Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of Thieno[2,3-*h*]-/[3,2-*h*]quinolines and Thieno[2,3-*f*]quinolines by Brønsted Acid mediated Cycloisomerisation

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General Information

If not otherwise cited, employed chemicals were purchased from commercial sources without further purifications. Solvents used for work-up and purification were distilled using standard procedures. Column chromatography was performed with silica gel (particle sizes 0.006 - 0.043 mm).

Melting point was carried out with Micro-Hot-Stage Galen TM III Cambridge Instrument without further corrections.

NMR measurements were performed with Bruker AVANCE 250 II (built 2006), Bruker AVANCE 300 III (built 2007) and AVANCE 500 (built 2001). NMR-peaks were calibrated using standard peaks of chloroform at 7.26 ppm for ^{1}H and at 77.16 ppm for ^{13}C. For peak descriptions, following abbreviations were used: s (singlet), d (doublet), t (triplet), dd (doublet doublet), td (triplet doublet), dt (doublet triplet), ddd (double doublet doublet).

IR measurement was completed with Nicolet 380 FT-IR spectrometer using ATR sampling technique. For peak descriptions, following abbreviations were used: w (weak), m (medium), s (strong).

GC/MS-measurements were conducted with Finnigan MAT 95-XP device using HP-5 capillary column with helium carrier gas and electron ionization (EI) scan technique at 70 eV.

For HRMS, Finnigan MAT 95 XP device was employed. Only signals with deviation of less than ±2 mDa were accounted as correct.

Synthesis of Thieno[2,3-*h*]-, Thieno[3,2-*h*]- and Benzothieno[3,2-*h*]quinolines

Synthesis of 3-bromo-2-heteroarylpyridines, 2a-c:

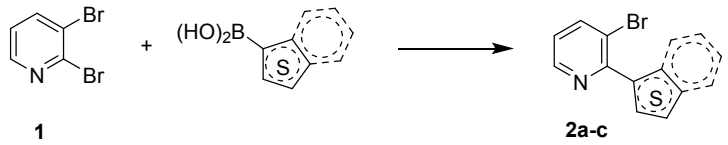


Table S1. Optimization of the regioselective Suzuki Coupling on 2,3-dibromopyridine

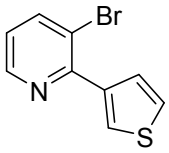
	Catalyst Ligand	**mol%**	**Boronic Acid eq.**	**Base**	**Solvent mixture**	**T (°C)**	**t (h)**	**Yield (%)**
1	$Pd(PPh_3)_4$	5	3.0	K_3PO_4	Toluene	80	20	-[a]
2	$PdCl_2(PPh_3)_2$	1.5	3.0	K_2CO_3	DME/H_2O (6:1)	80	5	-[a]
3	$Pd(PPh_3)_4$	5	1.5	K_2CO_3	DME/H_2O (6:1)	80	20	62
4	$PdCl_2(PPh_3)_2$	1.5	1.5	K_2CO_3	DME/H_2O (6:1)	80	20	71
5	**$Pd(PPh_3)_4$**	**5**	**1.3**	**K_2CO_3**	**1,4-Dioxan/H_2O (6:1)**	**80**	**4**	**98**
6	$Pd(OAC)_2$ PPh_3	5 1	1.3	K_2CO_3	MeCN/MeOH (2:1.6)	50	24	93

Conditions: 2,3-dibromopyridine (0.5 mmol), Boronic acid, Catalyst, Ligand, Base (2.0 eq.), solvents.

[a] Dimer as final product.

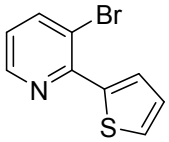
2,3-dibromopyridine (1.05 mmol, 248.7 mg), boronic acid (1.3 eq.), $Pd(PPh_3)_4$ (5 mol%) and K_2CO_3 (2.0 eq.) were dissolved in Dioxane/H_2O (6:1). The reaction mixture was stirred for 4 h at 80 °C. After cooling to room temperature, distilled water was added and the crude product was extracted with DCM. The collected organic phases were evaporated and the crude product was purified by column chromatography (Heptan/EtOAc 10:1) to obtain substrates **2a-c**.

3-bromo-2-(thiophen-3-yl)pyridine 2a



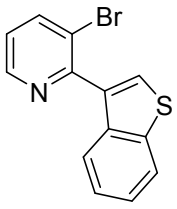
Following the synthesis instructions, the coupling with 3-thienylboronic acid (1.36 mmol, 174.7 mg) gave **2a** as colourless to light yellow oil (228 mg, 91 %). **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.58 (dd, ^3J = 4.6 = Hz, ^4J = 1.5 Hz, 1H, CH_{Pyr}), 7.97 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.96 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1H, CH_{Pyr}), 7.65 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.37 (dd, ^3J = 5.1 Hz, ^3J = 3.0 Hz, 1H, CH_{Thio}), 7.07 (dd, ^3J = 8.0 Hz, ^3J = 4.6 Hz, 1H, CH_{Pyr}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 153.2 (C_{Pyr}), 148.0, 141.8 (CH_{Pyr}), 140.4 (C_{Thio}), 129.0, 127.0, 124.9, 123.0 (CH_{Ar}), 119.3 (CBr) ppm. **IR** (ATR, cm^{-1}): ṽ = 3107 (w), 3043 (w), 2875 (w), 1567 (m), 1526 (w), 1439 (w), 1386 (m), 1358 (w), 1197 (w), 1135 (m), 1093 (m), 1052 (w), 1012 (s), 901 (w), 865 (m), 790 (s), 749 (s), 717 (m), 694 (w), 642 (m), 612 (w), 532 (m). **MS (EI, 70 eV)**: *m/z* (%) = 241 ($[M]^+$, 38), 239 (38), 161 (13), 160 (100), 132 (14), 116 (18), 109 (18), 89 (28), 87 (12), 86 (15), 82 (20), 81 (18), 76 (11), 75 (17), 74 (16), 69 (17), 63 (17), 62 (22), 61 (16), 58 (20), 57 (15), 51 (52), 50 (41), 45 (84), 39 (15), 38 (12), 37 (10). **HRMS (EI)** calcd. for $C_9H_6{}^{79}BrNS$ ($[M]^+$) 238.93988, found 238.93994; calcd. for $C_9H_6{}^{81}BrNS$ ($[M]^+$) 240.93784, found 240.93820.

3-bromo-2(thiophen-2-yl)pyridine 2b



Following the synthesis instructions the coupling with 2-thienylboronic acid (1.36 mmol, 174.7 mg) gave **2b** as colourless to light yellow oil (192 mg, 77 %). **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.50 (d, ^3J = 4.5 Hz, 1H, CH_{Pyr}), 8.15 (d, ^3J = 3.8 Hz, 1H, CH_{Thio}), 7.88 (dd, ^3J = 5.5 Hz, ^3J = 2.5 Hz, 1H, CH_{Thio}), 7.46 (dd, ^3J = 5.1 Hz, ^4J = 1.0 Hz, 1H, CH_{Thio}), 7.1 – 7.08 (m, 1H, CH_{Pyr}), 6.95 (dd, ^3J = 7.5 Hz, ^4J = 4.8 Hz, 1H, CH_{Pyr}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 150.5 (C_{Pyr}), 147.6 (CH_{Pyr}), 143.0 (C_{Thio}), 142.2, 129.1, 128.8, 127.6, 122.3 (CH_{Ar}), 117.2 (CBr) ppm. **IR** (ATR, cm^{-1}): ṽ = 3084 (w), 3028 (w), 2960 (m), 2902 (w), 2865 (w), 1602 (w), 1587 (w), 1550 (w), 1517 (w), 1488 (m), 1472 (m), 1400 (w), 1364 (m), 1263 (m), 1200 (w), 1130 (m), 1105 (m), 1074 (m), 1018 (m), 940 (w), 907 (m), 876 (m), 833 (s), 798 (m), 728 (s), 684 (m), 647 (w), 606 (s), 550 (m), 538 (m), 470 (w). **MS (EI, 70 eV):** *m/z* (%) = 241 ($[M]^+$, 100), 240 (14), 239 (98), 160 (74), 159 (12), 133 (11), 116 (20), 89 (18). **HRMS (EI)** calcd. for C_9H_6BrNS ($[M]^+$) 241.94561, found 241.94533.

2-(benzo[*b*]thiophen-3-yl)-3-bromopyridine 2c



Following the synthesis instructions, the coupling with benzo[b]thien-3-ylboronic acid resulted in (1.36 mmol, 243.0 mg) gave **2c** (303 mg, 98 %) as pink solid; mp: 80 – 83 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.69 (dd, ^3J = 4.6 Hz, ^4J = 1.5 Hz, 1H, CH_{Pyr}), 8.06 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, CH_{Pyr}), 7.94 – 7.89 (m, 1H, $CH_{b.Thio}$), 7.79 (s, 1H, $CH_{b.Thio}$), 7.78 – 7.73 (m, 1H, $CH_{b.Thio}$), 7.43 – 7.35 (m, 2H, $CH_{b.Thio}$), 7.21 (dd, ^3J = 8.1 Hz, ^3J = 4.6 Hz, 1H, CH_{Pyr}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 153.9 (C_{Pyr}), 148.1, 141.4 (CH_{Ar}), 139.9, 138.1, 134.9 (C_{Ar}),

128.1, 124.7, 124.6, 123.7, 123.7, 122.7 (CH_{Ar}), 121.4 (C_{Ar}) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3101 (w), 3044 (w), 2978 (w), 2923 (w), 1712 (m), 1662 (w), 1569 (m), 1521 (m), 1457 (m), 1429 (m), 1404 (m), 1343 (m), 1238 (m), 1122 (m), 1015 (m), 832 (m), 802 (m), 759 (s), 733 (s), 688 (m), 620 (m), 580 (m), 436 (m). **MS (EI, 70 eV):** *m/z* (%) = 291 ($[M]^+$, 100), 290 (80), 289 (99), 288 (68), 211 (12), 210 (67), 209 (35), 166 (30), 140 (10), 139 (25), 138 (10), 123 (13), 122 (13), 91 (13). **HRMS (ESI-TOF)** calcd. for $C_{13}H_8{}^{79}BrNS$ ($[M+H]^+$) 289.96296, found 291.96336; calcd. for $C_{13}H_8{}^{81}BrNS$ ($[M+H]^+$) 291.96091, found 291.96130.

Synthesis of Starting Materials 3a-u:

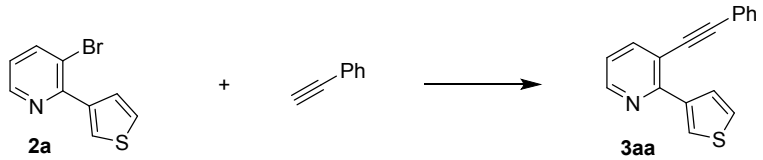


***Table S2**. Optimization of the Sonogashira reaction on 3-bromo-2-thien-3-ylpyridine.*

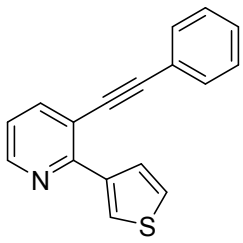
	Catalyst Ligand	**mol%**	**CuI mol%**	**Alkyne eq.**	**Base**	**Solvent mixture**	**T (°C)**	**t (h)**	**Yield (%)**
1	$PdCl_2(PPh_3)_2$	5	10	1.2	NEt_3	MeCN	50	24	17
2	$PdCl_2(PPh_3)_2$	5	10	1.2	NEt_3	Toluene	100	24	26
3	$PdCl_2(MeCN)_2$ *n*$BuPAd_2$	2 4	2	1.2	NEt_3	1,4-Dioxan	90	20	70
4	$PdCl_2(MeCN)_2$ *n*BuXPhos	2 4	2	1.5	NEt_3	1,4-Dioxan	90	20	-
5	$PdCl_2(MeCN)_2$ P*t*Bu_3·HBF_4	2 4	2	1.5	NEt_3	1,4-Dioxan	90	20	59
6	$PdCl_2(MeCN)_2$ XPhos	2 4	2	1.5	-	NEt_3	80	22	54

7	$PdCl_2(MeCN)_2$ *n*BuXPhos	2 4	2	1.5	-	NEt_3	80	20	35
8	$PdCl_2(MeCN)_2$ P*t*Bu$_3$·HBF$_4$	2 4	2	1.5	-	NEt_3	80	22	75
9	$Pd(PPh_3)_4$	5	2	1.2	NEt_3	1,4-Dioxan	90	20	77
10	**$Pd(PPh_3)_4$**	**5**	**2**	**1.2**	**-**	**NEt_3**	**80**	**20**	**82**

Conditions: 0.38 mmol **2a**, Catalyst, Ligand, CuI, Alkyne, Base, solvent (4 mL), Argon atmosphere.

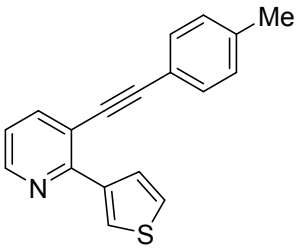
3-bromo-2-heteroarylpyridine, $Pd(PPh_3)_4$ (5 mol%) and CuI (2 mol%) were dissolved in NEt_3 under argon atmosphere. After the addition of alkyne (1.2 eq.), the reaction was stirred at 80 °C for 20 h. After cooling down to room temperature, washing with distilled water and extraction of the crude product with CH_2Cl_2 was performed. By evaporation of the collected organic phases and purification by column chromatography (Heptan/EtOAc, 8:1, 1 % NEt_3) the substrates **3aa-cf** were obtained.

3-(phenylethynyl)-2-(thiophen-3-yl)pyridine 3aa



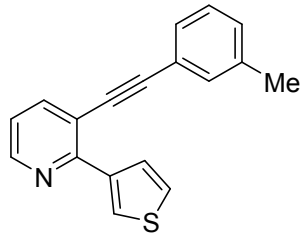
2a (0.36 mmol, 92 mg) reacted with phenylacetylene (0.436 mmol, 29 µL) to give **3aa** (247 mg, 82 %) as light yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.61 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.35 (dd, ^3J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.97 (dd, ^3J = 5.1 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.94 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.55 – 7.50 (m, 2H, CH_{Ph}), 7.42 – 7.36 (m, 4H, $CH_{Ph/Thio}$), 7.22 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 154.2 (C_{Pyr}), 148.5, 141.3 (CH_{Pyr}), 141.0 (C_{Thio}), 131.6 (CH_{Ph}), 128.9, 128.7 (CH_{Ar}), 128.6 (CH_{Ph}), 126.6, 124.8 (CH_{Ar}), 122.9 (C_{Ph}), 121.1 (CH_{Ar}), 116.9 (C_{Pyr}), 95.3, 87.9 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3101 (w), 3079 (w), 3027 (w), 1595 (w), 1552 (m), 1519 (w), 1488 (m), 1430 (s), 1370 (m), 1183 (w), 1102 (m), 1067 (m), 1024 (w), 913 (w), 903 (w), 874 (m), 845 (m), 806 (s), 750 (s), 688 (s), 641 (s), 546 (s), 490 (m). **MS (EI, 70 eV):** *m/z* (%) = 261 ([M]$^+$, 40), 260 (100), 259 (12), 216 (10), 150 (5), 130 (6), 126 (7), 109 (6), 74 (5), 51 (5), 45 (10), 39 (7). **HRMS (EI)** calcd. for $C_{17}H_{10}NS$ ([M]$^+$) 260.05285, found 260.05230.

2-(thiophen-3-yl)-3-(*p*-tolylethynyl)pyridine 3ab



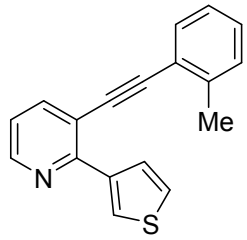
2a (0.36 mmol, 92 mg) reacted with 4-Ethynyltoluene (0.436 mmol, 33 µL) to give **3ab** (56 mg, 53 %) as yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.59 (dd, ^3J = 4.7 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.34 (dd, ^3J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.97 (dd, ^3J = 5.1 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.89 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.42 (d, ^3J = 8.1 Hz, 2H, $CH_{p\text{-}Tolyl}$), 7.38 (dd, ^3J = 5.1 Hz, ^3J = 3.0 Hz, 1H, CH_{Thio}), 7.19 (d, ^3J = 7.5 Hz, 2H, $CH_{p\text{-}Tolyl}$), 7.17 (dd, ^3J = 8.0 Hz, ^3J = 4.7 Hz, 1H, CH_{Pyr}), 2.39 (s, 3H,CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 154.1 (C_{Pyr}), 148.3, 141.3 (CH_{Ar}), 141.1, 139.2 (C_{Ar}), 131.5, 129.4 ($CH_{p\text{-}Tolyl}$), 128.7, 126.6, 124.8, 121.1 (CH_{Ar}), 119.8, 117.2 (C_{Ar}), 95.6, 87.3 (C_{Alkyne}), 21.7 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ 3105 (w), 2959 (w), 2916 (w), 2852 (w), 1556 (w), 1531 (w), 1506 (m), 1440 (m), 1362 (w), 1259 (w), 1105 (w), 1078 (m), 1036 (m), 1018 (m), 849 (m), 816 (s), 804 (s), 756 (s), 696 (m), 641 (m), 616 (m), 550 (m), 528 (m), 490 (m), 416 (m). **MS (EI, 70 eV)**: *m/z* (%) = 275 ($[M]^+$, 46), 274 (100), 273 (7), 272 (11), 260 (12), 259 (11), 163 (8), 139 (13), 136 (12), 130 (9), 63 (6), 45 (8), 39 (10). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{13}NS$ ($[M+H]^+$) 276.08415, found 276.08419.

2-(thiophen-3-yl)-3-(*m*-tolylethynyl)pyridine 3ac



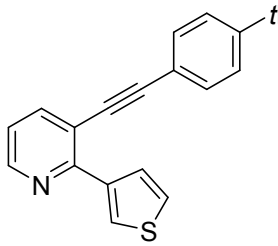
2a (0.36 mmol, 92 mg) reacted with 3-Ethynyltoluene (0.436 mmol, 33 µL) to give **3ac** (60 mg, 57 %) as yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.60 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.35 (dd, ^3J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.97 (dd, ^3J = 5.1 Hz, ^3J = 1.3 Hz, 1H, CH_{Thio}), 7.90 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.39 (dd, ^3J = 5.1 Hz, ^3J = 3.0 Hz, 1H, CH_{Thio}), 7.36 – 7.32 (m, 2H, $CH_{m\text{-}Tolyl}$), 7.30 – 7.24 (m, 1H, 3-Tolyl), 7.20 (d, ^4J = 1.0 Hz, 1H, $CH_{m\text{-}Tolyl}$), 7.17 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 2.37 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 154.1 (C_{Pyr}), 148.5, 141.3 (CH_{Ar}), 141.1, 138.3 (C_{Ar}), 132.1, 129.8, 128.73, 128.7, 128.5, 126.6, 124.8 (CH_{Ar}), 122.7 (C_{Ar}), 121.1 (CH_{Ar}), 117.0 (C_{Ar}), 95.6, 87.6 (C_{Alkyne}), 21.42 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3108 (w), 3034 (w), 2919 (w), 2854 (w), 2205 (w), 1599 (m), 1574 (m), 1552 (m), 1525 (s), 1484 (s), 1433 (s), 1362 (m), 1135 (s), 1103 (m), 1078 (m), 866 (m), 804 (s), 782 (s), 754 (s), 687 (s), 638 (m), 440 (s). **MS (EI, 70 eV):** *m/z* (%) = 275 ($[M]^+$, 51), 274 (100), 273 (12), 260 (16), 259 (12). **HRMS (EI)** calcd. for $C_{18}H_{12}NS$ ($[M]^+$) 274.06850, found 274.06866.

2-(thiophen-3-yl)-3-(*o*-tolylethynyl)pyridine 3ad



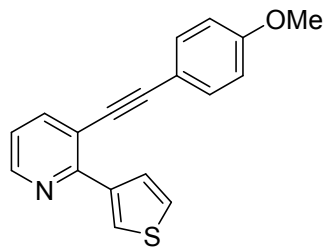
2a (0.36 mmol, 92 mg) reacted with 2-Ethynyltoluene (0.436 mmol, 33 µL) to give **3ad** (67 mg, 64 %) as yellow oil. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.61 (dd, ^{3}J = 4.8 Hz, ^{4}J = 1.8 Hz, 1H, CH_{Pyr}), 8.33 (dd, ^{3}J = 3.0 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Thio}), 7. 95 (dd, ^{3}J = 5.1 Hz, ^{4}J = 1.3 Hz 1H, CH_{Thio}), 7.93 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz 1H, CH_{Pyr}),7.50 (d, ^{3}J = 7.4 Hz, 1H, $CH_{o\text{-}Tolyl}$), 7.39 (dd, ^{3}J = 5.1 Hz, ^{3}J = 3.0 Hz, 1H, CH_{Thio}), 7.31 – 7.25 (m, 3H, $CH_{o\text{-}Tolyl}$), 7.21 (dd, ^{3}J = 7.8 Hz, ^{3}J = 4.8 Hz, 1H, CH_{Pyr}), 2.48 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 153.9 (C_{Pyr}), 148.4, 141.3 (CH_{Pyr}), 141.1, 140.2 (C_{Ar}), 132.0, 129.7, 128.9, 128.6, 126.5, 125.7, 124.8 (CH_{Ar}), 122.8 (C_{Ar}), 121.0 (CH_{Ar}), 117.1 (C_{Ar}), 94.4, 91.5 (C_{Alkyne}), 20.8 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3094 (w), 3033 (w), 2919 (w), 2207 (w), 1552 (m), 1525 (w),1485 (m), 1433 (s), 1362 (m), 1264 (m), 1239 (m), 1152 (w), 1112 (m), 1077 (m), 1038 (w), 903 (m), 870 (m), 853 (m), 804 (s), 751 (s), 713 (s), 638 (s), 616 (m), 450 (m). **MS (EI, 70 eV):** *m/z* (%) = 275 ($[M]^+$, 77), 274 (100), 273 (31), 272 (24), 243 (11), 242 (69), 241 (68), 240 (18), 230 (16), 216 (10), 164 (13), 163 (22), 139 (35), 115 (14) 110 (13), 109 (21), 89 (16), 87 (11), 75 (11), 74 (11), 63 (19), 51 (18), 45 (34), 39 (31). **HRMS (EI)** calcd. for $C_{18}H_{12}NS$ ($[M]^+$) 274.06850, found 274.06859.

3-((4-(*tert*-butyl)phenyl)ethynyl)-2-(thiophen-3-yl)pyridine 3ae



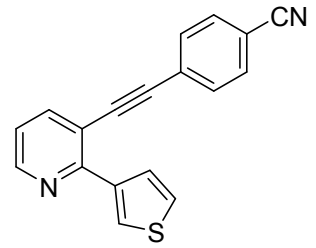
2a (0.36 mmol, 92 mg) reacted with 4-*tert*-Butylphenylacetylene (0.436 mmol, 79 µL) to give **3ae** (110 mg, 91 %) as brown solid; mp: 66 – 70 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.59 (dd, ^{3}J = 4.8, ^{4}J = 1.8 Hz, 1H, CH_{Pyr}), 8.35 (dd, ^{3}J = 3.0 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Thio}), 7.97 (dd, ^{3}J = 5.1 Hz, ^{4}J = 1.3 Hz, 1H, CH_{Thio}), 7.90 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz, 1H, CH_{Pyr}), 7.44 (m, 4H, CH_{Ar}), 7.38 (dd, ^{3}J = 5.1 Hz, ^{3}J = 3.1 Hz, 1H, CH_{Thio}), 7.17 (dd, ^{3}J = 7.8 Hz, ^{3}J = 4.8 Hz, 1H, CH_{Pyr}), 1.35 (s, 9H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 153.9 (C_{Pyr}), 148.4, 141.3 (CH_{Pyr}), 140.2, 141.1 (C_{Ar}), 132.0, 129.7, 128.9, 128.6, 126.5, 125.7, 124.8 (CH_{Ar}), 122.8 (C_{Ar}), 121.0 (CH_{Ar}), 117.1 (C_{Ar}), 94.4, 91.5 (C_{Alkyne}), 20.8 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3033 (w), 2959 (w), 2864 (w), 1574 (w), 1552 (w), 1523 (w), 1502 (w), 1437 (w), 1405 (w), 1359 (w), 1263 (w), 1100 (w), 890 (w), 855 (w), 833 (w), 805 (w), 754 (m), 662 (w), 645 (w), 568 (w), 511 (w), 449 (w). **MS (EI, 70 eV):** *m/z* (%) = 317 ($[M]^+$, 57), 316 (51), 303 (24), 302 (100), 286 (13), 274 (13), 260 (18), 137 (21). **HRMS (EI)** calcd. for $C_{11}H_{19}NS$ ($[M]^+$) 318.13110, found 318.13142.

3-((4-methoxyphenyl)ethynyl)-2-(thiophen-3-yl)pyridine 3af



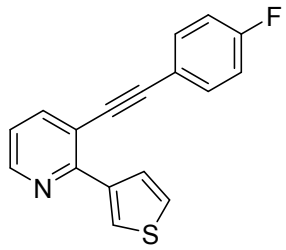
2a (0.36 mmol, 92 mg) reacted with 4-Ethynylanisole (0.436 mmol, 57 µL) to give **3af** (91 mg, 82 %) as light yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.57 (dd, ^3J = 4.7 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.32 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.95 (dd, ^3J = 5.1 Hz, ^4J = 1.2 Hz, 1H, CH_{Thio}), 7.88 (dd, ^3J = 7.8 Hz, ^3J = 1.8 Hz, 1H, CH_{Pyr}), 7.45 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.38 (dd, ^3J = 5.1 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.17 (dd, ^3J = 7.8 Hz, ^3J = 4.7 Hz, 1H, CH_{Pyr}), 6.90 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 3.84 (s, 3H, CH_3) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 160.2 (C_{OMe}), 154.1 (C_{Pyr}), 148.3 (CH_{Ar}), 141.3 (C_{Ar}), 141.1, 133.1, 128.8, 126.4, 124.8, 121.1 (CH_{Ar}), 117.3, 115.0 (C_{Ar}), 114.3 (CH_{Ar}), 95.5, 86.8 (C_{Alkyne}), 55.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3107 (w), 3033 (w), 3000 (w), 2955 (w), 2932 (w), 2835 (w), 2209 (w), 1603 (s), 1568 (m), 1552 (m), 1506 (s), 1434 (s), 1362 (w), 1288 (s), 1247 (s), 1173 (s), 1146 (m), 1102 (m), 1078 (m), 1026 (s), 828 (s), 804 (s), 754 (s), 690 (m), 635 (s), 540 (s), 530 (s), 492 (m). **MS (EI, 70 eV)**: *m/z* (%) = 291 ($[M]^+$, 100), 290 (58), 277 (12), 276 (44), 275 (15), 248 (28), 247 (60), 246 (21), 203 (10), 124 (11), 113 (9), 109 (9), 45 (12). **HRMS (ESI-TOF)** calcd. for $C_{18}H_{13}NOS$ ($[M+H]^+$) 292.0796, found 292.0791.

4-((2-(thiophen-3-yl)pyridin-3-yl)ethynyl)benzonitrile 3ag



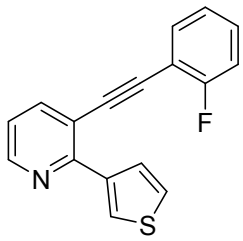
2a (0.36 mmol, 92 mg) reacted with 4-Ethynylbenzonitrile (0.436 mmol, 51 µL) to give **3ag** (73 mg, 71 %) as colourless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.64 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 8.21 (dd, ^4J = 3.0 Hz, ^4J = 1.2 Hz, 1H, CH_{Thio}), 7.92 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 7.88 (dd, ^3J = 5.1 Hz, ^4J = 1.2 Hz, 1H, CH_{Thio}), 7.66 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.58 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.40 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.23 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 154.8 (C_{Pyr}), 149.5, 141.4 (CH_{Ar}), 141.0 (C_{Ar}), 132.4, 132.1, 128.6 (CH_{Ar}), 127.7 (C_{Ar}), 126.7, 125.2, 121.3 (CH_{Ar}), 118.5 (CN), 116.0, 112.2 (C_{Ar}), 93.2, 92.2 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3089 (w), 3058 (w), 3025 (w), 2219 (m), 1601 (m), 1554 (w), 1523 (w), 1500 (w), 1432 (m), 1403 (w), 1271 (w), 1181 (w), 1105 (w), 880 (w), 841 (s), 802 (m), 748 (s), 688 (w), 628 (w), 554 (s), 499 (w), 478 (w). **MS (EI, 70 eV)**: *m/z* (%) = 286 ($[M]^+$, 37), 285 (100), 241 (9), 151 (10), 75 (9), 74 (12), 45 (16), 39 (11). **HRMS (ESI-TOF)** calcd. for $C_{18}H_{10}N2S$ ($[M+H]^+$) 287.0643, found 287.0649.

3-((4-fluorophenyl)ethynyl)-2-(thiophen-3-yl)pyridine 3ah



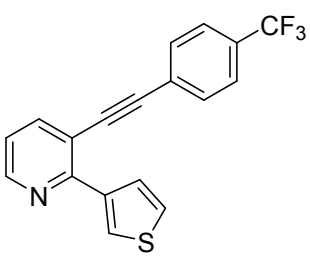
2a (0.36 mmol, 92 mg) reacted with 1-Ethynyl-4-fluorobenzene (0.436 mmol, 50 µL) to give **3ah** (77 mg, 77 %) as dark purple solid; mp: 57 – 60 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.60 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.29 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.94 (dd, ^3J = 5.1 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.88 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.52 – 7.45 (m, 2H, CH_{Ar}), 7.39 (dd, ^3J = 5.1 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.18 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 7.11 – 7.02 (m, 2H, CH_{Ar}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = −109.75 ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 162.9 (d, $^1J_{C,F}$ = 250.7 Hz, CF), 154.2 (C_{Pyr}), 148.6, 141.3 (CH), 141.1 (C_{Ar}), 133.5 (d, $^3J_{C,F}$ = 8.5 Hz, CH_{Ar}), 128.7, 126.6, 124.9, 121.2 (CH_{Ar}), 119.0 (d, $^4J_{C,F}$ = 3.5 Hz, C_{Ar}), 116.8 (C_{Ar}), 116.0 (d,$^2J_{C,F}$ = 22.2 Hz, CH_{Ar}), 94.2(C_{Alkyne}), 87.6 (d, $^5J_{C,F}$ = 1.5 Hz, C_{alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3041 (w), 2922 (w), 2852 (w), 2214 (w), 1600 (m), 1553 (m), 1528 (w), 1503 (m), 1436 (m), 1222 (m), 1152 (m), 904 (m), 868 (m), 854 (m), 831 (s), 803 (s), 756 (s), 653 (m), 642 (m), 548 (m), 517 (m), 502 (m). **MS (EI, 70 eV)**: *m/z* (%) = 278 ($[M]^+$, 100), 277 (10), 234 (10). **HRMS (ESI-TOF)** calcd. for $C_{17}H_{10}FNS$ ($[M+H]^+$) 280.05907, found 280.05874.

3-((2-fluorophenyl)ethynyl)-2-(thiophen-3-yl)pyridinen 3ai



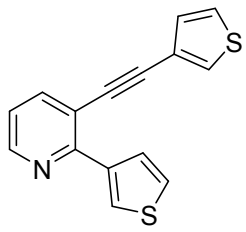
2a (0.36 mmol, 92 mg) reacted with 1-Ethynyl-2-fluorobenzene (0.436 mmol, 49 µl) to give **3ai** (66 mg, 66 %) as yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.60 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 8.42 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.97 (dd, ^3J = 5.1 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.92 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.49 (dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, CH_{Pyr}), 7.38 (dd, ^3J = 5.1 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.36 – 7.30 (m, 1H, CH_{Ar}), 7.21 – 7.09 (m, 3H, CH_{Ar}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = −109.12 ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 162.9 (d, $^1J_{C,F}$ = 252.3 Hz, CF), 154.1 (C), 148.9, 141.5 (CH_{Ar}), 140.9 (C_{Ar}), 133.3 (CH_{Ar}), 130.6 (d, $^3J_{C,F}$ = 8.0 Hz, CH_{Ar}), 128.7 (CH), 126.8 (d, $^4J_{C,F}$ = 1.5 Hz, CH_{Ar}), 124.8 (CH_{Ar}), 124.2 (d, $^3J_{C,F}$ = 3.7 Hz, CH_{Ar}), 121.1 (CH_{Ar}), 116.4 (C_{Ar}), 115.8 (d, $^2J_{C,F}$ = 20.7 Hz, CH_{Ar}), 111.5 (d, $^2J_{C,F}$ = 15.6 Hz, C_{Ar}), 92.8 (d, $^3J_{C,F}$ = 3.2 Hz, C_{Alkyne}), 88.9 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3299 (w), 3199 (w), 3145 (m), 1618 (m), 1562 (m), 1526 (s), 1484 (m), 1478 (s), 1470 (s), 1441 (m), 1389 (w), 1267 (w), 1241 (m), 1120 (w), 1103 (w), 884 (w), 869 (w), 827 (m), 819 (w), 773 (s), 769 (m). **MS (EI, 70 eV)**: *m/z* (%) = 279 ($[M]^+$, 44), 278 (100), 277 (10), 234 (10). **HRMS (EI)** calcd. for $C_{17}H_{10}FNS$ ($[M]^+$) 278.04342, found 278.04321.

2-(thiophen-3-yl)-3-((4-(trifluoromethyl)phenyl)ethynyl)pyridine 3aj



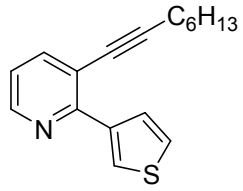
2a (0.36 mmol, 92 mg) reacted with 4-Ethynyl-α,α,α-trifluorotoluene (0.436 mmol, 71 µL) to yield the colourless solid **3aj** (99 mg, 83 %); mp: 91 – 93 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.63 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.25 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.92 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.91 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.74 – 7.52 (m, 4H, CH_{Ar}), 7.40 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.22 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}) ppm. **^{19}F NMR (471 MHz, $CDCl_3$)** δ = −62.86 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 154.7 (C_{Pyr}), 149.2, 141.4 (CH_{Ar}), 141.1 (C_{Ar}), 131.8 (CH_{Ar}), 130.6 (q, $^2J_{C,F}$ = 32.8 Hz, CCF_3), 128.7 (CH_{Ar}), 126.7 (C_{Ar}), 126.7 (CH_{Ar}), 125.6 (q, $^3J_{C,F}$ = 3.7 Hz, CH_{Ar}), 125.1 (CH_{Ar}), 123.6 (q, $^1J_{C,F}$ = 272.3 Hz, CF_3), 121.2 (CH_{Ar}), 116.3 (C_{Ar}), 93.6, 90.3 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3105 (w), 3056 (w), 1609 (m), 1556 (m), 1440 (m), 1401 (w), 1364 (w), 1317 (s), 1160 (s), 1105 (s), 1063 (s), 1012 (s), 839 (s), 804 (s), 758 (s), 717 (m), 703 (m), 643 (s), 593 (s), 550 (m), 521 (m), 492 (m), 422 (m). **MS (EI, 70 eV):** *m/z* (%) = 329 ($[M]^+$, 40), 328 (100), 260 (10), 259 (13), 130 (13), 109 (10), 75 (11), 69 (18), 45 (20), 39 (13). **HRMS (ESI-TOF)** calcd. for $C_{18}H_{10}F_3NS$ ($[M+H]^+$) 330.0564, found 330.0566.

2-(thiophen-3-yl)-3-(thiophen-3-ylethynyl)pyridine 3ak



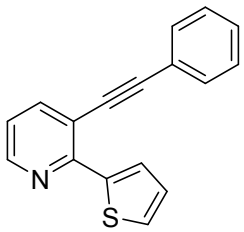
2a (0.36 mmol, 92 mg) reacted with 3-Ethynylthiophene (0.436 mmol, 43 µL) to yield the brown solid **3ak** (35 mg, 36 %); mp: 58 – 61 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.59 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.32 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.94 (dd, ^3J = 5.1 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.89 (dd ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.54 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.38 (dd, ^3J = 5.1 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.34 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.23 – 7.16 (m, 2H, $CH_{Pyr/Thio}$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 154.1 (C_{Pyr}), 148.4, 141.3 (CH_{Ar}), 140.9 (C_{Ar}), 129.6, 129.4, 128.7, 126.7, 125.9, 124.9 (CH_{Ar}), 122.0 (C_{Ar}), 121.2 (CH_{Ar}), 117.0 (C_{Ar}), 90.8, 87.4 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3099 (m), 2922 (w), 2209 (w), 1675 (m), 1572 (m), 1553 (m), 1519 (m), 1434 (m), 1404 (m), 1355 (m), 1261 (m), 1201 (m), 1106 (m), 1073 (m), 954 (m), 940 (m), 868 (m), 837 (m), 80 (s), 782 (s), 750 (s), 69 (m), 626 (m), 552 (m), 500 (m). **MS (EI, 70 eV)**: *m/z* (%) = 267 ($[M]^+$, 61), 266 (100), 222 (18). **HRMS (EI)** calcd. for $C_{15}H_8NS_2$ ($[M]^+$) 266.00927, found 266.00927.

3-(oct-1-yn-1-yl)-2-(thiophen-3-yl)pyridine 3al



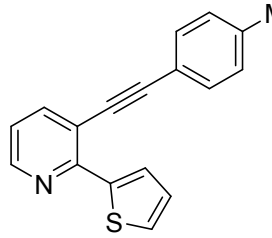
2a (0.36 mmol, 92 mg) reacted with 1-Octyne (0.436 mmol, 34 µL) to **3al** (54 mg, 56 %) as colourless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.52 (dd, ^3J = 4.7 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.29 (dd, ^3J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.91 (dd, ^3J = 5.1 Hz, ^4J = 1.2 Hz, 1H, CH_{Thio}), 7.76 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.33 (dd, ^3J = 5.1 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.10 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 2.46 (t, ^3J = 7.0 Hz, 2H, CH_2), 1.70 – 154 (m, 2H, CH_2), 1.51 – 1.37 (m, 2H, CH_2), 1.36 – 1.28 (m, 4H, CH_2), 0.91 (t, ^3J = 6.8 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 154.0 (C_{Pyr}), 147.8, 141.6 (CH_{Ar}), 141.2 (C_{Ar}), 128.7, 126.2, 124.5, 121.0 (CH_{Ar}), 117.7 (C_{Ar}), 97.1, 79.2 (C_{Alkyne}), 31.5, 28.8, 28.4, 22.7, 19.8 (CH_2), 14.2 (CH_3) ppm. **IR** (ATR, cm−1): ṽ = 2927 (m), 2856 (w), 2225 (w), 1575 (w), 1553 (w), 1526 (w), 1434 (s), 1404 (s), 1361 (s), 1262 (m), 1225 (m), 1110 (m), 866 (m), 805 (m), 756 (s), 690 (m), 638 (m), 618 (m), 541 (w). **MS (EI, 70 eV)**: *m/z* (%) = 269 ([M]$^+$, 7), 212 (23), 210 (11), 200 (22), 199 (100), 198 (67), 197 (19), 186 (14), 185 (13), 167 (11), 154 (25), 153 (11), 127 (10), 63 (14), 43 (26), 41 (35), 39 (16), 29 (28). **HRMS (EI)** calcd. for $C_{17}H_{19}NS$ ([M]$^+$) 269.12327, found 269.12304.

3-(phenylethynyl)-2-(thiophen-2-yl)pyridine 3ba



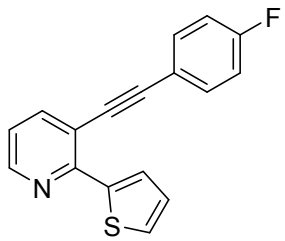
2b (0.36 mmol, 92 mg) reacted with Phenylacetylene (0.436 mmol, 34 µL) to **3ba** (53 mg, 56 %) as colourless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.55 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 8.41 (dd, ^3J = 3.8 Hz, ^4J = 1.1 Hz, 1H, CH_{Thio}), 7.88 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.63 – 7.58 (m, 2H, CH_{Ph}), 7.47 (dd, ^3J = 5.1 Hz, ^4J = 1.1 Hz, 1H, CH_{Thio}), 7.44 – 7.39 (m, 3H, CH_{Ph}), 7.17 (dd, ^3J = 5.1 Hz, ^3J = 3.8 Hz, 1H, CH_{Thio}), 7.14 (dd, ^3J = 7.8 Hz, ^3J = 4.7 Hz, 1H, CH_{Pyr}) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 152.3 (C_{Pyr}), 148.5 (CH_{Ar}), 144.2 (C_{Ar}), 141.7 (CH_{Ar}), 131.6 (CH_{Ph}), 129.0 (CH_{Ar}), 128.7 ($CH_{Ph/Ar}$), 128.3, 127.9 (CH_{Ar}), 122.9 (C_{Ar}), 120.9 (CH_{Ar}), 115.1 (C_{Ar}), 96.5, 87.7 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}) ṽ = 3067 (w), 2921 (w), 2851 (w), 1727 (w), 1587 (w), 1552 (m), 1525 (w), 1488 (w), 1435 (s), 1408 (s), 1263 (w), 1214 (m), 1101 (w), 1064 (m), 1024 (w), 973 (m), 857 (m), 843 (m), 802 (m), 765 (m), 752 (s), 736 (m), 699 (s), 688 (s), 666 (s), 620 (m), 606 (m), 550 (m), 532 (m), 515 (m), 495 (m), 443 (m). **MS (EI, 70 eV)**: *m/z* (%) = 261 ([M]$^+$, 97), 260 (100), 259 (18), 217 (10), 216 (32), 189 (11), 151 (11), 150 (18), 126 (39), 110 (15), 109 (35), 99 (10), 98 (17), 87 (15), 86 (11), 76 (14), 75 (14), 74 (20), 69 (11), 63 (17), 58 (20), 51 (30), 50 (14), 45 (32), 39 (23). **HRMS (EI)** calcd. for $C_{17}H_{11}N$ ([M]$^+$) 261.06067, found 261.06013.

2-(thiophen-2-yl)-3-(*p*-tolylethynyl)pyridine 3bb



2b (0.36 mmol, 92 mg) reacted with 4-Ethynyltoluene (0.436 mmol, 33 µL) to **3bb** (95 mg, 95 %) as colourless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.54 (dd, ^{3}J = 4.7 Hz, ^{4}J = 1.8 Hz, 1H, CH_{Pyr}), 8.41 (dd, ^{3}J = 3.8 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Thio}), 7.87 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz, 1H, CH_{Pyr}), 7.52 – 7.47 (m, 2H, $CH_{o\text{-}Tolyl}$), 7.46 (dd, ^{3}J = 5.1 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Thio}), 7.24 – 7.19 (m, 2H, CH_{Ph}), 7.16 (dd, ^{3}J = 5.1 Hz, ^{3}J = 3.8 Hz, 1H, CH_{Thio}), 7.13 (dd, ^{3}J = 7.8 Hz, ^{3}J = 4.8 Hz, 1H, CH_{Pyr}), 2.40 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 152.2 (C_{Pyr}), 148.3 (CH_{Ar}), 144.2 (C_{Ar}), 141.6 (CH_{Ar}), 139.3 (C_{Ar}), 131.5, 129.4 ($CH_{o\text{-}Tolyl}$), 128.6, 128.3, 127.9, 120.9 (CH_{Ar}), 119.8, 115.3 (C_{Ar}), 96.8, 87.1 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3048 (w), 3028 (w), 2917 (w), 2853 (w), 1707 (w), 1593 (m), 1581 (m), 1562 (m), 1478 (w), 1455 (w), 1416 (m), 1397 (m), 1377 (m), 1358 (m), 1259 (m), 1175 (m), 1160 (m), 1113 (m), 1088 (m), 1057 (w), 1037 (m), 1024 (m), 878 (m), 822 (m), 806 (s), 785 (s), 771 (s), 748 (s), 730 (m), 680 (m), 655 (w), 629 (m), 573 (m), 542 (w), 515 (m), 491 (m), 410 (s). **MS (EI, 70 eV):** *m/z* (%) = 275 ($[M]^+$, 100), 274 (66),273 (15), 272 (12), 259 (19), 230 (15), 139 (12), 136 (11). **HRMS (EI)** calcd. for $C_{18}H_{13}NS$ ($[M]^+$) 275.07630, found 275.07566.

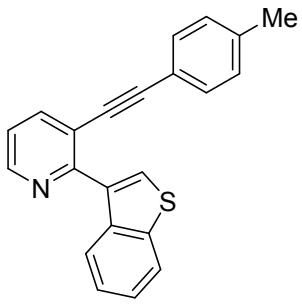
3-((4-fluorophenyl)ethynyl)-2-(thiophen-2-yl)pyridine 3bc



2b (0.36 mmol, 92 mg) reacted with 4-Fluorophenylactelyene (0.436 mmol, 50 µL) to get **3bc** (80 mg, 79 %) as colourless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.54 (dd, ^{3}J = 4.7 Hz, ^{4}J = 1.8 Hz, 1H, CH_{Pyr}), 8.34 (dd, ^{3}J = 3.8 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Thio}), 7.85 (dd, ^{3}J = 7.8, ^{4}J = 1.8 Hz, 1H, CH_{Pyr}), 7.56 (dd, ^{3}J = 9.0 Hz, $^{4}J_{H,F}$ = 5.3 Hz, 2H, CH_{Ar}), 7.46 (dd, ^{3}J = 5.1 Hz, ^{4}J = 1.1 Hz, 1H, CH_{Thio}), 7.15 (dd, ^{3}J = 5.1 Hz, ^{3}J = 3.8 Hz, 1H, CH_{Thio}), 7.13 (dd, ^{3}J = 7.8 Hz, ^{3}J = 4.8 Hz, 1H, CH_{Pyr}), 7.11 – 7.06 (m, 2H, CH_{Ar}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = −109.60 ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 163.0 (d, $^{1}J_{C,F}$ = 250.8 Hz, CF), 152.3 (C_{Pyr}), 148.6 (CH_{Ar}), 144.1 (C_{Ar}), 141.6 (CH_{Ar}), 133.5 (d, $^{3}J_{C,F}$ = 8.5 Hz, CH_{Ar}), 128.7, 128.2, 127.9, 120.9 (CH_{Ar}), 119.0 (d, $^{4}J_{C,F}$ = 3.5 Hz, C_{Ar}), 116.0 (d, $^{2}J_{C,F}$ = 22.2 Hz, CH_{Ar}), 114.9 (C_{Ar}), 95.4 (C_{Alkyne}), 87.4 (d, $^{5}J_{C,F}$ = 1.4 Hz, C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3062 (w), 2221 (w), 1902 (w), 1651 (w), 1597 (w), 1550 (w), 1504 (m), 1436 (m), 1409 (m), 1269 (w), 1234 (m), 1215 (m), 1092 (w), 1063 (w), 972 (w), 863 (w), 863 (w), 834 (m), 799 (m), 764 (m), 703 (m), 651 (m), 620 (w), 554 (m), 513 (m), 497 (w), 445 (w), 437 (w). **MS (EI, 70 eV)** *m/z* (%) = 279 ($[M]^+$,

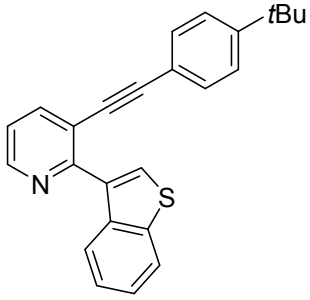
100), 278 (90), 277 (18), 234 (28), 144 (12), 117 (10), 109 (12). **HRMS (EI)** calcd. for $C_{17}H_{10}FNS$ ([M]$^+$) 279.05125, found 279.05063.

2-(benzo[*b*]thiophen-3-yl)-3-(*p*-tolylethynyl)pyridine 3ca



2c (0.36 mmol, 105 mg) reacted with 4-Ethynyltoluene (0.436 mmol, 33 µL) to get **3ca** (112 mg, 91 %) as brown oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.70 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.21 – 8.17 (m, 1H, $CH_{b.thio}$), 8.13 (s, 1H, $CH_{b.Thio}$), 7.98 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.95 – 7.91 (m, 1H, $CH_{b.Thio}$), 7.43 – 7.37 (m, 2H, $CH_{b.Thio}$), 7.29 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 7.18 – 7.13 (m, 2H, $CH_{p\text{-}Tolyl}$), 7.12 – 7.07 (m, 2H, $CH_{p\text{-}Tolyl}$), 2.34 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 155.5 (C_{Pyr}), 148.1, 140.6 (CH_{Ar}), 140.1, 139.1, 138.2, 134.8 (C_{Ar}), 131.5, 129.3 ($CH_{p\text{-}Tolyl}$), 128.5, 124.59, 124.6, 124.4, 122.6, 121.6 (CH_{Ar}), 119.6, 119.6 (C_{Ar}), 95.7, 86.7 (C_{Alkyne}), 21.7 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3053 (w), 3028 (w), 2918 (w), 2214 (w), 1905 (w), 1549 (w), 1430 (m), 1413 (m), 1340 (w), 1148 (w), 1094 (w), 1063 (w), 952 (w), 814 (s), 766 (s), 729 (s), 633 (m), 584 (m), 541 (m), 522 (m), 421 (m). **MS (EI, 70 eV):** *m/z* (%) = 325 ([M]$^+$, 93), 324 (100), 323 (21), 322 (169), 311 (14), 310 (55), 309 (48), 155 (14). **HRMS (EI)** calcd. for $C_{22}H_{14}NS$ ([M]$^+$) 325.08415, found 325.08395.

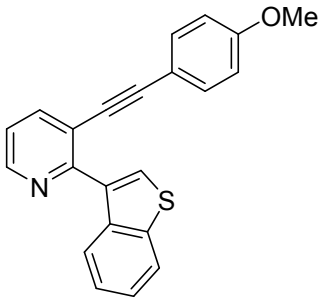
2-(benzo[*b*]thiophen-3-yl)-3-((4-(*tert*-butyl)phenyl)ethynyl)pyridine 3cb



2c (0.36 mmol, 105 mg) reacted with 4-*tert*-Butylphenylacetylene (0.436 mmol, 79 µL) to produce **3cb** (130 mg, 98 %) as light brown oil. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.70 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.24 – 8.16 (m, 1H, $CH_{b.Thio}$), 8.13 (s, 1H, $CH_{b.Thio}$), 7.98 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.96 – 7.89 (m, 1H, $CH_{b.Thio}$), 7.45 – 7.37 (m, 1H, $CH_{b.Thio}$), 7.32 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.29 (dd, ^3J = 7.9 Hz, ^3J = 4.7 Hz, 1H, $CH_{Pyr)}$, 7.21 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 1.30 (s, 9H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 155.6 (C_{Pyr}), 152.2 (C_{Ar}), 148.3, 140.6 (CH_{Ar}), 140.1, 138.3, 134.9 (C_{Ar}), 131.3, 128.4, 125.5, 124.6, 124.5, 124.5, 122.6, 121.6 (CH_{Ar}), 119.7, 119.5 (C_{Ar}), 95.6, 86.8 (C_{Alkyne}), 35.0 (C_{tBu}), 31.3 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3056 (w), 3033 (w), 2959 (m), 2864 (w), 2215 (w), 1603 (w), 1550 (w), 1506 (m), 1457 (m), 1430 (m), 1414 (m), 1362 (m), 1339 (w), 1265 (m), 1199 (w), 1092 (m), 1063 (w), 1018 (w), 952 (w), 907 (m), 832 (s), 802 (m), 767 (s), 729 (s), 645 (m), 560 (s), 422 (m). **MS (EI, 70 eV):** *m/z* (%) = 367 ([M]$^+$, 90), 366 (22), 353 (24), 352 (84), 350 (18), 337 (16), 336 (34), 311 (20), 310 (84),

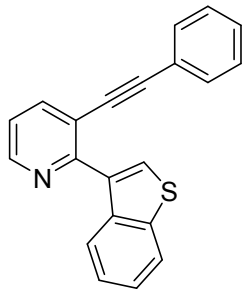
309 (39), 168 (20), 167 (25), 162 (69), 161 (51), 155 (23), 154 (19), 149 (28), 77 (18), 57 (20), 51 (18), 41 (100), 39 (61). **HRMS (ESI-TOF)** calcd. for $C_{25}H_{21}NS$ ([M+H]$^+$) 368.1473, found 368.1473.

2-(benzo[*b*]thiophen-3-yl)-3-((4-methoxyphenyl)ethynyl)pyridine 3cc



2c (0.36 mmol, 105 mg) reacted with 4-Ethynylanisole (0.436 mmol, 57 µL) to **3cc** (124 mg, 99 %) as light brown oil. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.68 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.22 – 8.16 (m, 1H, $CH_{b.Thio}$), 8.12 (s, 1H, $CH_{b.Thio}$), 7.96 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.96 – 7.90 (m, 1H, $CH_{b.Thio}$), 7.47 – 7.34 (m, 1H, $CH_{b.Thio}$), 7.28 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 7.19 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.81 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 3.79 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 160.1 (C_{Ar}), 155.5 (C_{Pyr}), 148.1, 140.3 (CH_{Ar}), 140.1, 138.3, 135.0 (C_{Ar}), 133.1, 128.3, 124.6, 124.5, 124.5, 122.6, 121.6 (CH_{Ar}), 119.6, 114.8 (C_{Ar}), 114.2 (CH_{Ar}), 95.5, 86.2 (C_{Alkyne}), 55.4 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3054 (w), 3000 (w), 2955 (w), 2932 (w), 2835 (w), 2539 (w), 2213 (w), 1733 (w), 1603 (s), 1568 (m), 1550 (m), 1506 (s), 1457 (m), 1430 (s), 1414 (m), 1286 (s), 1245 (s), 1173 (s), 1146 (m), 1094 (m), 1024 (s), 952 (m), 828 (s), 802 (s), 767 (s), 729 (s), 674 (m), 633 (m), 534 (s), 420 (m). **MS (EI, 70 eV)**: *m/z* (%) = 341 ([M]$^+$, 100), 340 (27), 327 (19), 326 (78), 325 (15), 310 (14), 309 (12), 298 (28), 297 (73), 296 (53), 270 (10), 159 (10), 148 (20). **HRMS (EI)** calcd. for $C_{22}H_{15}NOS$ ([M]$^+$) 341.08689, found 341.08652.

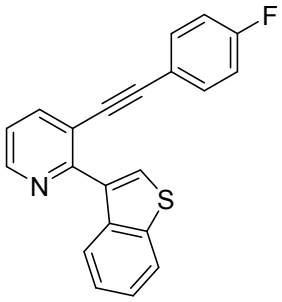
2-(benzo[*b*]thiophen-3-yl)-3-(phenylethynyl)pyridine 3cd



2c (0.36 mmol, 105 mg) reacted with Phenylacetylene (0.436 mmol, 34 µL) to **3cd** (126 mg, 98 %) as yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.73 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.28 – 8.24 (m, 1H, $CH_{b.Thio}$), 8.18 (s, 1H, $CH_{b.Thio}$), 7.99 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.99 – 7.94 (m, 1H, CH_{Ar}), 7.47 – 7.41 (m, 2H, CH_{Ar}), 7.33 – 7.30 (m, 5H, CH_{Ar}), 7.27 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 155.6 (C_{Pyr}), 148.3, 140.5 (CH_{Ar}), 140.0, 138.1, 134.8 (C_{Ar}), 131.5 (CH_{Ph}), 128. (CH_{Ar}), 128.4 (CH_{Ph}), 124.5, 124.5, 124.4 (CH_{Ar}), 122.6 (C_{Ar}), 122.5, 121.5 (CH_{Ar}), 119.1 (C_{Ar}), 95.3, 87.4 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3121 (w), 3053 (w), 3028 (w), 2216 (w), 1569 (w), 1546 (m), 1517 (m), 1488 (m), 1457 (m), 1430 (s), 1412 (m), 1342 (m), 1263 (w), 1224 (w), 1191 (w), 1150 (w), 1094 (w), 1062 (m), 1016 (m), 948 (w), 915 (w), 857 (m), 808 (m), 800 (m), 769 (s), 752 (s), 732 (s), 705 (m), 688 (s), 635 (s), 585 (m), 548 (m), 540

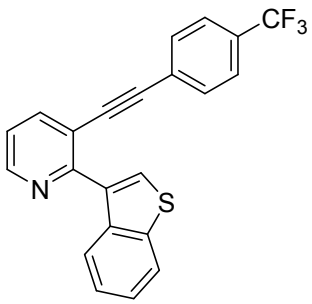
(m), 521 (m), 509 (m), 484 (m), 466 (m), 423 (s). **MS (EI, 70 eV):** *m/z* (%) = 311 ([M]$^+$, 59), 310 (100), 309 (36), 159 (12), 126 (13). **HRMS (EI)** calcd. for $C_{21}H_{12}NS$ ([M]$^+$) 310.06850, found 310.06910.

2-(benzo[*b*]thiophen-3-yl)-3-((4-fluorophenyl)ethynyl)pyridine 3ce



2c (0.36 mmol, 105 mg) reacted with 4-Fluorophenylacetylene (0.436 mmol, 50 µL) to yield **3ce** (104 mg, 82 %) as colourless solid; mp: 92 – 94 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.71 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.19 – 8.15 (m, 1H, $CH_{b.Thio}$), 8.09 (s, 1H, $CH_{b.Thio}$), 7.97 (dd, ^3J = 7.8 Hz, ^3J = 1.8 Hz, 1H, CH_{Pyr}), 7.96 – 7.90 (m, 1H, $CH_{b.Thio}$), 7.46 – 7.39 (m, 2H, CH_{Ar}), 7.29 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 7.24 – 7.18 (m, 2H, CH_{Ar}), 7.01 – 6.94 (m, 2H, CH_{Ar}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = −109.87 ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 162.8 (d, $^1J_{C,F}$ = 250.5 Hz, CF), 155.7 (C_{Pyr}), 148.5, 140.5 (CH_{Ar}), 140.1, 138.1, 135.0 (C_{Ar}), 133.5 (d, $^3J_{C,F}$ = 8.5 Hz, CH_{Ar}), 128.3, 124.6, 124.4, 122.6, 121.6 (CH_{Ar}), 119.1 (C_{Ar}), 118.8 (d, $^4J_{C,F}$ = 3.5 Hz, C_{Ar}), 115.8 (d, $^2J_{C,F}$ = 22.1 Hz, CH_{Ar}), 94.3 (C_{Alkyne}), 87.1 (d, $^5J_{C,F}$ = 1.5 Hz, C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3104 (w), 3059 (w), 1894 (w), 1601 (w), 1507 (m), 1458 (w), 1431 (m), 1411 (m), 1350 (w), 1231 (m), 1157 (m), 1090 (m), 1016 (w), 867 (w), 828 (m), 799 (m), 765 (m), 753 (m), 728 (m), 674 (m), 630 (m), 584 (m), 549 (m), 515 (m), 496 (m), 426 (m). **MS (EI, 70 eV)**: *m/z* (%) = 329 ([M]$^+$, 66), 328 (100), 327 (34), 326 (6), 325 (5), 284 (5), 168 (4), 157 (8), 74 (4), 69 (4). **HRMS (EI)** calcd. for $C_{21}H_{12}FNS$ ([M]$^+$) 328.05907, found 328.05890.

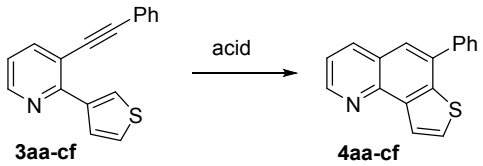
2-(benzo[*b*]thiophen-3-yl)-3-((4-(trifluoromethyl)phenyl)ethynyl)pyridine 3cf



2c (0.36 mmol, 105 mg) reacted with 4-(Trifluoromethyl)phenylacetylene (0.436 mmol, 71 µL) to yield **3cf** (135 mg, 98 %) as colorless solid; mp: 95 – 98 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.74 (dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 8.16 – 8.11 (m, 1H, $CH_{b.Thio}$), 8.05 (s, 1H, $CH_{b.Thio}$), 8.00 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.97 – 7.90 (m, 1H, $CH_{b.Thio}$), 7.53 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.45 – 7.38 (m, 2H, $CH_{b.Thio}$), 7.33 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 7.30 (d, ^3J = 8.0 Hz, 2H, CH_{Ar}) ppm. **^{19}F NMR (471 MHz, $CDCl_3$)** δ = −62.88 ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 156.1 (C_{Pyr}), 149.1, 140.7 (CH_{Ar}), 140.1, 138.1, 135.1 (C_{Ar}), 131.8 (CH_{Ar}), 130.4 (q, $^2J_{C,F}$ = 33.1 Hz, CCF_3), 128.5 (CH_{Ar}), 126.5 (q, $^5J_{C,F}$ = 1.4 Hz, C_{Ar}), 125.4 (q, $^3J_{C,F}$ = 3.8 Hz, CH_{Ar}), 124.7 (q, $^4J_{C,F}$ = 1.6 Hz, CH_{Ar}), 124.3 (CH_{Ar}), 124.0 (q, $^1J_{C,F}$ = 272.1 Hz, CF_3), 122.7, 121.7 (CH_{Ar}), 118.7 (C_{Ar}), 93.8, 89.7 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3054 (w), 2926 (w), 1613 (m), 1550 (w), 1513 (w), 1432 (m), 1412 (m), 1321 (s), 1156 (s), 1102 (s), 1065 (s), 1016 (s), 841 (s), 808 (s), 764 (s), 752 (s), 727 (s), 635 (m), 593 (s), 579 (m), 429 (m). **MS (EI, 70 eV)**:

m/z (%) = 379 ([M]$^+$, 70), 378 (100), 377 (15), 310 (25), 309 (32), 308 (12), 179 (10), 155 (29), 154 (20), 75 (10), 69 (18). **HRMS (ESI-TOF)** calcd. for $C_{22}H_{12}F_3NS$ ([M+H]$^+$) 380.0721, found 380.0725.

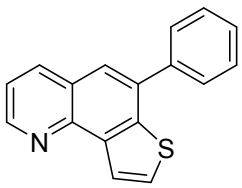
General procedure for the synthesis of benzo- and thieno[*h*]quinolines 4a-u:



3aa-cf **4aa-cf**

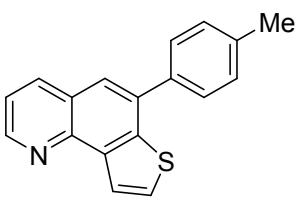
The starting materials **3aa-cf** were mixed with MsOH (30 eq.) under argon atmosphere. It was stirred for 3 h at room temperature. The reaction mixture was then neutralized with saturated Na_2CO_3 solution and washed. The crude products were then extracted with EtOAc and purified by column chromatography (Heptane/EtOAc, 5:1) to obtain the pure cyclization products **4aa-cf**.

6-phenylthieno[2,3-*h*]quinoline 4aa



According to the general rule, from **3aa** (0.38 mmol, 100 mg) was synthesized the light yellow solid **4aa** (95 mg, 95 %); mp: 141 – 144 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.98 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.45 (d, ^3J = 5.3 Hz, 1H, $CH_{Th.quin}$), 8.25 (dd, ^3J = 8.2 Hz, ^3J = 1.7 Hz, 1H, $CH_{Th.quin}$), 7.80 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 2H, CH_{Ph}), 7.67 (s, 1H, $CH_{Th.quin}$), 7.65 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.58 – 7.49 (m, 3H, CH_{Ph}), 7.47 (dd, ^3J = 8.2 Hz, ^3J = 4.4 Hz, 1H, $CH_{Th.quin}$) ppm. **^{13}C NMR (75 MHz, CDCl3)** δ = 149.2 ($CH_{Th.quin}$), 144.0, 140.8, 140.0, 138.0 ($C_{Th.quin}$), 136.5 ($CH_{Th.quin}$), 136.2 ($C_{Th.quin}$), 129.0, 128.6, 128.5 (CH_{Ph}), 127.0 ($CH_{Th.quin}$), 126.5 ($C_{Th.quin}$), 123.8, 123.3, 121.1 ($CH_{Th.quin}$) ppm. **IR** (ATR, cm^{-1}): ṽ = 3090 (w), 3061 (w), 3024 (w), 1587 (w), 1550 (w), 1484 (m), 1449 (w), 1441 (w), 1375 (w), 1360 (w), 1127 (m), 1072 (w), 1024 (w), 928 (m), 909 (w), 868 (m), 845 (m), 777 (m), 761 (m), 734 (s), 705 (s), 682 (m), 651 (m), 600 (m), 575 (m), 488 (m), 449 (m). **MS (EI, 70 eV)**: m/z (%) = 261 ([M]$^+$, 100), 260 (68), 259 (9), 233 (5), 131 (10), 130 (14), 69 (6), 51 (5), 45 (5), 39 (5). **HRMS (EI)** calcd. for $C_{17}H_{10}FNS$ ([M]$^+$) 261.06067, found 261.06010.

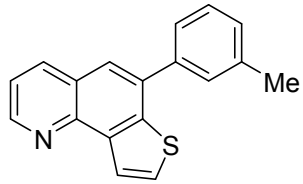
6-(*p*-tolyl)thieno[2,3-*h*]quinoline 4ab



According to the general rule, from **3ab** (0.38 mmol, 105 mg) was synthesized the brown solid **4ab** (86 mg, 82 %); mp: 133 – 138 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.97 (dd, ^3J = 4.4 Hz, ^3J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.44

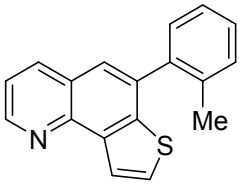
(d, ^3J = 5.5 Hz, 1H, $CH_{Th.quin}$), 8.25 (dd, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 1H, $CH_{Th.quin}$), 7.70 (d, ^3J = 8.1 Hz, 2H, $CH_{p\text{-}Tolyl}$), 7.66 (s, 1H, $CH_{Th.quin}$), 7.66 (d, ^3J = 5.2 Hz, 1H, $CH_{Th.quin}$), 7.46 (dd, ^3J = 8.2 Hz, ^3J = 4.4 Hz, 1H, $CH_{Th.quin}$), 7.35 (d, ^3J = 7.9 Hz, 2H, $CH_{p\text{-}Tolyl}$), 2.47 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.1 ($CH_{Th.quin}$), 144.0, 138.5, 138.0, 137.2 (C_{Ar}), 136.6 (CH_{Ar}), 136.3, 133.8 (C_{Ar}), 129.8, 128.4 ($CH_{p\text{-}Tolyl}$), 127.0 (CH_{Ar}), 126.6 (C_{Ar}), 123.8, 123.1, 121.1 (CH_{Ar}), 21.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3064 (w), 2917 (m), 2850 (m), 1737 (w), 1587 (w), 1550 (w), 1514 (w), 1180 (m), 1142 (m), 1128 (m), 1110 (m), 1040 (m), 1019 (m), 870 (m), 847 (m), 814 (m), 775 (m), 730 (m), 684 (m), 597 (m), 494 (m), 477 (m), 458 (m). **MS (EI, 70 eV):** *m/z* (%) = 275 ([M]$^+$, 100), 274 (42), 272 (12). **HRMS (EI)** calcd. for $C_{18}H_{13}NS$ ([M]$^+$) 275.07632, found 275.07616.

6-(*m*-tolyl)thieno[2,3-*h*]quinoline 4ac



According to the general rule, from **3ac** (0.38 mmol, 105 mg) was synthesized the yellow solid **4ac** (54 mg, 52 %); mp: 115 – 118 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.97 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.44 (d, ^3J = 5.5 Hz, 1H, $CH_{Th.quin}$), 8.24 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 7.66 (s, 1H, $CH_{Th.quin}$), 7.66 (d, ^3J = 5.0 Hz, 1H, $CH_{Th.quin}$), 7.63 – 7.58 (m, 2H, $CH_{m\text{-}Tolyl}$), 7.46 (dd, ^3J = 8.1 Hz, ^3J = 4.4 Hz, 1H, $CH_{Th.quin}$), 7.42 (d, ^3J = 8.0 Hz, 1H, $CH_{m\text{-}Tolyl}$), 7.30 (d, ^3J = 7.6 Hz, 1H, $CH_{m\text{-}Tolyl}$), 2.48 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.3 ($CH_{Th.quin}$), 144.2, 140.8, 140.0, 138.7, 138.1 (C_{Ar}), 136.4 (CH_{Ar}), 136.3 (C_{Ar}), 129.3, 129.2, 128.9, 126.9 (CH_{Ar}), 126.5 (C_{Ar}), 125.6, 123.8, 123.2, 121.1 (CH_{Ar}), 21.7 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3098 (w), 3078 (w), 2919 (w), 2851 (w), 1739 (w), 1603 (w), 1580 (w), 1550 (w), 1471 (m), 1373 (m), 1128 (m), 1070 (m), 934 (m), 912 (m), 872 (m), 789 (m), 728 (m), 709 (m), 681 (m), 651 (m), 507 (m), 482 (m), 463 (m). **MS (EI, 70 eV)**: *m/z* (%) = 275 ([M]$^+$, 100), 274 (42), 273 (10). **HRMS (EI)**: calcd. for $C_{18}H_{13}NS$ ([M]$^+$) 275.07632, found 275.07550.

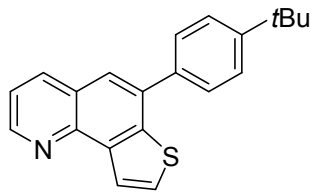
6-(*o*-tolyl)thieno[2,3-*h*]quinoline 4ad



According to the general rule, from **3ad** (0.38 mmol, 105 mg) was synthesized the yellow oil **4ad** (70 mg, 67 %). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ = 9.00 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.43 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 8.24 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 7.63 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.54 (s, 1H, $CH_{Th.quin}$), 7.48 (dd, ^3J = 8.2 Hz, ^3J = 4.4 Hz, 1H, $CH_{Th.quin}$), 7.44 – 7.31 (m, 4H, $CH_{o\text{-}Tolyl}$), 2.20 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.4 (CH_{Ar}), 144.2, 142.3, 139.4, 137.5 (C_{Ar}), 136.3 (CH_{Ar}), 136.3, 135.9 (C_{Ar}), 130.6, 129.6, 128.6, 127.2 (CH_{Ar}), 126.2 (C_{Ar}), 126.0, 123.8, 123.6, 121.0 (CH_{Ar}), 20.0 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3054 (w), 3023 (w), 2920 (w), 1600 (w), 1550 (w), 1485 (m), 1472 (m), 1472 (m), 1452 (m), 1374 (m), 1361 (m), 1352 (m), 1109 (m), 976 (m), 847 (s), 788 (m), 761 (s), 727 (s), 690 (m), 604 (m), 586 (m), 478 (m), 437 (m). **MS (EI, 70 eV):** *m/z* (%) = 275 ([M]$^+$, 100), 274 (52),

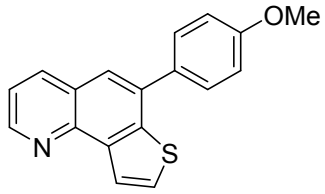
273 (14), 272 (12), 242 (23), 241 (24). **HRMS (EI)** calcd. for $C_{18}H_{13}NS$, ($[M]^+$) 275.07632, found 275.07599.

6-(4-(*tert*-butyl)phenyl)thieno[2,3-*h*]quinoline 4ae



According to the general rule, from **4ae** (0.38 mmol, 121 mg) was synthesized the brown solid **4ae** (111 mg, 92 %); mp: 111 – 112 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.97 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.45 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 8.25 (dd, ^3J = 8.2 Hz, ^4J = 1.8 Hz, 1H, $CH_{Th.quin}$), 7.76 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.68 (s, 1H, $CH_{Th.quin}$), 7.66 (d, ^3J = 5.5 Hz, 1H, $CH_{Th.quin}$), 7.57 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.46 (dd, ^3J = 8.2 Hz, ^3J = 4.4 Hz, 1H, $CH_{Th.quin}$), 1.42 (s, 9H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 151.6 (C_{Ar}), 149.2 ($CH_{Th.quin}$), 144.2, 140.8, 138.2, 137.1 (C_{Ar}), 136.4 (CH_{Ar}), 136.1 (C_{Ar}), 129.0, 128.5, 128.2, 126.7 (CH_{Ar}), 126.6 (C_{Ar}), 126.0, 123.8, 123.2, 121.1 (CH_{Ar}), 34.9 ($C_{t\mathrm{Bu}}$) 31.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3084 (w), 3028 (w), 2960 (m), 2902 (w), 2865 (w), 1602 (w), 1587 (w), 1550 (w), 1517 (w), 1488 (m), 1472 (m), 1400 (w), 1364 (m), 1263 (m), 1200 (w), 1130 (m), 1105 (m), 1074 (m), 1018 (m), 940 (w), 907 (m), 876 (m), 833 (s), 798 (m), 728 (s), 684 (m), 647 (w), 606 (s), 550 (m), 538 (m), 470 (w). **MS (EI, 70 eV)**: *m/z* (%) = 317 ($[M]^+$, 57), 303 (22), 302 (100), 274 (112), 260 (10), 137 (18). **HRMS (EI)** calcd. for $C_{21}H_{19}NS$ ($[M]^+$) 317.12327, found 317.12337.

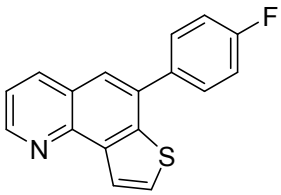
6-(4-methoxyphenyl)thieno[2,3-*h*]quinoline 4af



According to the general rule, from **3af** (0.38 mmol, 111 mg) was synthesized as an brown oil **4af** (91 mg, 82 %). **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.96 (dd, ^3J = 4.3 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.42 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 8.26 (dd, ^3J = 8.2 Hz, ^3J = 1.7 Hz, 1H, $CH_{Th.quin}$), 7.74 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 7.66 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.64 (s, 1H, $CH_{Th.quin}$), 7.47 (dd, ^3J = 8.2 Hz, ^3J = 4.4 Hz, 1H, $CH_{Th.quin}$), 7.08 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 3.91 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 160.0 (C_{OMe}), 149.3 ($CH_{Th.quin}$), 144.3, 141.0, 138.2 (C_{Ar}), 136.3 ($CH_{Th.quin}$), 135.9, 132.6 (C_{Ar}), 129.7 (CH_{Ar}), 126.8 ($CH_{Th.quin}$), 126.6 (C_{Ar}), 123.8, 123.0, 121.1 ($CH_{Th.quin}$), 114.5 (CH_{Ar}), 55.6 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3009 (w), 2959 (w), 2833 (w), 1603 (m), 1568 (w), 1513 (m), 1490 (m), 1451 (m), 1438 (m), 1372 (m), 1304 (w), 1284 (m), 1241 (s), 1177 (s), 1127 (m), 1111 (m), 1084 (m), 1028 (s), 938 (m), 890 (m), 835 (s), 812 (m), 787 (s), 777 (m), 734 (s), 723 (s), 686 (s), 624 (m), 596 (s), 556 (m), 517 (s), 464 (m). **MS (EI, 70 eV)**: *m/z* (%) = 291 ($[M]^+$, 100), 276 (17), 249 (7), 248 (29), 247 (32),

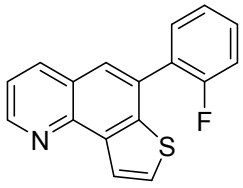
246 (13), 222 (5), 146 (6), 63 (5), 45 (6). **HRMS (EI)** calcd. for $C_{17}H_{10}FNS$ ($[M]^+$) 292.0796, found 292.0797.

6-(4-fluorophenyl)thieno[2,3-*h*]quinoline 4ah



According to the general rule, from **3ah** (0.38 mmol, 106 mg) was synthesized the colourless solid **4ah** (76 mg, 72 %); mp: 168 – 170 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.97 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.chin}$), 8.43 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 8.24 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 7.79 – 7.70 (m, 2H, CH_{Ar}), 7.65 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.62 (s, 1H, $CH_{Th.quin}$), 7.47 (dd, ^3J = 8.2 Hz, ^3J = 4.4 Hz, 1H, $CH_{Th.quin}$), 7.26 – 7.18 (m, 2H, CH_{Ar}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = −113.23 ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 163.0 (d, $^1J_{C,F}$ = 247.9 Hz, CF), 149.5 ($CH_{Th.quin}$), 144.2, 140.7, 138.3 ($C_{Th.quin}$), 136.4 ($CH_{Th.quin}$), 136.1 (d, $^4J_{C,F}$ = 3.3 Hz, C_{Ar}), 135.1 ($C_{Th.quin}$), 130.3 (d, $^3J_{C,F}$ = 8.1 Hz, CH_{Ar}), 127.0 ($CH_{Th.quin}$), 126.5 ($C_{Th.quin}$), 123.9, 123.4, 121.2 ($CH_{Th.quin}$), 116.0 (d, $^2J_{C,F}$ = 21.5 Hz, CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3034 (w), 1904 (w), 1762 (w), 1658 (w), 1512 (m), 1492 (m), 1473 (m), 1222 (m), 1160 (m), 1141 (m), 1130 (m), 1098 (m), 897 (m), 881 (m), 834 (m), 785 (m), 730 (m), 717 (m), 687 (m), 595 (m), 538 (m), 508 (m), 466 (m). **MS (EI, 70 eV)**: *m/z* (%) = 279 ($[M]^+$, 100), 278 (59). **HRMS (EI, 70 eV)** calcd. for $C_{17}H_{10}NFS$ ($[M]^+$) 279.05125, found 279.05089.

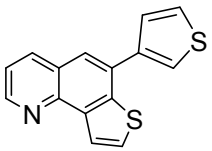
6-(2-fluorophenyl)thieno[2,3-*h*]quinoline 4ai



According to the general rule, from **3ai** (0.38 mmol, 106 mg) was synthesized the yellow solid **4ai** (55 mg, 52 %); mp: 87 – 89 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.61 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.04 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.85 (dd, ^3J = 8.3 Hz, ^4J = 1.6 Hz, 1H, $CH_{Th.quin}$), 7.32 (d, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.29 (dd, ^3J = 7.9 Hz, ^3J = 1.8 Hz, 1H, $CH_{Th.quin}$), 7.26 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.08 (dd, ^3J = 8.2 Hz, ^3J = 4.4 Hz, 2H,CH_{Ar}), 6.92 (dd, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, CH_{Ar}), 6.87 (dd, ^3J = 7.7 Hz, ^3J = 1.0 Hz, 1H, CH_{Ar}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = –114.31 ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 159.8 (d, ^1J = 248.3 Hz, CF), 149.7($CH_{Th.quin}$), 144.4, 141.4, 138.0 ($CH_{Th.quin}$), 136.4 ($CH_{Th.quin}$), 131.2 (d, ^4J = 3.0 Hz, CH_{Ar}), 130.4 (d, ^3J = 8.1 Hz, CH_{Ar}), 129.8 ($C_{Th.quin}$) 127.2 (d, ^2J = 15.2 Hz, C_{Ar}), 126.9 ($CH_{Th.quin}$), 126.0 ($CH_{Th.quin}$), 125.0 (d, ^3J = 2.0 Hz, $C_{Th.quin}$), 124.5 (d, ^3J = 3.7 Hz, CH_{Ar}), 123.7, 121.1 ($CH_{Th.quin}$), 116.4 (d, ^2J = 22.1 Hz, CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3056 (w), 3002 (w), 2922 (w), 2853 (w),

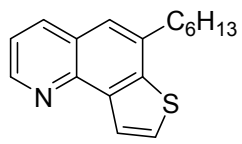
1934 (w), 1760 (w), 1577 (w), 1551 (w), 1481 (m), 1457 (m), 1361 (m),1210 (m), 1129 (m), 1104 (m), 1077 (w), 1035 (w), 942 (w), 917 (w), 882 (m), 849 (m), 783 (m), 673 (m), 646 (m). **MS (EI, 70 eV):** *m/z* (%) = 279 ([M]$^+$, 100), 278 (39), 260 (20). **HRMS (EI)** calcd. for $C_{17}H_{10}FNS$, ([M]$^+$) 279.05125, found 279.05121.

6-(thiophen-3-yl)thieno[2,3-*h*]quinoline 4ak



According to the general rule, from **3ak** (0.38 mmol, 102 mg) was synthesized the brown solid **4ak** (60 mg, 59 %); mp: 101 – 104 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.95 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.43 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 8.22 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 7.82 (dd, ^4J = 2.9 Hz, ^4J = 1.4 Hz, 1H, CH_{Thio}), 7.75 (s, 1H, $CH_{Th.quin}$), 7.66 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.59 (dd, ^3J = 5.0 Hz, ^4J = 1.4 Hz, 1H, CH_{Thio}), 7.50 (dd, ^3J = 5.0 Hz, ^4J = 2.9 Hz, 1H, CH_{Thio}), 7.45 (dd, ^3J = 8.2 Hz, ^3J = 4.4 Hz, 1H, $CH_{Th.quin}$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.3 ($CH_{Th.quin}$), 144.1, 140.5 140.3, 138.3 (C_{Ar}), 136.4 (CH_{Ar}), 130.8 (C_{Ar}), 127.7, 126.8, 126.5 (CH_{Ar}), 126.4 (C_{Ar}), 123.9, 123.5, 122.8, 121.2 (CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3092 (w), 3078 (w), 2919 (w), 2848 (w), 1582 (w), 1553 (w), 1494 (w), 1470 (w), 1373 (w), 1334 (m), 1258 (w), 1073 (w), 913 (m), 877 (m), 863 (m), 838 (m), 803 (m), 724 (m), 683 (m), 651 (m), 579 (m), 562 (m), 484 (w), 465 (m). **MS (EI, 70 eV)**: *m/z* (%) = 267 ([M]$^+$, 100), 266 (31). **HRMS (EI)** calcd. for $C_{15}H_8NS_2$ ([M]$^+$) 266.00927, found 266.00937.

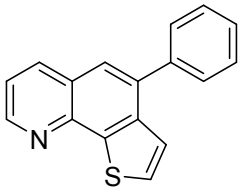
6-hexylthieno[2,3-*h*]quinoline 4al



According to the general rule, from **3al** (0.38 mmol, 102 mg) was synthesized at elevated temperature (120 °C) the brown solid **4al** (61 mg, 59 %); mp: 60 – 65 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.92 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.38 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 8.19 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 7.62 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.48 (s, 1H, $CH_{Th.quin}$), 7.44 (dd, ^3J = 8.2 Hz, ^3J = 4.4 Hz, 1H, $CH_{Th.quin}$), 3.02 (t, ^3J = 7.6 Hz, 2H, CH_2), 1.87 (dd, ^3J = 15.4 Hz, ^3J = 7.8 Hz, 2H, CH_2), 1.36 (ddd, ^3J = 9.5 Hz, ^3J = 4.7 Hz, ^3J = 1.6 Hz, 4H, CH_2), 1.27 (d, ^3J = 9.1 Hz, 2H, CH_2), 0.90 (t, ^3J = 7.0 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.6 ($CH_{Th.quin}$), 143.9, 141.9, 137.4, 136.2 (C_{Ar}), 136.0 (CH_{Ar}), 126.6 (C_{Ar}), 125.8, 123.9, 122.0, 120.8 (CH_{Ar}), 35.0, 31.8, 29.4, 29.2, 22.7 (CH_2), 14.2 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3044 (m), 2947 (m), 2926 (m), 2850 (m), 1937 (w), 1908 (w), 1879 (w), 1795 (w), 1673 (m), 1588 (m), 1492

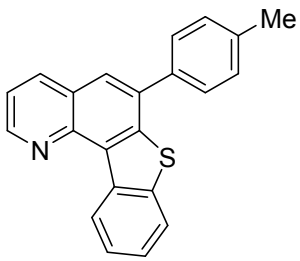
(m), 1452 (m), 1376 (m), 1132 (m), 1038 (m), 896 (m), 858 (m), 805 (w), 779 (m), 753 (s), 730 (s), 672 (m), 651 (m), 533 (w), 477 (w), 441 (w). **MS (EI, 70 eV)**: *m/z* (%) = 269 ([M]$^+$, 30), 210 (11), 200 (15), 199 (100), 198 (71), 154 (17), 43 (13), 41 (16). **HRMS (EI)** calcd. for $C_{17}H_{19}NS$ ([M]$^+$) 269.12327, found 269.12277.

4-phenylthieno[3,2-*h*]quinoline 4ba



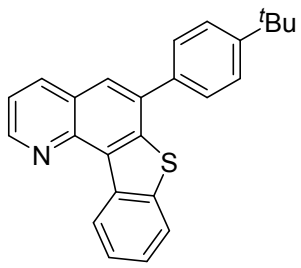
According to the general rule, from **3ba** (0.38 mmol, 100 mg) was synthesized the purple solid **4ba** (57 mg, 57 %); mp: 68 – 71 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.93 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.24 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 7.67 – 7.62 (m, 4H, CH_{Ar}), 7.57 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.56 – 7.44 (m, 4H, CH_{Ar}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.6 ($CH_{Th.quin}$), 144.2, 140.3, 139.4, 139.2, 137.3 (C_{Ar}), 136.6 (CH_{Ar}), 129.3, 128.7 (CH_{Ph}), 128.2, 128.0 (CH_{Ar}), 125.7 (C_{Ar}), 124.7, 124.2, 121.4 (CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3052 (w), 3023 (w), 2920 (w), 2850 (w), 1948 (w), 1889 (w), 1732 (w), 1492 (m), 1435 (m), 1332 (m), 1031 (m), 1010 (m), 994 (m), 973 (m), 874 (m), 852 (m), 784 (s), 692 (s), 766 (s), 646 (s), 577 (m), 432 (s), 416 (s). **MS (EI, 70 eV)**: *m/z* (%) = 262 ([M]$^+$, 19), 261 (100), 260 (33), 216 (15), 108 (12). **HRMS (ESI-TOF)** calcd. for $C_{17}H_{11}NS$ ([M+H]$^+$) 262.0690, found 262.0691.

6-(*p*-tolyl)benzo[4,5]thieno[2,3-*h*]quinoline 4ca



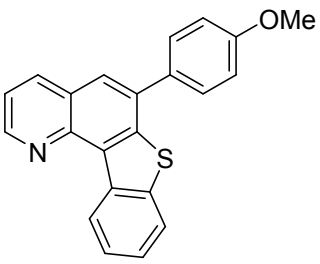
According to the general rule, from **3ca** (0.38 mmol, 124 mg) was synthesized the colourless solid **4ca** (92 mg, 74 %); mp: 161 – 164 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 9.91 (dd, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1H, $CH_{B.th.quin}$), 9.11 (dd, ^3J = 4.2 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 8.27 (d, ^3J = 8.2 Hz, ^4J = 0.9 Hz, 1H, $CH_{B.th.quin}$), 7.94 (d, ^3J = 8.0 Hz, 1H, $CH_{B.th.quin}$), 7.76 (s, 1H, $CH_{B.th.quin}$), 7.71 (d, ^3J = 8.0 Hz, 2H, $CH_{p\text{-}Tolyl}$), 7.68 – 7.60 (m, 1H, $CH_{B.th.quin}$), 7.56 – 7.52 (m, 1H, $CH_{B.th.quin}$), 7.48 (dd, ^3J = 8.2 Hz, ^3J = 4.3 Hz, 1H, $CH_{B.th.quin}$), 7.38 (d, ^3J = 8.2 Hz, 2H, $CH_{p\text{-}Tolyl}$), 2.50 (s, 1H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.6 ($CH_{B.th.quin}$), 145.8, 141.8, 139.6, 138.5, 137.2, 137.2 (C_{Ar}), 136.4 ($CH_{B.th.quin}$), 136.3, 131.2 (C_{Ar}), 129.7, 128.6 (CH_{Ar}), 128.0 ($CH_{B.th.quin}$), 126.8 (C_{Ar}), 126.1, 125.5, 125.1, 122.1, 120.6 ($CH_{B.th.quin}$), 21.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3053 (w), 3020 (w), 2916 (w), 1903 (w), 1795 (w), 1731 (w) 1656 (w), 1601 (w), 1583 (w), 1513 (w), 1485 (w), 1455 (w), 1439 (w), 1253 (w), 866 (w), 813 (m), 801 (m), 783 (w), 723 (m), 596 (w), 491 (w), 463 (w), 428 (w). **MS (EI, 70 eV)**: *m/z* (%) = 325 ([M]$^+$, 100), 324 (30), 323 (12), 162 (14), 91 (25), 73 (10), 69 (11), 65 (17), 63 (19), 51 (18), 45 (15), 39 (40). **HRMS (EI)** calcd. for $C_{22}H_{15}NS$ ([M]$^+$) 325.09197, found 325.0918.

6-(4-(*tert*-butyl)phenyl)benzo[4,5]thieno[2,3-*h*]quinoline 4cb



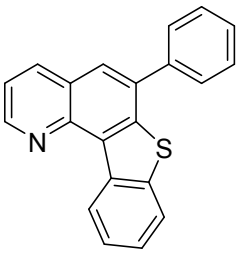
According to the general rule, from **3cb** (0.38 mmol, 140 mg) was synthesized the light brown solid **4cb** (119 mg, 85 %); mp: 192 – 194 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 9.91 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 1H, $CH_{B.th.quin}$), 9.11 (dd, ^3J = 4.3 Hz, ^3J = 1.8 Hz, 1H, $CH_{B.th.quin}$), 8.29 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 1H, $CH_{B.th.quin}$), 7.94 (d, ^3J = 7.9 Hz, 1H, $CH_{B.th.quin}$), 7.79 (s, 1H, $CH_{B.th.quin}$), 7.76 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.64 (ddd, ^3J = 8.2 Hz, ^3J = 7.1 Hz, ^4J = 1.1 Hz, 1H, $CH_{B.th.quin}$), 7.59 (d, ^3J = 8.4 Hz, 2H, CH_{Ar}), 7.53 (ddd, ^3J = 8.2 Hz, ^3J = 7.2 Hz, ^3J = 1.3 Hz, 1H, $CH_{B.th.quin}$), 7.50 (dd, ^3J = 8.1 Hz, ^3J = 4.3 Hz, 1H, $CH_{B.th.quin}$), 1.44 (s, 9H, CH_3). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 151.7 (C_{tBu}), 149.6 ($CH_{B.th.quin}$), 145.8, 141.8, 139.6, 137.2, 137.1 (C_{Ar}), 136.4 ($CH_{B.th.quin}$), 136.2, 131.2 (C_{Ar}), 128.4 (CH_{Ar}), 128.0 ($CH_{B.th.quin}$), 126.9 (C_{Ar}), 126.1 ($CH_{B.th.quin}$), 125.9 (CH_{Ar}), 125.6, 125.1, 122.1, 120.6 ($CH_{B.th.quin}$), 34.9 (C_{tBu}), 31.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3054 (w), 3027 (w), 2959 (m), 2866 (w), 1599 (w), 1583 (w), 1513 (w), 1486 (m), 1438 (m), 1403 (w), 1350 (m), 1265 (w), 1236 (w), 1201 (w), 1117 (m), 1020 (m), 925 (m), 876 (m), 859 (w), 828 (s), 804 (m), 775 (s), 752 (m), 729 (s), 643 (m), 602 (s), 548 (m), 536 (m), 503 (m), 429 (m). **MS (EI, 70 eV)**: *m/z* (%) = 367 ([M]$^+$, 88), 353 (21), 352 (100), 336 (16), 334 (12), 324 (14), 323 (10), 322 (13), 311 (15), 310 (17), 309 (10), 308 (12), 162 (15), 41 (11), 39 (10). **HRMS (ESI-TOF)** calcd. for $C_{25}H_{21}NS$ ([M+H]$^+$) 368.1473, found 368.1469.

6-(4-methoxyphenyl)benzo[4,5]thieno[2,3-*h*]quinoline 4cc



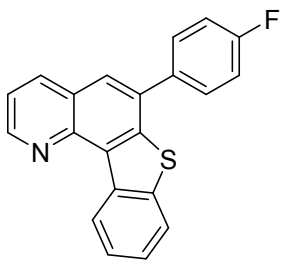
According to the general rule, from **3cc** (0.38 mmol, 130 mg) was synthesized the light brown solid **4cc** (84 mg, 65 %); mp: 207 – 210 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 9.90 (d, ^3J = 8.1 Hz, 1H, $CH_{B.th.quin}$), 9.10 (dd, ^3J = 4.2 Hz, ^4J = 1.6 Hz, 1H, $CH_{B.th.quin}$), 8.29 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1H, $CH_{B.th.quin}$), 7.94 (d, ^3J = 7.9 Hz, 1H, $CH_{B.th.quin}$), 7.75 (s, 1H, $CH_{B.th.quin}$), 7.75 (d, ^3J = 8.4 Hz, 2H, CH_{Ar}), 7.64 (t, ^3J = 7.6 Hz, 1H, $CH_{B.th.quin}$), 7.58 – 7.45 (m, 1H, $CH_{B.th.quin}$), 7.09 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 3.92 (s, 3H, CH_3) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 160.0 (C_{OMe}), 149.6 ($CH_{B.th.quin}$), 145.8, 142.0, 139.6, 137.2 (C_{Ar}), 136.4 ($CH_{B.th.quin}$), 136.0, 132.5, 131.2 (C_{Ar}), 129.9 (CH_{Ar}), 128.0 ($CH_{B.th.quin}$), 126.9 (C_{Ar}), 126.1, 125.4, 125.1, 122.2, 120.6 ($CH_{B.th.quin}$), 114.4 (CH_{Ar}), 55.6 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3017 (w), 2959 (m), 2922 (m), 2835 (m), 1603 (m), 1508 (s), 1486 (m), 1459 (m), 1436 (m), 1352 (m), 1284 (m), 1238 (s), 1175 (s), 1164 (m), 1160 (m), 1131 (m), 1125 (m), 1121 (m), 1105 (m), 1069 (m), 1024 (s), 975 (m), 925 (m), 878 (m), 861 (m), 826 (s), 791 (s), 754 (s), 729 (s), 715 (m), 713 (m), 641 (m), 626 (m), 596 (s), 542 (s), 511 (s), 427 (m). **MS (EI, 70 eV)**: *m/z* (%) = 341 ([M]$^+$, 100), 326 (12), 298 (25), 297 (30), 296 (12), 170 (9), 148 (14), 69 (5), 63 (5), 39 (6). **HRMS (EI)** calcd. for $C_{22}H_{15}NOS$ ([M]$^+$) 341.08743, found 341.086886.

6-phenylbenzo[4,5]thieno[2,3-*h*]quinoline 4cd



According to the general rule, from **3cd** (0.38 mmol, 118 mg) was synthesized the orange solid **4cd** (63 mg, 53%); mp: 176 – 182 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 9.92 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.3 Hz, 1H, $CH_{B.th.quin}$), 9.12 (dd, ^{3}J = 4.3 Hz, ^{4}J = 1.8 Hz, 1H, $CH_{B.th.quin}$), 8.28 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.8 Hz, 1H, $CH_{B.th.quin}$), 7.94 (dd, ^{3}J = 8.0 Hz, ^{4}J = 1.2 Hz, 1H, $CH_{B.th.quin}$), 7.81 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.5 Hz, 2H, CH_{Ph}), 7.78 (s, 1H, $CH_{B.th.quin}$), 7.65 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.1 Hz, ^{4}J = 1.2 Hz, 1H, $CH_{B.th.quin}$), 7.61 – 7.56 (m, 1H, $CH_{B.th.quin}$), 7.54 (m, 3H, CH_{Ph}), 7.49 (dd, ^{3}J = 8.2 Hz, ^{3}J = 4.3 Hz, 1H, $CH_{B.th.quin}$) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.7 ($CH_{B.th.quin}$), 145.8, 141.7, 140.1, 139.6, 137.1 (C_{Ar}), 136.5 (CH_{Ar}), 136.3, 131.2 (C_{Ar}), 129.0, 128.7 (CH_{Ph}), 128.6, 128.0 (CH_{Ar}), 126.8 (C_{Ar}), 126.1, 125.7, 125.1, 122.1, 120.6 (CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3045 (m), 3014 (m), 2918 (m), 2849 (m), 1731 (m), 1598 (m), 1583 (m), 1569 (m), 1351(m), 1119 (m), 1072 (m), 1041 (m), 1019 (m), 876 (m), 861 (m), 775 (s), 753 (s), 731 (s), 695 (s), 596 (m), 508 (m), 485 (m), 428 (m), 428 (m). **MS (EI, 70 eV)**: *m/z* (%) = 311 ($[M]^+$, 100), 310 (37), 155 (14). **HRMS (EI)** calcd. for $C_{21}H_{13}NS$ ($[M]^+$) 311.07632, found 311.07589.

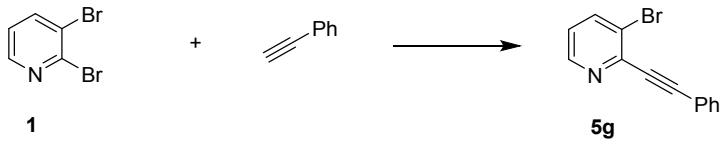
6-(4-fluorophenyl)benzo[4,5]thieno[2,3-*h*]quinoline 4ce



According to the general rule, from **3ce** (0.38 mmol, 125 mg) was synthesized the orange solid **4ce** (114 mg, 91 %); mp: 188 – 191 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 9.90 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.3 Hz, 1H, $CH_{B.th.quin}$), 9.13 (dd, ^{3}J = 4.3 Hz, ^{4}J = 1.8 Hz, 1H, $CH_{B.th.quin}$), 8.31 (dd, ^{3}J = 8.2 Hz, ^{4}J = 1.7 Hz, 1H, $CH_{B.th.quin}$), 7.94 (d, ^{3}J = 8.0 Hz, 1H, $CH_{B.th.quin}$), 7.78 (dd, ^{3}J = 8.8 Hz, $^{4}J_{H,F}$ = 5.3 Hz, 2H, CH_{Ar}), 7.77 (s, 1H, $CH_{B.th.quin}$), 7.68 – 7.61 (m, 1H, $CH_{B.th.quin}$), 7.55 (dd, ^{3}J = 5.1 Hz, ^{4}J = 2.1 Hz, 1H, $CH_{B.th.quin}$), 7.53 – 7.49 (m, 1H, $CH_{B.th.quin}$), 7.29 – 7.22 (m, 2H, CH_{Ar}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = –113.22 ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 163.0 (d, $^{1}J_{C,F}$ = 248.0 Hz, CF), 149.8 ($CH_{B.th.quin}$), 145.8, 141.5, 139.4, 137.1 ($C_{B.th.quin}$), 136.4 ($CH_{B.th.quin}$), 136.1 (d, $^{4}J_{C,F}$ = 3.3 Hz, C_{Ar}), 135.2, 131.3 ($C_{B.th.quin}$), 130.5 (d, $^{3}J_{C,F}$ = 8.2 Hz, CH_{Ar}), 128.1 ($CH_{B.th.quin}$), 126.7 ($C_{B.th.quin}$), 126.2, 125.7, 125.2,122.2, 120.7 ($CH_{B.th.quin}$), 116.0 (d, $^{2}J_{C,F}$ = 21.65 Hz, CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3062 (w), 3012 (w), 2920 (w), 1598 (m), 1506 (m), 1485 (m), 1458 (m), 1436 (m), 1285(m), 1156 (m), 1128 (m), 1070 (m), 924 (m), 835 (m), 819 (m), 783 (m), 732 (m), 694 (m), 593 (m), 512 (m), 430 (m). **MS (EI, 70 eV):** *m/z* (%) = 329 ($[M]^+$, 100), 328 (44), 164 (17), 75 (17), 69 (18), 63 (18), 63 (13), 57 (11), 51 (15), 50 (11), 45 (17), 39 (13). **HRMS (EI)** calcd. for $C_{21}H_{12}FNS$ ($[M]^+$) 329.06690, found 329.06658.

Synthesis of Thieno[2,3-*f*]quinolines

Optimisation – Synthesis of 3-bromo-2-(phenylethynyl)pyridine

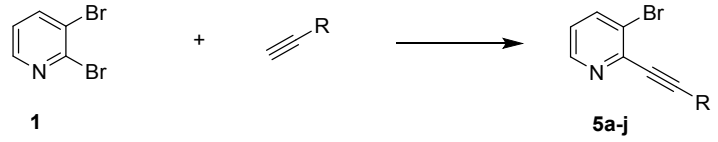


1 **5g**

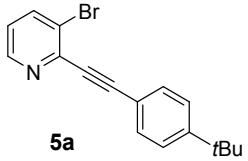
Table S3 *Optimisation – Synthesis of 3-bromo-2-(phenylethynyl)pyridine*

	Base	**T [°C]**	**t [h]**	**Yield [%]**
1	NEt_3	60	6	-
2	$HNiPr_2$	60	6	42
3	$HNiPr_2$	40	0.5	99

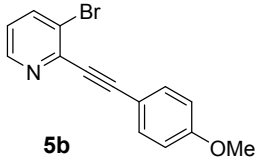
Table S4. *Site-Selective Sonogashira Reaction of 2,3-Dibromopyridine*



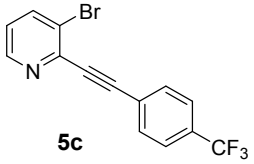
1 **5a-j**



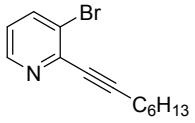
5a
90%



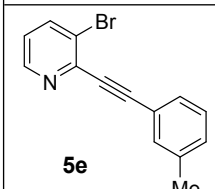
5b
95%



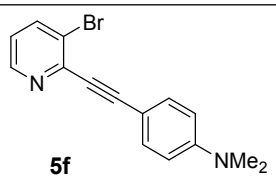
5c
94%



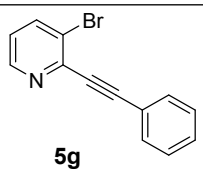
5d
94 %



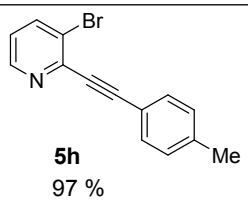
5e
96 %



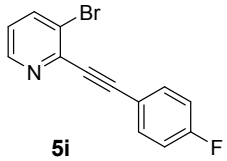
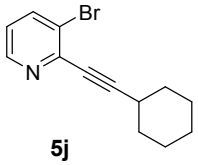
5f
55 %



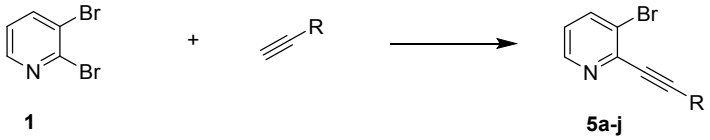
5g
99 %



5h
97 %

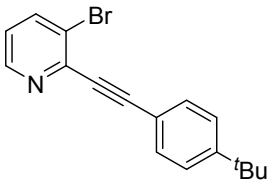
 **5i** 89 %	 **5j** 98 %		

Synthesis of 2-(alkynyl)-3-bromopyridines, 5a-j:



2,3-Dibromopyridine (1.0 mmol), $Pd(PPh_3)_4$ (5 mol%) and CuI (2 mol%) were dissolved in 6 mL of diisopropylamine ($HNiPr_2$) under an argon atmosphere. After addition of the corresponding alkyne (1.2 eq.) the reaction was stirred at 40 °C for 0.5 hours. After cooling to room temperature, the reaction mixture was washed with distilled water and extracted with ethyl acetate. The combined organic layers were collected and the solvent evaporated. The crude product was purified by column chromatography.

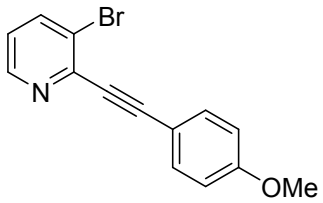
3-bromo-2-((4-(*tert*-butyl)phenyl)ethynyl)pyridine 5a



Following the general procedure, 2,3-dibromopyridine (1 mmol, 236.89 mg) and 4-*tert*-butylphenylacetylene (1.2 mmol, 216 µL) gave **5a** as a yellow solid (283 mg, 90 %), mp: 77 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.54 (dd, ^3J = 4.7, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.94 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.60 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.40 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.12 (dd, ^3J = 8.1, ^3J = 4.7 Hz, 1H, CH_{pyr}), 1.33 (s, 9H, $CH_{3\text{-}tBu}$) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 153.1 (C_{Ar}), 148.1 (CH_{pyr}), 143.8 (C_{pyr}), 140.2 (CH_{pyr}), 132.2 (CH_{Ar}), 125.6 (CH_{Ar}), 124.0 (C_{pyr}), 123.5 (CH_{pyr}), 118.9 (C_{Ar}), 95.3, 86.9 (C_{Alkyne}), 35.1 (C_{tBu}), 31.3 ($CH_{3\text{-}tBu}$) ppm. **IR** (ATR, cm^{-1}): ṽ = 2959 (m), 2901 (m), 2860 (m), 2217 (m), 1562 (s), 1508 (m), 1422 (s),

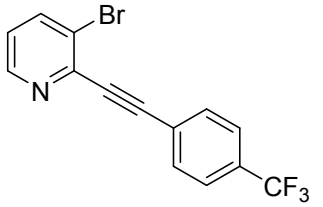
1362 (m), 1265 (m), 1123 (m), 1102 (m), 1059 (m), 1018 (s), 847 (s), 830 (s), 787 (s), 748 (s), 622 (m), 567 (s). **MS (EI, 70 eV):** *m/z* (%) = 315 ([M]$^+$, 32), 313 ([M]$^+$, 33), 300 (97), 298 (100), 117 (24), 151 (24), 95 (36), 51 (36), 41 (67), 39 (37). **HRMS (EI):** calcd. for $C_{17}H_{16}N_1Br_1$ (M)$^+$ 313.04606, found 313.04585; calcd. for $C_{17}H_{16}N_1{}^{81}Br_1$ (M)$^+$ 315.04402, found 315.04406.

3-bromo-2-((4-methoxyphenyl)ethynyl)pyridine 5b



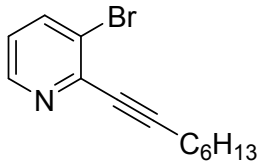
Following the general procedure, 2,3-dibromopyridine (1 mmol, 236.89 mg) and 4-methoxyphenylacetylene (1.2 mmol, 156 µL) gave **5b** as an orange oil (273.5 mg, 95 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.52 (dd, ^3J = 4.6, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.90 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.58 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 7.08 (dd, ^3J = 8.1, ^3J = 4.6 Hz, 1H, CH_{pyr}), 6.89 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 3.83 (s, 3H, CH_3) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 160.65 (C_{Ar}), 148.4 (CH_{pyr}), 144.2 (C_{pyr}), 139.9 (CH_{pyr}), 133.9 (CH_{Ar}), 123.6 (C_{pyr}), 123.3 (CH_{pyr}), 114.3 (CH_{Ar}), 114.1 (C_{Ar}), 94.6, 86.7 (C_{Alkyne}), 55.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3044 (w), 2957 (w), 2918 (w), 2835 (w), 2217 (m), 1603 (s), 1564 (s), 1508 (s), 1434 (m), 1416 (s), 1288 (s), 1247 (s), 1177 (m), 1156 (s), 1125 (m), 1014 (s), 828 (s), 789 (s), 748 (s), 530 (s). **MS (EI, 70 eV):** *m/z* (%) = 289 ([M]$^+$, 98), 287 ([M]$^+$, 100), 274 (31), 272 (31), 246 (7), 244 (8), 165 (33), 164 (28), 138 (17), 137 (9). **HRMS (ESI-TOF):** calcd. for $C_{14}H_{10}O_1N_1Br_1$ ([M+H]$^+$) 288.0024, found 288.0027.

3-bromo-2-((4-(trifluoromethyl)phenyl)ethynyl)pyridine 5c



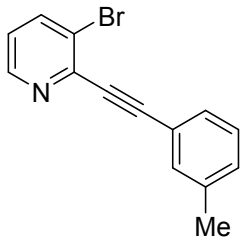
Following the general procedure, 2,3-dibromopyridine (1 mmol, 236.89 mg) and 4-trifluoromethylphenylacetylene (1.2 mmol, 196 µL) gave **5c** as a yellow solid (306.2 mg, 94 %), mp: 75 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.57 (dd, ^3J = 4.6, ^4J = 1.4 Hz, 1H, CH_{pyr}), 7.95 (dd, ^3J = 8.2, ^4J = 1.4 Hz, 1H, CH_{pyr}), 7.75 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.64 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.17 (dd, ^3J = 8.2, ^3J = 4.6 Hz, 1H, CH_{pyr}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -62.95 (s, 3F, CF_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.6 (CH_{pyr}), 143.3 (C_{pyr}), 140.1 (CH_{pyr}), 132.6 (CH_{Ar}), 131.1 (q, $^2J_{C,F}$ = 33.0 Hz, C_{Ar}), 125.9 (C_{Ar}), 125.9 (C_{pyr}), 125.5 (q, $^3J_{C,F}$ = 3.8 Hz, CH_{Ar}), 124.2 (CH_{pyr}), 123.9 (q, $^1J_{C,F}$ = 272.3 Hz, CF_3), 92.0, 89.4 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3046 (w), 2225 (w), 1418 (m), 1403 (m), 1315 (s), 1154 (s), 1102 (s), 1057 (s), 1018 (s), 1010 (s), 975 (m), 835 (s), 787 (s), 748 (s), 721 (m), 655 (m). **MS (EI, 70 eV):** *m/z* (%) = 327 ([M]$^+$, 99), 325 ([M]$^+$, 100), 246 (27), 226 (60), 199 (24), 177 (42), 150 (20), 98 (23), 51 (39), 50 (20). **HRMS (EI):** calcd. for $C_{14}H_7N_1Br_1F_3$ (M)$^+$ 324.97085 found 324.97135; calcd. for $C_{14}H_7N_1{}^{81}Br_1F_3$ (M)$^+$ 326.96880, found 326.96935.

3-bromo-2-(oct-1-yn-1-yl)pyridine 5d



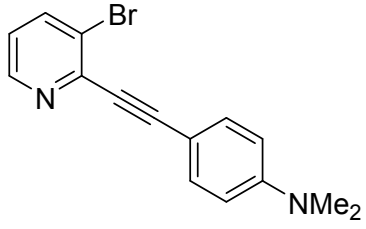
Following the general procedure, 2,3-dibromopyridine (1 mmol, 236.89 mg) and 1-octyne (1.2 mmol, 0.177 mL) gave **5d** as a brown oil (261.6 mg, 94 %). **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.47 (dd, ^3J = 4.7, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.86 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.06 (dd, ^3J = 8.1 Hz, ^3J = 4.7 Hz, 1H, CH_{pyr}), 2.50 (t, ^3J = 7.0 Hz, 2H, CH_2), 1.73 – 1.60 (m, 2H, CH_2), 1.56 – 1.44 (m, 2H, CH_2), 1.35 – 1.29 (m, 4H, CH_2), 0.90 (t, ^3J = 7.0 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.2 (CH_{pyr}), 144.3 (C_{pyr}), 139.8 (CH_{pyr}), 123.6 (C_{pyr}), 123.2 (CH_{pyr}), 96.8, 79.4 (C_{Alkyne}), 31.5, 28.7, 28.3, 22.7, 19.7 (CH_2), 14.2 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2953 (m), 2928 (m), 2856 (m), 2232 (m), 1566 (m), 1422 (s), 1125 (m), 1069 (m), 1016 (s), 789 (s), 750 (s), 723 (m), 645 (m). **MS (EI, 70 eV):** *m/z* (%) = 267 ([M]$^+$, 2), 265 ([M]$^+$, 2), 224 (24), 222 (25), 210 (48), 208 (47), 197 (34), 195 (30), 186 (100), 158 (37), 117 (28), 116 (59), 115 (69), 114 (30), 102 (27), 89 (43), 88 (41), 75 (26), 63 (36), 62 (34), 51 (39), 43 (70), 41 (94), 39 (56), 29 (74). **HRMS (EI):** calcd. for $C_{13}H_{16}N_1Br_1$ (M)$^+$ 265.04606 found 265.04569; calcd. for $C_{13}H_{16}N_1{}^{81}Br_1$ (M)$^+$ 267.04402, found 267.04374.

3-bromo-2-(*m*-tolylethynyl)pyridine 5e



Following the general procedure, 2,3-dibromopyridine (1 mmol, 236.89 mg) and 3-methylphenylacetylene (1.2 mmol, 155 µL) gave **5e** as a yellow solid (262.3 mg, 96 %), mp: 65 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.54 (dd, ^3J = 4.6, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.92 (dd, ^3J = 8.2, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.48 – 7.46 (m, 1H, CH_{Ar}), 7.48 – 7.43 (m, 1H, CH_{Ar}), 7.30 – 7.23 (m, 1H, CH_{Ar}), 7.23 – 7.18 (m, 1H, CH_{Ar}), 7.11 (dd, ^3J = 8.2, ^3J = 4.6 Hz, 1H, CH_{pyr}), 2.37 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.4 (CH_{pyr}), 144.0 (C_{pyr}), 139.9 (CH_{pyr}), 138.3 (C_{Ar}), 132.9, 130.4, 129.4, 128.5 (CH_{Ar}), 123.9 (C_{Ar}), 123.6 (CH_{pyr}), 121.9 (C_{pyr}), 94.5, 87.3 (C_{Alkyne}), 21.4 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3039 (w), 2963 (w), 2924 (w), 2209 (w), 1558 (w), 1484 (m), 1430 (m), 1401 (m), 1125 (m), 1057 (m), 1014 (s), 898 (m), 804 (s), 779 (s), 748 (s), 684 (s), 554 (m), 439 (m). **MS (EI, 70 eV):** *m/z* (%) = 273 ([M]$^+$, 96), 271 ([M]$^+$, 100), 192 (16), 191 (49), 190 (21), 165 (13), 164 (13), 163 (16), 96 (11), 82 (13). **HRMS (EI):** calcd. for $C_{14}H_{10}N_1Br_1$ (M)$^+$ 270.99911 found 270.99903; calcd. for $C_{14}H_{10}N_1{}^{81}Br_1$ (M)$^+$ 272.99707, found 272.99724.

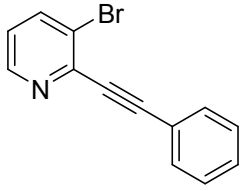
4-((3-bromopyridin-2-yl)ethynyl)-*N*,*N*-dimethylaniline 5f



Following the general procedure, 2,3-dibromopyridine (1 mmol, 236.89 mg) and 4-dimethylaminophenylacetylene (1.2 mmol, 174 mg) gave **5f** as a yellow crystalline solid (166 mg, 55 %), mp: 92-94 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.50 (dd, ^3J = 4.7, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.88 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1H, CH_{pyr}), 7.52 (d, ^3J = 9.0 Hz,

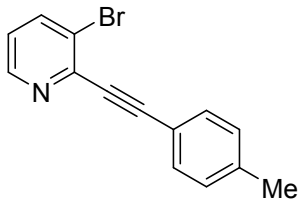
2H, CH_{Ar}), 7.03 (dd, ^3J = 8.1, ^3J = 4.7 Hz, 1H, CH_{pyr}), 6.65 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 3.00 (s, 6H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 150.9 (C_{Ar}), 148.3 (CH_{pyr}), 144.6 (C_{pyr}), 139.8 (CH_{pyr}), 133.7 (CH_{Ar}), 123.3 (C_{pyr}), 122.7 (CH_{pyr}), 111.8 (CH_{Ar}), 108.5 (C_{Ar}), 96.6, 86.5 (C_{alkyne}), 40.2 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2897 (m), 2852 (m), 2815 (m), 2205 (s), 1601 (s), 1562 (s), 1523 (s), 1420 (s), 1366 (s), 1226 (s), 1197 (s), 1152 (s), 1125 (s), 1059 (s), 1018 (s), 816 (s), 806 (s), 787 (s), 746 (s), 525 (s). **MS (EI, 70 eV):** *m/z* (%) = 302 ([M]$^+$, 97), 301 (69), 300 ([M]$^+$, 100), 299 (56), 286 (11), 284 (11), 177 (14), 151 (11), 150 (14), 110 (13), 97 (7). **HRMS (ESI-TOF):** calcd. for $C_{15}H_{13}N_2Br_1$ ([M+H]$^+$) 301.0340 found 301.0342.

3-bromo-2-(phenylethynyl)pyridine 5g



Following the general procedure, 2,3-dibromopyridine (1 mmol, 236.89 mg) and phenylacetylene (1.2 mmol, 148 µL) gave **5g** as a colorless oil (261 mg, 99 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.55 (dd, ^3J = 4.6, ^4J = 1.3 Hz, 1H, CH_{pyr}), 7.92 (dd, ^3J = 8.1, ^4J = 1.3 Hz, 1H, CH_{pyr}), 7.65 (dd, ^3J = 7.4, ^4J = 2.2 Hz, 2H, CH_{Ar}), 7.41 – 7.35 (m, 3H, CH_{Ar}), 7.12 (dd, ^3J = 8.1, ^3J = 4.6 Hz, 1H, CH_{pyr}) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 148.4 (CH_{pyr}), 143.9 (C_{pyr}), 140.0 (CH_{pyr}), 132.3, 129.5, 128.6 (CH_{Ar}), 124.0 (C_{pyr}), 123.7 (CH_{pyr}), 122.1 (C_{Ar}), 94.2, 87.6 (C_{alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3044 (w), 2219 (m), 1562 (m), 1490 (s), 1432 (m), 1418 (s), 1059 (m), 1018 (s), 789 (s), 750 (s), 732 (m), 686 (s), 565 (m), 546 (m), 521 (m). **MS (EI, 70 eV):** *m/z* (%) = 259 ([M]$^+$, 99), 258 (18), 257 ([M]$^+$, 100), 178 (31), 177 (29), 152 (12), 151 (42), 150 (26), 89 (10), 75 (16), 51 (11). **HRMS (ESI-TOF):** calcd. for $C_{13}H_8N_1Br_1$ ([M+H]$^+$) 257.9918 found 257.9919.

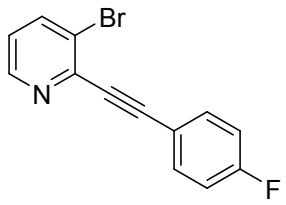
3-bromo-2-(*p*-tolylethynyl)pyridine 5h



Following general procedure, 2,3-dibromopyridine reacted with 4-Ethynyltoluene (1.2 mmol, 152 µL) to form the colorless oil **5h** (264 mg, 97 %). **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.53 (dd, ^3J = 4.7 Hz, ^4J = 1.5 Hz, 1H, CH_{Pyr}), 7.91 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1H, CH_{Pyr}), 7.54 (d, ^3J = 8.2 Hz, 2H, $CH_{p\text{-}Tolyl}$), 7.18 (d, ^3J = 8.5 Hz, 2H, $CH_{p\text{-}Tolyl}$), 7.10 (dd, ^3J = 8.1 Hz, ^3J = 4.7 Hz, 1H, CH_{Pyr}), 2.38 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.2 (CH_{Pyr}), 143.9 (C_{Ar}), 140.1 (CH_{Pyr}), 139.9 (C_{Ar}), 132.3, 129.3 ($CH_{p\text{-}Tolyl}$), 123.9 (C_{Ar}), 123.5 (CH_{Pyr}), 119.0 (C_{Ar}), 94.87, 87.01 (C_{Alkyne}), 21.8 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3035 (w), 2916 (w), 2854 (w), 2215 (m), 1564 (m), 1508 (m), 1432 (m), 1420 (s), 1156 (m), 1123 (m), 1057 (m), 1014 (s), 812 (s), 777 (s), 744 (s), 701 (m), 688 (m), 635 (m), 519 (s), 511 (s), 418 (s). **MS (EI, 70 eV)**: *m/z* (%) = 273 ($C_{14}H_{10}{}^{81}BrN$ [M]$^+$, 92), 272 (24), 271 ($C_{14}H_{10}{}^{79}BrN$ [M]$^+$, 100), 270 (12),

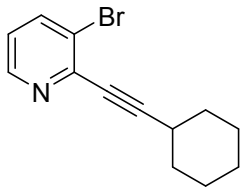
192 (20), 191 (51), 190 (26), 165 (16), 164 (18), 163 (28), 140 (19), 139 (12), 115 (17), 113 (10), 99 (10), 98 (11), 87 (14), 74 (10), 63 (14), 51 (29), 50 (23), 39 (20). **HRMS (EI)** calcd. for $C_{14}H_{10}{}^{79}BrN$ ([M]$^+$) 270.99911, found 270.99904; calcd. for $C_{14}H_{10}{}^{81}BrN$ 272.99707, found 272.99733.

3-bromo-2-((4-fluorophenyl)ethynyl)pyridine 5i



Following the general procedure A, 2,3-dibromopyridine reacted with 4-Fluorophenylacetylene (1.2 mmol, 137 µL) to form the colorless solid **5i** (244 mg, 89 %); mp: 90 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.54 (dd, ^3J = 4.7 Hz, ^4J = 1.5 Hz, 1H, CH_{Pyr}), 7.92 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1H, CH_{Pyr}), 7.63 (dd, ^3J = 8.9 Hz, ^3J = 5.4 Hz, 1H, CH_{Pyr}), 7.13 (dd, ^3J = 8.1 Hz, $^4J_{H,F}$ = 4.7 Hz, 2H, CH_{Ar}), 7.07 (t_{pseudo}, ^3J = 8.8 Hz, 1H, CH_{Ar}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = −108.86 ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 163.4 (d, $^1J_{C,F}$ = 251.3 Hz, CF), 148.3 (CH_{Pyr}), 143.6 (C_{pyr}), 140.1 (CH_{Pyr}), 134.4 (d, $^3J_{C,F}$ = 8.7 Hz, CH_{Ar}), 123.9 (C_{Pyr}), 123.7 (CH_{Pyr}), 118.2 (d, $^4J_{C,F}$ = 3.6 Hz, C_{Ar}), 116.0 (d, $^2J_{C,F}$ = 22.2 Hz, CH_{Ar}), 93.3 (C_{Alkyne}), 87.2 (d, $^5J_{C,F}$ = 1.3 Hz, C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3060 (w), 3039 (w), 2217 (m), 1595 (w), 1564 (m), 1502 (m), 1418 (m), 1212 (m), 1152 (m), 1131 (m), 1094 (m), 1059 (m), 1016 (s), 832 (s), 789 (s), 746 (s), 694 (m), 637 (m), 523 (s), 509 (s). **MS (EI, 70 eV)**: *m/z* (%) = 277 ($C_{13}H_7{}^{81}BrFN$ [M]$^+$, 100), 276 (18), 275 ($C_{13}H_7{}^{79}BrFN$ [M]$^+$, 96), 196 (32), 195 (27), 170 (10), 169 (38), 168 (33), 145 (43), 123 (10), 110 (11), 99 (14), 98 (26), 86 (12), 75 (11), 74 (13), 70 (12), 57 (11), 51 (27), 50 (35), 39 (11). **HRMS (EI)** calcd. for $C1_3H_7{}^{79}BrFN$ ([M]$^+$) 274.97404, found 274.97476; calcd. for $C_{13}H_7{}^{81}BrFN$ ([M]$^+$) 276.97200, found 276.97165.

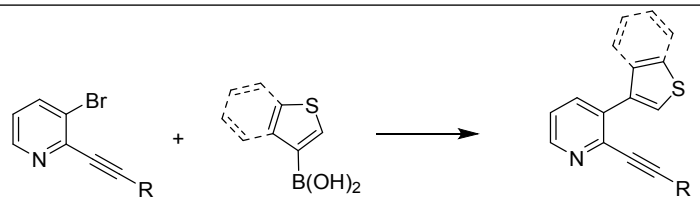
3-bromo-2-(cyclohexylethynyl)pyridine 5j



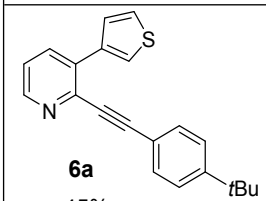
Following the general procedure, 2,3-dibromopyridine reacted with Cyclohexylacetylene (1.2 mmol, 157 µL) to form the colorless oil **5j** (259 mg, 98 %). **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.46 (dd, ^3J = 4.7 Hz, ^4J = 1.5 Hz, 1H, CH_{Pyr}), 7.86 (dd, ^3J = 8.1 Hz, ^3J = 1.5 Hz, 1H, CH_{Pyr}), 7.05 (dd, ^3J = 8.1 Hz, ^3J = 4.7 Hz, 1H, CH_{Pyr}), 2.82 – 2.62 (m, 1H, CH_{Cy}), 1.99 – 1.85 (m, 2H, CH_2), 1.83 – 1.74 (m, 2H, CH_2), 1.72 – 1.50 (m, 3H, CH_2), 1.47 – 1.32 (m, 3H, CH_2) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 148.2 (CH_{Pyr}), 144.3 (C_{Pyr}), 139.8 (CH_{Pyr}), 123.8 (C_{Pyr}), 123.1 (CH_{Pyr}), 100.5, 79.5 (C_{Alkyne}), 32.2 (CH_2), 29.8 (CH_{Cy}), 26.0, 24.8 (CH_2) ppm. **IR** (ATR, cm^{-1}): ṽ = 2930 (s), 2854 (m), 2223 (w), 1717 (w), 1566 (m), 1420 (s), 1337 (m), 1302 (m), 1257 (m), 1127 (m), 1063 (m), 1018 (s), 968 (m), 936 (m), 791 (s), 750 (s), 635 (m), 567 (m), 519 (m), 447 (m). **MS (EI, 70 eV):** *m/z* (%) = 265 ($C_{13}H_{14}{}^{81}BrN$ [M]$^+$, 15), 263 ($C_{13}H_{14}{}^{79}BrN$ [M]$^+$, 15), 236 (87), 234 (90), 210 (40), 208 (47), 197 (48), 195 (49), 184 (33), 156 (45), 154 (48), 141 (37), 128 (65), 115 (35), 102 (36), 101 (35), 87 (31), 78 (32), 77 (52), 76 (33), 75 (59), 74 (37), 67 (38), 63 (43), 51 (82), 50 (42), 41 (100), 39 (99), 29 (46). **HRMS (ESI-TOF)** calcd. for $C_{13}H_{14}{}^{79}BrN$ ([M+H]$^+$) 264.0388, found 264.0384

Synthesis of 2-(alkynyl)-3-thiophenpyridines, 6a-s (conditions A):

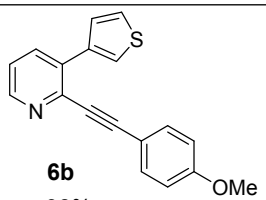
Table S5. *Synthesis of 2-alkynyl-3-thienylpyridines*



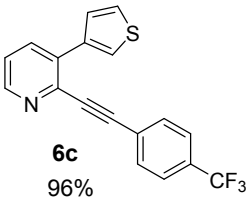
5a-j **6a-v**



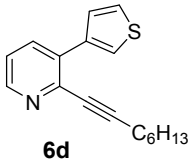
6a
45%



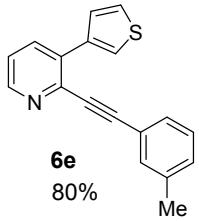
6b
98%



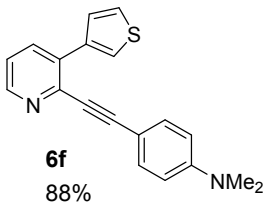
6c
96%



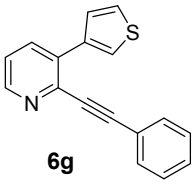
6d
81%



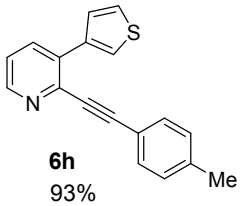
6e
80%



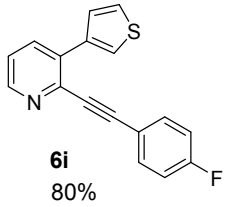
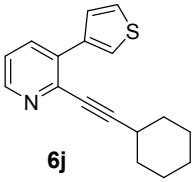
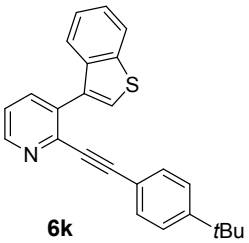
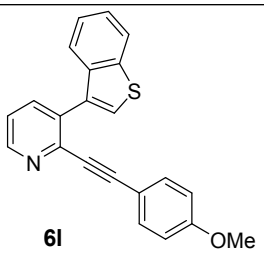
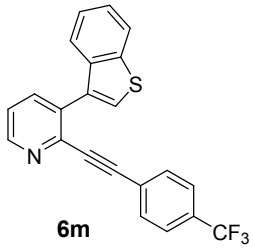
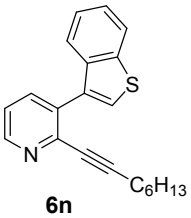
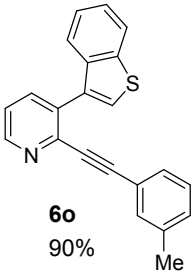
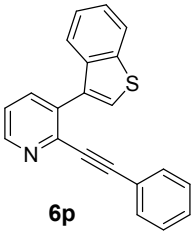
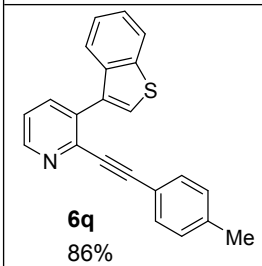
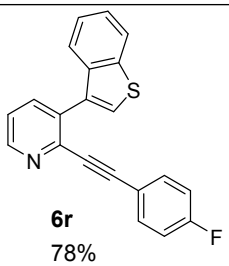
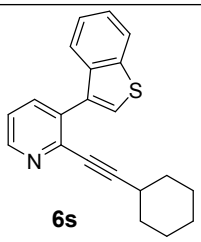
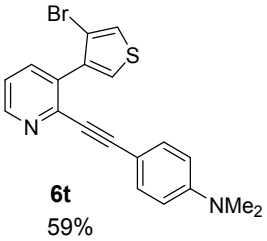
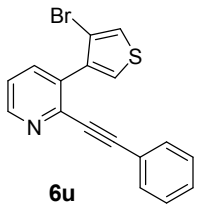
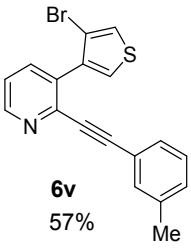
6f
88%



6g
77%

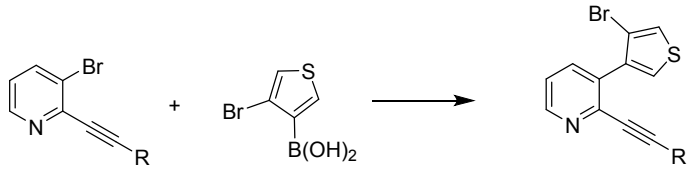


6h
93%

 **6i** 80%	 **6j** 81%	 **6k** 94%	 **6l** 93%
 **6m** 78%	 **6n** 73%	 **6o** 90%	 **6p** 87%
 **6q** 86%	 **6r** 78%	 **6s** 83%	 **6t** 59%
 **6u** 61%	 **6v** 57%		

2-(alkynyl)-3-bromopyridine (0.525 mmol), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (2.0 eq.) and the corresponding 3-thienylboronic acid (1.7 eq.) were dissolved in 1,4-dioxane (3.0 mL) and water (0.5 mL) under an argon atmosphere. The reaction was stirred overnight at 90 °C. Afterwards the reaction mixture was washed with distilled water and extracted with ethyl acetate. The combined organic layers were collected and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography to yield desired compounds.

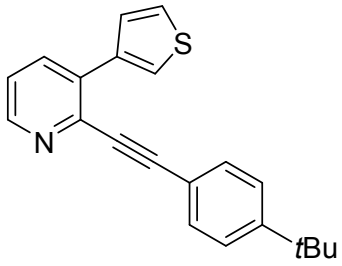
Synthesis of 2-(alkynyl)-3-(3-bromothiophen)pyridines, **6t-v** (conditions B):



5e-g **6t-v**

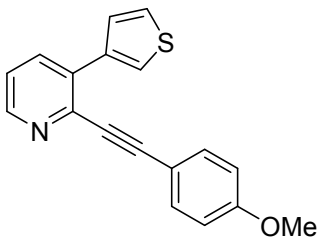
2-(alkynyl)-3-bromopyridine (0.5 mmol), $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), K_2CO_3 (2 eq.) and 4-bromo-3-thiopheneboronic acid (1.1 eq) were dissolved in CH_3CN (1.5 mL) and water (0.5 mL) under an argon atmosphere. The reaction was stirred 24 hours at 100 °C. After cooling to room temperature, the reaction mixture was washed with distilled water and extracted with ethyl acetate. The combined organic layers were collected and the solvent evaporated. The crude product was purified by column chromatography to yield desired compounds.

2-((4-(*tert*-butyl)phenyl)ethynyl)-3-(thiophen-3-yl)pyridine 6a



Following the general procedure, **5a** (0.525 mmol, 165.0 mg) reacted with 3-thiopheneboronic acid (0.893 mmol, 114.2 mg) to yield **6a** as a yellow oil (78.4 mg, 45 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.45 (dd, ^3J = 4.6, ^4J = 1.6 Hz, 1H, CH_{pyr}), 7.66 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1H, CH_{pyr}), 7.63 (dd, ^4J = 2.9, ^4J = 1.4 Hz, 1H, CH_{thioph}), 7.42 (dd, ^3J = 4.9, ^4J = 1.4 Hz, 1H, CH_{thioph}), 7.35 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.31 (dd, ^3J = 4.9, ^4J = 2.9 Hz, 1H, CH_{thioph}), 7.26 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.15 (dd, ^3J = 7.8, ^3J = 4.6 Hz, 1H, CH_{pyr}), 1.21 (s, 9H, CH_3) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 152.4 (C_{Ar}), 148.3 (CH_{pyr}), 140.9 (C_{pyr}), 138.4 (C_{thioph}), 136.4 (CH_{pyr}), 134.4 (C_{pyr}), 131.7 (CH_{Ar}), 128.4 (CH_{thioph}), 125.5 (CH_{Ar}), 125.4 (CH_{thioph}), 124.6 (CH_{pyr}), 122.7 (CH_{thioph}), 119.4 (C_{Ar}), 92.7, 88.4 (C_{Alkyne}), 34.9 (C_{tBu}), 31.2 (CH_3) ppm. **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 2959 (m), 2924 (w), 2864 (w), 2217 (w), 1424 (s), 1362 (m), 1102 (m), 855 (m), 835 (s), 779 (s), 647 (s), 626 (m), 563 (s). **MS (EI, 70 eV):** *m/z* (%) = 317 ($[M]^+$, 42), 303 (22), 302 (100), 286 (17), 274 (11), 273 (17), 260 (27), 136 (32), 63 (10), 41 (30), 39 (18). **HRMS (EI):** calcd. for $C_{21}H_{19}N_1S_1$ $(M)^+$ 317.12327 found 317.12326.

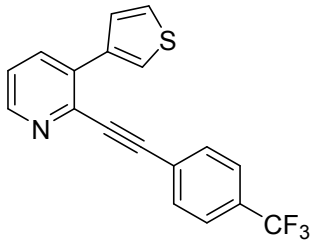
2-((4-methoxyphenyl)ethynyl)-3-(thiophen-3-yl)pyridine 6b



Following the general procedure, **5b** (0.525 mmol, 151.3 mg) reacted with 3-thiopheneboronic acid (0.8925 mmol, 114.2 mg) to yield **6b** as a yellow oil (150 mg, 98 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.55 (dd, ^3J = 4.7, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.78 (dd, ^3J = 7.9, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.74 (dd, ^4J = 3.0, ^4J = 1.3 Hz, 1H, CH_{thioph}), 7.52 (dd, ^3J = 5.0, ^4J = 1.3 Hz,

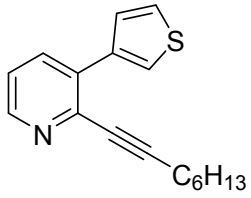
1H, CH_{thioph}), 7.44 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.42 (dd, ^3J = 5.0, ^4J = 3.0 Hz, 1H, CH_{thioph}), 7.27 (dd, ^3J = 7.9, ^3J = 4.7 Hz, 1H, CH_{pyr}), 6.86 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 3.81 (s, 3H, CH_3) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 160.4 (C_{Ar}), 148.2 (CH_{pyr}),141.0 (C_{pyr}), 138.5(C_{thioph}), 136.6 (CH_{pyr}), 134.3 (C_{pyr}), 133.6 (CH_{Ar}), 128.4, 125.5 (CH_{thioph}), 124.6 (CH_{pyr}), 122.7 (CH_{thioph}), 114.5 (C_{Ar}), 114.2 (CH_{Ar}), 93.1, 87.8 (C_{alkyne}), 55.4 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2209 (m), 1603 (s), 1506 (s), 1440 (m), 1424 (s), 1288 (s), 1247 (s), 1173 (s), 1152 (s), 1107 (s), 1024 (s), 830 (s), 777 (s), 647 (s), 532 (s). **MS (EI, 70 eV):** *m/z* (%) = 292 (19), 291 ($[M]^+$, 100), 290 (19), 276 (33), 275 (14), 249 (10), 248 (38), 247 (65), 246 (18), 203 (7), 124 (7), 45 (10). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{13}O_1N_1S_1$ ($[M+H]^+$) 292.0796 found 292.0798.

3-(thiophen-3-yl)-2-((4-(trifluoromethyl)phenyl)ethynyl)pyridine 6c



Following the general procedure, **5c** (0.525 mmol, 171.2 mg) reacted with 3-thiopheneboronic acid (0.8925 mmol, 114.2 mg) to give **6c** as a yellow solid (165.3 mg, 96 %), mp: 50-52 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.60 (dd, ^3J = 4.7, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.82 (dd, ^3J = 7.9, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.71 (dd, ^4J = 2.9, ^4J = 1.4 Hz, 1H, CH_{thioph}), 7.59 (s, 4H, CH_{Ar}), 7.51 (dd, ^3J = 5.0, ^4J = 1.4 Hz, 1H, CH_{thioph}), 7.45 (dd, ^3J = 5.0, ^4J = 2.9 Hz, 1H, CH_{thioph}), 7.34 (dd, ^3J = 7.9, ^3J = 4.7 Hz, 1H, CH_{pyr}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -62.92 (s, 3F, CF_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.7 (CH_{pyr}), 140.3 (C_{pyr}), 138.4 (C_{thioph}), 136.7 (CH_{pyr}), 135.1 (C_{pyr}), 132.3 (CH_{Ar}), 130.8 (q, $^2J_{C,F}$ = 33.0 Hz, C_{Ar}), 128.4 (CH_{thioph}), 125.8 (CH_{thioph}), 125.5 (q, $^3J_{C,F}$ = 3.8 Hz, CH_{Ar}), 124.8 (CH_{thioph}), 124.2 (q, $^1J_{C,F}$ = 272.0 Hz, CF_3), 124.8 (C_{Ar}), 123.5 (CH_{pyr}), 91.0, 90.6 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 1613 (m), 1426 (m), 1323 (s), 1166 (s), 1102 (s), 1065 (s), 1016 (s), 835 (s), 785 (s), 767 (s), 717 (m), 694 (m), 659 (s), 651 (s), 591 (s). **MS (EI, 70 eV):** *m/z* (%) = 330 (33), 329 ($[M]^+$, 100), 328 (99), 310 (11), 284 (12), 260 (29), 259 (30), 258 (26), 130 (7), 108 (8). **HRMS (EI):** calcd. for $C_{18}H_{10}F_3N_1S_1$ $(M)^+$ 329.04806 found 329.04708.

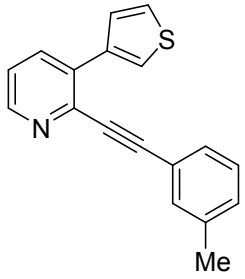
2-(oct-1-yn-1-yl)-3-(thiophen-3-yl)pyridine 6d



Following the general procedure, **5d** (0.525 mmol, 139.74 mg) and 3-thiopheneboronic acid (0.8925 mmol, 114.2 mg) gave **6d** as a brown solid (114.7 mg, 81 %), mp: 50 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.48 (dd, ^3J = 4.7, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.73 (dd, ^3J = 7.9, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.68 (dd,

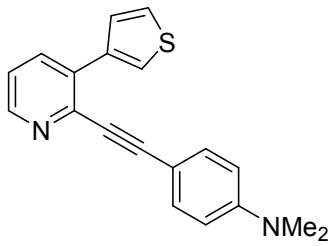
^4J = 3.0, ^4J = 1.3 Hz, 1H, CH_{thioph}), 7.45 (dd, ^3J = 5.0, ^4J = 1.3 Hz, 1H, CH_{thioph}), 7.37 (dd, ^3J = 5.0, ^4J = 3.0 Hz, 1H, CH_{thioph}), 7.23 (dd, ^3J = 7.9, ^3J = 4.7 Hz, 1H, CH_{pyr}), 2.41 (t, ^3J = 7.0 Hz, 2H, CH_2), 1.65 – 1.48 (m, 2H, CH_2), 1.44 – 1.30 (m, 2H, CH_2), 1.33 – 1.22 (m, 4H, CH_2), 0.87 (t, ^3J = 6.9 Hz, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 148.1 (CH_{pyr}), 141.1 (C_{pyr}), 138.6 (C_{thioph}), 136.5 (CH_{pyr}), 134.0 (C_{pyr}), 128.3, 125.3, 124.4 (CH_{thioph}), 122.5 (CH_{pyr}), 95.0, 80.3 (C_{Alkyne}), 31.5, 28.8, 28.2, 22.6, 19.7 (CH_2), 14.2 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2953 (w), 2926 (m), 2856 (m), 2228 (w), 1556 (w), 1449 (m), 1426 (s), 1354 (w), 1189 (w), 1113 (w), 863 (m), 779 (s), 721 (m), 649 (s). **MS (EI, 70 eV):** *m/z* (%) = 269 ([M]$^+$, 4), 268 (5), 212 (46), 210 (19), 200 (25), 199 (100), 198 (61), 197 (20), 186 (29), 173 (44), 172 (20), 154 (20), 63 (11), 43 (20), 41 (32), 39 (15), 29 (24). **HRMS (EI):** calcd. for $C_{17}H_{18}N_1S_1$ (M)$^+$ 268.11545 found 268.11546; calcd. for $C_{17}H_{19}N_1S_1$ (M)$^+$ 269.12327 found 269.12268.

3-(thiophen-3-yl)-2-(*m*-tolylethynyl)pyridine 6e



Following the general rule, **5e** (0.525 mmol, 142.88 mg) and 3-thiopheneboronic acid (0.8925 mmol, 114.2 mg) gave **6e** as a yellow oil (116 mg, 80 %). **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.57 (dd, ^3J = 4.7, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.80 (dd, ^3J = 7.9, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.75 (dd, ^4J = 3.0, ^4J = 1.3 Hz, 1H, CH_{thioph}), 7.53 (dd, ^3J = 5.0, ^4J = 1.3 Hz, 1H, CH_{thioph}), 7.44 (dd, ^3J = 5.0, ^4J = 3.0 Hz, 1H, CH_{thioph}), 7.33 – 7.28 (m, 2H, CH_{Ar}), 7.29 (dd, ^3J = 7.9, ^3J = 4.7 Hz, 1H, CH_{pyr}), 7.26 – 7.19 (m, 1H, CH_{Ar}), 7.19 – 7.14 (m, 1H, CH_{Ar}), 2.34 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 148.6 (CH_{pyr}), 141.0 (C_{pyr}), 138.6 (C_{thioph}), 138.2 (C_{Ar}), 136.5 (CH_{pyr}), 134.5 (C_{pyr}), 132.6, 130.0, 129.2, 128.5 (CH_{Ar}), 128.4, 125.5 (CH_{thioph}), 124.7 (CH_{pyr}), 122.9 (CH_{thioph}), 122.4 (C_{Ar}), 92.6, 88.8 (C_{Alkyne}), 21.4 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3097 (w), 3037 (w), 2918 (w), 2207 (w), 1556 (m), 1484 (m), 1449 (m), 1426 (s), 1397 (m), 1356 (m), 1111 (m), 863 (m), 777 (s), 688 (s), 647 (s), 618 (m), 563 (m), 519 (m), 441 (m). **MS (EI, 70 eV):** *m/z* (%) = 276 (20), 275 ([M]$^+$, 92), 274 (100), 273 (20), 272 (13), 260 (25), 259 (15), 230 (8), 136 (8). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{13}N_1S_1$ ([M+H]$^+$) 276.0847 found 276.0848.

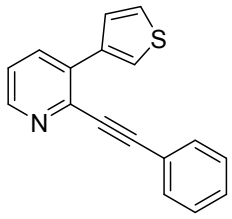
***N*,*N*-dimethyl-4-((3-(thiophen-3-yl)pyridin-2-yl)ethynyl)aniline 6f**



Following the general procedure, **5f** (0.525 mmol, 158.12 mg) reacted with 3-thiopheneboronic acid (0.8925 mmol, 114.2 mg) to give **6f** as a brown oil (140.1 mg, 88 %). **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.53 (dd, ^3J = 4.7, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.77 (dd, ^4J = 3.0, ^4J = 1.3 Hz, 1H, CH_{thioph}), 7.76 (dd, ^3J = 7.7, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.55 (dd, ^3J = 5.0, ^4J = 1.3 Hz,

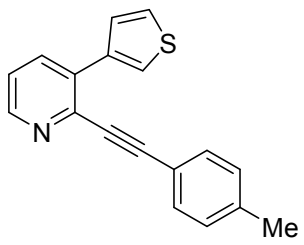
1H, CH_{thioph}), 7.42 (dd, ^3J = 5.0, ^4J = 3.0 Hz, 1H, CH_{thioph}), 7.38 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 7.22 (dd, ^3J = 7.7, ^4J = 4.7 Hz, 1H, CH_{pyr}), 6.64 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 2.99 (s, 6H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 150.7 (C_{Ar}), 148.4 (CH_{pyr}), 141.7 (C_{pyr}), 138.9 (C_{thioph}), 136.3 (CH_{pyr}), 133.7 (C_{pyr}), 133.3 (CH_{Ar}), 128.6, 125.2, 124.5 (CH_{thioph}), 122.1 (CH_{pyr}), 111.8 (CH_{Ar}), 109.1 (C_{Ar}), 94.4, 87.7 (C_{Alkyne}), 40.2 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3039 (w), 2891 (w), 2854 (w), 2802 (w), 2201 (m), 1603 (s), 1519 (s), 1424 (s), 1354 (s), 1185 (s), 1148 (s), 1125 (m), 1109 (s), 944 (m), 814 (s), 779 (s), 732 (s), 690 (m), 647 (s), 528 (s). **MS (EI, 70 eV):** *m/z* (%) = 305 (23), 304 ($[M]^+$, 100), 303 (47), 288 (13), 287 (25), 261 (6), 260 (20), 259 (14), 258 (6), 151 (6), 130 (8) **HRMS (ESI-TOF):** calcd. for $C_{19}H_{16}N_2S_1$ ($[M+H]^+$) 305.1112 found 305.1113; calcd. for $C_{19}H_{16}N_2S_1$ ($[M+Na]^+$) 327.0926 found 327.0933.

2-(phenylethynyl)-3-(thiophen-3-yl)pyridine 6g



According to the synthesis instructions **5g** (0.525 mmol, 135.5 mg) reacted with 3-thienylboronic acid (0.893 mmol, 114.3 mg) to form the brown oil **6g** (106 mg, 77 %). **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.54 (dd, ^3J = 4.7 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 7.75 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 7.71 (dd ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.50 (dd, ^3J = 5.0 Hz, ^3J = 1.3 Hz, 1H, CH_{Thio}), 7.51 – 7.47 (m, 2H, CH_{Ph})7.40 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.35 – 7.30 (m, 3H, CH_{Ph}), 7.24 (dd, ^3J = 7.9 Hz, ^4J = 4.7 Hz, 1H, CH_{Pyr}) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.4 (CH_{Pyr}), 140.7, 138.4(C_{Ar}), 136.3 (CH_{Ar}), 134.4 (C_{Ar}), 131.9 (CH_{Ph}), 129.0 (CH_{Ar}), 128.4 (CH_{Ph}), 128.3, 125.4, 124.6, 122.9 (CH_{Ar}), 122.4 (C_{Ar}), 92.2, 89.0 (C_{Alkyny}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3100 (w), 3055 (w), 2220 (w), 1597 (w), 1556 (m), 1490 (m), 1424 (s), 1356 (m), 1189 (m), 1111 (m), 1068 (w), 1022 (w), 899 (m), 868 (w), 851 (m), 779 (s), 752 (s), 730 (m), 686 (s), 647 (s), 561 (m), 550 (m), 524 (m), 458 (w). **MS (EI, 70 eV)**: *m/z* (%) = 261 ($[M]^+$, 70), 260 (100), 259 (15), 258 (3), 233 (3), 232 (3), 228 (4), 227 (3), 216 (8), 214 (3), 189 (4), 130 (5), 108 (8), 95 (3), 63 (3). **HRMS (EI)** calcd. for $C_{17}H_{10}NS$ ($[M]^+$) 260.05285, found 260.05265.

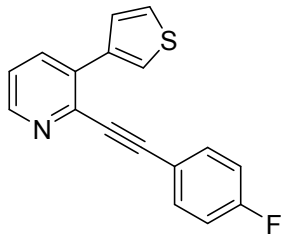
3-(thiophen-3-yl)-2-(*p*-tolylethynyl)pyridine 6h



According to the synthesis instructions **5h** (0.525 mmol, 142.9 mg) reacted with 3-thienylboronic acid (0.893 mmol, 114.3 mg) to form the light brown oil **6h** (133 mg, 93 %). **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.56 (dd, ^3J = 4.8 Hz, ^3J = 1.7 Hz, 1H, CH_{Pyr}), 7.79 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H,

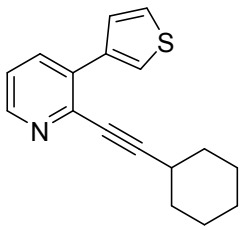
CH_{Pyr}), 7.75 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.53 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.43 (dd, ^3J = 5.1 Hz, ^4J = 2.9 Hz, 1H, CH_{Thio}), 7.40 (d, ^3J = 8.2 Hz, 2H, $CH_{p\text{-}Tolyl}$), 7.28 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 7.18 – 7.11 (m, 2H, $CH_{p\text{-}Tolyl}$), 2.36 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.4 (CH_{Pyr}), 140.9, 139.5, 138.5 (C_{Ar}), 136.6 (CH_{Ar}), 134.5 (C_{Ar}), 132.0, 129.3 ($CH_{p\text{-}Tolyl}$), 128.4, 125.5, 124.7, 122.8 (CH_{Ar}), 119.4 (C_{Ar}), 93.0, 88.4 (C_{Alkyne}), 21.7 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2920 (s), 2850 (m), 2219 (w), 1717 (m), 1558 (w), 1508 (m), 1451 (m), 1426 (m), 1360 (m), 1271 (m), 1181 (m), 1115 (m), 1026 (m), 855 (m), 816 (s), 781 (s), 649 (s), 528 (m), 418 (m). **MS (EI, 70 eV)**: *m/z* (%) = 275 ([M]$^+$, 98), 274 (100), 273 (24), 272 (13), 271 (6), 260 (17), 259 (15), 228 (6), 140 (7), 63 (7), 45 (9). **HRMS (EI)** calcd. for $C_{18}H_{13}NS$ ([M]$^+$) 275.07632, found 275.07550.

2-((4-fluorophenyl)ethynyl)-3-(thiophen-3-yl)pyridine 6i



According to the synthesis instructions **5i** (0.525 mmol, 144.9 mg) reacted with 3-thienylboronic acid (0.893 mmol, 114.3 mg) to form the colourless oil **6i** (115 mg, 80%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.55 (d, ^3J = 3.9 Hz, 1H, CH_{Pyr}), 7.78 (dd, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 1H, CH_{Pyr}), 7.70 (dd, ^4J = 2.9 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.50 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.48 – 7.44 (m, 2H, CH_{Ar}), 7.42 (dd, ^3J = 5.0 Hz, ^3J = 3.0 Hz, 1H, CH_{Thio}), 7.28 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 7.05 – 6.98 (m, 2H, CH_{Ar}) ppm. **^{19}F NMR (471 MHz, $CDCl_3$)** δ = −109.32 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 163.0 (d, $^1J_{C,F}$ = 250.9 Hz, CF), 148.4 (CH_{Pyr}), 140.6, 138.4 (C_{Ar}), 136.6 (CH_{Ar}), 134.6 (C_{Ar}), 134.0 (d, $^3J_{C,F}$ = 8.4 Hz, CH_{Ar}), 128.3, 125.6, 124.7, 123.0 (CH_{Ar}), 118.5 (d, $^4J_{C,F}$ = 3.6 Hz, C_{Ar}), 115.9 (d, $^2J_{C,F}$ = 22.1 Hz, CH_{Ar}), 91.4, 88.6 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 2922 (s), 2852 (m), 2221 (w), 1712 (m), 1599 (m), 1506 (s), 1426 (m), 1230 (s), 1154 (s), 1115 (m), 1092 (m), 837 (s), 781 (s), 719 (m), 694 (m), 649 (m), 530 (m), 517 (m). **MS (EI, 70 eV):** *m/z* (%) = 279 ([M]$^+$, 100), 278 (99), 277 (22), 246 (6), 234 (11), 207 (7), 63 (6), 45 (12). **HRMS (EI)** calcd. for $C_{17}H_{10}FNS$ ([M]$^+$) 279.05125, found 279.05067.

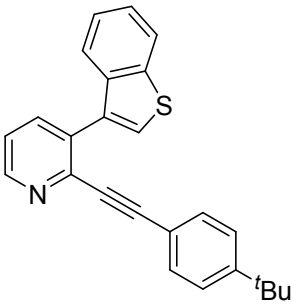
2-(cyclohexylethynyl)-3-(thiophen-3-yl)pyridine 6j



According to the synthesis instructions **5j** (0.525 mmol, 138.7 mg) reacted with 3-thienylboronic acid (0.893 mmol, 114.3 mg) to form the colourless oil **6j** (98 mg, 81 %). **^{1}H NMR (250 MHz, CDCl3)** δ = 8.49 (dd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 7.72 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 7.69 (dd, ^4J = 3.0 Hz,

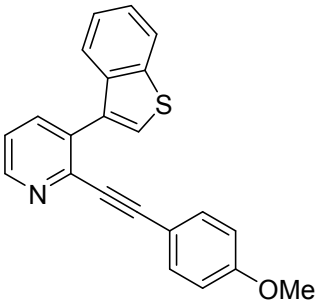
^4J = 1.3 Hz, 1H, CH_{Thio}), 7.46 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Thio}), 7.37 (dd, ^3J = 5.0 Hz, ^4J = 3.0 Hz, 1H, CH_{Thio}), 7.22 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 2.70 – 2.53 (m, 1H, CH_{Cy}), 1.94 – 1.79 (m, 2H, CH_2), 1.75 – 1.60 (m, 2H, CH_2), 1.60 – 1.43 (m, 3H, CH_2), 1.42 – 1.18 (m, 3H, CH_2) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 148.3 (CH_{Pyr}), 141.5, 138.8 (C_{Ar}), 136.3 (CH_{Ar}), 134.1 (C_{Ar}), 128.4, 125.2, 124.4, 122.4 (CH_{Ar}), 98.2, 80.4 (C_{Alkyne}), 32.1 (CH_2), 29.9 (CH_{Cy}), 26.0, 25.0 (CH_2) ppm. **IR** (ATR, cm^{-1}): ṽ = 2926 (m), 2850 (m), 2219 (w), 1556 (m), 1447 (m), 1424 (s), 1352 (m), 1300 (w), 1220 (w), 1189 (w), 1111 (w), 1084 (w), 1022 (w), 960 (w), 888 (w), 861 (m), 779 (s), 647 (s), 577 (m). **MS (EI, 70 eV)**: *m/z* (%) = 267 ($[M]^+$, 41), 266 (83), 239 (22), 238 (64), 24 (49), 223 (47), 222 (21), 212 (79), 211 (26), 210 (82), 199 (50), 198 (24), 186 (86), 185 (32), 173 (27), 172 (23), 166 (23), 63 (20), 56 (23), 45 (28), 41 (100), 39 (60). **HRMS (ESI-TOF)** calcd. for $C_{17}H_{17}NS$ ($[M+H]^+$) 268.1160, found 268.1165.

3-(benzo[*b*]thiophen-3-yl)-2-((4-(*tert*-butyl)phenyl)ethynyl)pyridine 6k



According to the synthesis instructions, **5a** (0.525 mmol, 164.25 mg) and 3-benzothiopheneboronic acid (0.8925 mmol, 158.87 mg) produced **6k** as a yellow oil (182.0 mg, 94 %), mp: 125 - 127 ºC. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.68 (dd, ^3J = 4.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 8.00 – 7.94 (m, 1H, $CH_{benzothioph}$), 7.83 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.75 – 7.69 (m, 1H, $CH_{benzothioph}$), 7.67 (s, 1H, CH_{thioph}), 7.43 – 7.38 (m, 2H, $CH_{benzothioph}$), 7.36 (dd, ^3J = 7.8, ^3J = 4.8 Hz, 1H, CH_{pyr}), 7.23 (d, ^3J = 8.6 Hz, 2H, (CH_{Ar}), 7.04 (d, ^3J = 8.6 Hz, 2H, (CH_{Ar}), 1.26 (s, 9H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 152.4 (C_{Ar}), 149.2 (CH_{Ar}), 143.0, 140.1, 138.2 (C_{Ar}), 137.6 (CH_{Ar}), 134.3, 133.9 (C_{Ar}), 131.8, 126.5, 125.4, 124.7, 124.6, 123.2, 123.0, 122.5 (CH_{Ar}), 119.2(C_{Ar}), 93.3, 88.0 (C_{alkyne}), 34.9 (C_{tBu}), 31.2(CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3089 (w), 3062 (w), 2953 (m), 2862 (w), 2219 (w), 1508 (m), 1426 (m), 1412 (s), 1362 (m), 1094 (m), 849 (m), 826 (s), 802 (m), 783 (s), 767 (s), 760 (m), 754 (s), 732 (s), 565 (s), 424 (m). **MS (EI, 70 eV):** *m/z* (%) = 368 (12), 367 ($[M]^+$, 42), 366 (100), 352 (12), 351 (13), 350 (21), 336 (21), 310 (16), 161 (10). **HRMS (ESI-TOF):** calcd. for $C_{25}H_{21}N_1S_1$ ($[M+H]^+$) 368.1473, found 368.1473.

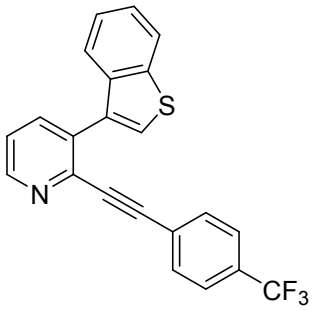
3-(benzo[*b*]thiophen-3-yl)-2-((4-methoxyphenyl)ethynyl)pyridine 6l



Following the general procedure 1B, **5b** (0.525 mmol, 151.27 mg) and 3-benzothiopheneboronic acid (0.8925 mmol, 158.87 mg) gave **6l** as a

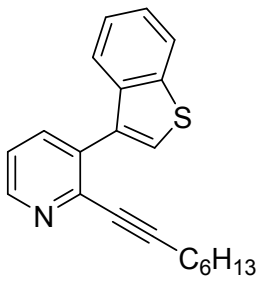
yellow solid (165.9 mg, 93 %), mp: 106-108 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.66 (dd, ^3J = 4.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.99 – 7.94 (m, 1H, $CH_{benzothioph}$), 7.82 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.74 – 7.69 (m, 1H, $CH_{benzothioph}$), 7.67 (s, 1H, CH_{thioph}), 7.42 – 7.36 (m, 2H, $CH_{benzothioph}$), 7.34 (dd, ^3J = 7.8, ^3J = 4.8 Hz, 1H, CH_{pyr}), 7.02 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 6.73 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 3.76 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 160.2 (C_{Ar}), 149.2 (CH_{Ar}), 143.1, 140.1, 138.2 (C_{Ar}), 137.5 (CH_{Ar}), 134.1, 134.0 (C_{Ar}), 133.5, 126.4, 124.6, 124.5, 123.3, 122.9, 122.3 (CH_{Ar}), 114.3 (C_{Ar}), 114.0 (CH_{Ar}), 93.4, 87.6 (C_{alkyne}), 55.4 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2840 (w), 2215 (m), 1603 (m), 1508 (s), 1424 (m), 1290 (m), 1249 (s), 1024 (s), 832 (s), 789 (s), 758 (s), 729 (s), 542 (s), 525 (s), 418 (s), **MS (EI, 70 eV):** *m/z* (%) = 342 (13), 341 ($[M]^+$, 47), 340 (100), 325 (11), 298 (25), 297 (80), 296 (38), 155 (11), 149 (46), 148 (10), 135 (16), 114 (14), 63 (12), 39 (12). **HRMS (ESI-TOF):** calcd. for $C_{22}H_{15}N_1O_1S_1$ ($[M+H]^+$) 342.0952, found 342.0955.

3-(benzo[*b*]thiophen-3-yl)-2-((4-(trifluoromethyl)phenyl)ethynyl)pyridine 6m



Following the synthesis rule, **5c** (0.525 mmol, 171.21 mg) reacted with 3-benzothiopheneboronic acid (0.8925 mmol, 158.87 mg) to yield **6m** as a yellow solid (154.9 mg, 78 %), mp: 162-164 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.71 (dd, ^3J = 4.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.99 – 7.97 (m, 1H, $CH_{benzothioph}$), 7.86 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.72 – 7.69 (m, 1H, $CH_{benzothioph}$), 7.64 (s, 1H, CH_{thioph}), 7.45 (dd, ^3J = 8.7, ^4J = 0.8 Hz, 2H, CH_{Ar}), 7.41 (dd, ^3J = 7.8, ^3J = 4.8 Hz, 1H, CH_{pyr}), 7.41 – 7.37 (m, 2H, $CH_{benzothioph}$), 7.13 (dd, ^3J = 8.7, ^4J = 0.8 Hz, 2H, CH_{Ar}) ppm. **^{19}F NMR (471 MHz, $CDCl_3$)** δ = -62.95 (s, 3F, CF_3) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 149.4 (CH_{Ar}), 142.2, 140.1, 138.0 (C_{Ar}), 137.8 (CH_{Ar}), 135.0, 133.7 (C_{Ar}), 132.1 (CH_{Ar}), 130.5 (q, $^2J_{C,F}$ = 33.0 Hz, C_{Ar}), 126.6 (CH_{Ar}), 126.0 (C_{Ar}), 124.8 (CH_{Ar}), 125.3 (q, $^3J_{C,F}$ = 3.8 Hz, CH_{Ar}), 124.6 (CH_{Ar}), 123.9 (q, $^1J_{C,F}$ = 272.3 Hz, CF_3), 123.2, 123.2, 123.0 (CH_{pyr}), 91.2, 90.5(C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3079 (w), 1611 (w), 1552 (w), 1426 (m), 1325 (s), 1160 (s), 1146 (m), 1115 (s), 1102 (s), 1065 (s), 1014 (m), 837 (s), 800 (s), 760 (s), 736 (s), 711 (m), 701 (s), 596 (m). **MS (EI, 70 eV):** *m/z* (%) = 380 (9), 379 ($[M]^+$, 30), 378 (100), 309 (10), 308 (13), 155 (10), 139 (7), 114 (7), 69 (9). **HRMS (ESI-TOF):** calcd. for $C_{22}H_{12}N_1S_1F_3$ ($[M+H]^+$) 380.0721, found 380.0715.

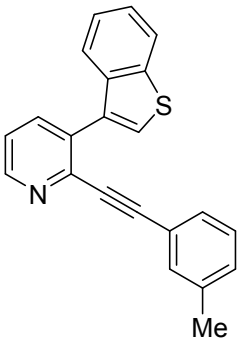
3-(benzo[*b*]thiophen-3-yl)-2-(oct-1-yn-1-yl)pyridine 6n



According the general procedure, **5d** (0.525 mmol, 139.75 mg) and 3-benzothiopheneboronic acid (0.8925 mmol, 158.87 mg) gave **6n** as a red oil

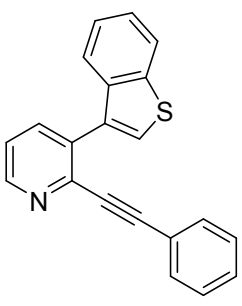
(121.8 mg, 73 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.60 (dd, ^3J = 4.8, ^4J = 1.8 Hz, 1H, CH_{pyr}), 7.92 – 7.90 (m, 1H, $CH_{benzothioph}$), 7.74 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1H, CH_{pyr}), 7.64 – 7.61 (m, 1H, $CH_{benzothioph}$), 7.57 (s, 1H, CH_{thioph}), 7.40 – 7.33 (m, 2H, $CH_{benzothioph}$), 7.30 (dd, ^3J = 7.8, ^3J = 4.8 Hz, 1H, CH_{pyr}), 2.17 (t, ^3J = 7.0 Hz, 2H, CH_2), 1.25 – 1.13 (m, 4H, CH_2), 1.12 – 1.02 (m, 4H, CH_2), 0.83 (t, ^3J = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 149.0 (CH_{Ar}), 143.2, 140.1, 138.2 (C_{Ar}), 137.6 (CH_{Ar}), 134.1, 133.9 (C_{Ar}), 126.1, 124.5, 124.3, 123.2, 122.8, 122.1 (CH_{Ar}), 95.1, 79.9 (C_{alkyne}), 31.4, 28.4, 27.9, 22.5, 19.4 (CH_2), 14.2 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3056 (w), 2953 (m), 2926 (m), 2856 (m), 2228 (w), 1552 (m), 1457 (m), 1440 (m), 1426 (s), 1414 (s), 1337 (w), 1102 (m), 837 (m), 806 (m), 783 (m), 775 (m), 758 (s), 732 (s), 699 (m), 433 (m). **MS (EI, 70 eV):** *m/z* (%) = 319 ($[M]^+$, 27), 318 (21), 290 (13), 276 (22), 263 (18), 262 (70), 261 (13), 260 (39), 250 (33), 249 (100), 248 (97), 247 (95), 246 (58), 236 (51), 235 (25), 224 (23), 223 (97), 222 (46), 221 (14), 176 (12). **HRMS (ESI-TOF):** calcd. for $C_{21}H_{21}N_1S_1$ ($[M+H]^+$) 320.1473, found 320.1474.

3-(benzo[*b*]thiophen-3-yl)-2-(*m*-tolylethynyl)pyridine 6o



Following the general procedure, **5e** (0.525 mmol, 142.88 mg) and 3-benzothiopheneboronic acid (0.8925 mmol, 158.87 mg) gave **6o** as an orange oil (153.8 mg, 90 %). **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.68 (dd, ^3J = 4.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.99 – 7.95 (m, 1H, CH_{Ar}), 7.84 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.74 – 7.70 (m, 1H, CH_{Ar}), 7.67 (s, 1H, CH_{Pyr}), 7.45 – 7.35 (m, 2H, CH_{Ar}), 7.37 (dd, ^3J = 7.8, ^3J = 4.8 Hz, 1H, CH_{pyr}), 7.13 – 7.04 (m, 2H, CH_{Ar}), 6.95 – 6.90 (m, 1H, CH_{Ar}), 6.84 – 6.82 (m, 1H, CH_{Ar}), 2.23 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.2 (CH_{pyr}), 142.9, 140.2, 138.2, 138.0 (C_{Ar}), 137.6 (CH_{pyr}), 134.4, 133.9 (C_{Ar}), 132.6, 129.9, 129.0, 128.2, 126.5, 124.6, 124.6, 123.3, 122.9, 122.6 (CH_{Ar}), 122.0 (C_{Ar}), 93.3, 88.3 (C_{Alkyne}), 21.3 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3052 (w), 2918 (w), 2207 (w), 1550 (m), 1484 (m), 1426 (s), 1405 (m), 1096 (m), 841 (m), 781 (s), 758 (s), 732 (s), 709 (m), 688 (s), 569 (m), 441 (m), 424 (s). **MS (EI, 70 eV):** *m/z* (%) = 326 (8), 325 ($[M]^+$, 32), 324 (100), 323 (8), 310 (9), 309 (8), 308 (7), 162 (9), 161 (8), 155 (14), 139 (8), 114 (8), 63 (8), 39 (9). **HRMS (ESI-TOF):** calcd. for $C_{22}H_{15}N_1S_1$ ($[M+H]^+$) 326.1003, found 326.1006.

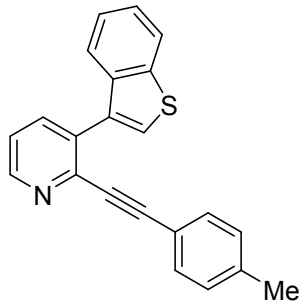
3-(benzo[*b*]thiophen-3-yl)-2-(phenylethynyl)pyridine 6p



According to the synthesis instructions **5g** (0.525 mmol, 135.5 mg) reacted with benzothiophene-3-boronic acid (0.893 mmol, 259.1 mg) to form the light yellow oil **6p** (136 mg, 87 %). **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.60 (dd,

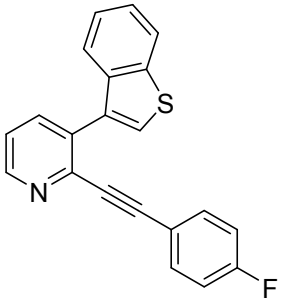
^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 7.94 – 7.82 (m, 1H, $CH_{B.thio}$), 7.75 (dd, ^3J = 7.8 Hz, ^3J = 1.7 Hz, 1H, CH_{Pyr}), 7.69 – 7.60 (m, 1H, $CH_{B.thio}$), 7.59 (s, 1H, $CH_{B.thio}$), 7.40 – 7.27 (m, 3H, CH_{Ar}), 7.20 – 7.08 (m, 3H, CH_{Ar}), 7.07 – 6.96 (m, 2H, CH_{Ar}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.2 (CH_{Pyr}), 142.7, 140.1, 138.2 (C_{Ar}), 137.6 (CH_{Ar}), 134.4, 133.8 (C_{Ar}), 132.0 (CH_{Ph}), 129.0 (CH_{Ar}), 128.3 (CH_{Ph}), 126.5, 124.7, 124.5, 123.2, 123.0, 122.7 (CH_{Ar}), 122.2 (C_{Ar}), 92.9, 88.5 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3066 (w), 3060 (w), 3058 (m), 3021 (w), 2217 (m), 1552 (m), 1521 (w), 1496 (w), 1466 (m), 1400 (w), 1387 (s), 1071 (w), 783 (w), 765 (m), 746 (m), 741 (m), 710 (w), 677 (m). **MS (EI, 70 eV)**: *m/z* (%) = 311 ([M]$^+$, 30), 310 (100), 309 (12), 308 (9), 307 (3), 282 (3), 155 (13), 154 (6), 133 (3). **HRMS (ESI-TOF)** calcd. for $C_{21}H_{13}NS$ ([M+H]$^+$) 312.0847, found 312.0850.

3-(benzo[*b*]thiophen-3-yl)-2-(*p*-tolylethynyl)pyridine 6q



According to the synthesis instructions **5h** (0.525 mmol, 142.9 mg) reacted with benzothiophene-3-boronic acid (0.893 mmol, 259.1 mg) to form the light brown oil **6q** (147 mg, 86 %). **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.67 (dd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 8.04 – 7.92 (m, 1H, $CH_{B.thio}$), 7.83 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 7.74 – 7.68 (m, 1H, $CH_{B.thio}$), 7.67 (s, 1H, $CH_{B.thio}$), 7.46 – 7.30 (m, 3H, CH_{Ar}), 7.07 – 6.92 (m, 4H, CH_{Ar}), 2.29 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.2 (CH_{Pyr}), 143.0, 140.1, 139.3, 138.2 (C_{Ar}), 137.6 ($C_{HAr)}$, 134.3, 133.9 (C_{Ar}), 131.9, 129.1 ($CH_{p\text{-}Tolyl)}$, 126.5, 124.6, 124.5, 123.2, 122.9, 122.5 (CH_{Ar}), 119.2 (C_{Ar}), 93.4, 88.0 (C_{Alkyne}), 21.6 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3161 (w), 3146 (m), 3076 (w), 3021 (m), 2308 (m), 1616 (m), 1584 (m), 1558 (m), 1545 (m), 1459 (m), 1444 (s), 1176 (w), 1115 (w), 1061 (w), 840 (m), 837 (w), 818 (w), 797 (m), 770 (m), 740 (m). **MS (EI, 70 eV):** *m/z* (%) = 325 ([M]$^+$, 100), 324 (76), 323 (28), 310 (43), 299 (15), 285 (17), 249 (12), 184 (14), 108 (36), 66 (69), 52 (45), 51 (10). **HRMS (EI)** calcd. for $C_{22}H_{15}NS$ ([M]$^+$) 325.09252, found 325.09197.

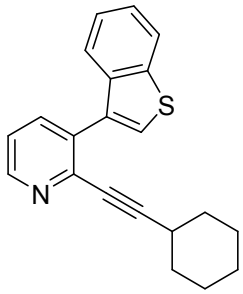
3-(benzo[*b*]thiophen-3-yl)-2-((4-fluorophenyl)ethynyl)pyridine 6r



According to the synthesis instructions **5i** (0.525 mmol, 144.9 mg) reacted with benzothiophene-3-boronic acid (0.893 mmol, 259.1 mg) to form the yellow oil **6r** (135 mg, 78 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.68 (dd,

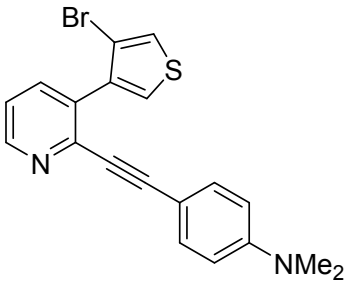
^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 8.02 – 7.92 (m, 1H, $CH_{B.thio}$), 7.84 (dd, ^3J = 7.8 Hz, ^3J = 1.7 Hz, 1H, CH_{Pyr}), 7.70 (dd, ^3J = 7.2 Hz, ^4J = 1.3 Hz, 1H, $CH_{B.thio}$), 7.65 (s, 1H, $CH_{B.thio}$), 7.44 – 7.36 (m, 2H, $CH_{B.thio}$), 7.38 (dd, ^3J = 7.7 Hz, ^3J = 5.1 Hz, 1H, CH_{Pyr}), 7.11 – 6.99 (m, 2H, CH_{Ar}), 6.89 (t_{pseudo}, ^3J = 8.8 Hz, 2H, CH_{Ar}) ppm. **^{19}F NMR (471 MHz, $CDCl_3$)** δ = −109.61 ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 163.0 (d, $^1J_{C,F}$ = 250.8 Hz, CF), 149.3 (CH_{Pyr}), 142.7, 140.1, 138.2 (C_{Ar}), 137.7 (CH_{Ar}), 134.5 (C_{Ar}), 133.93 (d, $^3J_{C,F}$ = 8.5 Hz, CH_{Ar}), 133.9 (C_{Ar}), 126.5, 124.7, 124.6, 123.2, 123.0, 122.7 (CH_{Ar}), 118.4 (d, $^4J_{C,F}$ = 3.5 Hz, C_{Ar}), 115.7 (d, $^2J_{C,F}$ = 22.1 Hz, CH_{Ar}), 91.9, 77.4 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3060 (w), 3021 (w), 2219 (m), 1580 (m), 1552(m), 1521 (w), 1496 (w), 1479 (s), 1400 (w), 1387 (m), 1211 (m), 1206 (s), 1127 (m), 1071 (w), 818 (m), 808 (w), 779 (w), 766 (w), 739 (m), 710 (w), 506 (w). **MS (EI, 70 eV)**: *m/z* (%) = 329 ([M]$^+$, 100), 328 (88), 327 (34), 303 (12), 285 (17), 253 (13), 184 (14), 108 (30), 70 (35), 52 (44), 50 (17). **HRMS (EI)** calcd. for $C_{21}H_{12}FNS$ ([M]$^+$) 329.06745, found 329.06690.

3-(benzo[*b*]thiophen-3-yl)-2-(cyclohexylethynyl)pyridine 6s



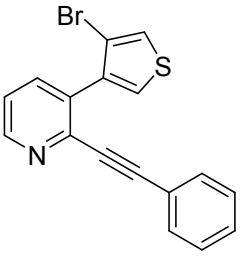
According to the synthesis instructions **5j** (0.525 mmol, 138.7 mg) reacted with benzothiophene-3-boronic acid (0.893 mmol, 259.1 mg) to form the light yellow oil **6s** (121 mg, 83 %). **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.60 (dd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, CH_{Pyr}), 7.97 – 7.86 (m, 1H, $CH_{B.thio}$), 7.75 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, CH_{Pyr}), 7.66 – 7.59 (m, 1H, $CH_{B.thio}$), 7.57 (s, 1H, $CH_{B.thio}$), 7.40 – 7.34 (m, 2H, $CH_{B.thio}$), 7.30 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 1H, CH_{Pyr}), 2.48 – 2.30 (m, 1H, CH_{Cy}), 1.59 – 1.46 (m, 2H, CH_2), 1.45 – 1.31 (m, 3H, CH_2), 1.22 – 1.06 (m, 5H, CH_2) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.0 (CH_{Pyr}), 143.5, 140.1, 138.3 (C_{Ar}), 137.5 (CH_{Ar}), 134.2, 134.1 (C_{Ar}), 126.0, 124.5, 124.3, 123.3, 122.8, 122.1 (CH_{Ar}), 98.8, 78.0 (C_{Alkyne}), 31.8 (CH_2), 29.4 (CH_{Cy}), 25.9, 24.5 (CH_2) ppm. **IR** (ATR, cm^{-1}): ṽ = 3054 (w), 2926 (s), 2850 (m), 2221 (w), 1550 (m), 1519 (w), 1445 (m), 1426 (s), 1412 (s), 1348 (m), 1259 (w), 1187 (w), 1146 (w), 1100 (m), 1055 (w), 1018 (w), 962 (w), 936 (w), 888 (w), 847 (m), 835 (m), 756 (s), 732 (s), 628 (m), 575 (w), 422 (m). **MS (EI, 70 eV)**: *m/z* (%) = 317 ([M]$^+$, 84), 316 (100), 288 (34), 274 (29), 273 (27), 262 (27), 260 (63), 259 (29), 248 (24), 247 (24), 236 (88), 235 (37), 223 (55), 222 (36), 41 (47), 39 (28). **HRMS (ESI-TOF)** calcd. for $C_{21}H_{19}NS$ ([M+H]$^+$) 318.1316, found 318.1317.

4-((3-(4-bromothiophen-3-yl)pyridin-2-yl)ethynyl)-*N*,*N*-dimethylaniline 6t



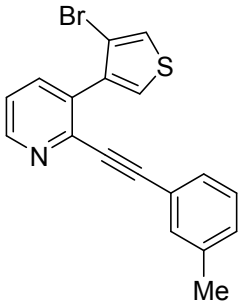
According to the general procedure, **5f** (0.5 mmol, 150.59 mg) and 4-bromo-3-thiopheneboronic acid (0.55 mmol, 113.77 mg) gave **6t** as a yellow solid (113.0 mg, 59 %), mp: 163-164 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.59 (dd, ^3J = 4.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.70 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.54 (d, ^4J = 3.5 Hz, 1H, CH_{thioph}), 7.40 (d, ^4J = 3.5 Hz, 1H, CH_{thioph}), 7.24 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 7.24 (dd, ^3J = 7.8, ^3J = 4.8 Hz, 1H, CH_{pyr}), 6.59 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 2.97 (s, 6H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 150.7 (C_{Ar}), 149.4 (CH_{Ar}), 143.8, 138.6 (C_{Ar}), 137.7, 133.4 (CH_{Ar}), 133.1 (C_{Ar}), 126.0, 123.4, 121.3 (CH_{Ar}), 112.4 (C_{Ar}), 111.8 (CH_{Ar}), 108.9 (C_{Ar}), 94.9, 86.9 (C_{Alkyne}), 40.2 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3095 (w), 2889 (m), 2205 (m), 1607 (s), 1523 (s), 1422 (s), 1368 (s), 1344 (s), 1187 (s), 1150 (s), 1109 (m), 1065 (m), 923 (s), 853 (m), 802 (s), 795 (s), 769 (s), 519 (s), 507 (s). **MS (EI, 70 eV):** *m/z* (%) = 384 ($[M]^+$, 100), 383 (60), 382 (98), 381 (40), 287 (15), 260 (13), 259 (34), 191 (30), 129 (14). **HRMS (ESI-TOF):** calcd. for $C_{19}H_{15}N_2Br_1S_1$ ($[M+H]^+$) 383.0218, found 383.0211.

3-(4-bromothiophen-3-yl)-2-(phenylethynyl)pyridine 6u



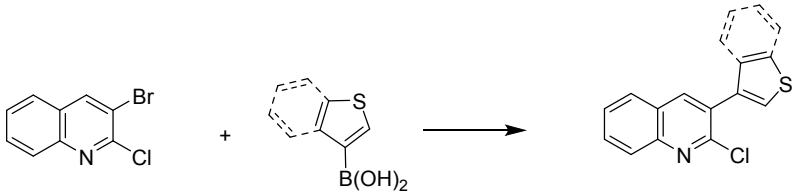
Following the general procedure, **5g** (0.5 mmol, 129.06 mg) and 4-bromo-3-thiopheneboronic acid (0.55 mmol, 113.77 mg) gave **6u** as a yellow solid (104.0 mg, 61 %), mp: 95-97 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.65 (dd, ^3J = 4.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.74 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.53 (d, ^4J = 3.4 Hz, 1H, CH_{thioph}), 7.43 (d, ^4J = 3.4 Hz, 1H, CH_{thioph}), 7.40 – 7.35 (m, 2H, CH_{Ar}), 7.32 (dd, ^3J = 7.8, ^3J = 4.8 Hz, 1H, CH_{pyr}), 7.32 – 7.29 (m, 3H, CH_{Ar}) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.6 (CH_{Ar}), 143.0, 138.3 (C_{Ar}), 137.9 (CH_{Ar}), 134.0 (C_{Ar}), 132.1, 129.1, 128.5, 126.1, 123.7 (CH_{Ar}), 122.4 (C_{Ar}), 122.3 (CH_{Ar}), 112.3 (C_{Ar}), 92.7, 88.2 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}):ṽ = 3099 (m), 2215 (m), 1556 (m), 1490 (m), 1420 (s), 1346 (m), 1259 (w), 1201 (m), 1111 (m), 1026 (m), 921 (m), 855 (m), 820 (s), 797 (s), 771 (s), 752 (s), 684 (s), 530 (m), 501 (m). **MS (EI, 70 eV):** *m/z* (%) = 341 ($[M]^+$, 3), 339 ($[M]^+$, 3), 261 (21), 260 (100), 259 (30), 216 (8), 214 (8), 130 (12). **HRMS (EI):** calcd. for $C_{17}H_{10}N_1Br_1S_1$ $(M)^+$ 338.97118, found 338.97071; calcd. for $C_{17}H_{10}N_1{}^{81}Br_1S_1$ $(M)^+$ 340.96914, found 340.96961.

3-(4-bromothiophen-3-yl)-2-(*m*-tolylethynyl)pyridine 6v



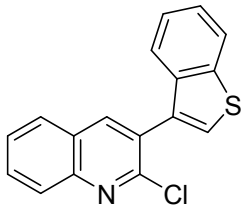
Following the general procedure, **5e** (0.5 mmol, 136.07 mg) reacted with 4-bromo-3-thiopheneboronic acid (0.55 mmol, 113.77 mg) to form the brown solid **6v** (101.7 mg, 57 %), mp: 91 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.64 (dd, ^3J = 4.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.74 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1H, CH_{pyr}), 7.54 (d, ^4J = 3.4 Hz, 1H, CH_{thioph}), 7.42 (d, ^4J = 3.4 Hz, 1H, CH_{thioph}), 7.31 (dd, ^3J = 7.8, ^3J = 4.8 Hz, 1H, CH_{pyr}), 7.20 – 7.16 (m, 3H, CH_{Ar}), 7.16 – 7.11 (m, 1H, CH_{Ar}), 2.31 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, DMSO)** δ = 149.5 (CH_{Ar}), 141.9, 138.1, 137.9 (C_{Ar}), 137.8 (CH_{Ar}), 134.0 (C_{Ar}), 131.8, 130.2, 128.7, 128.5, 127.2, 124.6, 122.9 (CH_{Ar}), 121.3, 111.3 (C_{Ar}), 91.8, 88.0 (C_{alkyne}), 20.7 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3087 (m), 2207 (m), 1556 (m), 1486 (m), 1422 (s), 1405 (m), 1344 (m), 1111 (m), 1045 (m), 915 (m), 855 (m), 818 (s), 800 (s), 783 (s), 771 (s), 686 (s), 672 (m), 554 (m), 511 (m), 443 (m). **MS (EI, 70 eV):** *m/z* (%) = 355 ($[M]^+$, 5), 353 ($[M]^+$, 5), 276 (6), 275 (21), 274 (100), 273 (32), 272 (18), 271 (5), 260 (4), 259 (21), 136 (11), 123 (4). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{12}N_1Br_1S_1$ ($[M+H]^+$) 353.9952, found 353.9952.

Synthesis of 3-(benzo[*b*]thiophen-3-yl)-2-chloroquinoline and 2-chloro-3-(thiophen-3-yl)quinoline:



3-bromo-2-chloroquinoline (0.83 mmol), K_3PO_4 (3.0 eq.) and the corresponding 3-thienylboronic acid (1.0 eq.) were dissolved in 1,4-dioxane (3.0 mL) and water (0.75 mL). Reaction mixture were degassed for 10 minutes and the $Pd(dppf)Cl_2$ (5 mol %) was added under an argon atmosphere. The reaction was stirred during 3 hours at 100 °C. After cooling, the reaction mixture was washed with distilled water and extracted with ethyl acetate (EtOAc). The combined organic layers were collected and the solvent evaporated. The crude product was purified by column chromatography to yield desired compounds.

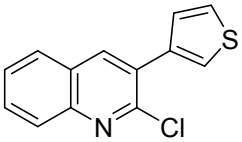
3-(benzo[*b*]thiophen-3-yl)-2-chloroquinoline



Following the general procedure D, 3-bromo-2-chloroquinoline (0.83 mmol, 199.62 mg) and benzo[*b*]thiophen-3-ylboronic acid (0.83 mmol, 147.76 mg)

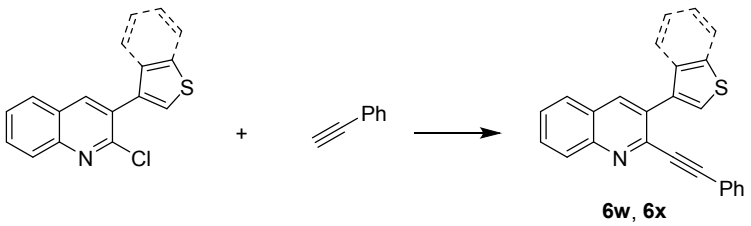
gave **MB-950** as a crystalline yellow solid (197 mg, 80%), mp: 98-100 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.23 (s, 1H, CH_{pyr}), 8.12 (dd, ^3J = 8.5, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.99 – 7.92 (m, 1H, CH_{Ar}), 7.86 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.80 (ddd, ^3J = 8.5, ^3J = 6.9, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.62 (ddd, ^3J = 8.1, ^3J = 6.9, ^4J = 1.2 Hz, 1H), 7.58 (s, 1H, CH_{thiop}), 7.57 – 7.52 (m, 1H, CH_{Ar}), 7.46 – 7.36 (m, 2H, CH_{Ar}). **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 150.6, 147.4 (C_{Ar}), 140.0 (CH_{Ar}), 138.5, 133.0 (C_{Ar}), 130.9 (CH_{Ar}), 129.0 (C_{Ar}), 128.6, 127.7, 127.6 (CH_{Ar}), 127.1 (C_{Ar}), 126.9, 124.9, 124.7, 123.0, 123.0 (CH_{Ar}). **IR** (ATR, cm^{-1}): ṽ = 3074 (w), 3054 (w), 1484 (m), 1426 (m), 1321 (m), 1210 (m), 1133 (m), 1067 (m), 1045 (s), 878 (m), 855 (m), 822 (m), 750 (s), 732 (s), 692 (s), 641 (m), 598 (s), 474 (s), 447 (m), 418 (m). **MS (EI, 70 eV):** *m/z* (%) = 297 (38), 296 (20), 295 ($[M]^+$, 100), 261 (9), 260 (43), 259 (24), 216 (25), 214 (11), 130 (10). **HRMS (ESI-TOF):** calcd. for $C_{17}H_{10}N_1Cl_1S_1$ ($[M+H]^+$) 296.0301, found 296.0305.

2-chloro-3-(thiophen-3-yl)quinoline



Following the general procedure D, 3-bromo-2-chloroquinoline (0.83 mmol, 199.62 mg) and thiophen-3-ylboronic acid (0.83 mmol, 106.2 mg) gave **MB-953** as a crystalline white solid (120 mg, 59%), mp: 73-74 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.18 (s, 1H, CH_{pyr}), 8.05 (dd, ^3J = 8.5, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.83 (dd, ^3J = 8.2, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.74 (ddd, ^3J = 8.5, ^3J = 6.9, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.58 (ddd, ^3J = 8.2, ^3J = 6.9, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.57 (dd, ^4J = 3.1, ^4J = 1.4 Hz, 1H, CH_{thiop}), 7.44 (dd, ^3J = 5.0, ^4J = 3.1 Hz, 1H, CH_{thiop}), 7.40 (dd, ^3J = 5.0, ^4J = 1.4 Hz, 1H, CH_{thiop}). **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 149.5, 146.9 (C_{Ar}), 138.6 (CH_{Ar}), 137.8 (C_{Ar}), 130.6 (CH_{Ar}), 129.9 (C_{Ar}), 129.0, 128.5, 127.6, 127.5 (CH_{Ar}), 127.4 (C_{Ar}), 125.7, 125.4 (CH_{Ar}). **IR** (ATR, cm^{-1}): ṽ = 1484 (m), 1414 (m), 1327 (m), 1131 (m), 1088 (s), 991 (m), 921 (m), 849 (s), 812 (m), 789 (s), 777 (s), 750 (s), 701 (m), 690 (m), 651 (s), 639 (s), 596 (s), 480 (s), 443 (m). **MS (EI, 70 eV):** *m/z* (%) = 247 ([M]+, 37), 246 (16), 245 ([M]+, 100), 211 (8), 210 (46), 209 (20), 166 (7), 164 (6), 139 (10). **HRMS (EI):** calcd. for $C_{13}H_8N_1Cl_1S_1$ $(M)^+$ 245.00605, found 245.00583, calcd. for $C_{13}H_8N_1{}^{37}Cl_1S_1$ $(M)^+$ 247.00310, found 247.00314.

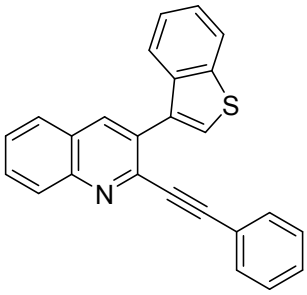
Synthesis of 3-(benzo[*b*]thiophen-3-yl)-2-(phenylethynyl)quinolines **6w-x**:



6w, **6x**

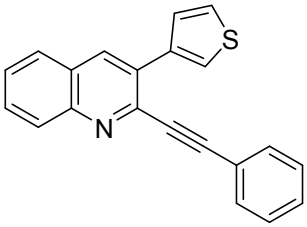
3-(benzo[*b*]thiophen-3-yl)-2-chloroquinoline (0.4 mmol), $Pd(PPh_3)_4$ (5 mol %) and CuI (2 mol %) were dissolved in 2.4 mL of $HNiPr_2$ under an argon atmosphere. After addition of the alkyne (1.2 eq.) the reaction was stirred at 70 °C for 20 h. After cooling to room temperature, the reaction mixture was washed with distilled water and extracted with ethyl acetate (EtOAc). The combined organic layers were collected and the solvent evaporated. The crude product was purified by column chromatography.

3-(benzo*[b]*thiophen-3-yl)-2-(phenylethynyl)quinoline 6w



According to the general procedure, 3-(benzo[*b*]thiophen-3-yl)-2-chloroquinoline (0.4 mmol, 118.31 mg) and phenylacetylene (0.48 mmol, 0.053 mL) gave **6w** as a yellow solid (112.8 mg, 78%), mp: 166-167 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.27 (s, 1H, CH_{pyr}), 8.22 (dd, ^3J = 8.4, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.99 (dd, ^3J = 8.2, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.85 (dd, ^3J = 8.2, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.78 (ddd, ^3J = 8.4, ^3J = 6.9, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.75 (dd, ^3J = 8.1, ^4J = 1.4 Hz, 1H CH_{Ar}), 7.71 (s, 1H, CH_{thiop}), 7.60 (ddd, ^3J = 8.2, ^3J = 6.9, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.42 (ddd, ^3J = 8.1, ^3J = 7.1, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.38 (ddd, ^3J = 8.2, ^3J = 7.1, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.26 (dd, ^3J = 7.5, ^3J = 1.4 Hz, 1H, CH_{Ar}), 7.20 (dd, ^3J = 8.4, ^3J = 7.5 Hz, 2H, CH_{Ar}), 7.07 (dd, ^3J = 8.4, ^4J = 1.4 Hz, 2H, CH_{Ar}) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 147.7, 143.6, 140.1, 138.7 (C_{Ar}), 136.9 (CH_{Ar}), 134.1 (C_{Ar}), 132.2 (CH_{Ar}), 131.5 (C_{Ar}), 130.4, 129.3, 129.2, 128.3, 127.7, 127.7 (CH_{Ar}), 127.1 (C_{Ar}), 126.5, 124.7, 124.6, 123.3, 122.9 (CH_{Ar}), 122.1 (C_{Ar}), 93.5, 89.1 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3050 (m), 2215 (w), 1593 (m), 1490 (m), 1428 (m), 1144 (m), 1131 (m), 913 (m), 849 (m), 810 (m), 760 (s), 748 (s), 740 (s), 703 (m), 684 (s), 620 (m), 525 (m), 474 (m), 464 (m), 431 (m). **MS (EI, 70 eV):** *m/z* (%) = 362 (12), 361 (41), 360 ($[M]^+$, 100), 359 (13), 358 (15), 357 (3), 187 (2), 180 (10), 163 (2), 158 (3). **HRMS (EI):** calcd. for $C_{25}H_{14}N_1S_1$ $(M)^+$ 360.08415, found 360.08316.

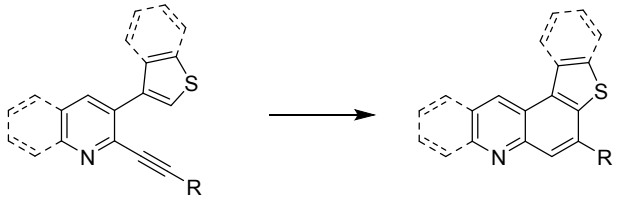
2-(phenylethynyl)-3-(thiophen-3-yl)quinoline 6x



Following the general procedure, 2-chloro-3-(thiophen-3-yl)quinoline (0.4 mmol, 98.3 mg) reacted with phenylacetylene (0.48 mmol, 0.053 mL) to yield **6x** as a yellow solid (90.2 mg, 72%), mp: 98-99 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.2 (d, ^4J = 0.9 Hz, 1H, CH_{pyr}), 8.2 (ddd, ^3J = 8.5, ^4J = 2.0, ^4J = 0.9 Hz, 1H, CH_{Ar}), 7.8 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.8 (dd, ^4J = 3.0, ^4J = 1.3 Hz, 1H, CH_{thiop}), 7.7 (ddd, ^3J = 8.5, ^3J = 7.0, ^4J = 1.5 Hz, 1H, CH_{Ar}), 7.6 (dd, ^3J = 5.0, ^4J = 1.3 Hz, 1H, CH_{thiop}), 7.6 (ddd, ^3J = 8.1, ^3J = 7.0, ^4J = 2.0 Hz, 1H, CH_{Ar}), 7.6 – 7.5 (m, 2H, CH_{Ar}), 7.5 (dd, ^3J = 5.0, ^4J = 3.0 Hz, 1H,

CH_{thiop}), 7.4 – 7.3 (m, 3H, CH_{Ar}) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 147.2, 142.3, 138.8 (C_{Ar}), 135.5, 132.3 (CH_{Ar}), 132.0 (C_{Ar}), 130.1, 129.3, 129.1, 128.9, 128.5, 127.7, 127.6 (CH_{Ar}), 127.4 (C_{Ar}), 125.5, 124.7 (CH_{Ar}), 122.4 (C_{Ar}), 93.0, 89.5 (C_{Alkyne}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3099 (w), 3054 (w), 2211 (w), 1574 (w), 1490 (m), 1420 (m), 1350 (m), 1148 (m), 913 (m), 859 (m), 791 (s), 750 (s), 727 (s), 686 (s), 666 (s), 643 (s), 620 (s), 528 (m), 495 (m), 476 (m). **MS (EI, 70 eV):** *m/z* (%) = 312 (21), 311 ([M]$^+$, 83), 310 (100), 309 (14), 308 (8), 278 (4), 266 (4), 155 (7), 139 (4), 133 (7). **HRMS (EI):** calcd. for $C_{21}H_{13}N_1S_1$ $(M)^+$ 311.07632, found 311.07550.

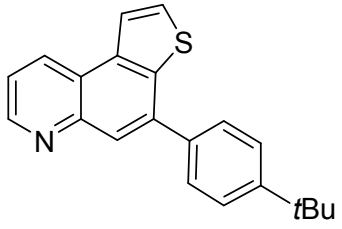
Synthesis of thieno[3,2-*f*]quinolines 7a-x:



6a-x **7a-x**

A degassed and argon flushed Schlenk tube was charged with corresponding starting material (0.3 mmol) and MsOH (50 eq.). The reaction was stirred at 120 °C for 1 h. After cooling to room temperature, the reaction mixture was washed with a 10 % sodium hydroxide solution and extracted with ethyl acetate. The combined organic layers were collected and the solvent evaporated. The crude product was purified by column chromatography.

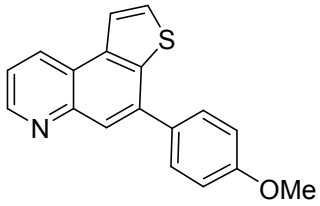
4-(4-(*tert*-butyl)phenyl)thieno[3,2-*f*]quinoline 7a



According to the general procedure, the reaction of **6a** (0.195 mmol, 62 mg) and MsOH (9.75 mmol, 630 µL), affords product **7a** as a yellow oil (51.8 mg, 84 %). **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.95 (dd, ^3J = 4.4, ^4J = 1.7 Hz, 1H, CH_{pyr}), 8.68 – 8.61 (m, 1H, CH_{pyr}), 8.08 (br s, 1H, CH_{Ar}), 8.03 (dd, ^3J = 5.5, ^5J = 0.8 Hz, 1H, CH_{thioph}), 7.80 (d, ^3J = 8.4 Hz, 2H, CH_{Ar}), 7.70 (dd, ^3J = 5.5, ^6J = 0.9 Hz, 1H, CH_{thioph}), 7.58 (d, ^3J = 8.4 Hz, 2H, CH_{Ar}), 7.51 (dd, ^3J = 8.3, ^3J = 4.4 Hz, 1H, CH_{pyr}), 1.42 (s, 9H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 151.9 (C_{Ar}), 149.2 (CH_{Ar}), 147.4, 139.0, 138.1, 136.9, 136.2 (C_{Ar}), 132.2, 128.2, 127.9, 126.0, 124.8 (CH_{Ar}), 123.6 (C_{Ar}), 122.2, 121.0 (CH_{Ar}), 34.9 (C_{tBu}), 31.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2959 (m), 2901 (m), 2866 (w), 1735 (m), 1486 (m), 1475 (s), 1360 (s), 1238 (s), 909 (m), 884 (m), 835 (s), 769 (s), 734 (s), 686 (s), 608 (s), 550 (s). **MS (EI, 70 eV):**

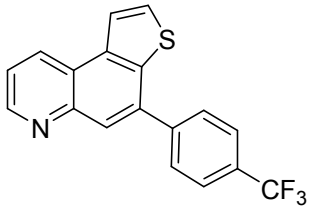
m/z (%) = 317 ([M]$^+$, 55), 303 (23), 302 (100), 286 (13), 274 (19), 273 (16), 260 (19), 137 (46), 41 (29), 39 (16) **HRMS (EI):** calcd. for $C_{21}H_{19}N_1S_1$ (M)$^+$ 317.12327 found 317.12319.

4-(4-methoxyphenyl)thieno[3,2-*f*]quinoline 7b



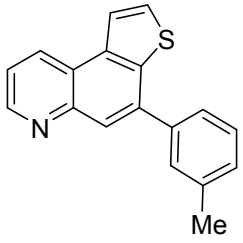
According to the general procedure, the reaction of **6b** (0.3 mmol, 87.41 mg) and MsOH (15.0 mmol, 1.0 mL), affords product **7b** as a yellow solid (80.1 mg, 92 %), mp: 161-163 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.94 (dd, ^3J = 4.4, ^4J = 1.7 Hz, 1H, CH_{pyr}), 8.64 (ddd, ^3J = 8.3, ^4J = 1.7, ^5J = 0.9 Hz, 1H, CH_{pyr}), 8.03 (br s, 1H, CH_{Ar}), 8.02 (d, ^3J = 5.5 Hz, 1H, CH_{thioph}), 7.78 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 7.69 (dd, ^3J = 5.5, J = 0.5 Hz, 1H, CH_{thioph}), 7.51 (dd, ^3J = 8.3, ^3J = 4.4 Hz, 1H, CH_{pyr}), 7.08 (d, J = 8.8 Hz, 2H, CH_{Ar}), 3.90 (s, 3H, CH_3). **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 160.1 (C_{Ar}), 149.1 (CH_{Ar}), 147.4, 138.8, 138.2, 136.2, 132.3 (C_{Ar}), 132.2, 129.7, 127.9, 124.5 (CH_{Ar}), 123.5 (C_{Ar}), 122.2, 120.9, 114.5 (CH_{Ar}), 55.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2920 (m), 2833 (m), 1601 (m), 1488 (m), 1247 (s), 1179 (s), 1028 (s), 828 (s), 812 (s), 769 (s), 740 (s), 723 (s), 688 (s), 602 (s), 556 (s), 517 (s). **MS (EI, 70 eV):** *m/z* (%) = 292 (20), 291 ([M]$^+$, 100), 276 (19), 248 (24), 247 (30), 246 (14), 146 (5), 123 (4). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{13}O_1N_1S_1$ ([M+H]$^+$) 292.0796 found 292.0798.

4-(4-(trifluoromethyl)phenyl)thieno[3,2-*f*]quinoline 7c



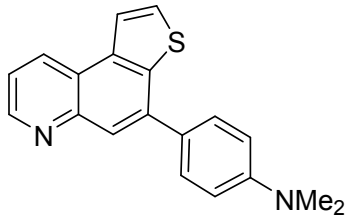
According to the general procedure, the reaction of **6c** (0.3 mmol, 98.72 mg) and MsOH (15.0 mmol, 1.0 mL), affords product **7c** as a yellow solid (93.8 mg, 95 %), mp: 127-129 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.99 (br s, 1H, CH_{pyr}), 8.67 (dd, ^3J = 8.3, ^4J = 1.6 Hz, 1H, CH_{pyr}), 8.07 (d, ^3J = 5.4 Hz, 1H, CH_{thioph}), 8.06 (s, 1H, CH_{Ar}), 7.95 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.82 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.73 (d, ^3J = 5.4 Hz, 1H, CH_{thioph}), 7.57 (dd, ^3J = 8.3, ^3J = 4.3 Hz, 1H, CH_{pyr}) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -62.54 (s, 3F, CF_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.8 (CH_{Ar}), 147.4, 143.5, 137.4, 136.6 (C_{Ar}), 132.0 (CH_{Ar}), 130.8 (d, $^2J_{C,F}$ = 33.0 Hz, C_{Ar}), 128.9, 128.1 (CH_{Ar}), 126.1 (d, $^3J_{C,F}$ = 3.8 Hz, CH_{Ar}), 125.8 (CH_{Ar}), 124.3 (q, $^1J_{C,F}$ = 272.0 Hz, CF_3), 124.1 (C_{Ar}), 122.4, 121.7 (CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 1323 (s), 1152 (m), 1102 (s), 1065 (s), 1016 (s), 909 (m), 841 (s), 832 (s), 812 (m), 802 (m), 769 (s), 734 (s), 684 (s), 618 (s), 542 (m), 482 (m). **MS (EI, 70 eV):** *m/z* (%) = 330 (25), 329 ([M]$^+$, 100), 328 (41), 310 (6), 260 (9), 259 (12), 268 (6), 232 (6), 154 (6), 69 (5). **HRMS (EI):** calcd. for $C_{18}H_{10}F_3N_1S_1$ (M)$^+$ 329.04806 found 329.04776.

4-(*m*-tolyl)thieno[3,2-*f*]quinoline 7e



According to the general procedure, the reaction of **6e** (0.18 mmol, 51.6 mg) and MsOH (9.3 mmol, 600µ mL), affords product **7e** as a colourless oil (43.0 mg, 87 %). **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.96 (dd, ^3J = 4.3, ^4J = 1.7 Hz, 1H, CH_{pyr}), 8.63 (ddd, ^3J = 8.3, ^4J = 1.7, ^5J = 0.8 Hz, 1H, CH_{pyr}), 8.04 (br s, 1H, CH_{Ar}), 8.03 (d, ^3J = 5.5 Hz, 1H, CH_{thioph}), 7.69 (dd, ^3J = 5.5, J = 0.5 Hz, 1H, CH_{thioph}), 7.66 – 7.63 (m, 2H, CH_{Ar}), 7.51 (dd, ^3J = 8.3, ^3J = 4.3 Hz, 1H, CH_{pyr}), 7.48 – 7.41 (m, 1H, CH_{Ar}), 7.33 – 7.28 (m, 1H, CH_{Ar}), 2.48 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.6 (CH_{Ar}), 147.8, 140.0, 138.9, 138.8, 138.0, 136.3 (C_{Ar}), 131.8, 129.5, 129.3, 128.9, 127.8, 125.6, 125.4 (CH_{Ar}), 123.6 (C_{Ar}), 122.2, 121.1 (CH_{Ar}), 21.7 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3035 (w), 2918 (w), 2854 (w), 1601 (m), 1558 (m), 1475 (s), 1354 (m), 878 (m), 824 (m), 787 (s), 769 (s), 734 (s), 705 (s), 680 (s), 616 (m), 579 (m), 474 (m), 433 (m). **MS (EI, 70 eV):** *m/z* (%) = 276 (28), 275 ($[M]^+$, 100), 274 (42), 273 (13), 272 (10), 259 (10), 137 (14), 123 (5). **HRMS (EI):** calcd. for $C_{18}H_{13}N_1S_1$ $(M)^+$ 275.07632 found 275.07595.

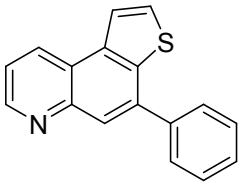
***N*,*N*-dimethyl-4-(thieno[3,2-*f*]quinolin-4-yl)aniline 7f**



According to the general procedure, the reaction of **6f** (0.071 mmol, 21.5 mg) and MsOH (3.53 mmol, 240 µL), affords product **7f** as a yellow solid (14.3 mg, 66 %). mp: 196-199 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.93 (dd, ^3J = 4.3, ^4J = 1.7 Hz, 1H, CH_{pyr}), 8.63 (ddd, ^3J = 8.3, ^4J = 1.7, J = 0.8 Hz, 1H, CH_{pyr}), 8.03 (d, ^3J = 5.5 Hz, 1H, CH_{thioph}), 8.02 (br s, 1H, CH_{Ar}), 7.77 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 7.69 (dd, ^3J = 5.5, J = 0.6 Hz, 1H, CH_{thioph}), 7.48 (dd, ^3J = 8.3, ^3J = 4.3 Hz, 1H, CH_{pyr}), 6.89 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 3.06 (s, 6H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 150.8 (C_{Ar}), 149.4 (CH_{Ar}), 147.9, 139.2, 138.3, 136.2 (C_{Ar}), 131.9, 129.4 (CH_{Ar}), 127.7 (C_{Ar}), 127.7, 124.2, 122.2, 120.6, 112.6 (CH_{Ar}), 40.6 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3093 (w), 3058 (m), 1605 (s), 1523 (s), 1486 (s), 1358 (s), 1222 (m), 1189 (s), 1170 (m), 1065 (m), 812 (s), 781 (s), 744 (s), 727 (s), 699 (s), 600 (s), 546 (s), 515 (s), 488 (m), 478 (s). **MS (EI, 70 eV):** *m/z* (%) = 305 (22), 304 ($[M]^+$,

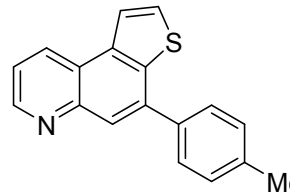
100), 303 (47), 288 (14), 260 (16), 259 (12), 151 (13). **HRMS (EI):** calcd. for $C_{19}H_{16}N_2S_1$ $(M)^+$ 304.10287 found 304.10219.

4-phenylthieno[3,2-*f*]quinoline 7g



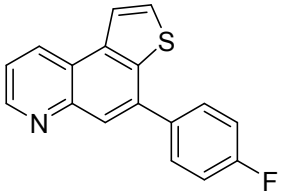
Starting material **6g** (0.38 mmol, 100 mg) cyclized to a light yellow solid **7g** (99 mg, 99 %); mp: 109 – 113 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.95 (dd, ^3J = 4.3 Hz, ^4J = 1.6 Hz, 1H, $CH_{th.quin}$), 8.58 (d, ^3J = 8.3 Hz, 1H, CH_{Ar}), 8.05 (s, 1H, $CH_{th.quin}$), 7.98 (d, ^3J = 5.6 Hz, 1H, $CH_{th.quin}$), 7.89 – 7.78 (m, 2H, CH_{Ar}), 7.65 (d, ^3J = 5.5 Hz, 1H, $CH_{th.quin}$), 7.59 – 7.43 (m, 4H, CH_{Ar}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.6 ($CH_{th.quin}$), 147.7, 140.0, 138.7, 137.8, 136.3 (C_{Ar}), 131.7 (CH_{Ar}), 129.0 (CH_{Ph}), 128.7 (CH_{Ar}), 128.5 (CH_{Ph}), 127.7, 125.4 (CH_{Ar}), 123.5 (C_{Ar}), 122.1, 121.1 (CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3095 (w), 3052 (w), 2974 (w), 2922 (w), 1598 (w), 1558 (w), 1485 (m), 1474 (m), 1358 (m), 1145 (m), 1074 (m), 105 (w), 924 (w), 873 (m), 847 (w), 759 (m), 734 (m), 704 (m), 683 (m), 643 (m), 604 (m), 575 (m), 540 (m), 448 (m). **MS (EI, 70 eV)**: *m/z* (%) = 261 ($[M]^+$, 100), 260 (50), 259 (13), 130 (13). **HRMS (EI)** calcd. for $C_{17}H_{11}NS$ $([M]^+)$ 261.06122, found 261.06067.

4-(*p*-tolyl)thieno[3,2-*f*]quinoline 7h



Starting material **6h** (0.38 mmol, 105 mg) cyclised to colourless oil **7h** (80 mg, 76 %). **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 8.95 (dd, ^3J = 4.3 Hz, ^4J = 1.7 Hz, 1H, $CH_{Th.quin}$), 8.63 (ddd, ^3J = 8.3 Hz, ^4J = 1.7 Hz, ^5J = 0.7 Hz, 1H, $CH_{Th.quin}$), 8.03 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 8.02 (s, 1H, $CH_{Th.quin}$), 7.74 (d, ^3J = 8.2 Hz, 2H, $CH_{4\text{-}Tolyl}$), 7.69 (d, ^3J = 5.5 Hz, 1H, $CH_{Th.quin}$), 7.50 (dd, ^3J = 8.3 Hz, ^3J = 4.3 Hz, 1H, $CH_{Th.quin}$), 7.37 (d, ^3J = 7.8 Hz, 2H, $CH_{4\text{-}Tolyl}$), 2.47 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.7 ($CH_{Th.quin}$), 147.9, 138.8, 138.6, 138.0, 137.2, 136.3 (C_{Ar}), 131.7 ($CH_{Th.quin}$), 129.8, 128.4 ($CH_{4\text{-}Tolyl}$), 127.8, 125.3 ($CH_{Th.quin}$), 123.6 (C_{Ar}), 122.2, 121.1 ($CH_{Th.quin}$), 21.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3025 (w), 2918 (w), 2856 (w), 1601 (m), 1556 (m), 1515 (w), 1488 (m), 1473 (s), 1358 (s), 1323 (m), 1210 (m), 1185 (m), 1148 (m), 1137 (m), 1113 (m), 1090 (m), 1067 (w), 1020 (m), 936 (w), 909 (m), 882 (m), 853 (m), 816 (s), 769 (s), 738 (s), 684 (s), 602 (s), 542 (s), 495 (s), 453 (s). **MS (EI, 70 eV):** *m/z* (%) = 275 ($[M]^+$, 96), 274 (100), 273 (19), 260 (24), 249 (25), 235 (13), 158 (18), 66 (69), 52 (10). **HRMS (EI)** calcd. for $C_{18}H_{13}NS$ $([M]^+)$ 275.07687, found 275.07632.

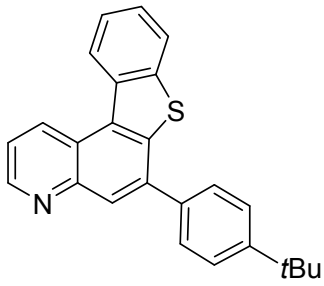
4-(4-fluorophenyl)thieno[3,2-*f*]quinoline 7i



Starting material **6i** (0.38 mmol, 106 mg) gave cyclised product **7i** (82 mg, 77 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 9.00 (dd, ^3J = 4.3 Hz, ^4J = 1.6 Hz, 1H, $CH_{Th.quin}$), 8.66 (dd, ^3J = 8.2 Hz, ^5J = 0.6 Hz, 1H, $CH_{Th.quin}$), 8.07 (d, ^3J = 5.4 Hz,

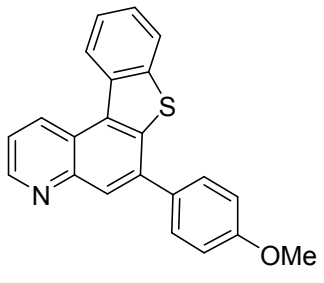
1H, $CH_{Th.quin}$), 8.03 (s, 1H, $CH_{Th.quin}$), 7.83 (dd, ^3J = 8.7 Hz, $^4J_{H,F}$ = 5.3 Hz, 2H, CH_{Ar}), 7.73 (d, ^3J = 5.4 Hz, 1H, $CH_{Th.quin}$), 7.56 (dd, ^3J = 8.3 Hz, ^3J = 4.3 Hz, 1H, $CH_{Th.quin}$), 7.29 (d, ^3J = 9.1 Hz, 2H, CH_{Ar}) ppm. **^{19}F NMR (471 MHz, $CDCl_3$)** δ = −113.09 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 163.1 (d, $^1J_{C,F}$ = 248.1 Hz, CF), 149.8 ($CH_{Th.quin}$), 147.8, 137.8, 137.7, 136.4 ($C_{Th.quin}$), 136.1 (d, $^4J_{C,F}$ = 3.5 Hz, C_{Ar}), 131.8 ($CH_{Th.quin}$), 130.3 (d, $^3J_{C,F}$ = 8.2 Hz, CH_{Ar}), 127.8, 125.5 ($CH_{Th.quin}$), 123.7 ($C_{Th.quin}$), 122.3, 121.3 ($CH_{Th.quin}$), 116.1 (d, $^2J_{C,F}$ = 21.5 Hz, CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3079 (m), 1599 (m), 1558 (m), 1513 (s), 1490 (s), 1477 (s), 1360 (m), 1321 (m), 1296 (m), 1224 (s), 1152 (s), 1098 (m), 909 (m), 870 (m), 855 (m), 832 (s), 808 (s), 785 (s), 764 (s), 738 (s), 717 (m), 682 (s), 598 (s), 540 (s), 507 (s), 472 (m), 457 (m), 416 (s). **MS (EI, 70 eV):** *m/z* (%) = 279 ($[M]^+$, 100), 278 (82), 277 (31), 253 (24), 235 (13), 158 (14), 70 (43), 50 (14). **HRMS (EI, 70 eV):** calcd. for $C_{17}H_{10}FNS$ ($[M]^+$) 279.05180, found 279.05125.

6-(4-(*tert*-butyl)phenyl)benzo[4,5]thieno[3,2-*f*]quinoline 7k



According to the general procedure, the reaction of **6k** (0.3 mmol, 110.25 mg) and MsOH (15.0 mmol, 1.0 mL), affords product **7k** as a yellow solid (70.3 mg, 64 %), mp: 187-189 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 9.28 (d, ^3J = 8.7 Hz, 1H, $CH_{benzothioph}$), 8.98 (dd, ^3J = 4.3, ^4J = 1.6 Hz, 1H, CH_{pyr}), 8.73 (br-d, ^3J = 8.0 Hz, 1H, $CH_{benzothioph}$), 8.15 (d, ^5J = 0.6 Hz, 1H, CH_{Ar}), 7.94 (ddd, ^3J = 7.7, ^4J = 1.6, ^5J = 0.6 Hz, 1H, CH_{pyr}), 7.77 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.59 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.60 – 7.53 (m, 1H, $CH_{benzothioph}$), 7.57 (dd, ^3J = 7.7, ^3J = 4.3 Hz, 1H, CH_{pyr}), 7.53 – 7.45 (m, 1H, $CH_{benzothioph}$), 1.44 (s, 9H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 151.8 (C_{Ar}), 149.0 (CH_{Ar}), 148.1, 140.4, 139.6, 138.9, 137.0, 136.7 (C_{Ar}), 131.0 (CH_{Ar}), 129.5 (C_{Ar}), 128.4, 128.1, 126.0, 125.8, 125.1 (CH_{Ar}), 124.9 (C_{Ar}), 124.4, 123.3, 121.2 (CH_{Ar}), 34.9 (C_{tBu}), 31.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2959 (m), 1482 (m), 1459 (w), 1263 (w), 1193 (w), 1144 (m), 1117 (m), 917 (m), 886 (m), 830 (s), 806 (m), 754 (s), 723 (s), 705 (w), 624 (m), 606 (s), 550 (s), 538 (m), 511 (m), 418 (m). **MS (EI, 70 eV):** *m/z* (%) = 368 (21), 367 ($[M]^+$, 73), 354 (8), 353 (27), 352 (100), 336 (14), 324 (19), 323 (18), 311 (11), 310 (18), 309 (9), 176 (10), 162 (37). **HRMS (EI):** calcd. for $C_{25}H_{21}N_1S_1$ $(M)^+$ 367.13892, found 367.13849.

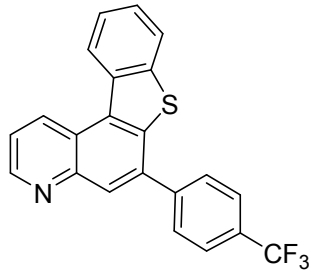
6-(4-methoxyphenyl)benzo[4,5]thieno[3,2-*f*]quinoline 7l



According to the general procedure, the reaction of **6l** (0.1025 mmol, 35.0 mg) and MsOH (5.12 mmol, 340 µL), affords product **7l** as a white solid (18.6 mg, 53 %), mp: 200-202 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 9.34 (br-d, ^3J = 8.5 Hz, 1H, $CH_{benzothioph}$), 9.00 (dd, ^3J = 4.3, 1.5 Hz, 1H, CH_{pyr}), 8.79 (br-d, ^3J = 8.3 Hz, 1H, $CH_{benzothioph}$), 8.12 (br s, 1H, CH_{Ar}), 7.98 (dd, ^3J = 7.9, 1.5 Hz, 1H, CH_{pyr}), 7.77 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 7.65 – 7.58

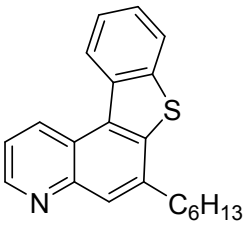
(m, 1H, $CH_{benzothioph}$), 7.61 (dd, ^3J = 7.9, ^3J = 4.3 Hz, 1H, CH_{pyr}), 7.56 – 7.48 (m, 1H, $CH_{benzothioph}$), 7.10 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 3.93 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 160.2 (C_{Ar}), 149.1 (CH_{Ar}), 148.2, 140.5, 139.8, 138.8, 136.9, 132.4 (C_{Ar}), 131.1, 130.0 (CH_{Ar}), 129.5 (C_{Ar}), 128.0, 125.9, 125.2 (CH_{Ar}), 124.9 (C_{Ar}), 124.5, 123.5, 121.3, 114.5 (CH_{Ar}), 55.6 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2988 (w), 2835 (m), 1609 (m), 1515 (s), 1482 (s), 1438 (m), 1288 (m), 1249 (s), 1181 (s), 1032 (s), 915 (m), 880 (s), 828 (s), 808 (s), 750 (s), 732 (m), 715 (s), 604 (s), 546 (s), 507 (s), 420 (m). **MS (EI, 70 eV):** *m/z* (%) = 342 (24), 341 ([M]$^+$, 100), 326 (12), 298 (20), 297 (36), 296 (22), 171 (13), 149 (24), 135 (9). **HRMS (EI):** calcd. for $C_{22}H_{15}N_1O_1S_1$ $(M)^+$ 341.08689, found 341.08709.

6-(4-(trifluoromethyl)phenyl)benzo[4,5]thieno[3,2-*f*]quinoline 7m



According to the general procedure, the reaction of **6m** (0.12 mmol, 46.0 mg) and MsOH (6.06 mmol, 390 µL), affords product **7m** as a white solid (43.0 mg, 94 %), mp: 202 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 9.31 (dd, ^3J = 8.7, ^4J = 1.5 Hz, 1H, CH_{pyr}), 8.99 (dd, ^3J = 4.3, ^4J = 1.5 Hz, 1H, CH_{pyr}), 8.75 (ddd, ^3J = 8.3, ^4J = 1.2, ^5J = 0.5 Hz, 1H, $CH_{benzothiop}$), 8.12 (s, 1H, CH_{Ar}), 7.94 (ddd, ^3J = 8.2, ^4J = 1.4, ^5J = 0.5 Hz, 1H, $CH_{benzothiop}$), 7.89 (dd, ^3J = 8.0, ^4J = 0.8 Hz, 2H, CH_{Ar}), 7.80 (m, 2H, CH_{Ar}), 7.62 (dd, ^3J = 8.7, ^3J = 4.3 Hz, 1H, CH_{pyr}), 7.59 (ddd, ^3J = 8.3, ^3J = 7.2, ^4J = 1.4 Hz, 1H, $CH_{benzothiop}$), 7.50 (ddd, ^3J = 8.2, ^3J = 7.2, ^4J = 1.2 Hz, 1H, $CH_{benzothiop}$). **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -62.54 (s, 3F, CF_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.3 (CH_{Ar}), 147.8, 143.4, 140.3, 138.8, 137.5, 136.6 (C_{Ar}), 131.2 (CH_{Ar}), 130.2 (q, $^2J_{C,F}$ = 33.3 Hz, C_{Ar}), 129.2, 128.6, 126.2 (CH_{Ar}), 126.1 (d, $^3J_{C,F}$ = 3.8 Hz, CH_{Ar}), 125.4, 124.5 (CH_{Ar}), 124.3 (q, $^1J_{C,F}$ = 272.3 Hz, CF_3), 123.5 (CH_{Ar}), 121.9 (CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3052 (w), 2922 (w), 1929 (w), 1613 (w), 1484 (w), 1407 (m), 1325 (s), 1261 (m), 1168 (m), 1098 (s), 1065 (s), 1016 (s), 915 (s), 841 (s), 808 (s), 752 (s), 719 (s), 676 (m), 624 (m), 608 (m). **MS (EI, 70 eV):** *m/z* (%) = 380 (25), 379 ([M]$^+$, 100), 378 (25), 309 (10), 189 (11), 179 (15), 155 (10), 69 (17). **HRMS (EI):** calcd. for $C_{22}H_{12}N_1F_3S_1$ $(M)^+$ 379.06371, found 379.06323.

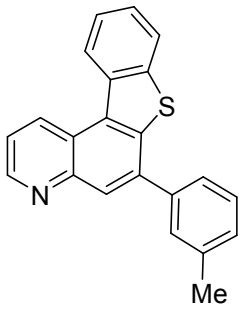
6-hexylbenzo[4,5]thieno[3,2-*f*]quinoline 7n



According to the general procedure, the reaction of **6n** (0.22 mmol, 71.0 mg) and MsOH (11.1 mmol, 740 µL), affords product **7n** as a yellow solid (50.0 mg, 71 %), mp: 49-51 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 9.27 (ddd, ^3J = 8.6, ^4J = 1.6, ^5J = 0.8 Hz, 1H, $CH_{benzothioph}$), 8.95 (dd, ^3J = 4.2, ^4J = 1.5 Hz, 1H, CH_{pyr}), 8.74 (br-d, ^3J = 8.2 Hz, 1H, $CH_{benzothioph}$), 8.03 (ddd, ^3J = 7.8, ^4J = 1.5, ^5J = 0.8 Hz, 1H, CH_{pyr}), 7.98 (d, ^5J = 0.8 Hz, 1H, CH_{Ar}), 7.63 – 7.56 (m, 1H, $CH_{benzothioph}$), 7.56 (dd, ^3J = 7.8, ^3J = 4.2 Hz, 1H, CH_{pyr}), 7.55 – 7.48 (m, 1H, $CH_{benzothioph}$), 3.06 (t, ^3J = 7.7 Hz, 2H, CH_2), 2.00 – 1.87 (m, 2H, CH_2), 1.56 – 1.43 (m, 2H, CH_2), 1.43 – 1.28 (m, 4H, CH_2), 0.91 (t, ^3J = 7.1 Hz, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**

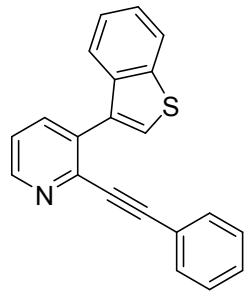
δ = 147.6 (CH_{Ar}), 147.0, 139.2, 138.7, 137.8, 135.9 (C_{Ar}), 129.8 (CH_{Ar}), 127.7 (C_{Ar}), 125.8, 124.6, 124.0, 123.3 (CH_{Ar}), 123.2 (C_{Ar}), 122.4, 119.7 (CH_{Ar}), 34.1, 30.7, 28.2, 27.8, 21.6 (CH_2), 13.1 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2957 (m), 2926 (s), 2852 (m), 1486 (m), 1457 (m), 1247 (m), 1195 (m), 1076 (m), 1030 (m), 868 (m), 808 (s), 760 (s), 750 (s), 732 (s), 715 (s), 596 (m), 575 (s), 501 (m), 441 (m), 416 (m). **MS (EI, 70 eV):** *m/z* (%) = 319 ($[M]^+$, 32), 262 (13), 260 (9), 250 (21), 249 (100), 248 (51), 247 (19), 222 (7). **HRMS (EI):** calcd. for $C_{21}H_{21}N_1S_1$ $(M)^+$ 319.13892, found 319.13890.

6-(*m*-tolyl)benzo[4,5]thieno[3,2-*f*]quinoline 7o



According to the general procedure, the reaction of **6o** (0.077 mmol, 25 mg) and MsOH (3.84 mmol, 256 µL), affords product **7o** as a yellow solid (20.0 mg, 80 %), mp: 128-130 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 9.36 (d, ^3J = 8.4 Hz, 1H, $CH_{benzothioph}$), 9.01 (dd, ^3J = 4.3, ^4J = 1.6 Hz, 1H, CH_{pyr}), 8.80 (d, ^3J = 8.2 Hz, 1H, $CH_{benzothioph}$), 8.15 (s, 1H, CH_{Ar}), 7.99 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1H, CH_{pyr}), 7.66 – 7.47 (m, 6H, CH_{Ar}), 7.33 (d, ^3J = 7.8 Hz, 1H, CH_{Ar}), 2.50 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.1 (CH_{Ar}), 148.1, 140.5, 139.9, 139.7, 139.2, 138.8, 136.8 (C_{Ar}), 131.2, 129.6 (CH_{Ar}), 129.5 (C_{Ar}), 129.5, 128.9, 128.1, 125.9, 125.8, 125.2 (CH_{Ar}), 125.1 (C_{Ar}), 124.5, 123.5, 121.4 (CH_{Ar}), 21.7 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 2916 (w), 2852 (w), 1585 (w), 1545 (w), 1482 (m), 1346 (m), 1321 (m), 1263 (m), 1030 (m), 886 (m), 808 (s), 785 (s), 756 (s), 727 (s), 705 (s), 608 (m), 507 (s), 427 (s). **MS (EI, 70 eV):** *m/z* (%) = 326 (25), 325 ($[M]^+$, 100), 324 (26), 162 (30), 155 (11), 148 (9), 146 (10). **HRMS (EI):** calcd. for $C_{22}H_{15}N_1S_1$ $(M)^+$ 325.09197, found 325.09208.

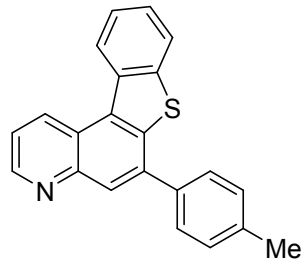
6-phenylbenzo[4,5]thieno[3,2-*f*]quinoline 7p



Starting material **6p** (0.38 mmol, 118 mg) cyclised to yellow solid **7p** (64 mg, 54 %); mp: 135 – 139 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 9.35 (d, ^3J = 8.0 Hz, 1H, $CH_{B.th.quin}$), 9.01 (dd, ^3J = 4.2 Hz, ^4J = 1.6 Hz, 1H, $CH_{B.th.quin}$), 8.80 (d, ^3J = 7.8 Hz, 1H, $CH_{B.th.quin}$), 8.16 (s, 1H, $CH_{B.th.quin}$), 7.98 (d, ^3J = 7.8 Hz, 1H, $CH_{B.th.quin}$), 7.86 – 7.79 (m, 2H, CH_{Ph}), 7.65 (dd, ^3J = 9.0 Hz, ^3J = 4.7 Hz, 1H, $CH_{B.th.quin}$), 7.63 – 7.51 (m, 5H, CH_{Ar}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.2($CH_{B.th.quin}$), 148.1, 140.5, 134.0, 139.0, 137.6, 136.8 (C_{Ar}), 131.1 ($CH_{B.th.quin}$), 129.6 (C_{Ar}), 129.1, 128.8, 128.8 (CH_{Ph}), 128.3, 125.9, 125.2 ($CH_{B.th.quin}$), 125.1 (C_{Ar}), 124.5, 123.5, 121.5 ($CH_{B.th.quin}$) ppm. **IR** (ATR, cm^{-1}) ṽ = 3046 (w), 3031 (w), 2920 (w), 1572 (w), 1545 (w), 1480 (m), 1428 (m), 1348 (m), 1319 (m), 1259 (m), 1195 (w), 1158 (m), 1142 (m), 1069 (m), 1028 (m), 915 (m), 907 (m), 808 (m), 748 (s), 717 (s), 694 (s), 604 (s), 567

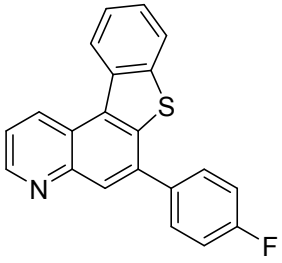
(m), 546 (s), 505 (m), 449 (m), 420 (m). **MS (EI, 70 eV)**: *m/z* (%) = 311 ([M]$^+$, 100), 310 (32), 309 (12), 282 (7), 155 (19), 141 (5). **HRMS (EI, 70 eV)** calcd. for $C_{21}H_{13}NS$ ([M]$^+$) 311.07632, found 311.07570.

6-(*p*-tolyl)benzo[4,5]thieno[3,2-*f*]quinoline 7q



Starting material **6q** (0.38 mmol, 124 mg) cyclised to yellow solid **7q** (85 mg, 69 %); mp: 152 – 155 °C. **^{1}H NMR (300 MHz, CDCl^3)** δ = 9.33 (dd, ^3J = 8.7 Hz, ^4J = 1.5 Hz, 1H, $CH_{B.th.quin}$), 9.00 (dd, ^3J = 4.2 Hz, ^3J = 1.6 Hz, 1H, $CH_{B.th.quin}$), 8.78 (d, ^3J = 8.1 Hz, 1H, $CH_{B.th.quin}$), 8.14 (s, 1H, $CH_{B.th.quin}$), 7.97 (dd, ^3J = 7.9 Hz, ^3J = 1.3 Hz, 1H, $CH_{B.th.quin}$), 7.72 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.62 (d, ^3J = 8.5 Hz, 1H, $CH_{B.th.quin}$), 7.60 (dd, ^3J = 8.4 Hz, ^3J = 2.6 Hz, 1H, $CH_{B.th.quin}$), 7.42 – 7.36 (m, 2H, CH_{Ar}), 2.49 (s, 3H, CH_3) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ = 149.1 ($CH_{B.th.quin}$), 148.1, 140.5, 139.7, 139.1, 138.8, 137.1, 136.8 (C_{Ar}), 131.1 ($CH_{B.th.quin}$), 129.8 (CH_{Ar}), 129.5 (C_{Ar}), 128.6 (CH_{Ar}), 128.1, 125.9, 125.2 ($CH_{B.th.quin}$), 125.0 (C_{Ar}), 124.4, 123.4, 121.3 ($CH_{B.th.quin}$), 21.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3025 (w), 2916 (w), 2850 (w), 1548 (w), 1513 (w), 1482 (m), 1348 (m), 1321 (m), 1300 (w), 1259 (w), 1185 (m), 1111 (m), 1069 (w), 1043 (w), 1020 (w), 913 (m), 816 (s), 806 (s), 748 (s), 715 (s), 602 (s), 546 (m), 530 (m), 488 (s), 457 (m), 418 (m). **MS (EI, 70 eV):** *m/z* (%) = 325 ([M]$^+$, 100), 324 (30), 323 (13), 310 (6), 309 (7), 162 (5), 161 (6), 155 (5), 91 (5). HRMS (ESI-TOF) calcd. for $C_{22}H_{15}NS$ ([M+H]$^+$) 326.1003, found 326.1002.

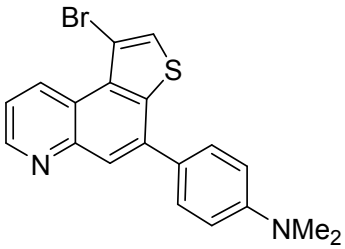
6-(4-fluorophenyl)benzo[4,5]thieno[3,2-*f*]quinoline 7r



Starting material **6r** (0.38 mmol, 125 mg) cyclised to white solid **7r** (89 mg, 71 %); mp: 204 – 205 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ = 9.34 (d, ^3J = 8.5 Hz, 1H, $CH_{B.th.quin}$), 9.01 (dd, ^3J = 4.2 Hz, ^4J = 1.5 Hz, 1H, $CH_{B.th.quin}$), 8.79 (d, ^3J = 8.3 Hz, 1H, $CH_{B.th.quin}$), 8.11 (s, 1H, $CH_{B.th.quin}$), 7.98 (d, ^3J = 7.8 Hz, 1H, $CH_{B.th.quin}$), 7.84 – 7.73 (m, 2H, CH_{Ar}), 7.65 – 7.59 (m, 2H, $CH_{B.th.quin}$), 7.56 – 7.48 (m, 1H, $CH_{B.th.quin}$), 7.34 – 7.16 (m, 2H, CH_{Ar}) ppm. **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 163.2 (d, $^1J_{C,F}$ = 248.3 Hz, CF), 149.3 ($CH_{B.th.quin}$), 148.0, 140.3, 139.4, 138.0, 136.8 (C_{Ar}), 136.0 (d, $^4J_{C,F}$ = 3.0 Hz, C_{Ar}), 131.1 ($CH_{B.th.quin}$), 130.5 (d, $^3J_{C,F}$ = 8.3 Hz, CH_{Ar}), 129.7 (C_{Ar}), 128.3, 126.0, 125.3 ($CH_{B.th.quin}$), 125.1 (C_{Ar}), 124.5, 123.5, 121.6 ($CH_{B.th.quin}$), 116.1 (d, $^2J_{C,F}$ = 21.5 Hz, CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3039 (m), 2920 (m), 2850 (m), 1601 (m), 1550 (w), 1508 (s), 1482 (s), 1405 (m), 1348 (m), 1319 (m), 1302 (m),

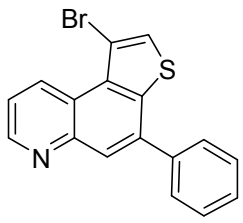
1263 (m), 1220 (s), 1158 (s), 1096 (s), 1069 (m), 1014 (m), 913 (s), 832 (s), 818 (s), 806 (s), 750 (s), 715 (s), 602 (s), 546 (m), 528 (s), 501 (s), 422 (s). **MS (EI, 70 eV)**: *m/z* (%) = 329 ([M]$^+$, 100), 328 (32), 327 (11), 301 (5), 300 (9), 164 (15), 74 (5). **HRMS (ESI-TOF)** calcd. for $C_{21}H_{12}FNS$ ([M+H]$^+$) 330.0753, found 330.0748.

-(1-bromothieno[3,2-*f*]quinolin-4-yl)-*N*,*N*-dimethylaniline 7t



According to the general procedure C, the reaction of **6t** (0.14 mmol, 53.7 mg) and MsOH (7.0 mmol, 454 µL), affords product **7t** as a yellow solid (44 mg, 83 %), mp: 199-202 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 9.97 (ddd, ^3J = 8.6, ^4J = 1.6, ^5J = 0.8 Hz, 1H, CH_{pyr}), 8.96 (dd, ^3J = 4.3, ^4J = 1.6 Hz, 1H, CH_{pyr}), 8.02 (s, 1H, CH_{thioph}), 7.68 (d, ^5J = 0.8 Hz, 1H, CH_{Ar}), 7.67 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.51 (dd, ^3J = 8.6, ^3J = 4.3 Hz, 1H, CH_{pyr}), 6.87 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 3.06 (s, 6H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 150.9 (C_{Ar}), 149.5 (CH_{Ar}), 148.4, 139.2, 138.7 (C_{Ar}), 130.7 (CH_{Ar}), 130.3 (C_{Ar}), 129.5, 126.6, 126.1 (CH_{Ar}), 123.9, 123.7 (C_{Ar}), 120.1, 112.5 (CH_{Ar}), 107.3 (C_{Ar}), 40.5 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3093 (m), 2805 (m), 1611 (s), 1595 (m), 1525 (s), 1477 (s), 1465 (m), 1445 (m), 1360 (s), 1313 (s), 1234 (m), 1195 (s), 915 (s), 878 (m), 810 (s), 795 (s), 764 (s), 606 (s), 546 (s), 513 (s). **MS (EI, 70 eV):** *m/z* (%) = 384 ([M]$^+$, 100), 383 (60), 382 ([M]$^+$, 97), 381 (40), 287 (15), 260 (15), 259 (38), 191 (31), 129 (16). **HRMS (ESI-TOF):** calcd. for $C_{19}H_{15}N_2Br_1S_1$ ([M+H]$^+$) 383.0218, found 383.0216.

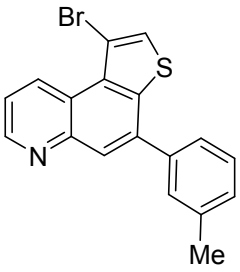
1-bromo-4-phenylthieno[3,2-*f*]quinoline 7u



According to the general procedure, the reaction of **6u** (0.258 mmol, 88.0 mg) and MsOH (12.9 mmol, 840 µL), affords product **7u** as a white solid (68.2 mg, 77 %), mp: 166 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 9.99 (dd, ^3J = 8.6, ^4J = 1.6 Hz, 1H, CH_{pyr}), 8.98 (dd, ^3J = 4.3, ^4J = 1.6 Hz, 1H, CH_{pyr}), 8.06 (s, 1H, CH_{thioph}), 7.74 (dd, ^3J = 7.9, ^4J = 1.7 Hz, 2H, CH_{Ar}), 7.68 (s, 1H, CH_{Ar}), 7.59 – 7.54 (m, 2H, CH_{Ar}), 7.55 (dd, ^3J = 8.6, ^3J = 4.3 Hz, 1H, CH_{pyr}), 7.54 – 7.47 (m, 1H, CH_{Ar}) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.7 (CH_{Ar}), 148.1, 138.9, 138.7, 138.4 (C_{Ar}), 130.7 (CH_{Ar}), 130.5 (C_{Ar}), 129.1, 129.0, 128.7, 127.1, 126.7 (CH_{Ar}), 124.2 (C_{Ar}), 120.7 (CH_{Ar}), 107.4 (C_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3093 (m), 3023 (m), 1480 (m), 1463 (m), 1434 (m), 1313 (m), 1201 (m), 1072 (m), 1032 (m), 915 (s), 861 (m), 841 (m),

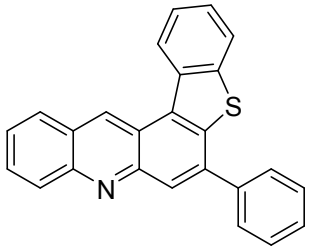
806 (m), 762 (s), 752 (s), 696 (s), 608 (s), 577 (s), 548 (s). **MS (EI, 70 eV):** *m/z* (%) = 341 ([M]$^+$, 100), 339 ([M]$^+$, 96), 260 (54), 259 (41), 232 (26), 189 (23), 130 (34), 116 (20), 94 (20). **HRMS (EI):** calcd. for $C_{17}H_{10}N_1Br_1S_1$ $(M)^+$ 338.97118, found 338.97149; calcd. for $C_{17}H_{10}N_1{}^{81}Br_1S_1$ $(M)^+$ 340.96914, found 340.97009.

1-bromo-4-(*m*-tolyl)thieno[3,2-*f*]quinoline 7v



Following the general procedure, the reaction of **6v** (0.11 mmol, 39.0 mg) and MsOH (5.5 mmol, 356 µL), affords product **7v** as a white solid (32 mg, 82 %), mp: 138-140 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 9.98 (ddd, ^3J = 8.6, ^4J = 1.6, ^5J = 0.8 Hz, 1H, CH_{pyr}), 8.98 (dd, ^3J = 4.3, ^4J = 1.6 Hz, 1H, CH_{pyr}), 8.04 (s, 1H, CH_{thioph}), 7.68 (d, ^5J = 0.8 Hz, 1H, CH_{Ar}), 7.58 – 7.53 (m, 2H, CH_{Ar}), 7.54 (dd, ^3J = 8.6, ^3J = 4.3 Hz, 1H, CH_{pyr}), 7.43 (t, ^3J = 7.8 Hz, 1H, CH_{Ar}), 7.31 (d, ^3J = 7.8 Hz, 1H, CH_{Ar}), 2.47 (s, 3H, CH_3) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.8 (CH_{Ar}), 148.2, 138.9, 138.8, 138.5 (C_{Ar}), 130.6 (CH_{pyr}), 130.4 (C_{Ar}), 129.7, 129.4, 129.0, 127.1, 126.6, 125.7, 124.2 (C_{Ar}), 120.6 (CH_{Ar}), 107.4 (C_{Ar}), 21.7 (CH_3) ppm. **IR** (ATR, cm^{-1}): ṽ = 3095 (w), 3044 (m), 1554 (m), 1480 (m), 1467 (m), 1313 (s), 1203 (m), 919 (s), 870 (s), 857 (m), 781 (s), 764 (s), 725 (m), 699 (s), 624 (s), 581 (m), 546 (s), 503 (m), 433 (m). **MS (EI, 70 eV):** *m/z* (%) = 355 ([M]$^+$, 91), 354 (22), 353 ([M]$^+$, 92), 274 (37), 273 (23), 272 (28), 259 (35), 136 (100). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{12}N_1Br_1S_1$ ([M+H]$^+$) 353.9952, found 353.9952.

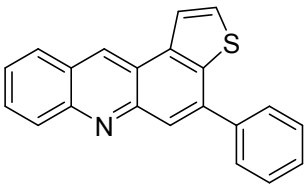
6-phenylbenzo[4,5]thieno[3,2-*a*]acridine 7w



According to the general procedure, **6w** (0.13 mmol, 46.5 mg) and MsOH (6.45 mmol, 420 µL) were mixed and stirred during 6 hours, affords product **7w** as a yellow solid (43.4 mg, 93 %), mp: 193-195 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 9.81 (s, 1H, CH_{pyr}), 8.94 (dd, ^3J = 8.3, ^4J = 1.4 Hz, 1H, CH_{Ar}), 8.29 (dd, ^3J = 8.7, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.25 (d, ^5J = 0.9 Hz, 1H, CH_{Ar}), 8.17 (dd, ^3J = 8.4, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.99 (dd, ^3J = 8.1, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.86 (dd, ^3J = 8.0, ^4J = 1.6 Hz, 2H, CH_{Ar}), 7.83 (ddd, ^3J = 8.7, ^3J = 6.6, ^4J = 1.4 Hz, 1H, CH_{Ar}), 7.67 (ddd, ^3J = 8.4, ^3J = 7.1, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.63 (ddd, ^3J = 8.3, ^3J = 6.6, ^4J = 1.2 Hz, 1H, CH_{Ar}), 7.60 – 7.53 (m, 3H, CH_{Ar}), 7.53 (ddd, ^3J = 8.1, ^3J = 7.1, ^4J = 1.1 Hz, 1H, CH_{Ar}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.0, 147.7, 140.4, 140.2, 139.8, 139.3, 137.1 (C_{Ar}), 130.8, 130.3, 129.2, 129.1, 129.0 (CH_{Ar}), 128.9 (C_{Ar}), 128.7, 128.6, 128.0 (CH_{Ar}), 126.6 (C_{Ar}), 126.4, 125.7, 125.4, 124.3 (CH_{Ar}), 123.6 (C_{Ar}), 123.5 (CH_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3054 (w), 3029 (w), 1498 (m), 1447 (m), 1286 (w), 1129 (m), 884 (m), 767 (m), 729 (s), 713 (s), 694 (s), 670 (m), 596 (s), 563 (m), 530 (m), 462 (m),

422 (m). **MS (EI, 70 eV):** *m/z* (%) = 362 (27), 361 ([M]+, 100), 360 (32), 359 (14), 358 (6), 357 (4), 332 (2), 180 (16), 179 (6), 166 (2). **HRMS (EI):** calcd. for $C_{25}H_{15}N_1S_1$ $(M)^+$ 361.09197, found 361.09125.

4-phenylthieno[3,2-*a*]acridine 7x

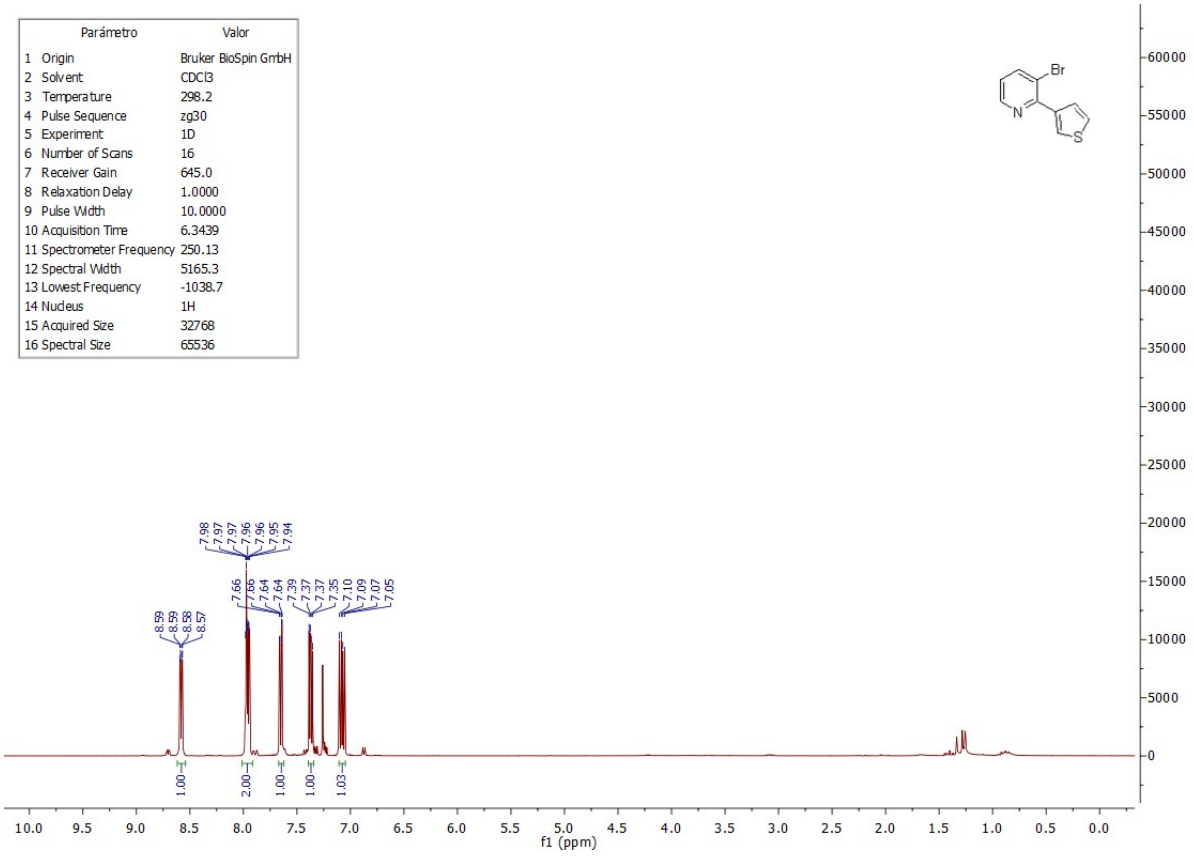


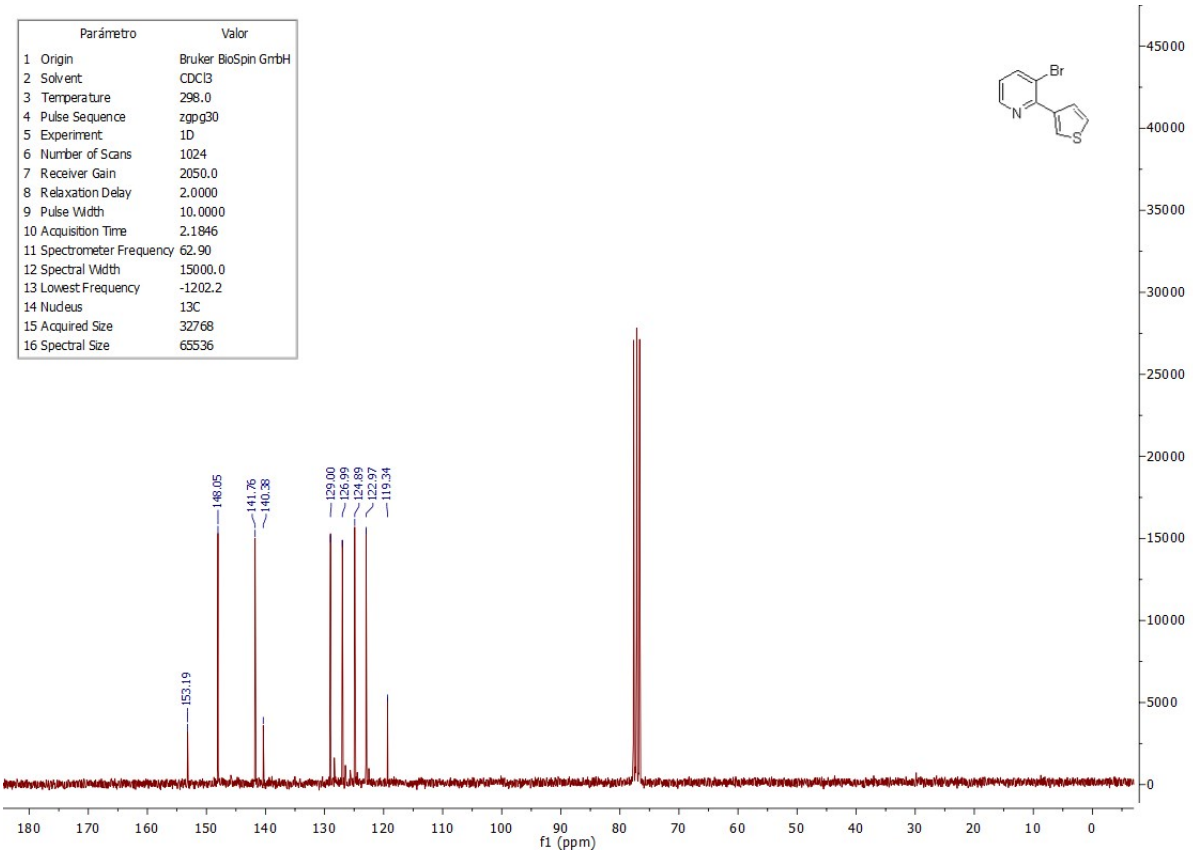
According to the general procedure, **6x** (0.13 mmol, 40.2 mg) and MsOH (6.45 mmol, 420 µmL) were mixed and stirred during 6 hours, affords product **7x** as a yellow solid (36.95 mg, 92 %), mp: 148-150 °C. **^{1}H NMR (250 MHz, $CDCl_3$)** δ = 9.14 (br s, 1H, CH_{pyr}), 8.28 (ddd, ^3J = 8.8, ^4J = 1.9, ^5J = 0.9 Hz, 1H, CH_{Ar}), 8.18 (d, ^3J = 5.4 Hz, 1H, CH_{thioph}), 8.13 (br s, 1H, CH_{Ar}), 8.07 (ddd, ^3J = 8.4, ^4J = 1.6, ^5J = 0.7 Hz, 1H, CH_{Ar}), 7.89 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 2H, CH_{Ar}), 7.81 (ddd, ^3J = 8.8, ^3J = 6.8, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.72 (dd, ^3J = 5.4, ^6J = 0.6 Hz, 1H, CH_{thioph}), 7.62 – 7.47 (m, 4H, CH_{Ar}) ppm. **^{13}C NMR (63 MHz, $CDCl_3$)** δ = 149.0, 148.4, 140.1, 139.9, 137.3, 136.2 (C_{Ar}), 131.1, 130.1, 129.4, 129.1, 128.9, 128.5, 128.2, 127.6 (CH_{Ar}), 126.5 (C_{Ar}), 126.1, 125.3, 123.0 (CH_{Ar}), 122.5 (C_{Ar}) ppm. **IR** (ATR, cm^{-1}): ṽ = 3052 (w), 1480 (m), 1438 (m), 1360 (m), 1092 (m), 905 (m), 878 (m), 868 (m), 789 (m), 746 (s), 711 (s), 690 (s), 672 (s), 655 (m), 620 (m), 600 (s), 560 (m), 528 (m), 468 (m), 437 (m). **MS (EI, 70 eV):** *m/z* (%) = 312 (24), 311 ($[M]^+$, 100), 310 (40), 309 (14), 308 (5), 155 (11), 133 (6). **HRMS (EI):** calcd. for $C_{21}H_{13}N_1S_1$ $(M)^+$ 311.07632, found 311.07647.

NMR-Spectra

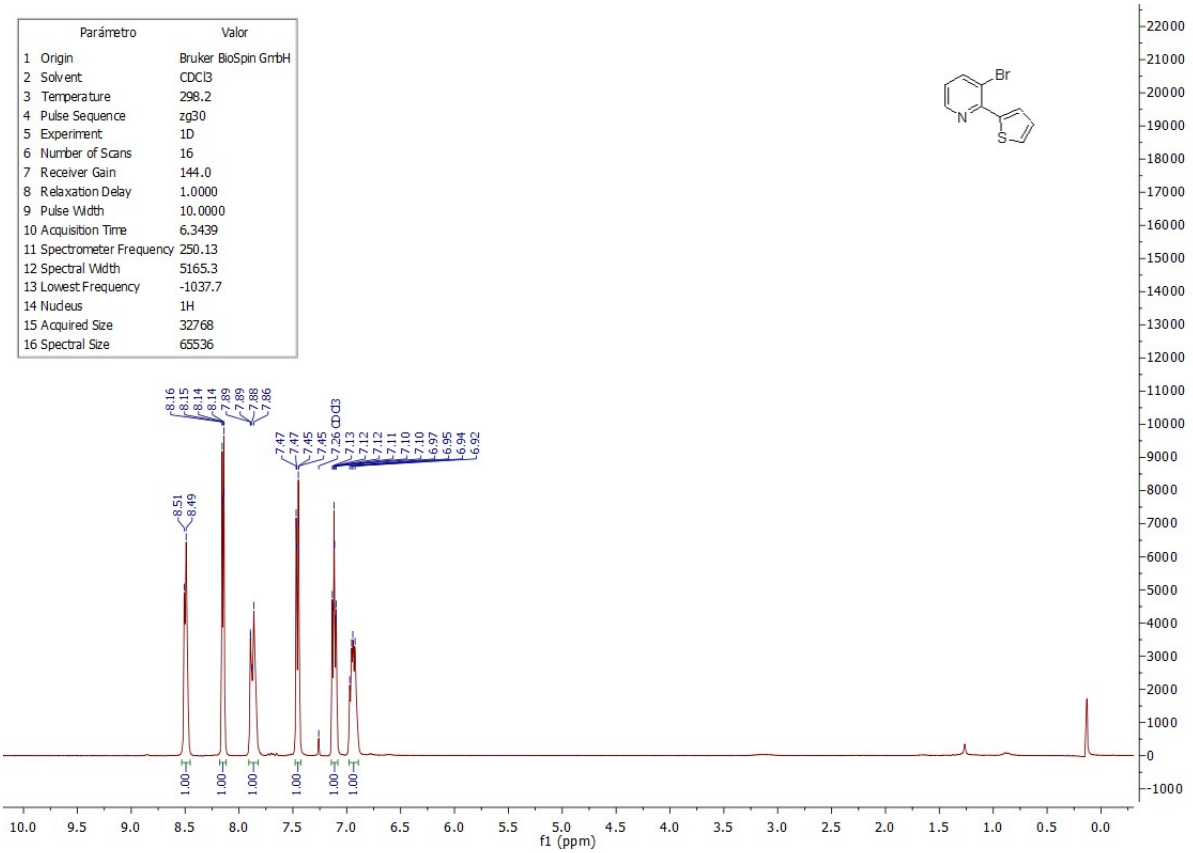
3-bromo-2-(thiophen-3-yl)pyridine **2a**

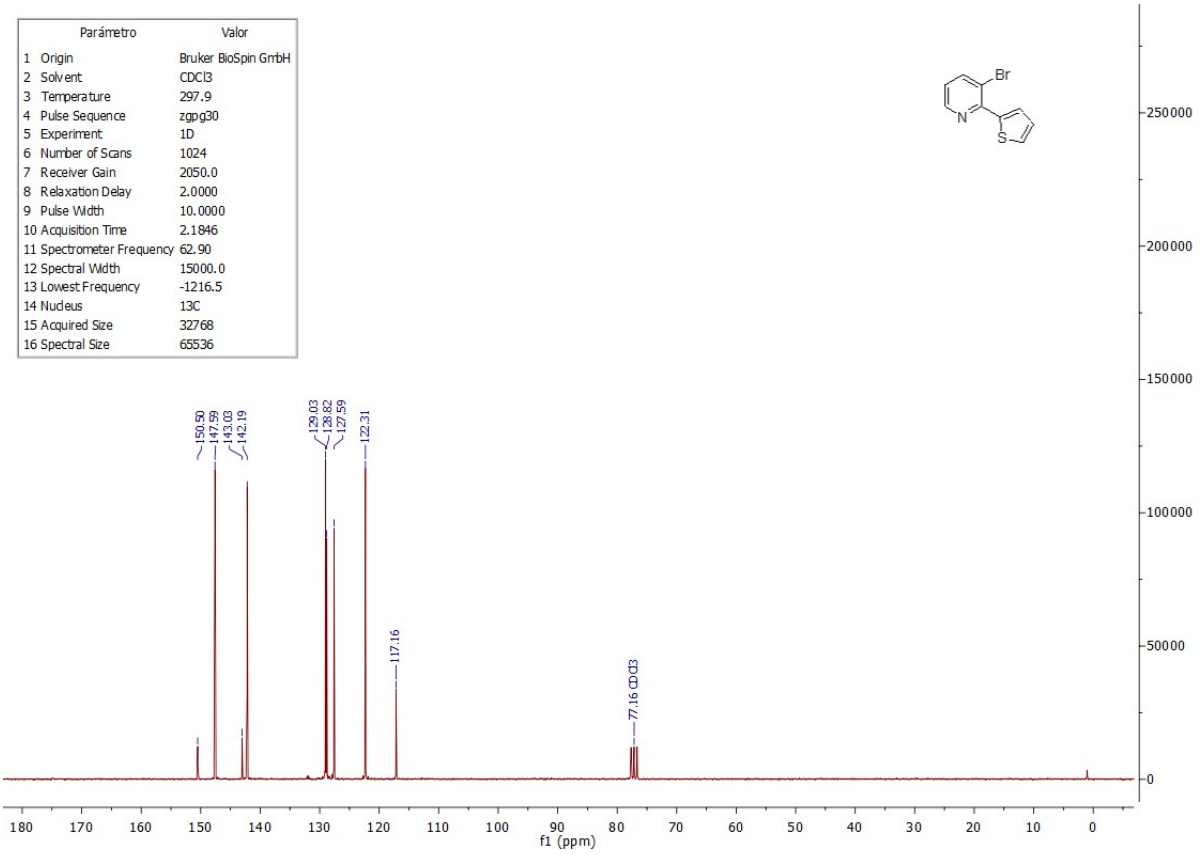
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	645.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.7
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536



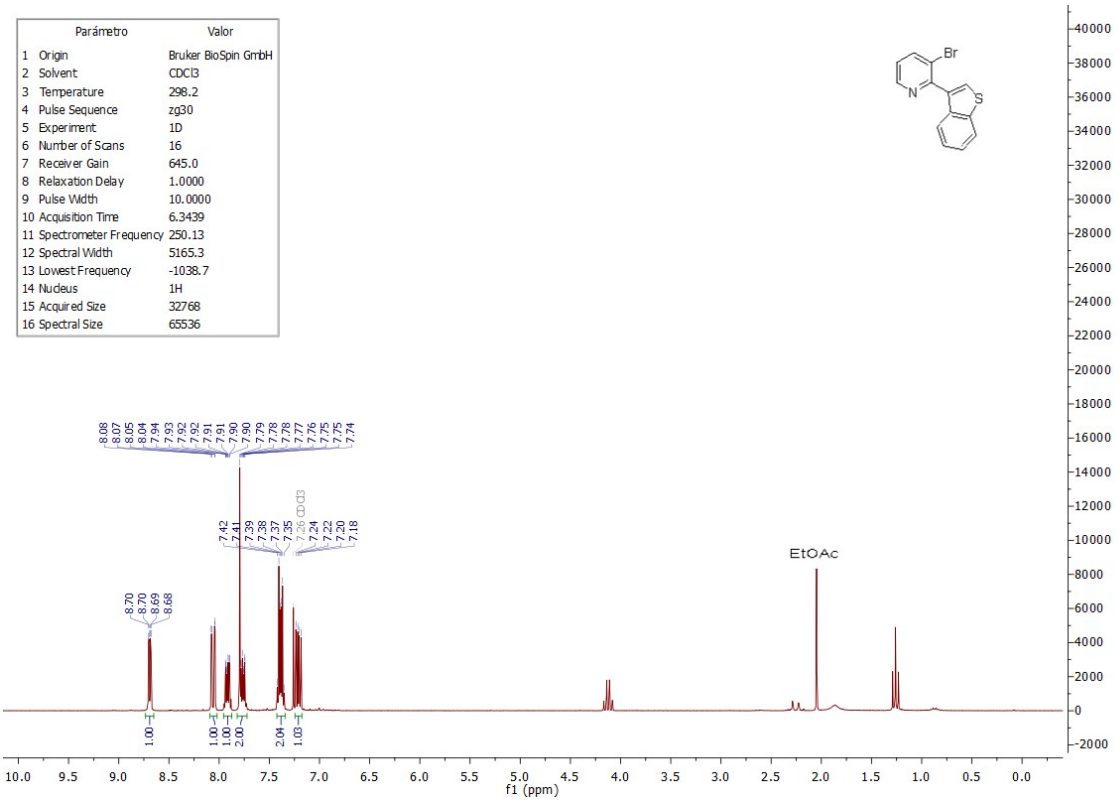


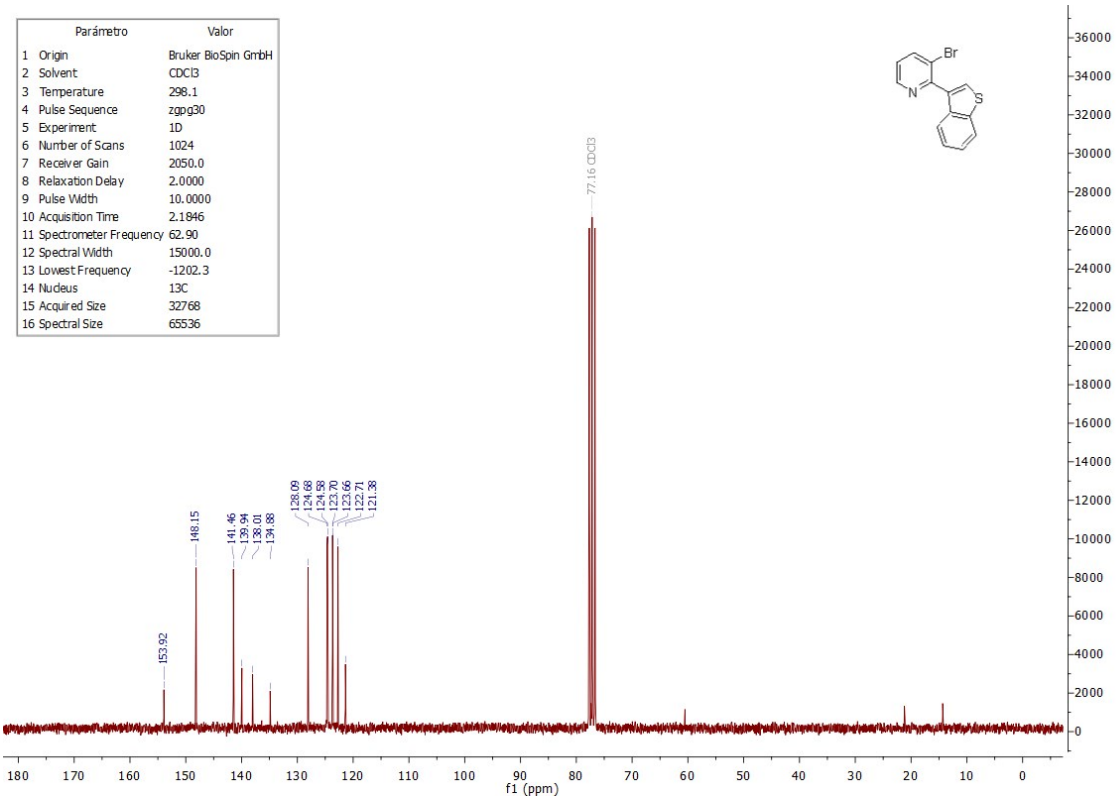
3-bromo-2(thiophen-2-yl)pyridine **2b**



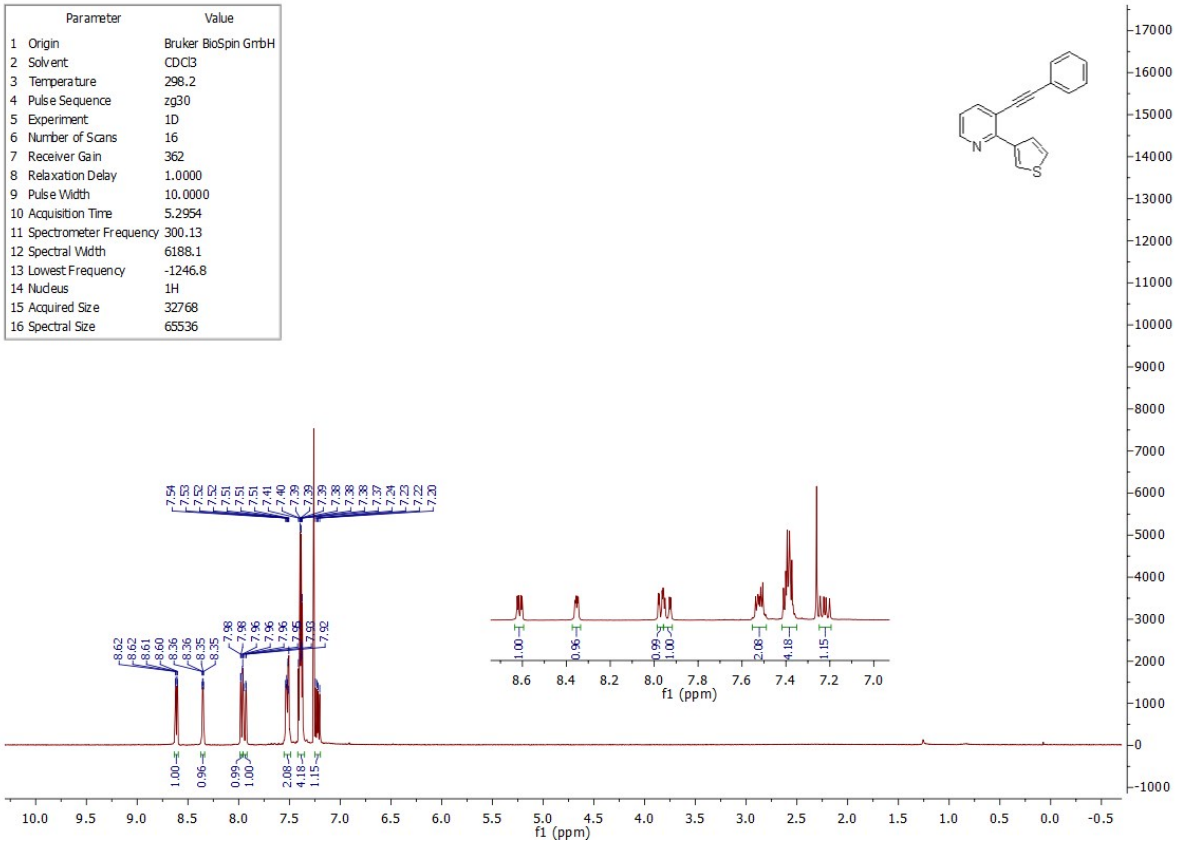


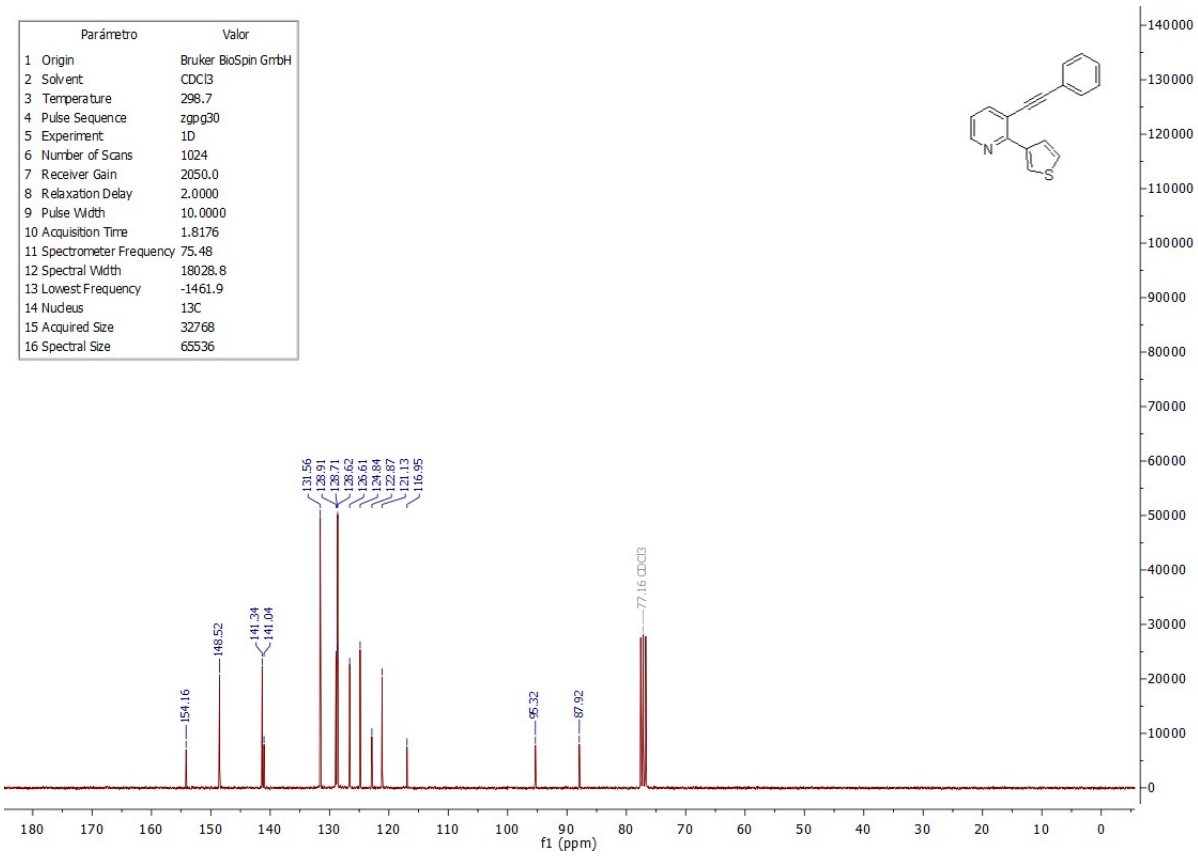
2-(benzo[*b*]thiophen-3-yl)-3-bromopyridine **2c**





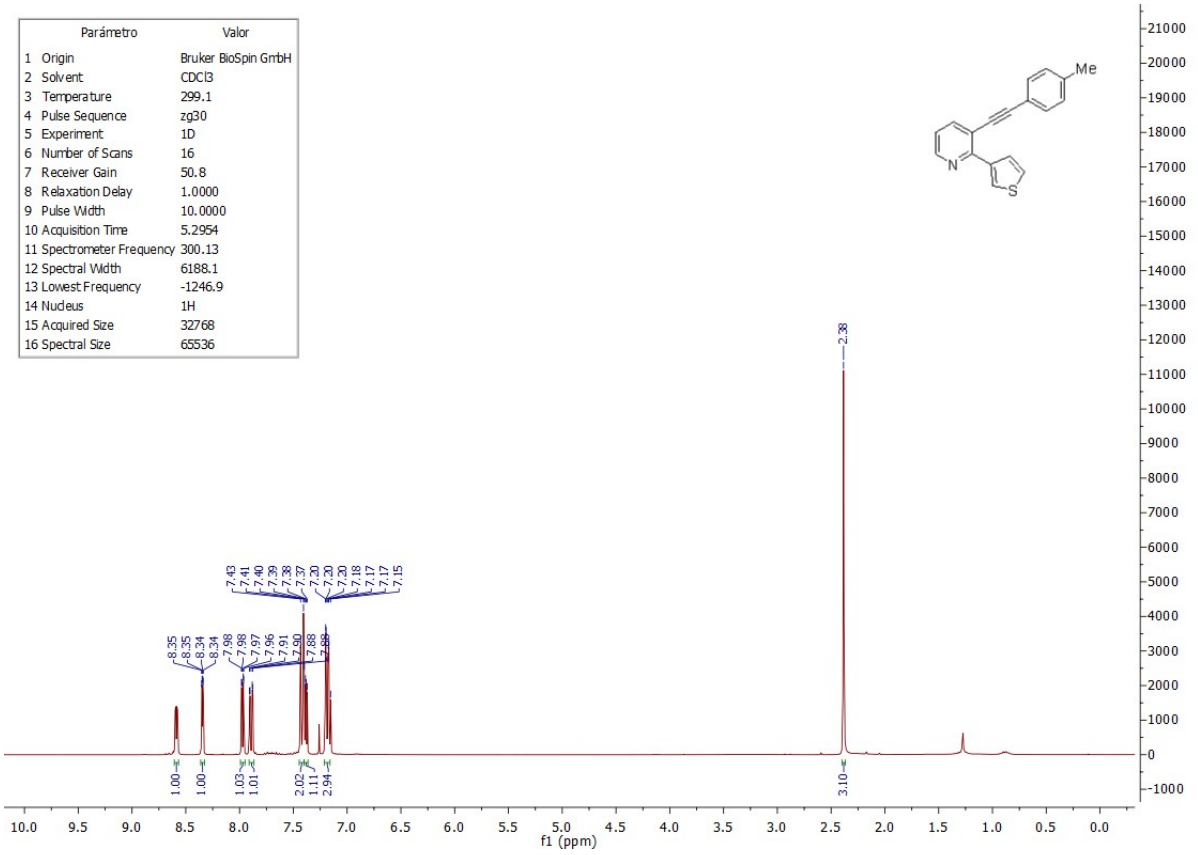
3-(phenylethynyl)-2-(thiophen-3-yl)pyridine **3a**



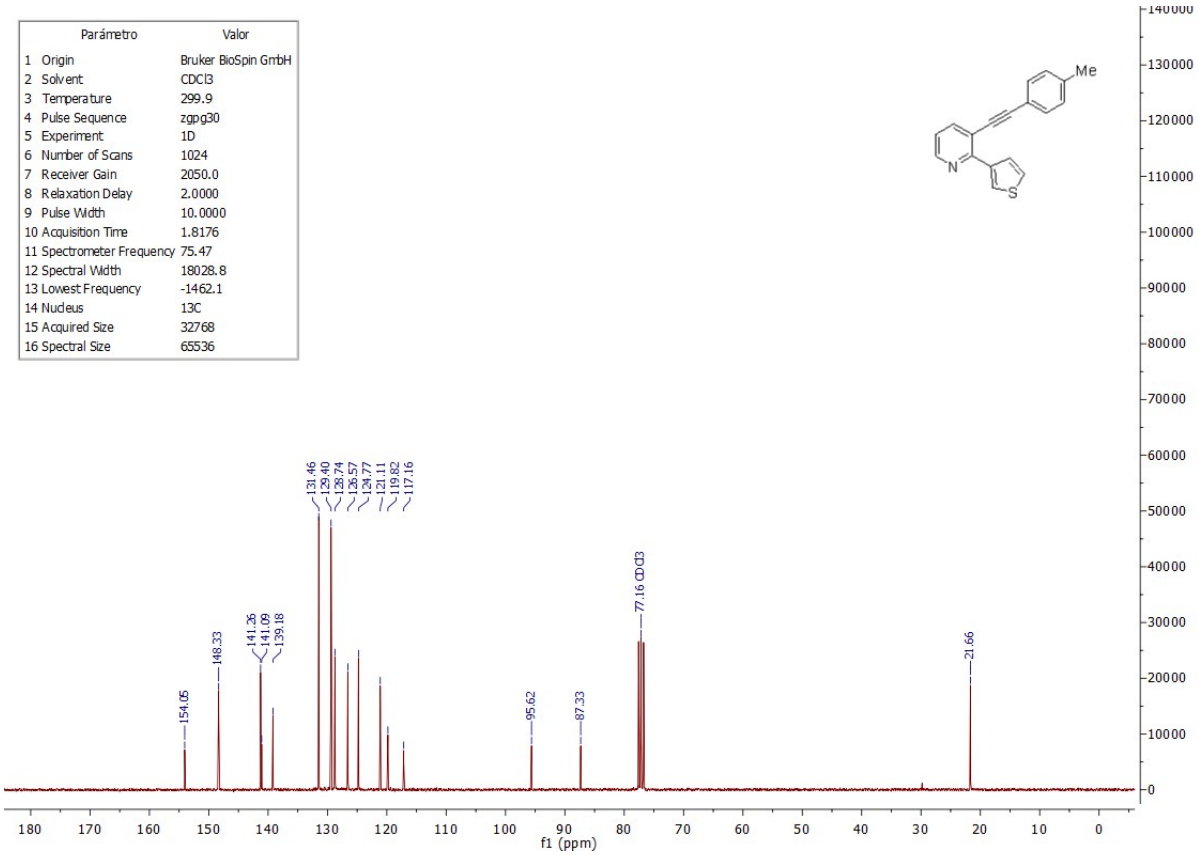


2-(thiophen-3-yl)-3-(**p**-tolylethynyl)pyridine **3b**

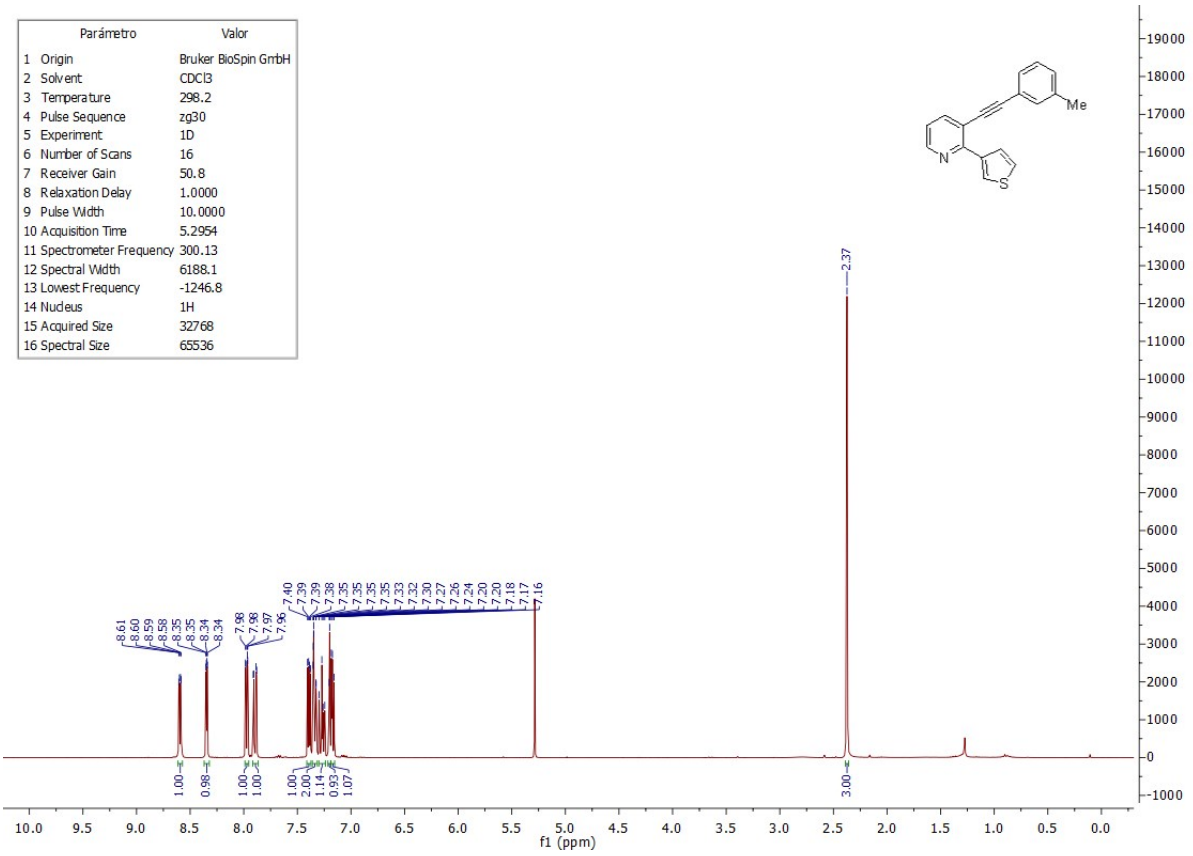
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	299.1
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	50.8
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1246.9
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

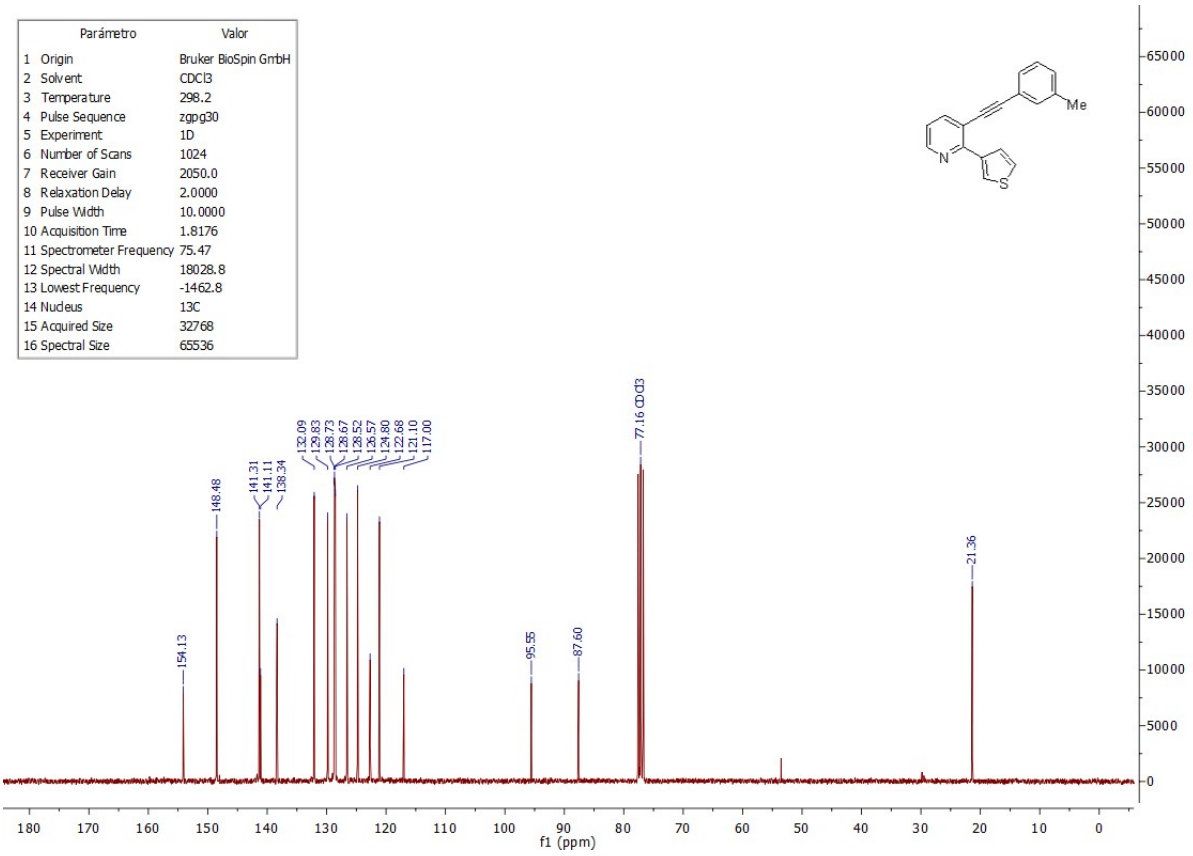


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	299.9
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1462.1
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

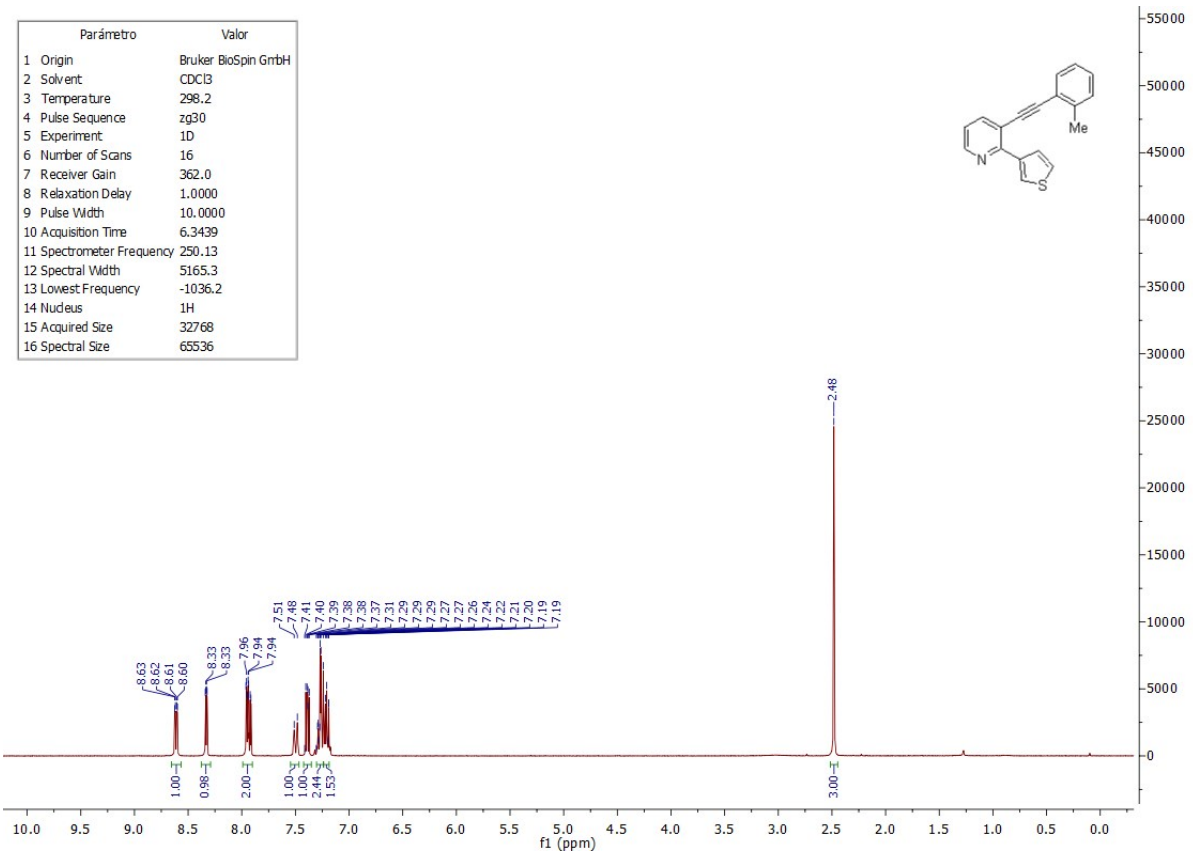


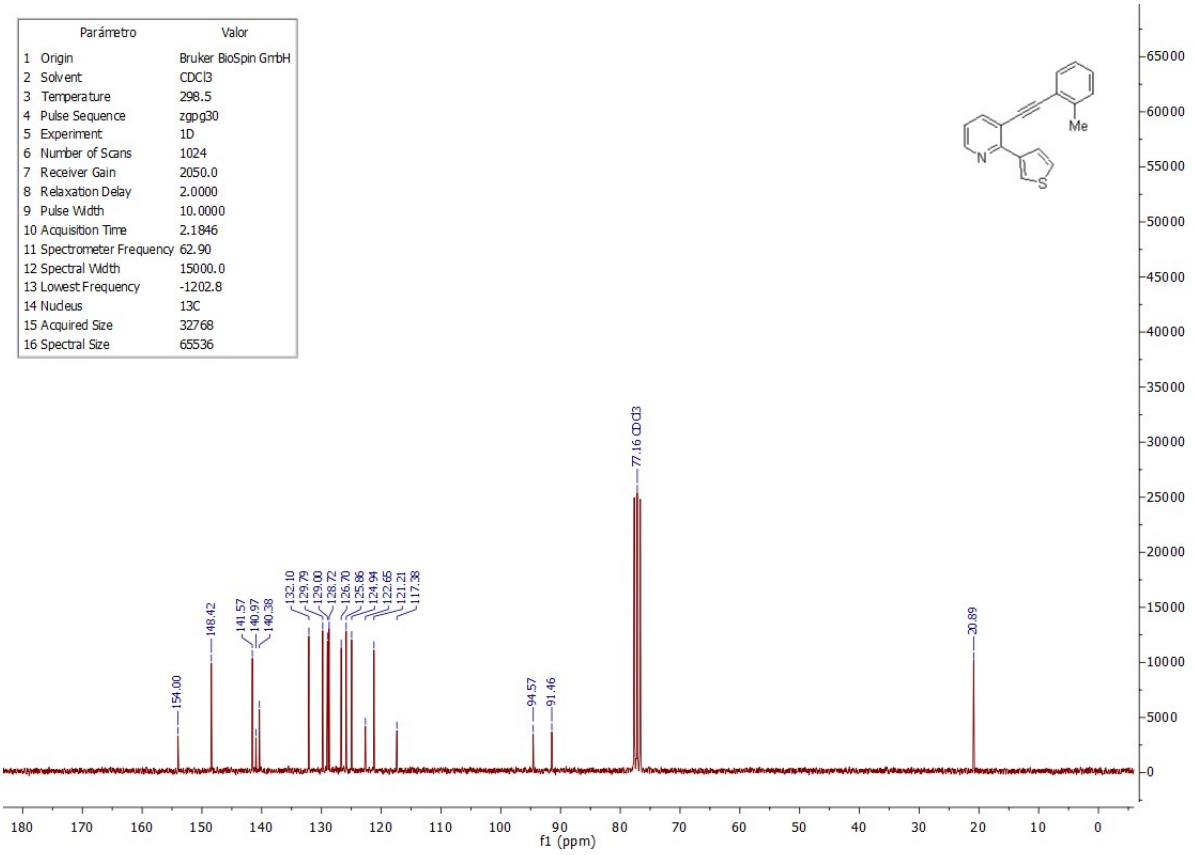
2-(thiophen-3-yl)-3-(*m*-tolylethynyl)pyridine **3c**



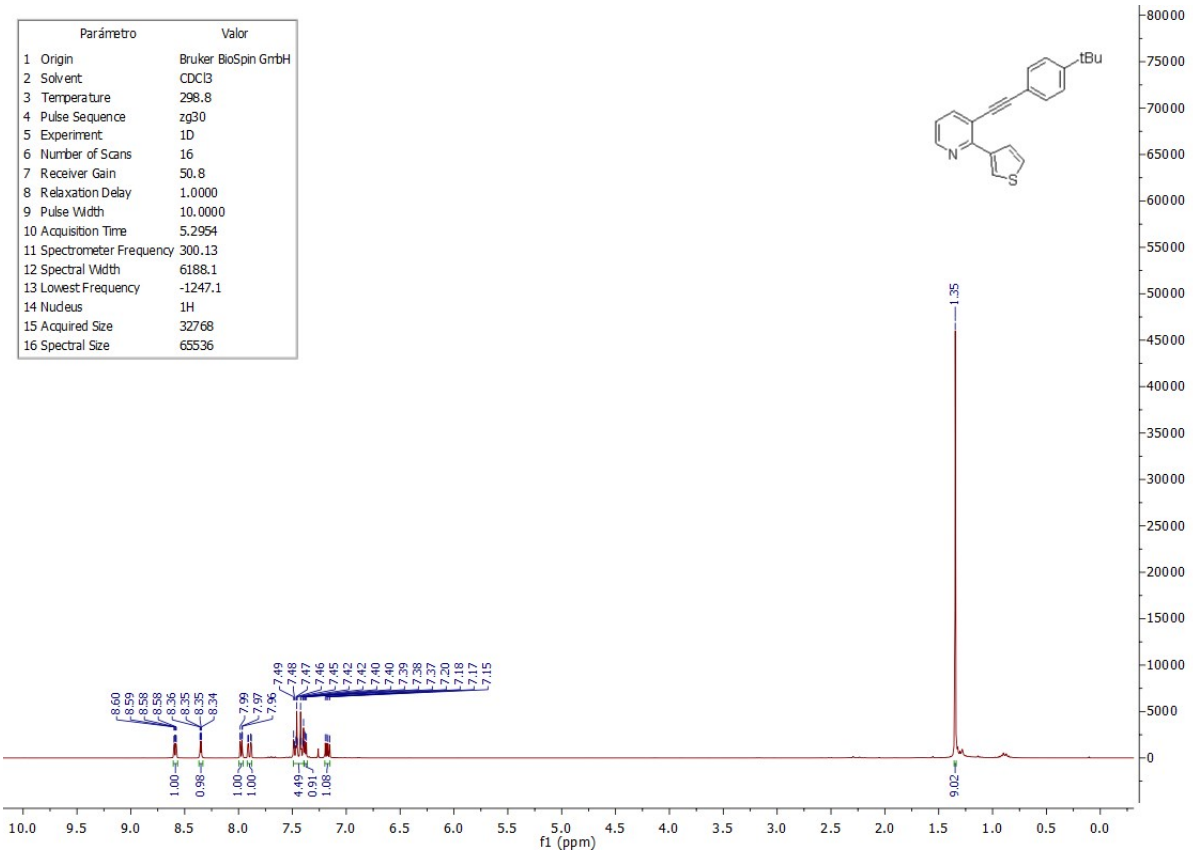


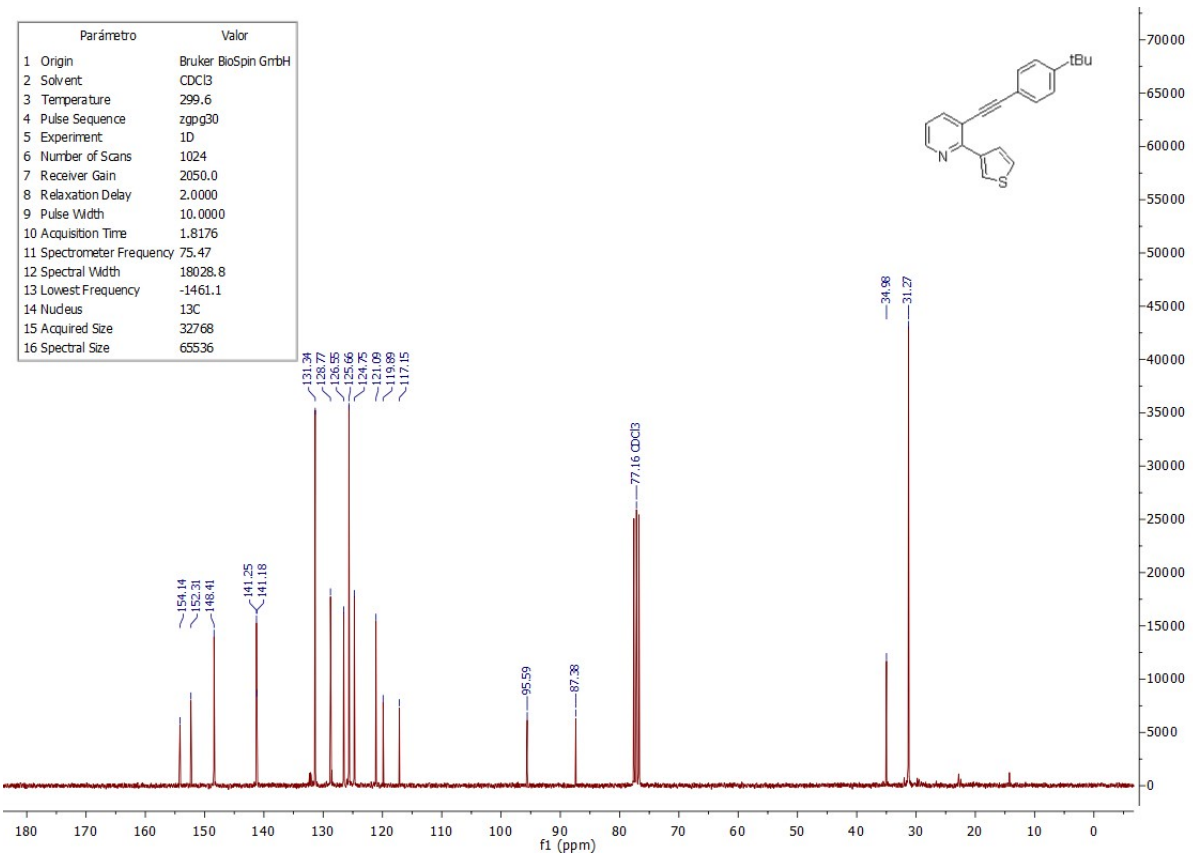
2-(thiophen-3-yl)-3-(*o*-tolylethynyl)pyridine **3d**





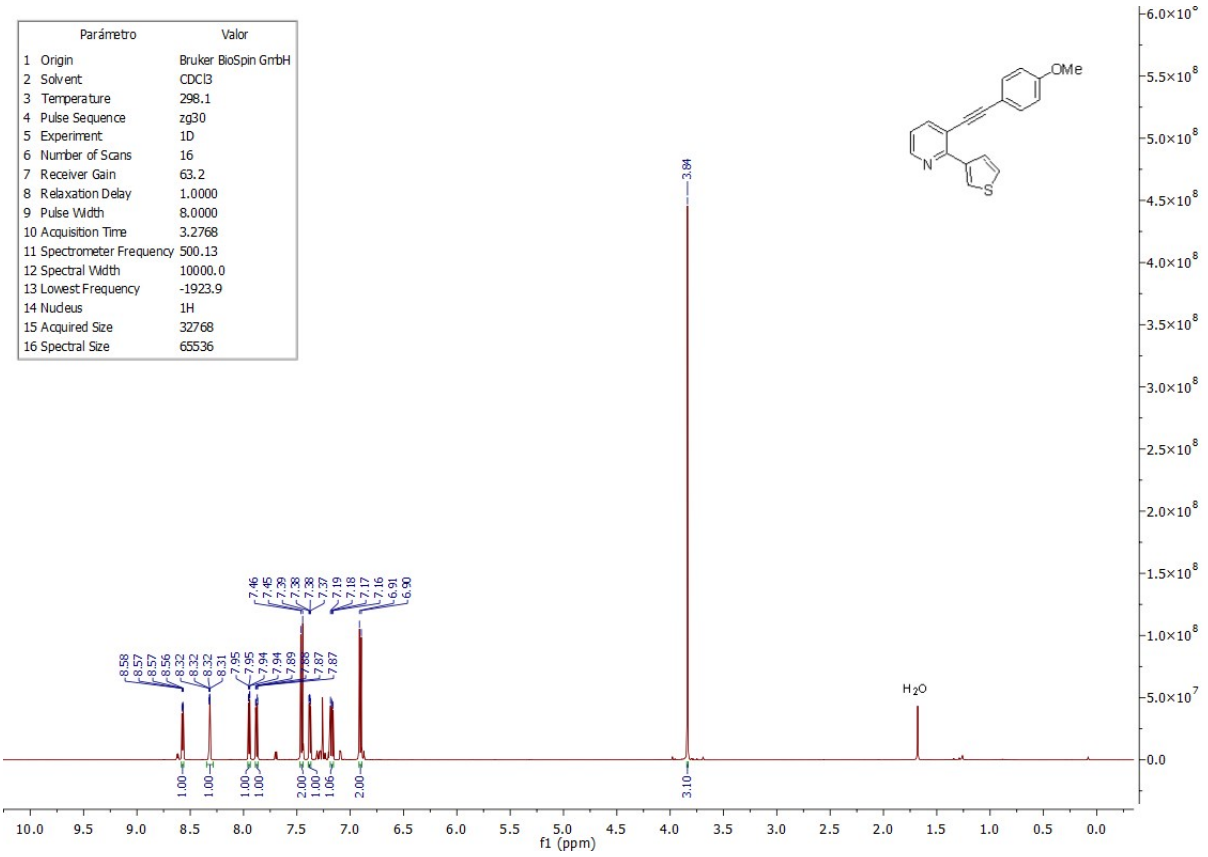
3-((4-(*tert*-butyl)phenyl)ethynyl)-2-(thiophen-3-yl)pyridine **3e**



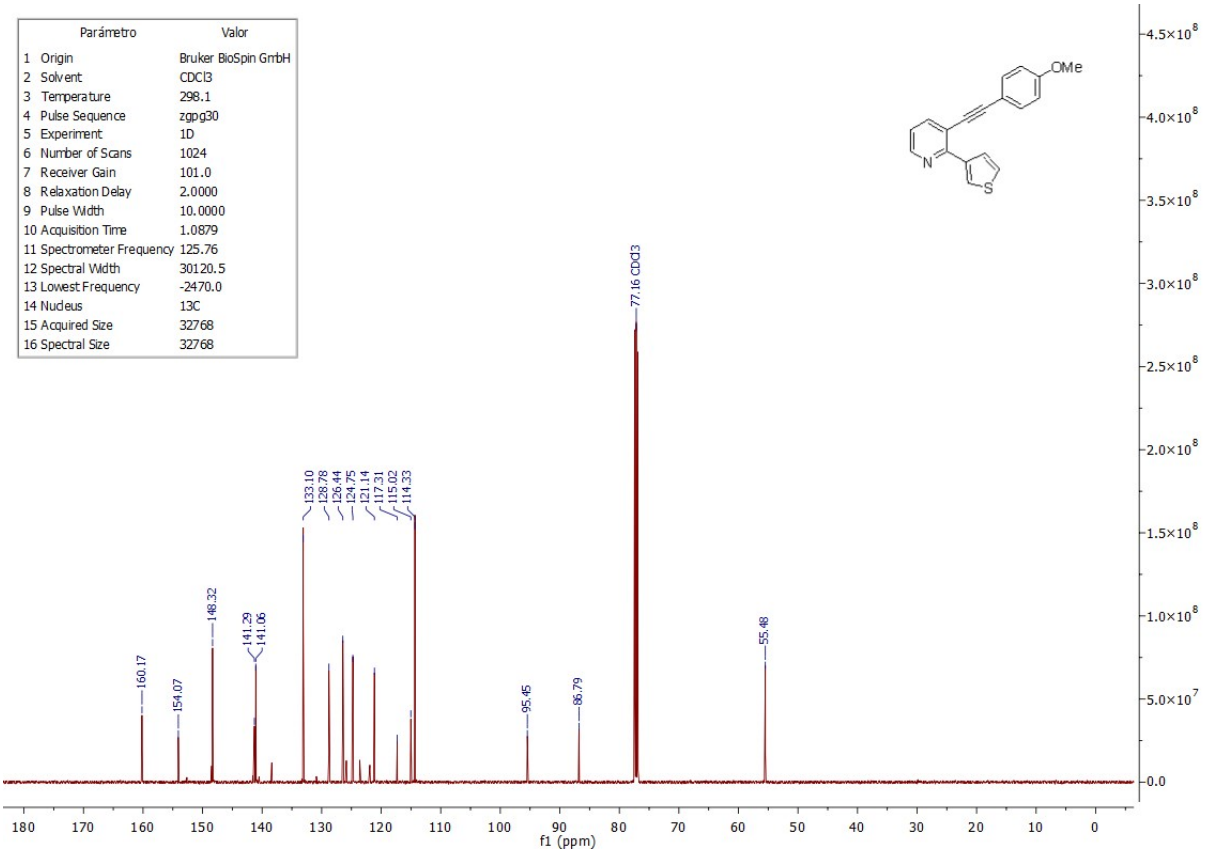


3-((4-methoxyphenyl)ethynyl)-2-(thiophen-3-yl)pyridine **3f**

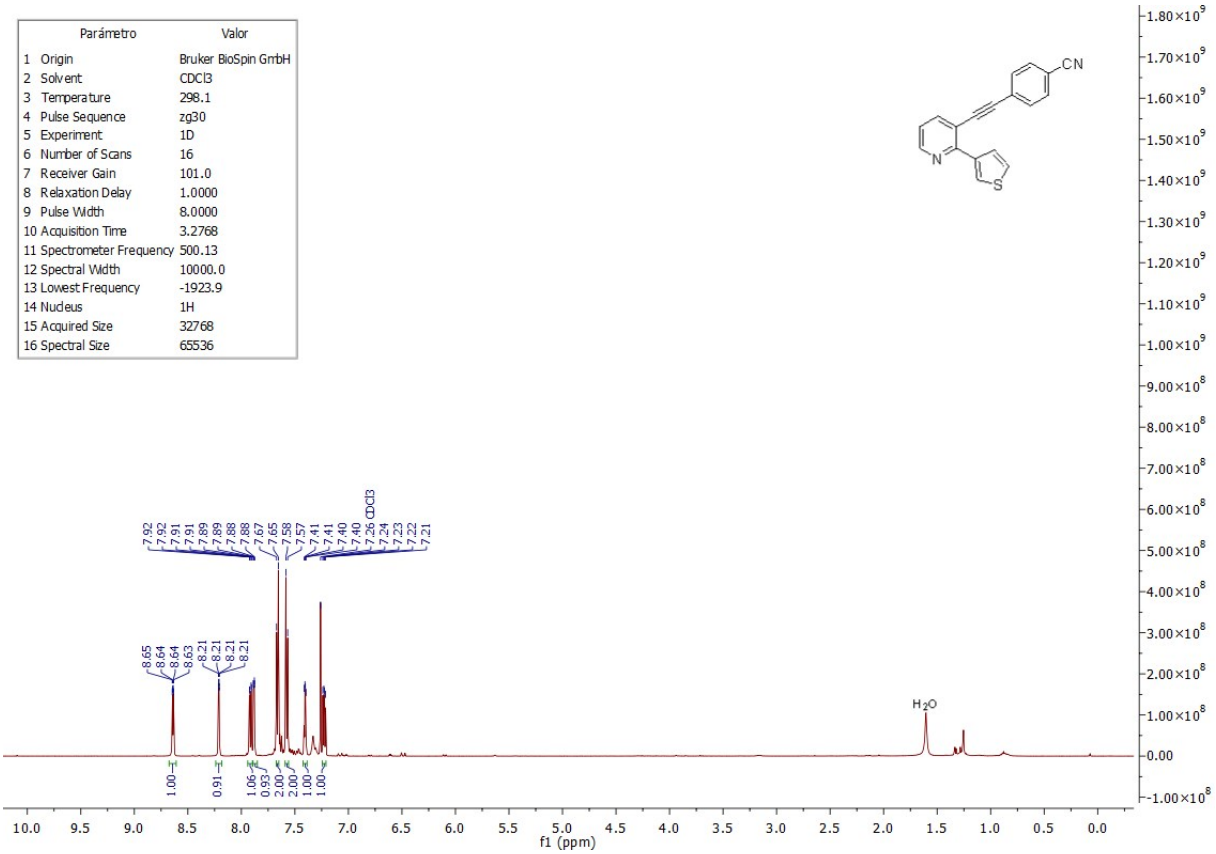
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	63.2
8 Relaxation Delay	1.0000
9 Pulse Width	8.0000
10 Acquisition Time	3.2768
11 Spectrometer Frequency	500.13
12 Spectral Width	10000.0
13 Lowest Frequency	-1923.9
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

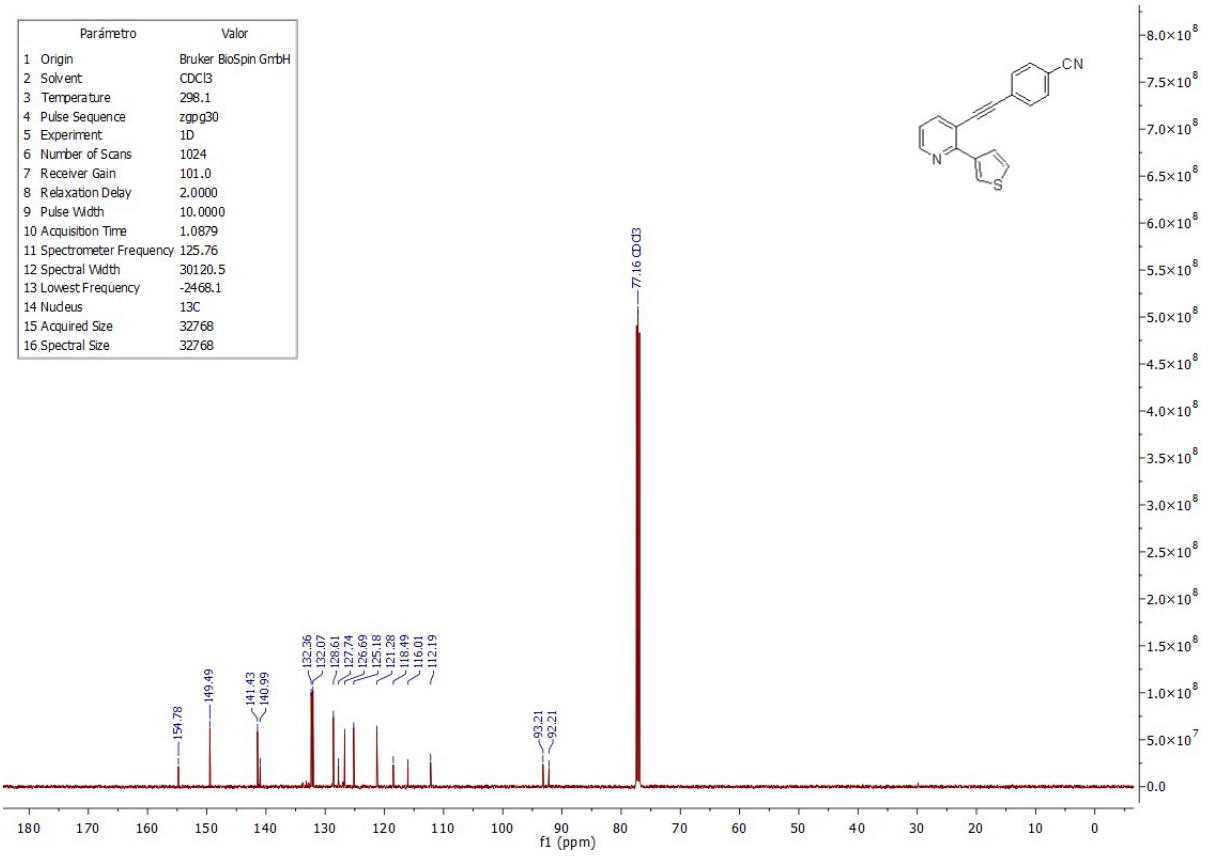


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	101.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.0879
11 Spectrometer Frequency	125.76
12 Spectral Width	30120.5
13 Lowest Frequency	-2470.0
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768

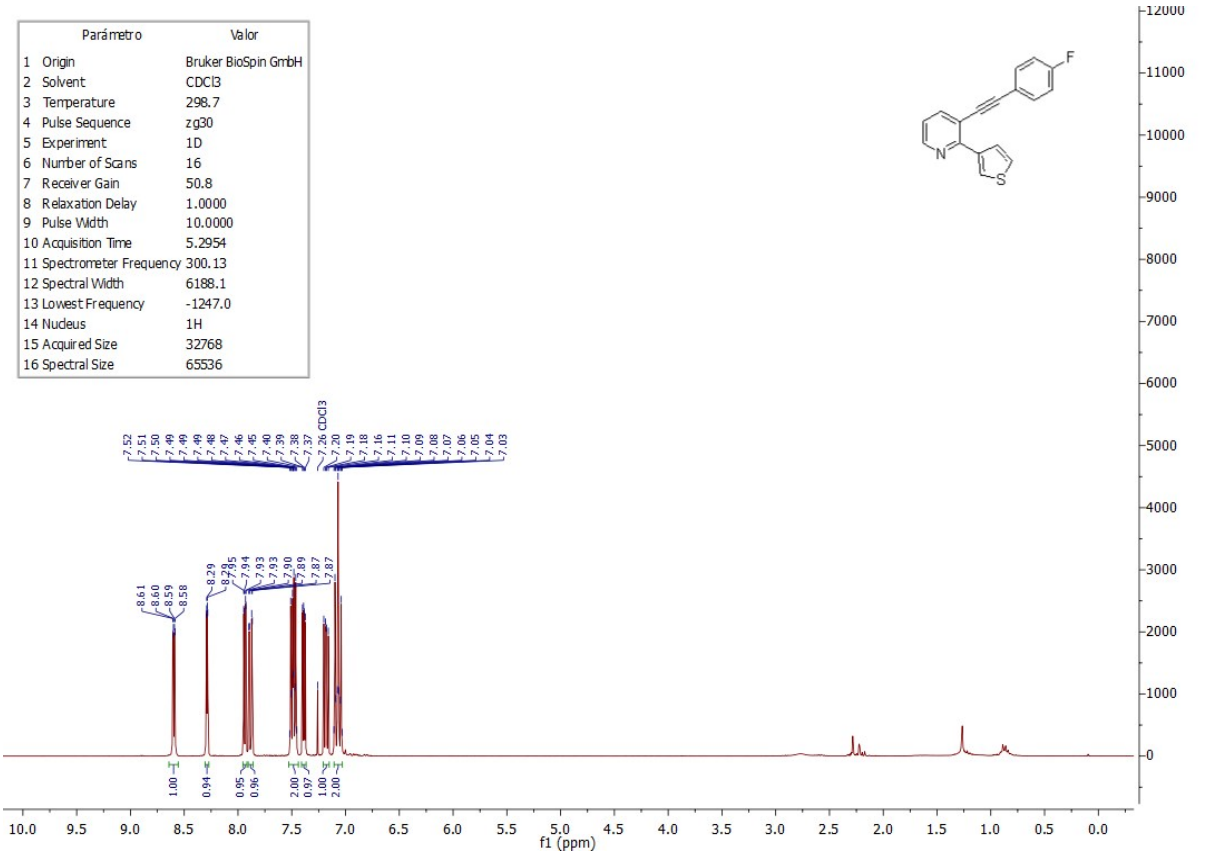


4-((2-(thiophen-3-yl)pyridin-3-yl)ethynyl)benzonitrile **3g**

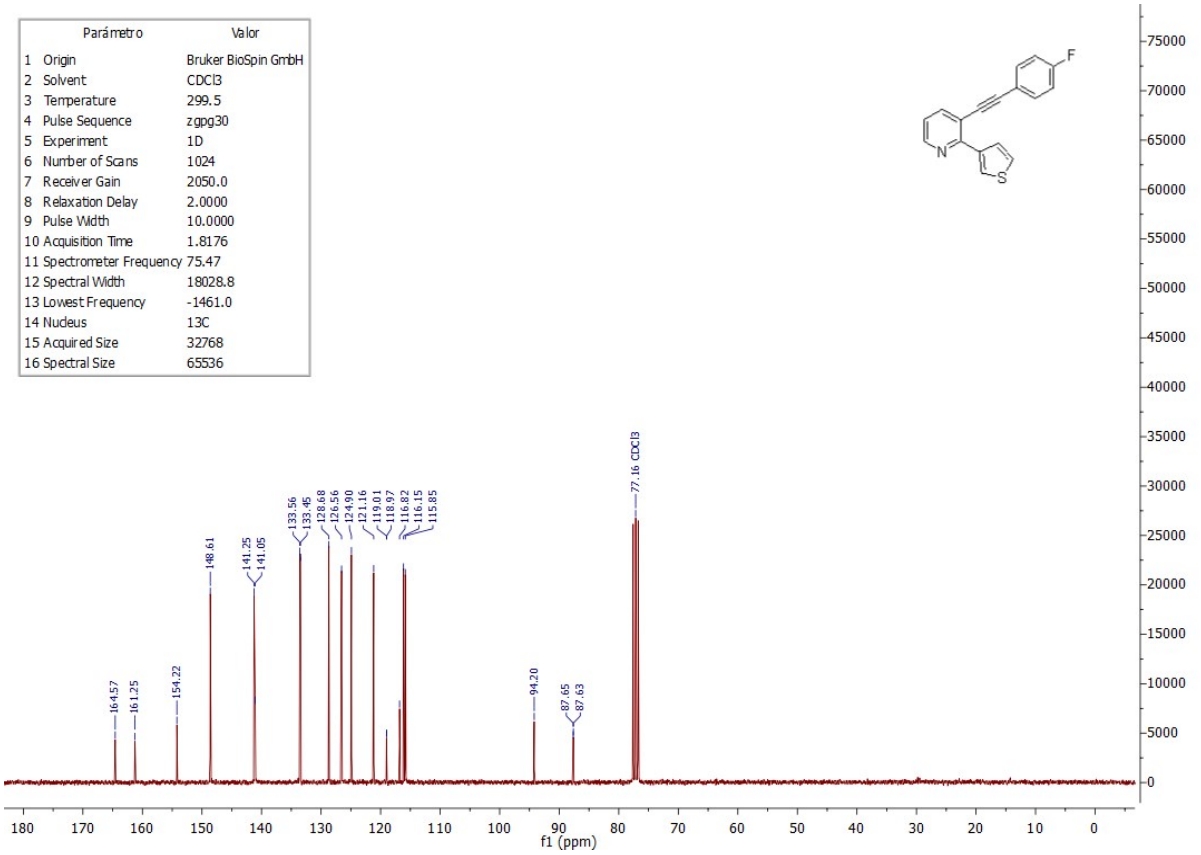




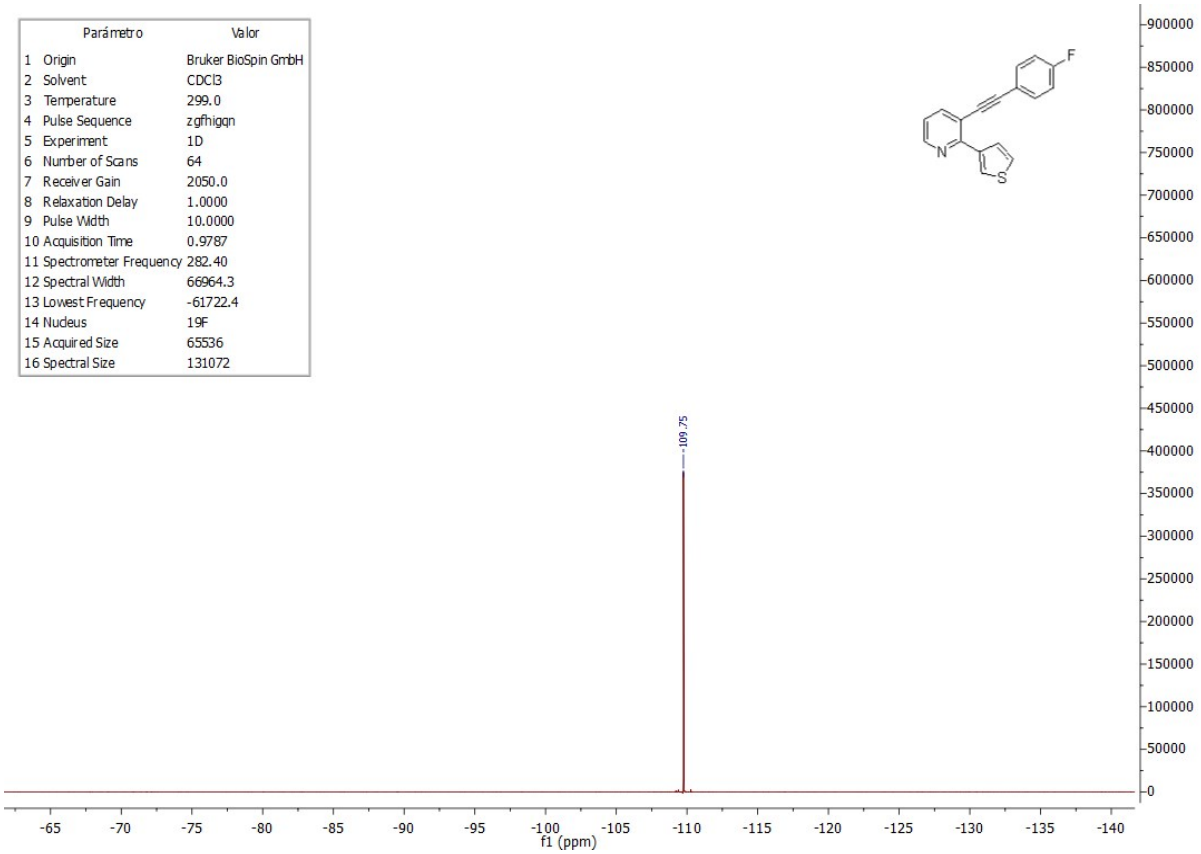
3-((4-fluorophenyl)ethynyl)-2-(thiophen-3-yl)pyridine **3h**



Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	299.5
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1461.0
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

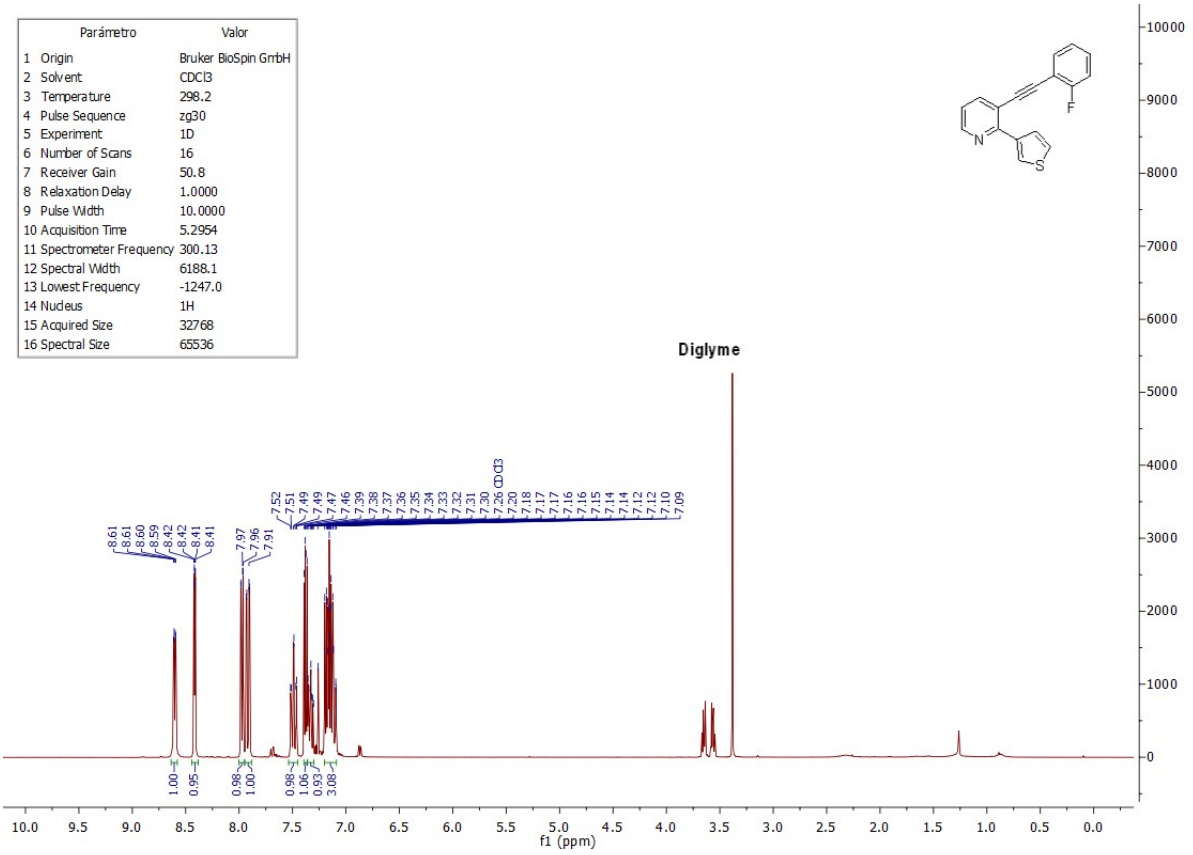


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	299.0
4 Pulse Sequence	zgfhigqn
5 Experiment	1D
6 Number of Scans	64
7 Receiver Gain	2050.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	0.9787
11 Spectrometer Frequency	282.40
12 Spectral Width	66964.3
13 Lowest Frequency	-61722.4
14 Nucleus	19F
15 Acquired Size	65536
16 Spectral Size	131072

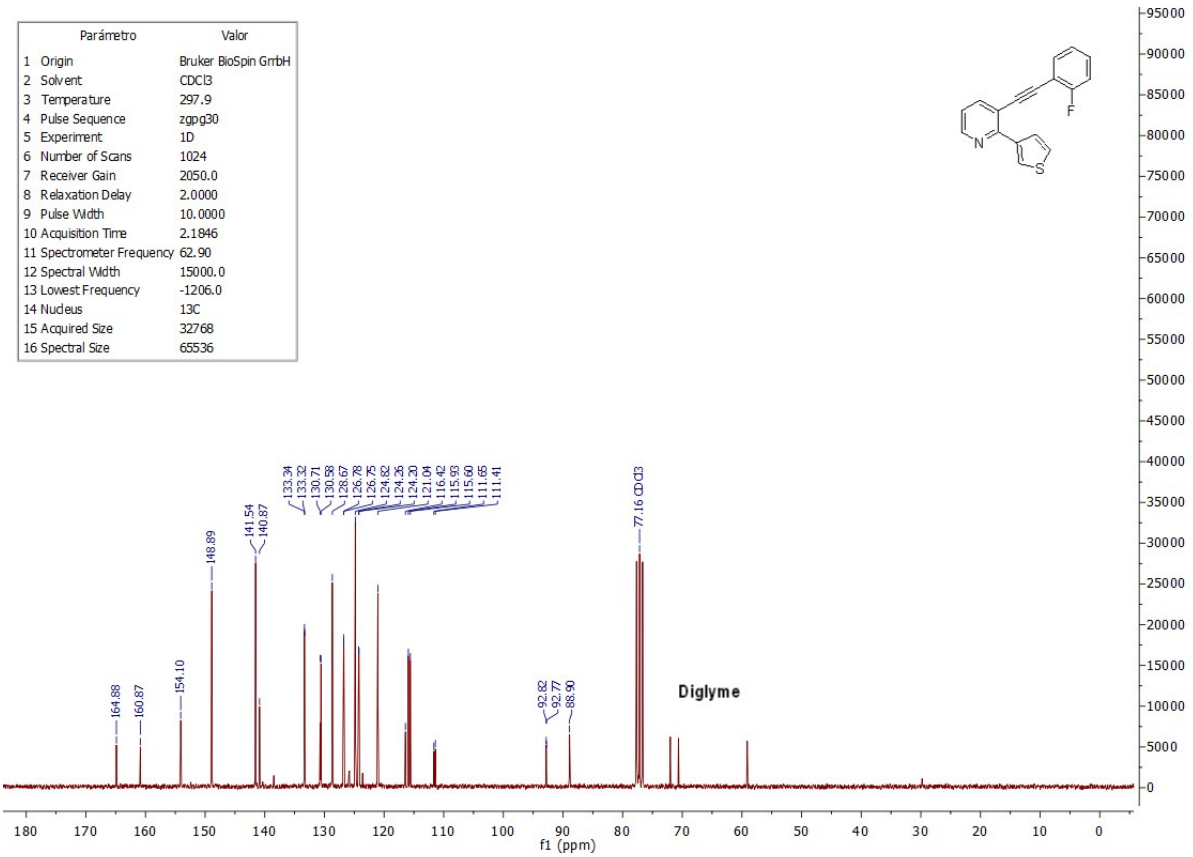


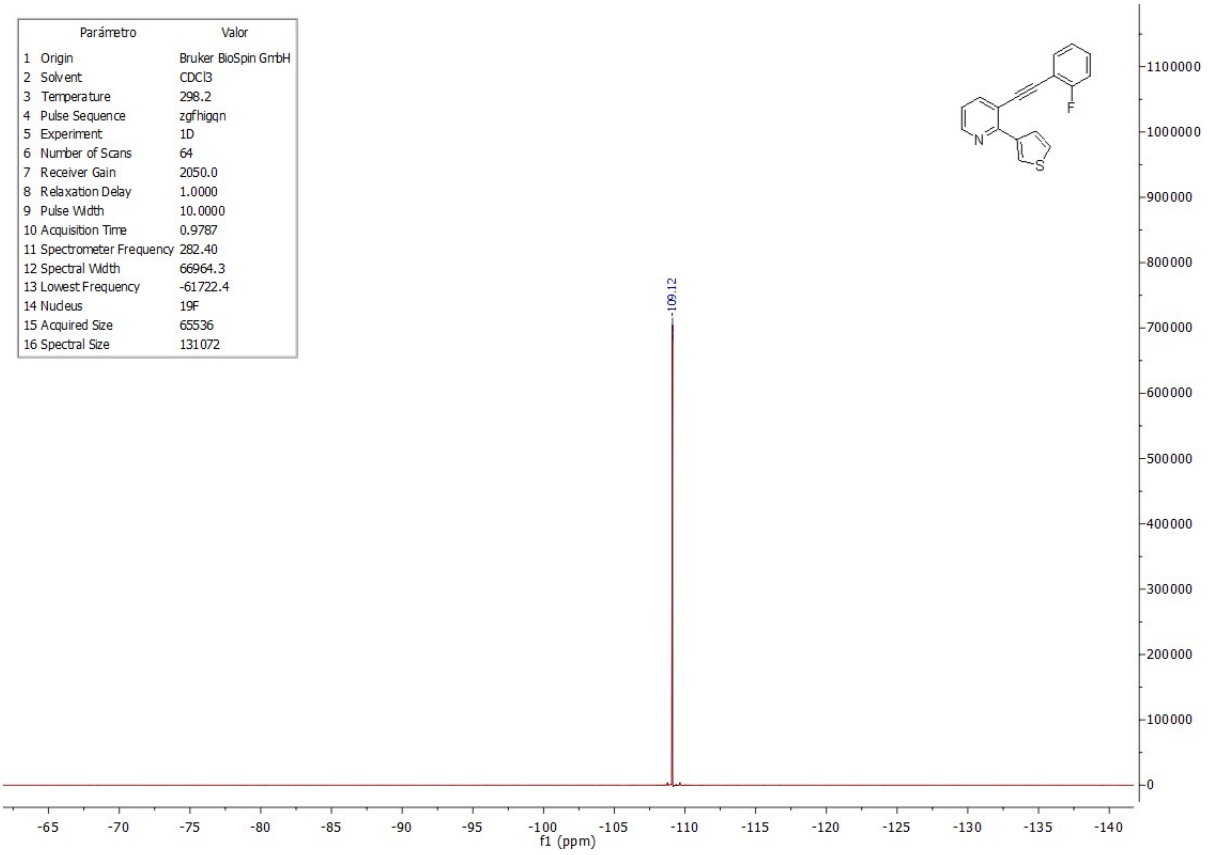
3-((2-fluorophenyl)ethynyl)-2-(thiophen-3-yl)pyridinen **3i**

Parámetro	Valor
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	50.8
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



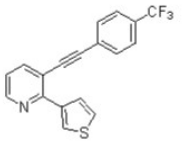
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.9
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1206.0
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

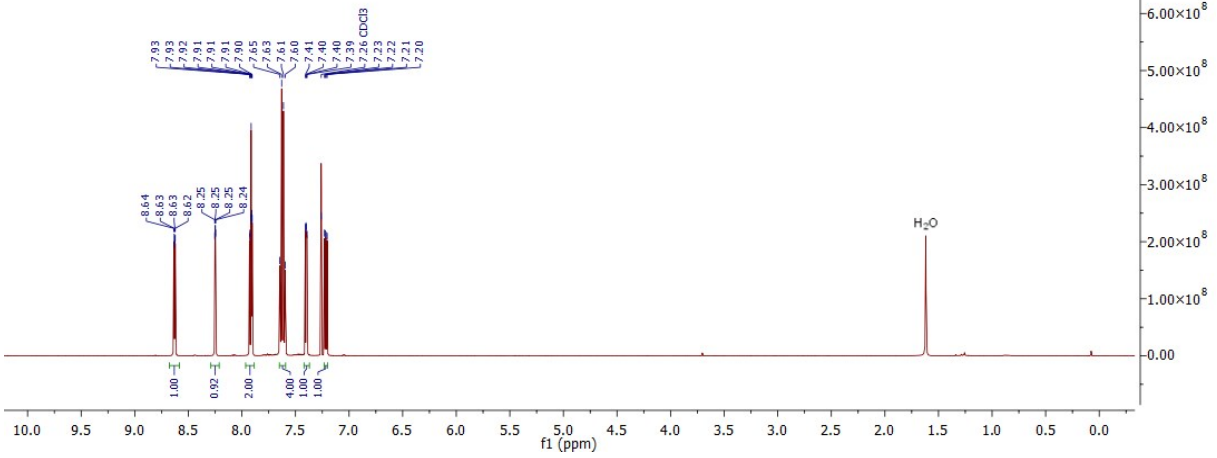




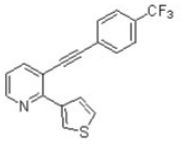
2-(thiophen-3-yl)-3-((4-(trifluoromethyl)phenyl)ethynyl)pyridine **3j**

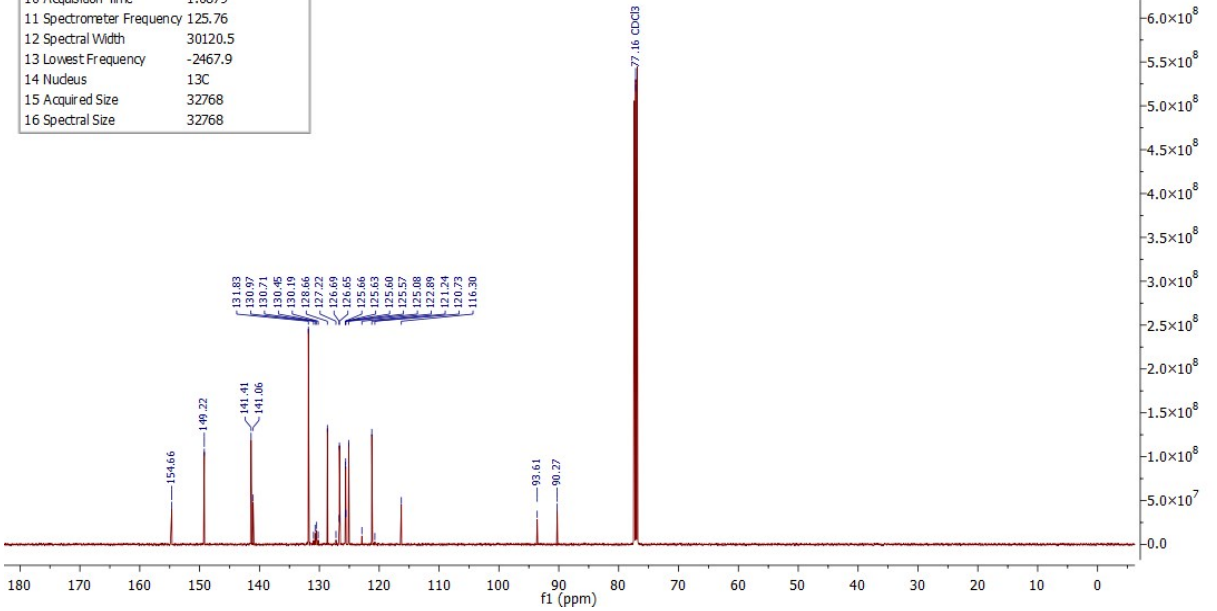
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	101.0
8 Relaxation Delay	1.0000
9 Pulse Width	8.0000
10 Acquisition Time	3.2768
11 Spectrometer Frequency	500.13
12 Spectral Width	10000.0
13 Lowest Frequency	-1923.9
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

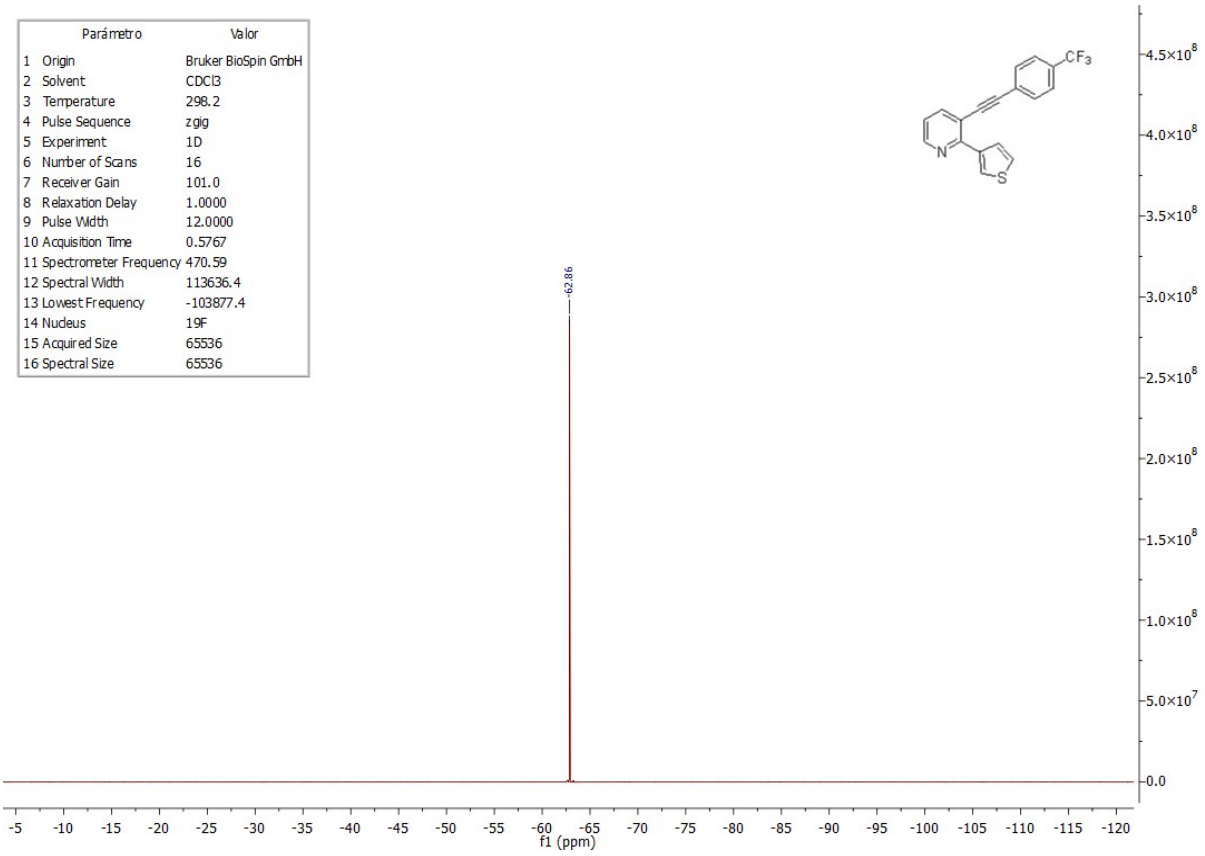




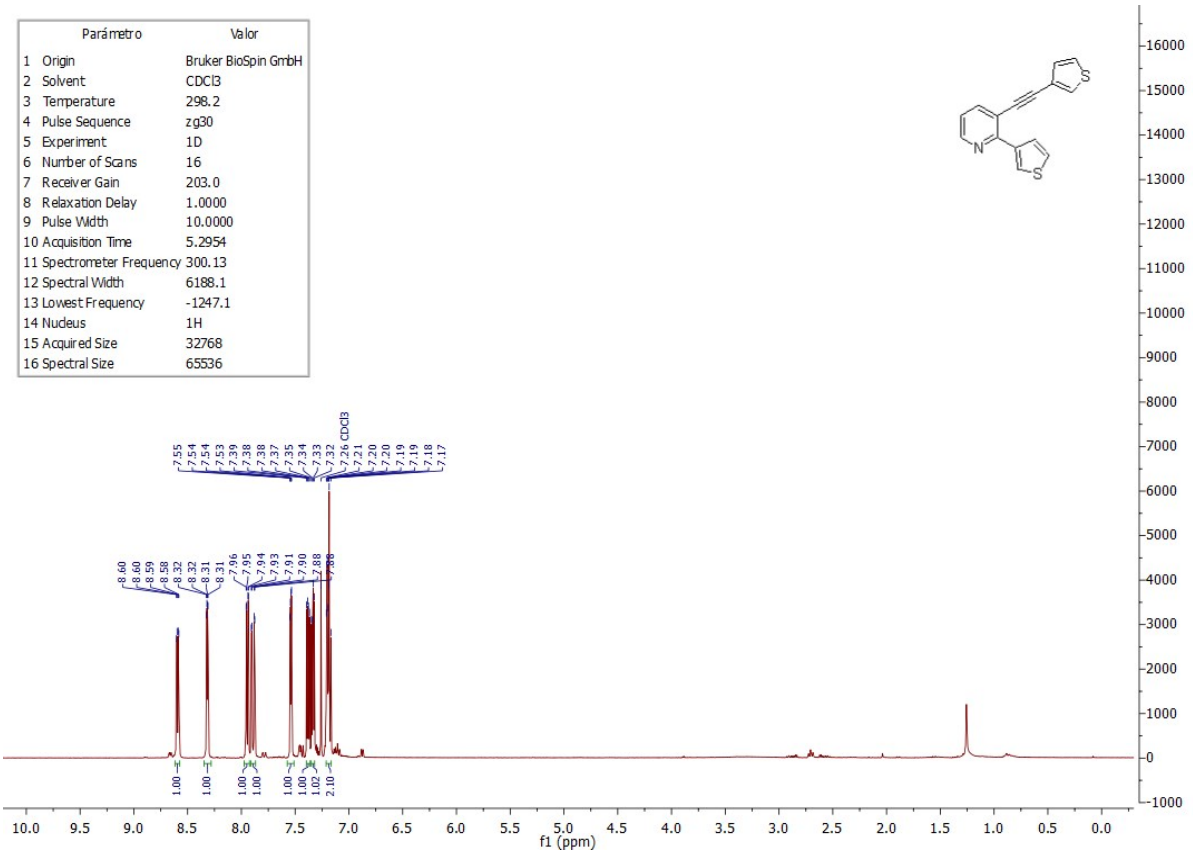
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	2048
7 Receiver Gain	101.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.0879
11 Spectrometer Frequency	125.76
12 Spectral Width	30120.5
13 Lowest Frequency	-2467.9
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768

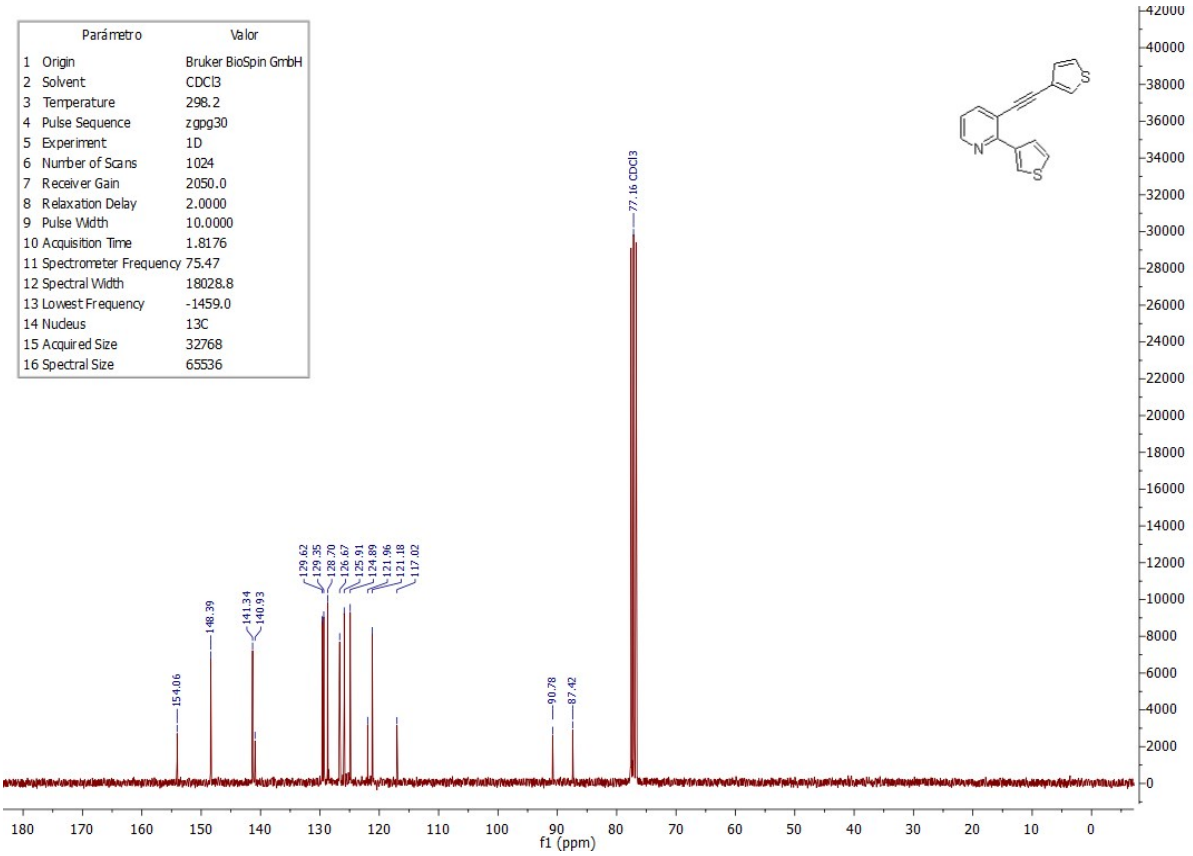






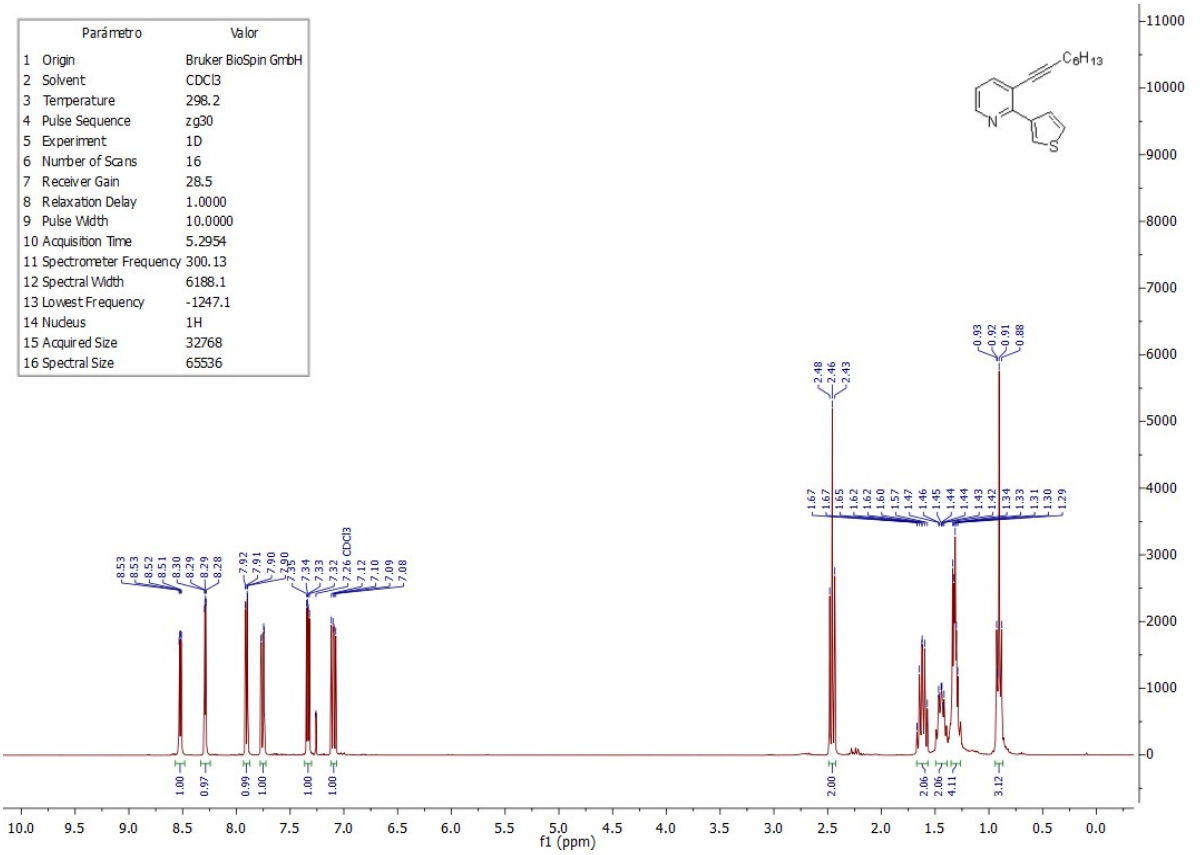
2-(thiophen-3-yl)-3-(thiophen-3-ylethynyl)pyridine **3k**



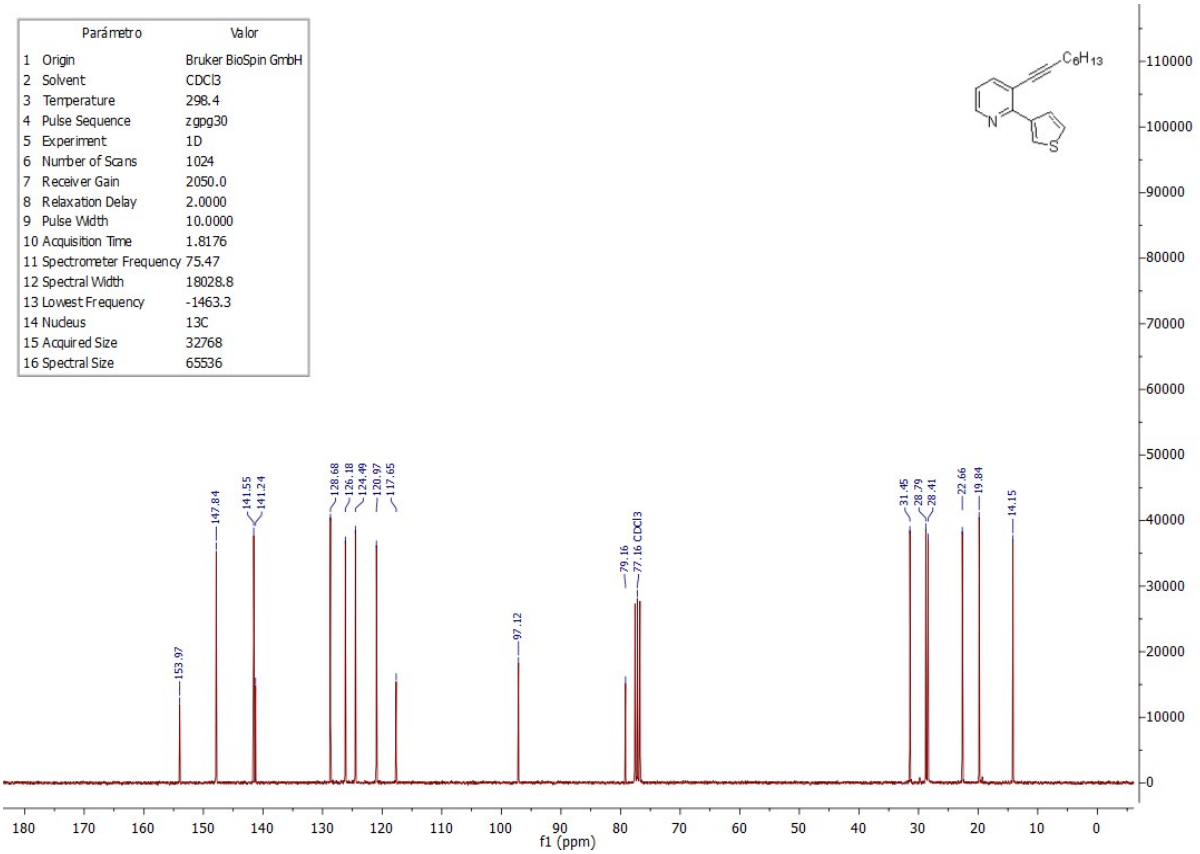


3-(oct-1-yn-1-yl)-2-(thiophen-3-yl)pyridine **3l**

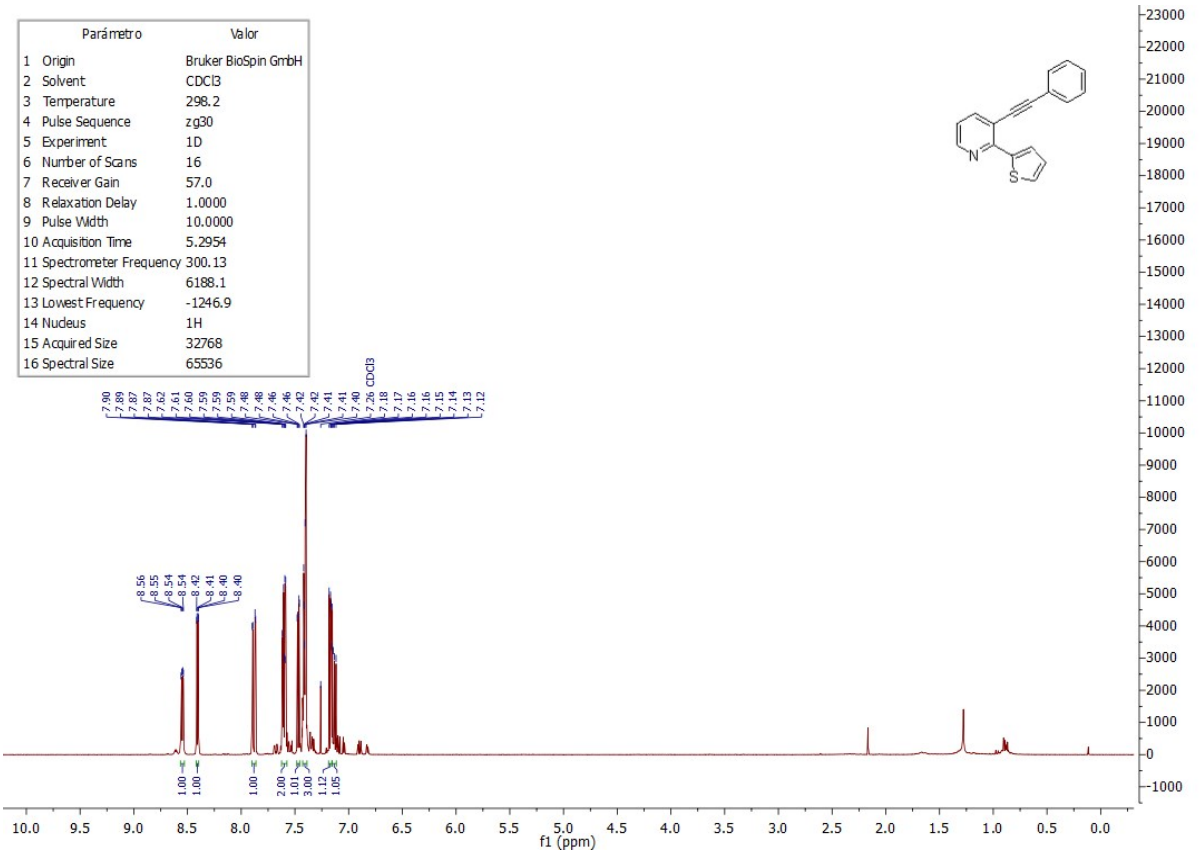
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	28.5
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1247.1
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

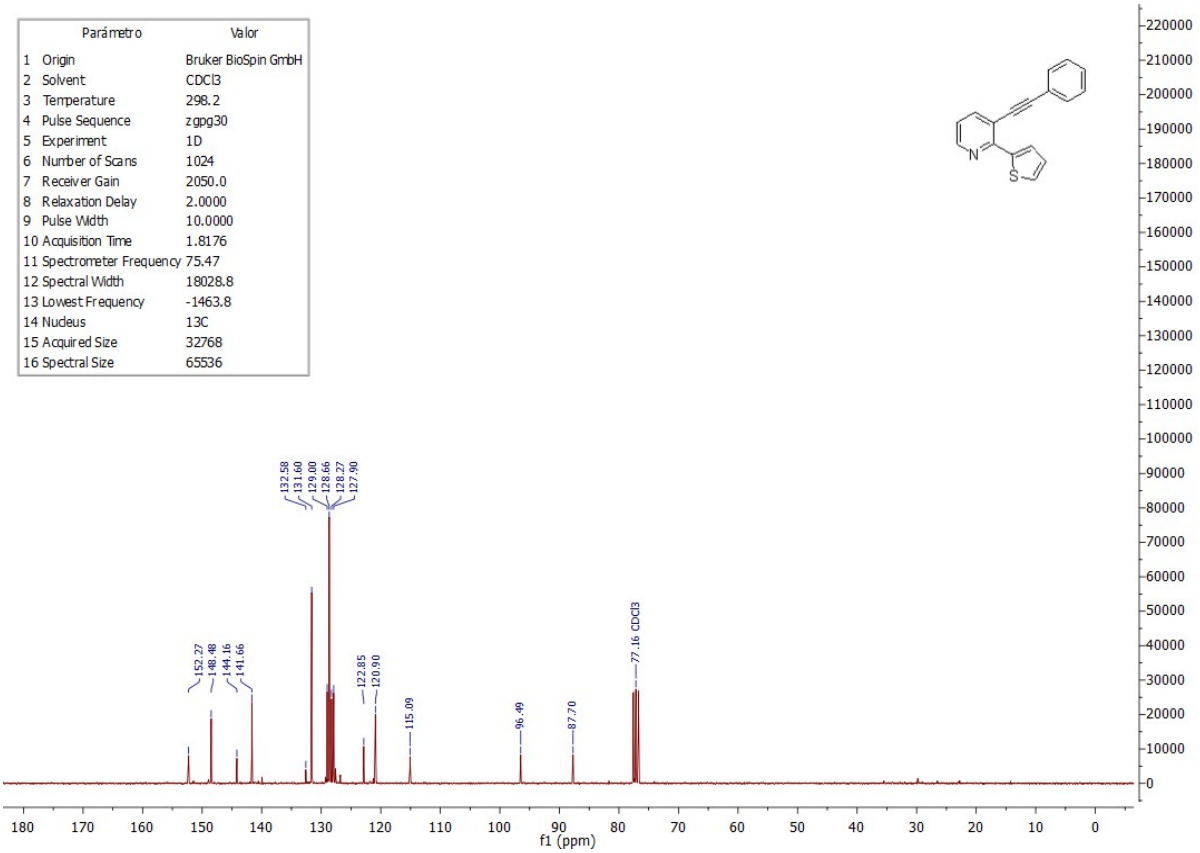


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.4
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1463.3
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

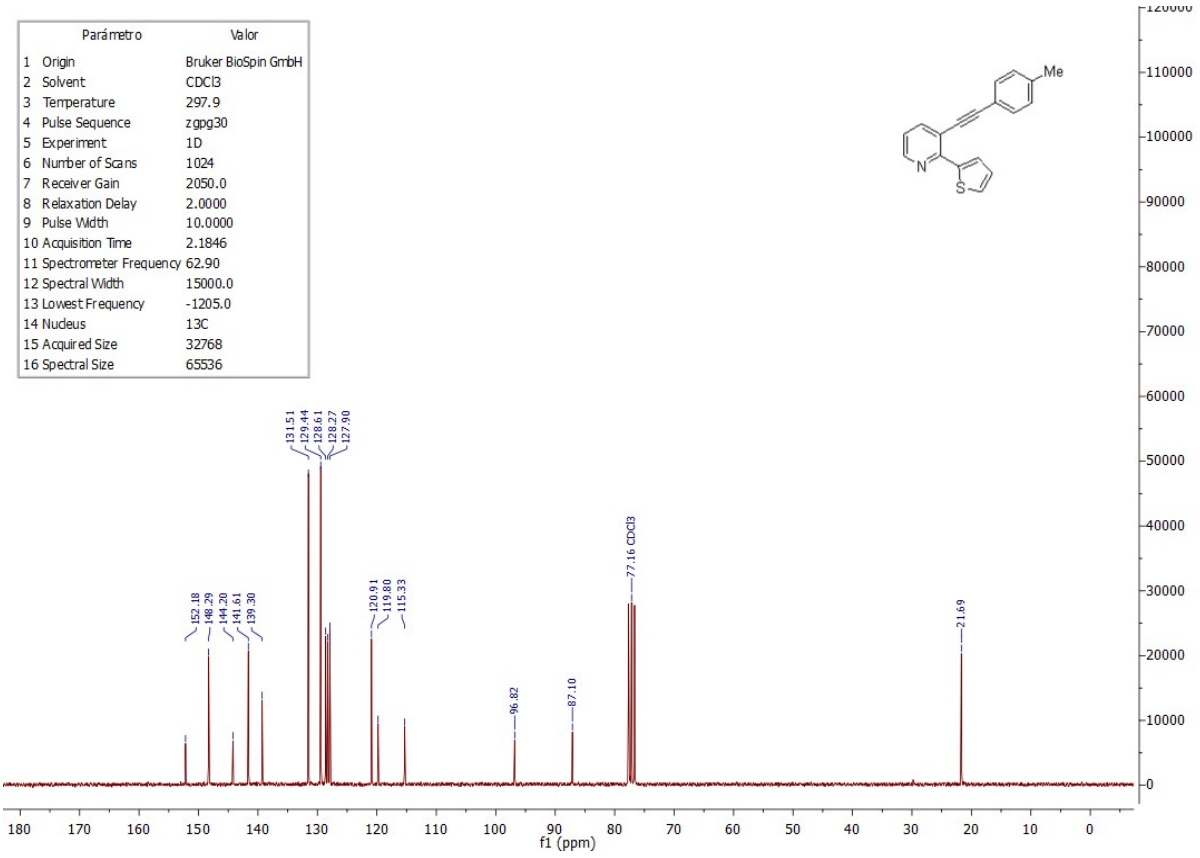


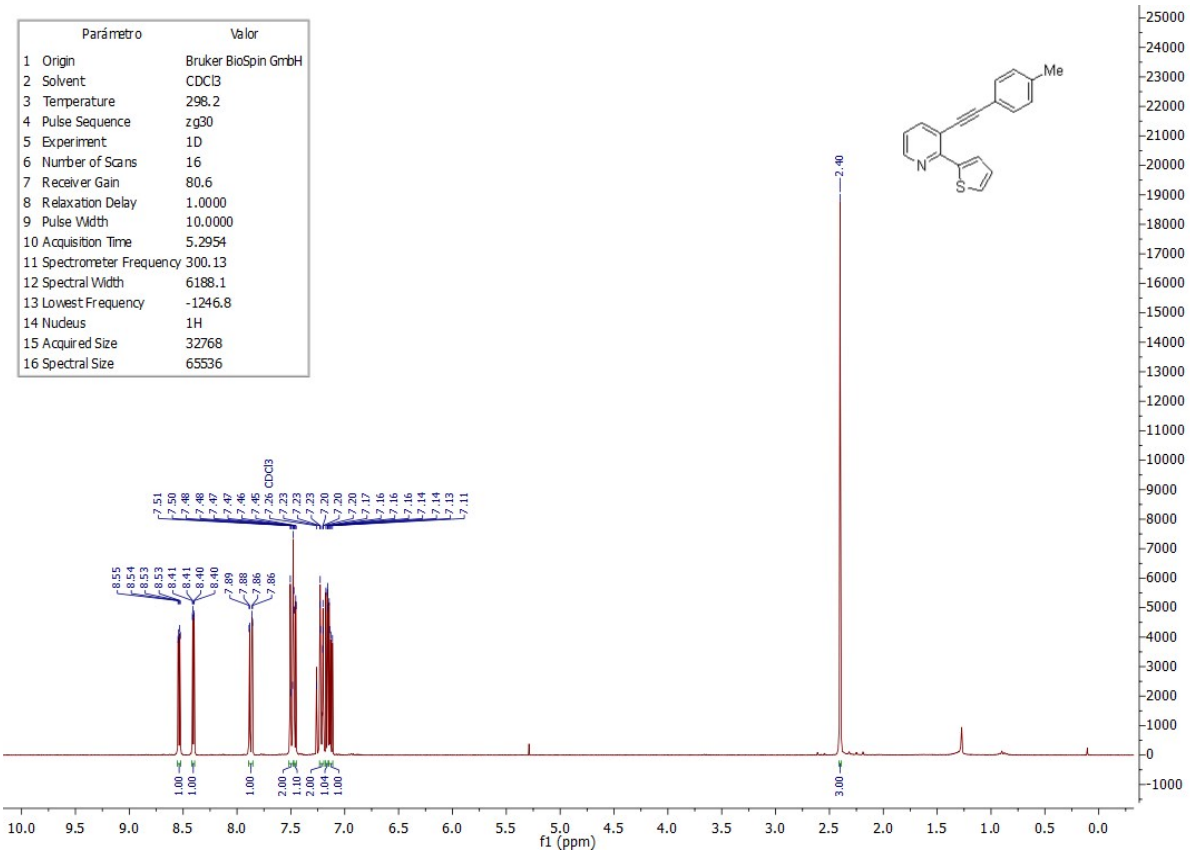
3-(phenylethynyl)-2-(thiophen-2-yl)pyridine **3m**





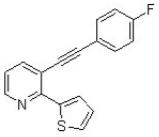
2-(thiophen-2-yl)-3-(*p*-tolylethynyl)pyridine **3n**

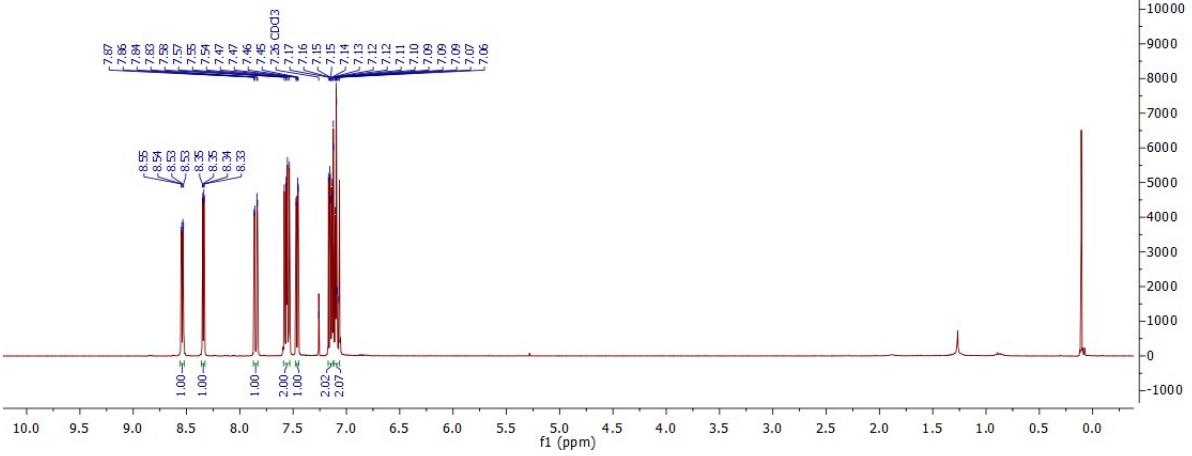




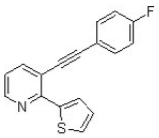
3-((4-fluorophenyl)ethynyl)-2-(thiophen-2-yl)pyridine **3o**

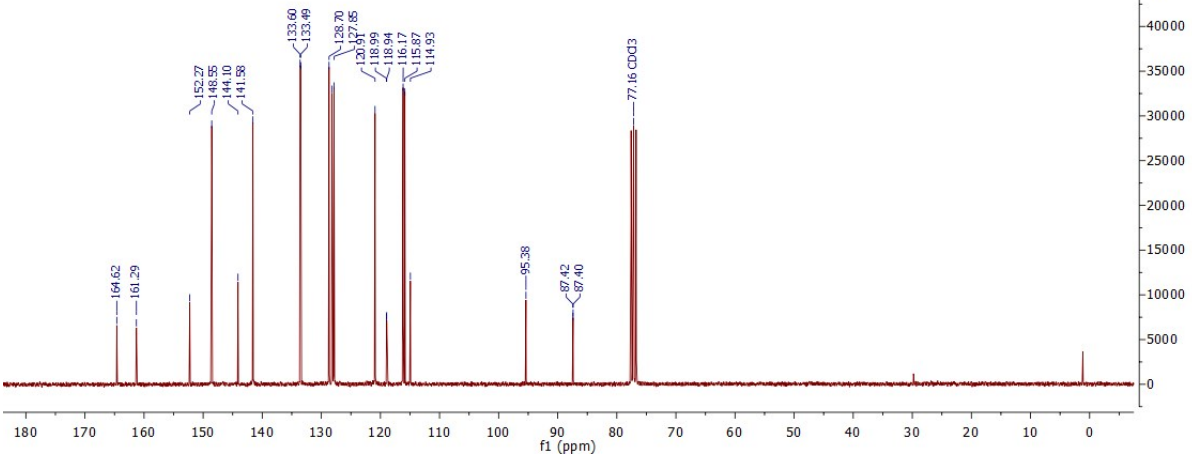
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	50.8
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1247.0
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

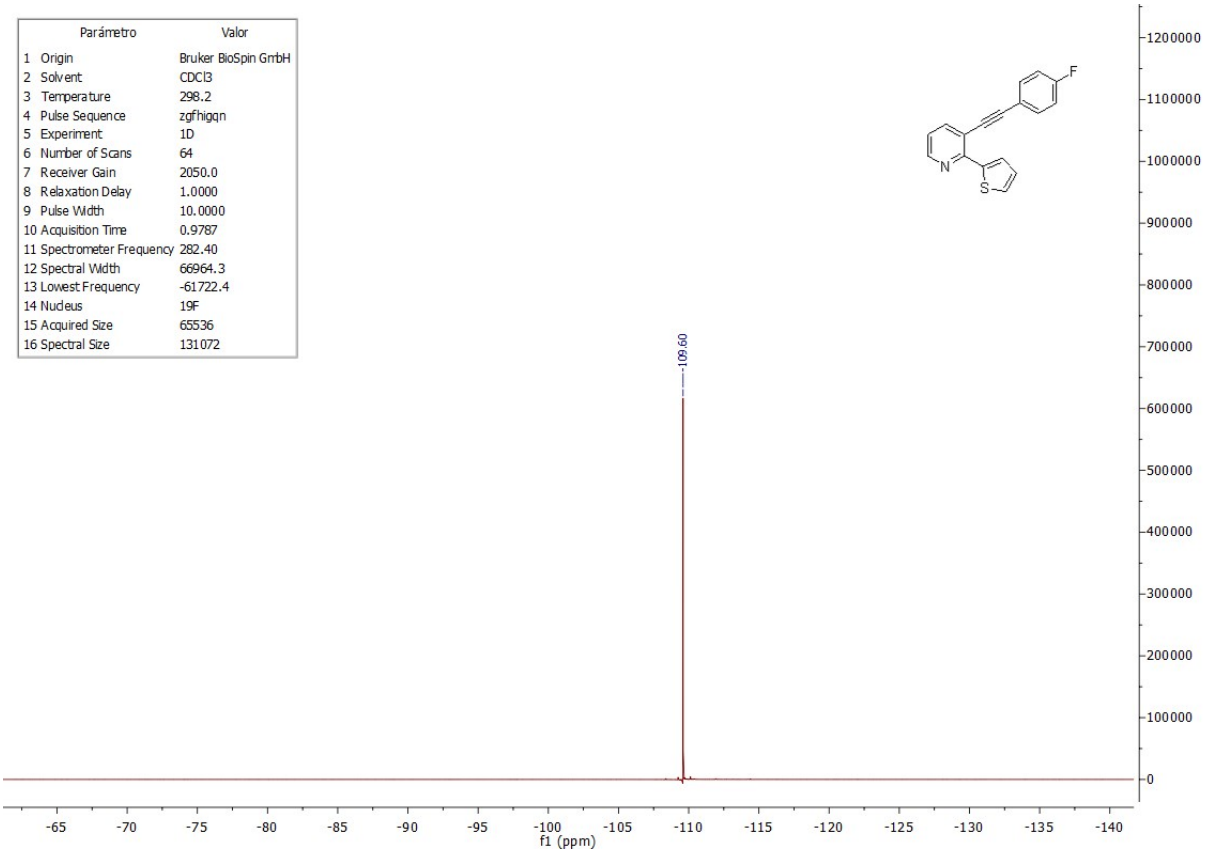




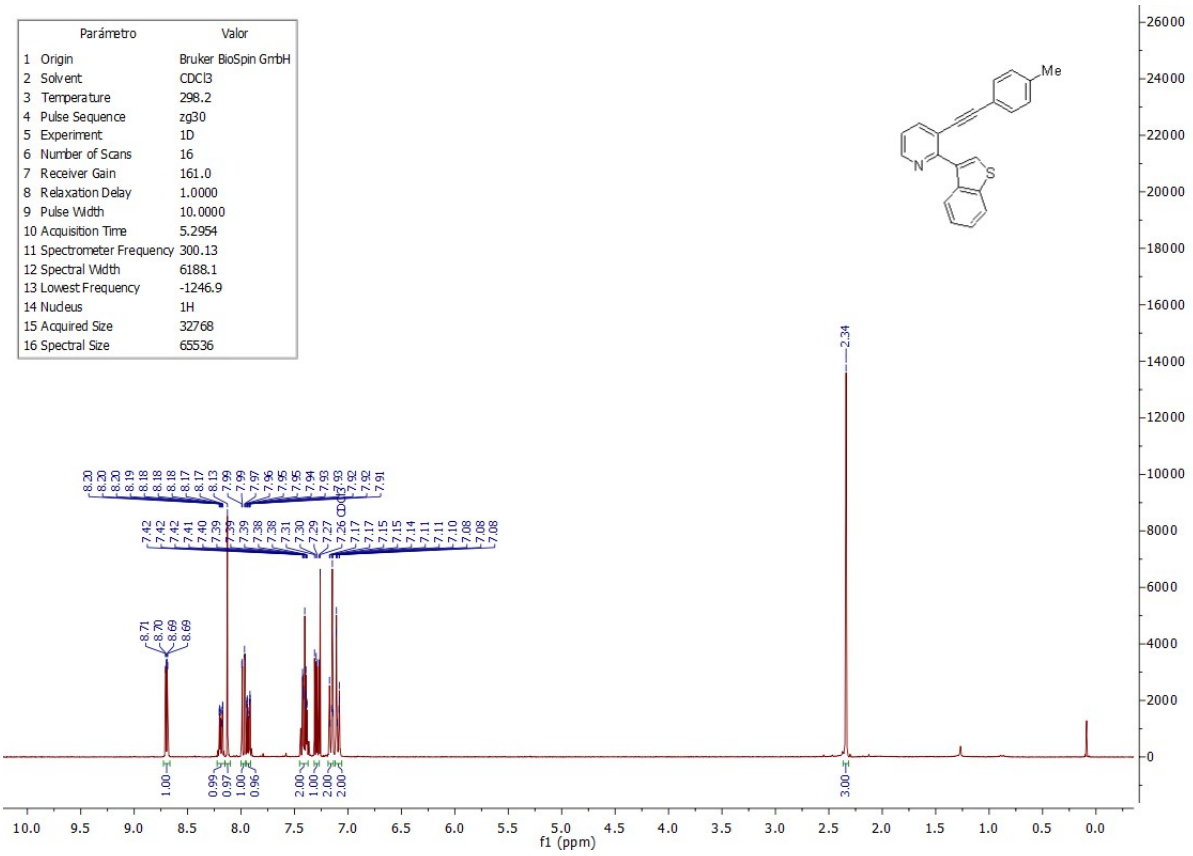
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1463.1
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

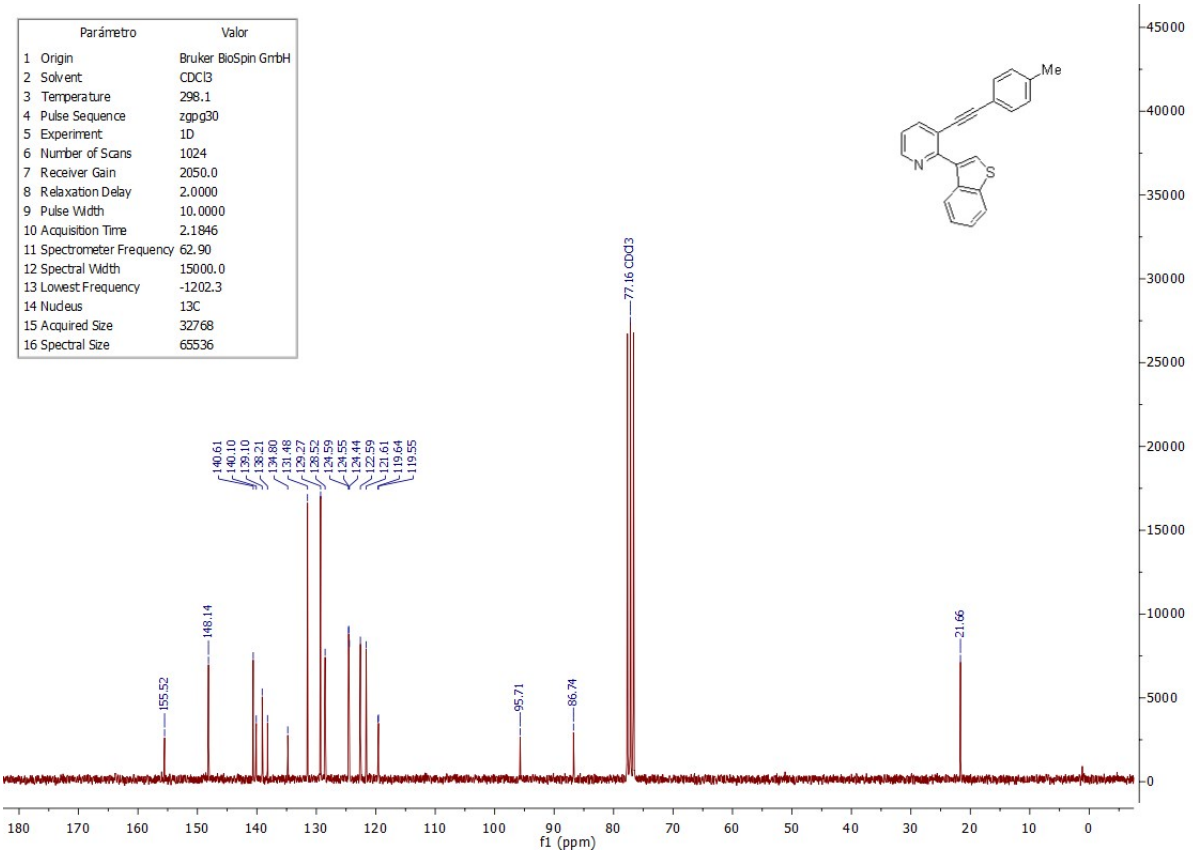






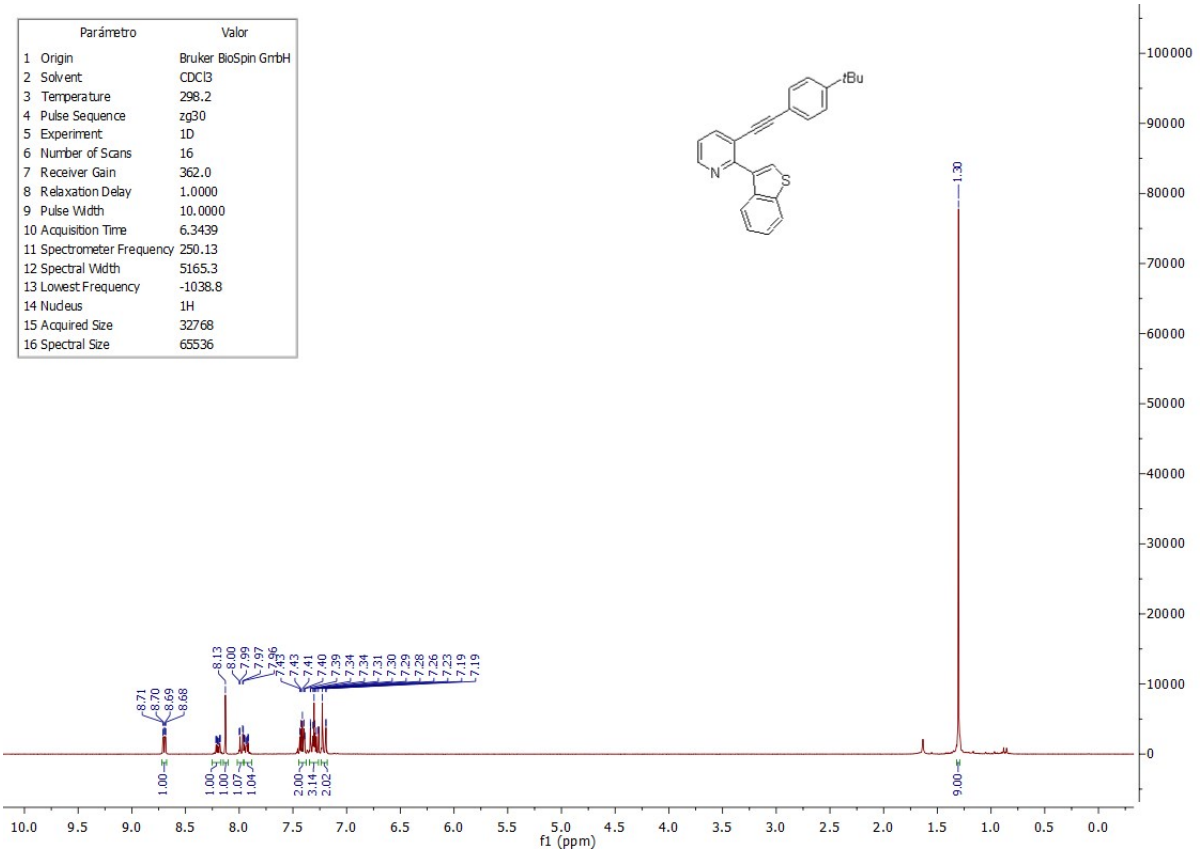
2-(benzo[b]thiophen-3-yl)-3-(*p*-tolylethynyl)pyridine **3p**



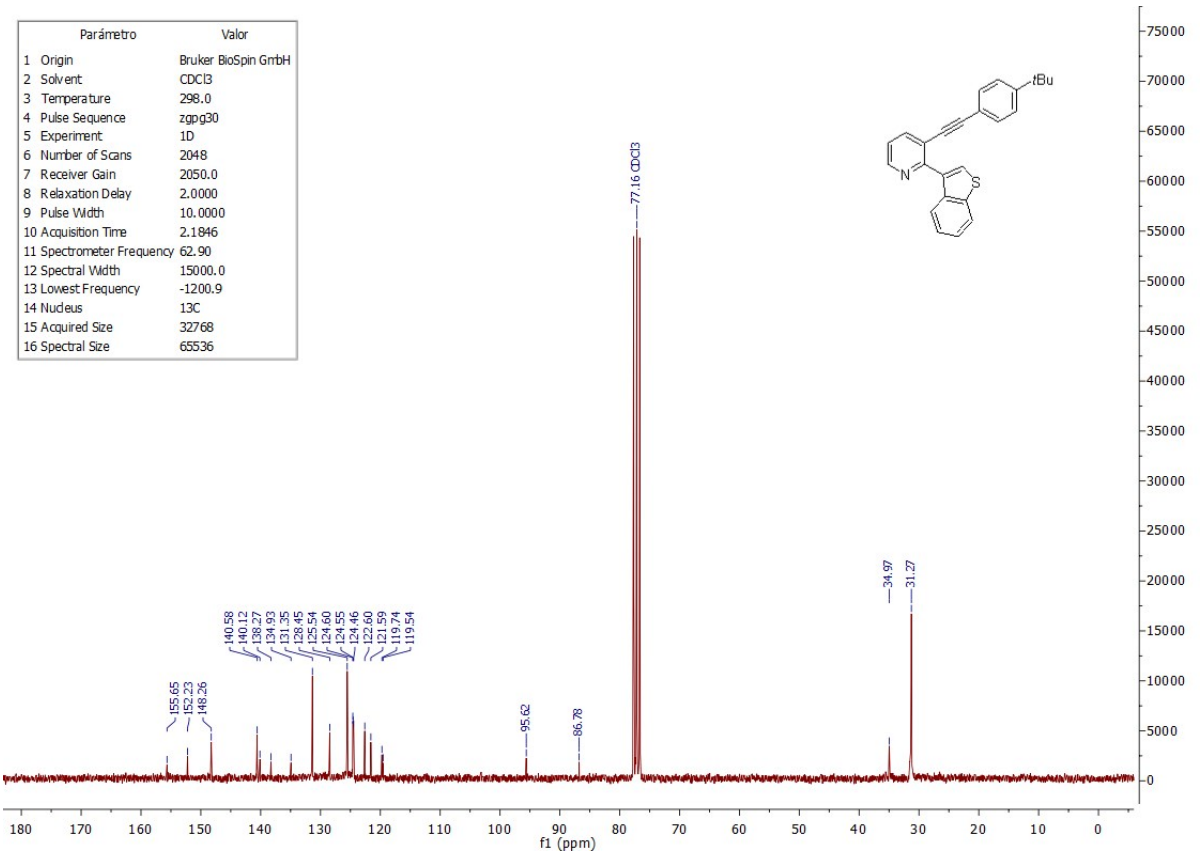


2-(benzo[*b*]thiophen-3-yl)-3-((4-(*tert*-butyl)phenyl)ethynyl)pyridine **3q**

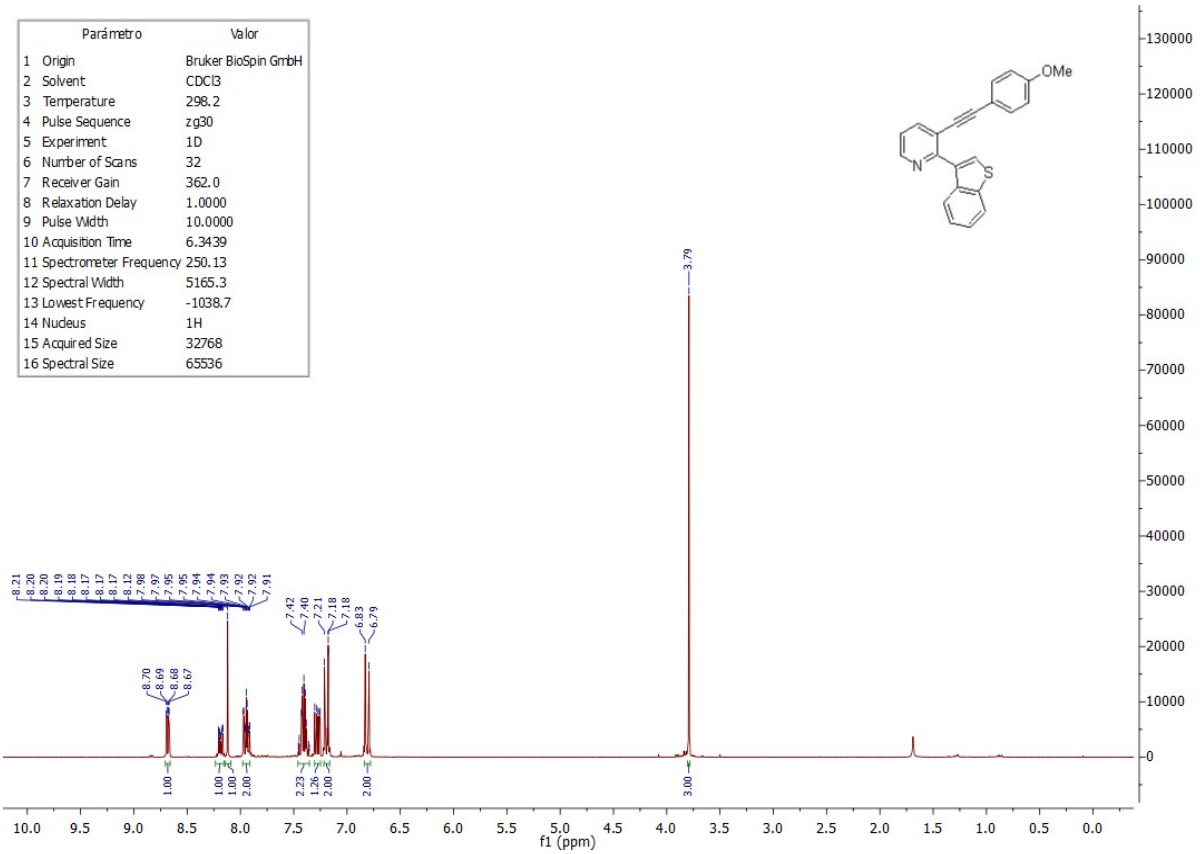
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	362.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.8
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

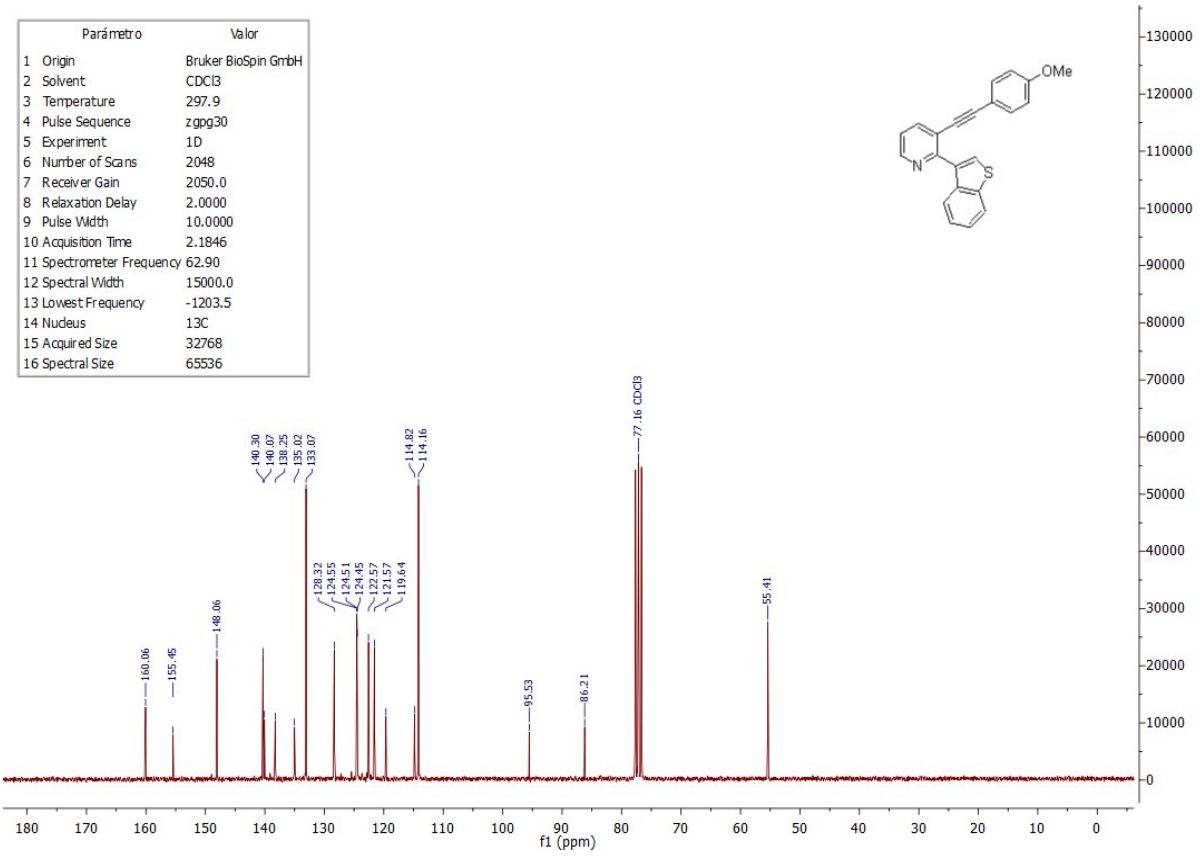


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	2048
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1200.9
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

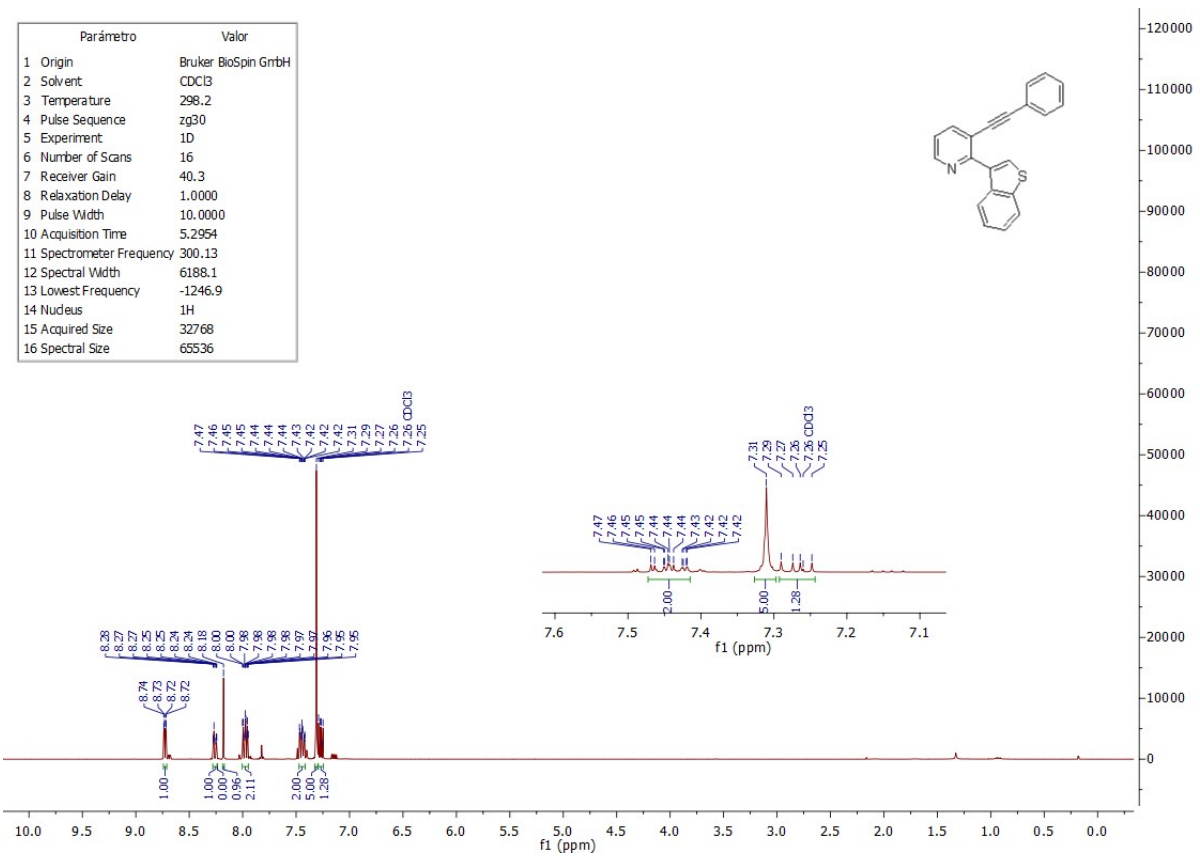


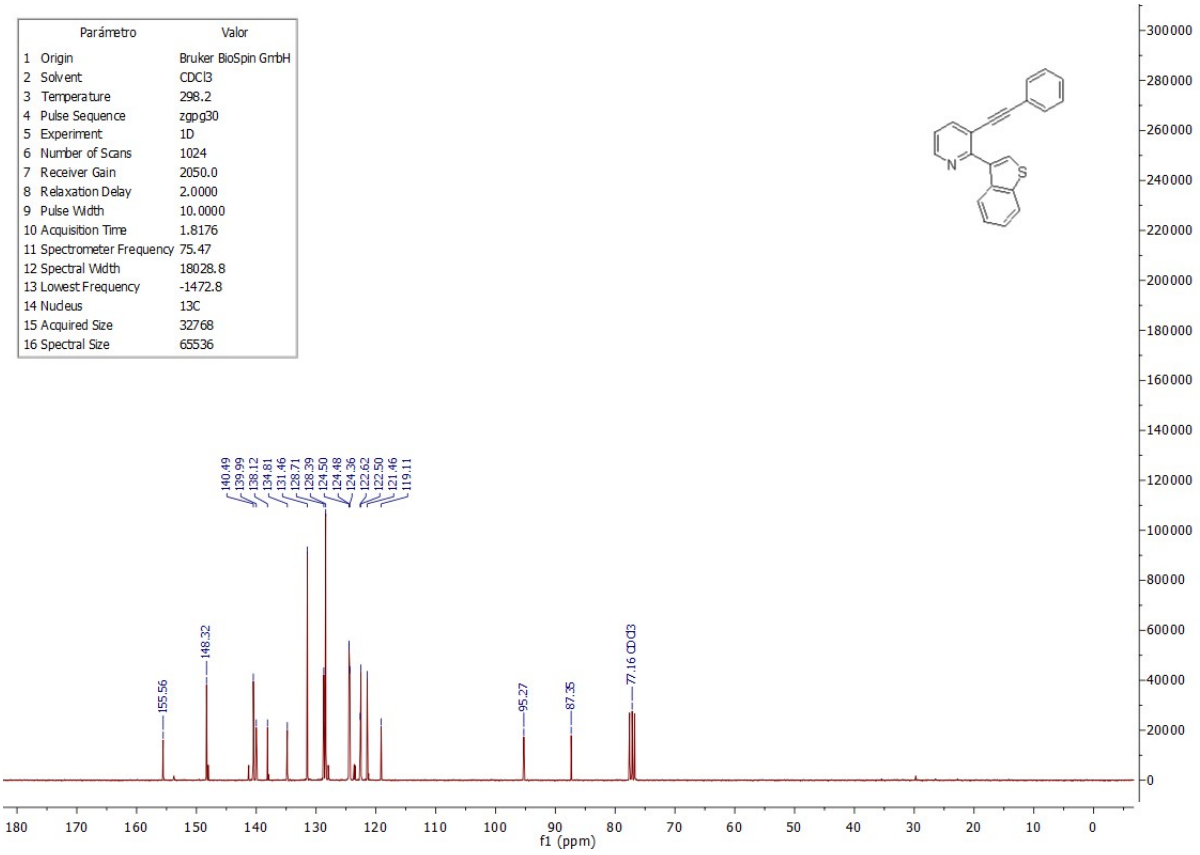
2-(benzo[*b*]thiophen-3-yl)-3-((4-methoxyphenyl)ethynyl)pyridine **3r**





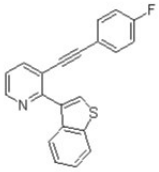
2-(benzo[*b*]thiophen-3-yl)-3-(phenylethynyl)pyridine **3s**

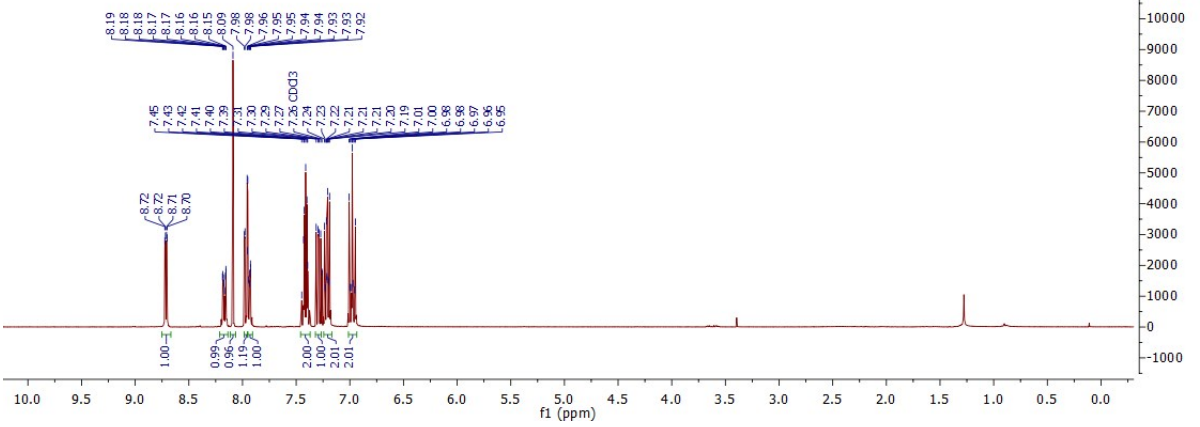




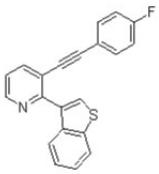
2-(benzo[*b*]thiophen-3-yl)-3-((4-fluorophenyl)ethynyl)pyridine **3t**

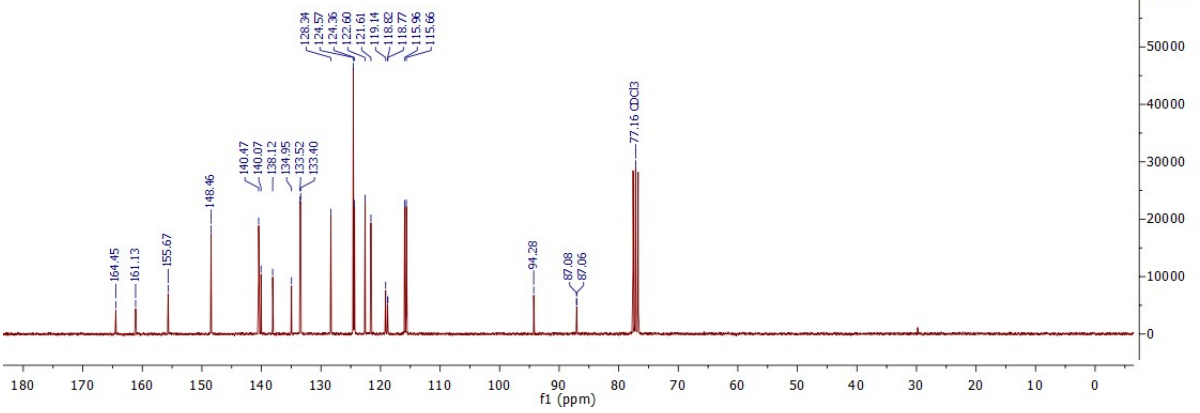
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	57.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1246.8
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

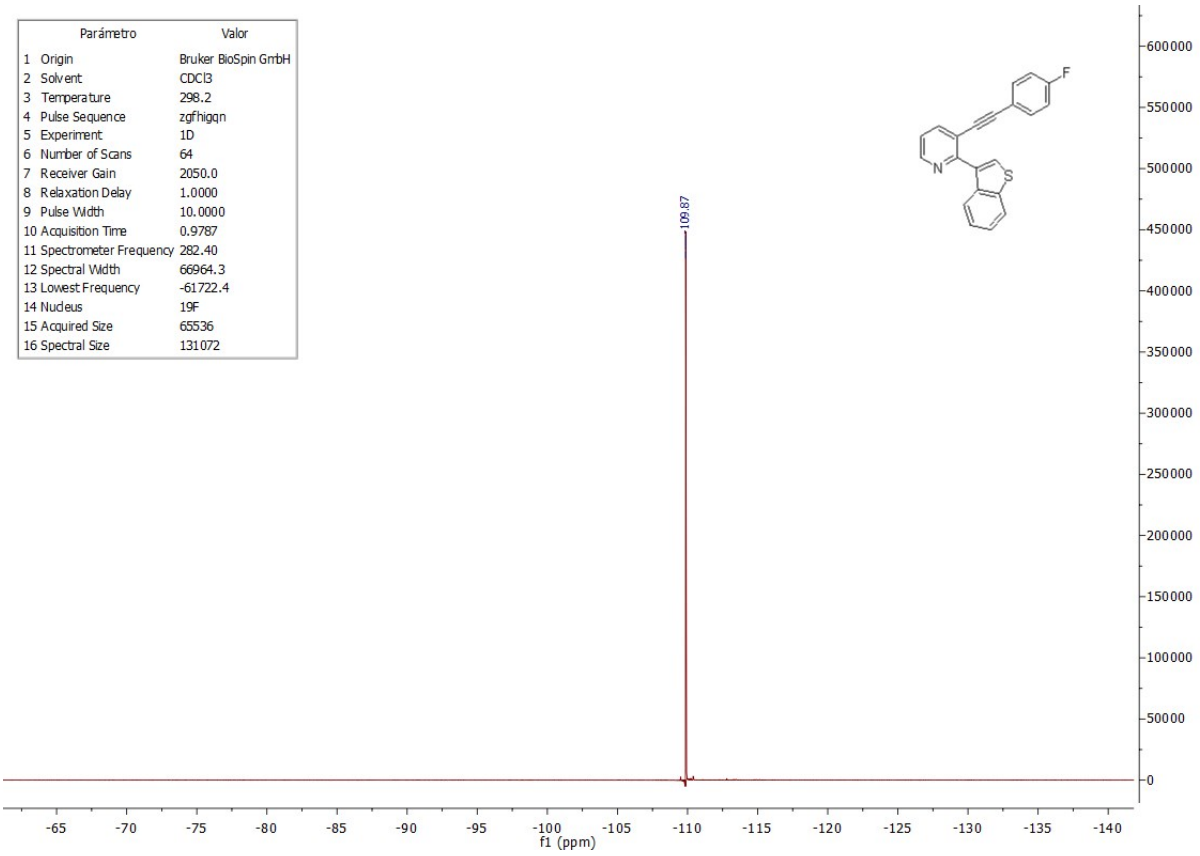




Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1462.6
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

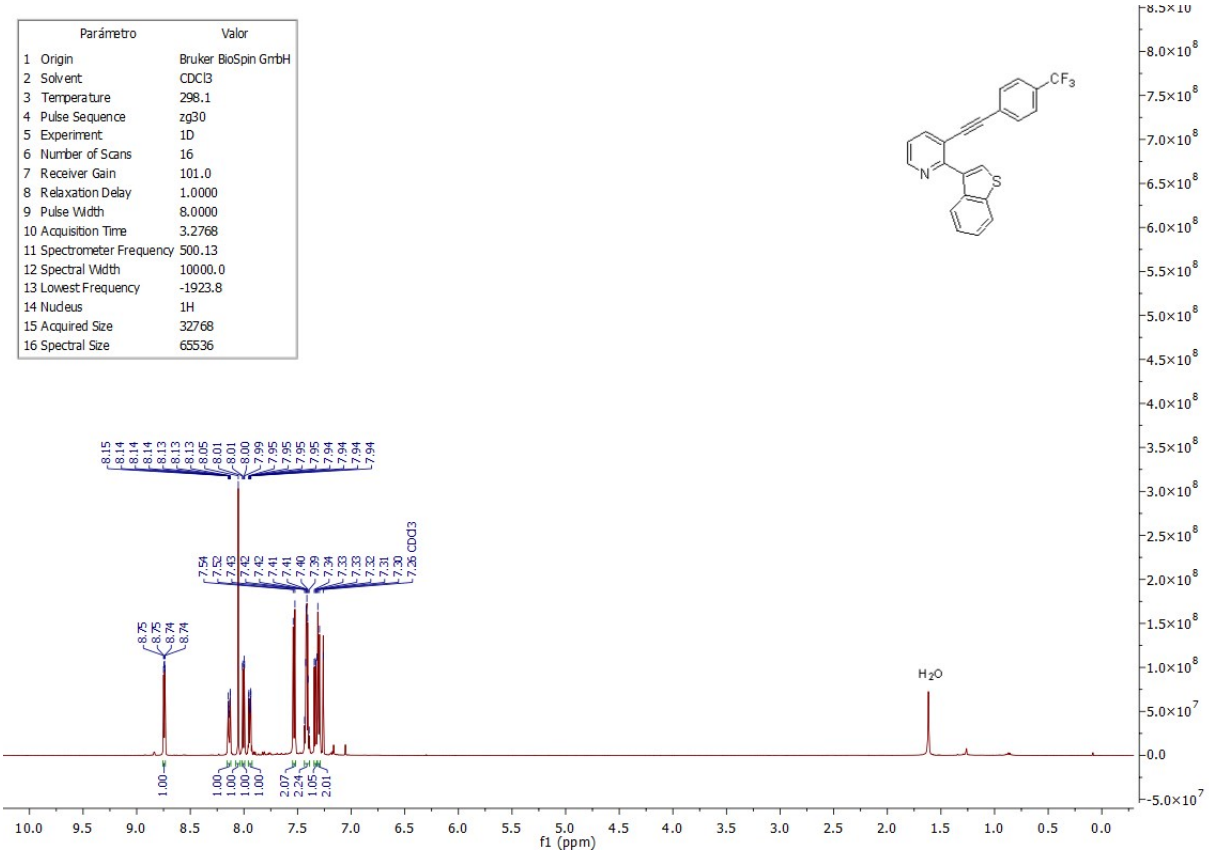




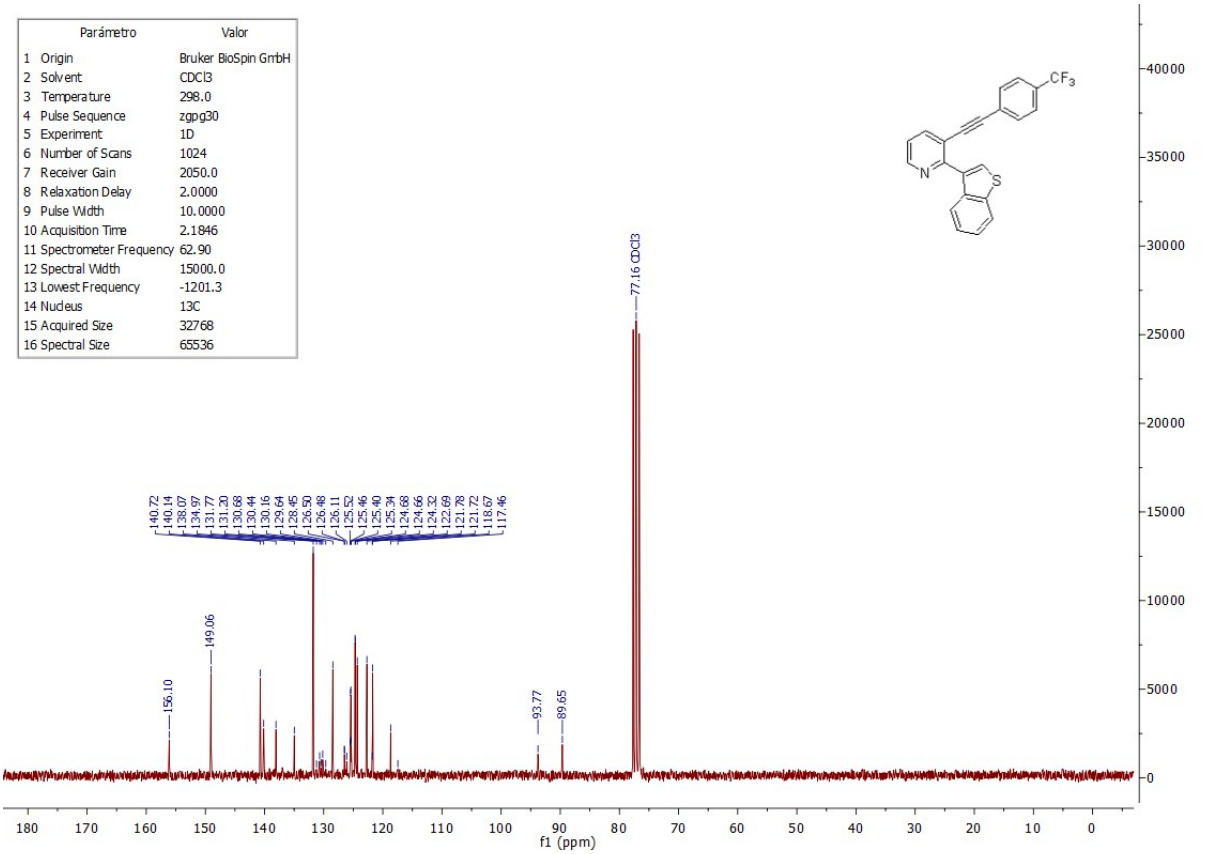


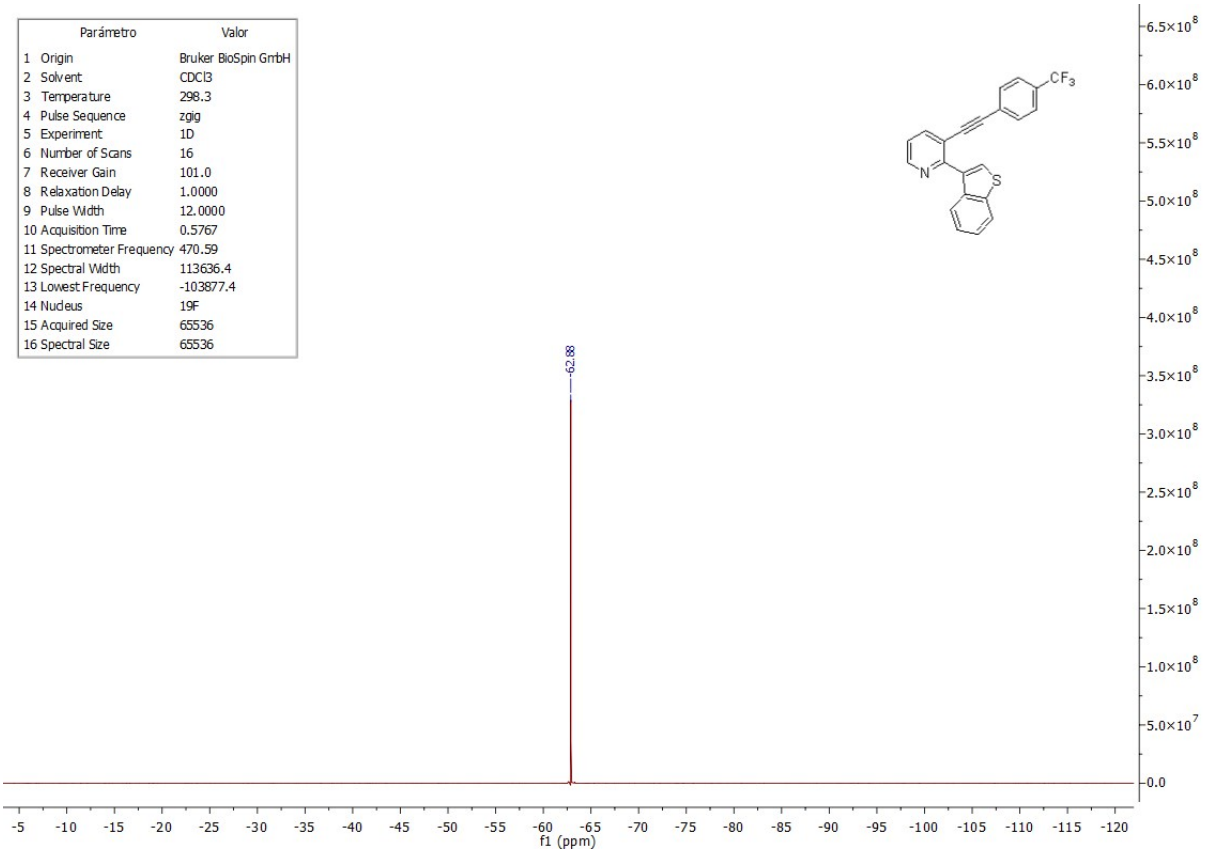
2-(benzo[*b*]thiophen-3-yl)-3-((4-(trifluoromethyl)phenyl)ethynyl)pyridine **3u**

Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	101.0
8 Relaxation Delay	1.0000
9 Pulse Width	8.0000
10 Acquisition Time	3.2768
11 Spectrometer Frequency	500.13
12 Spectral Width	10000.0
13 Lowest Frequency	-1923.8
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

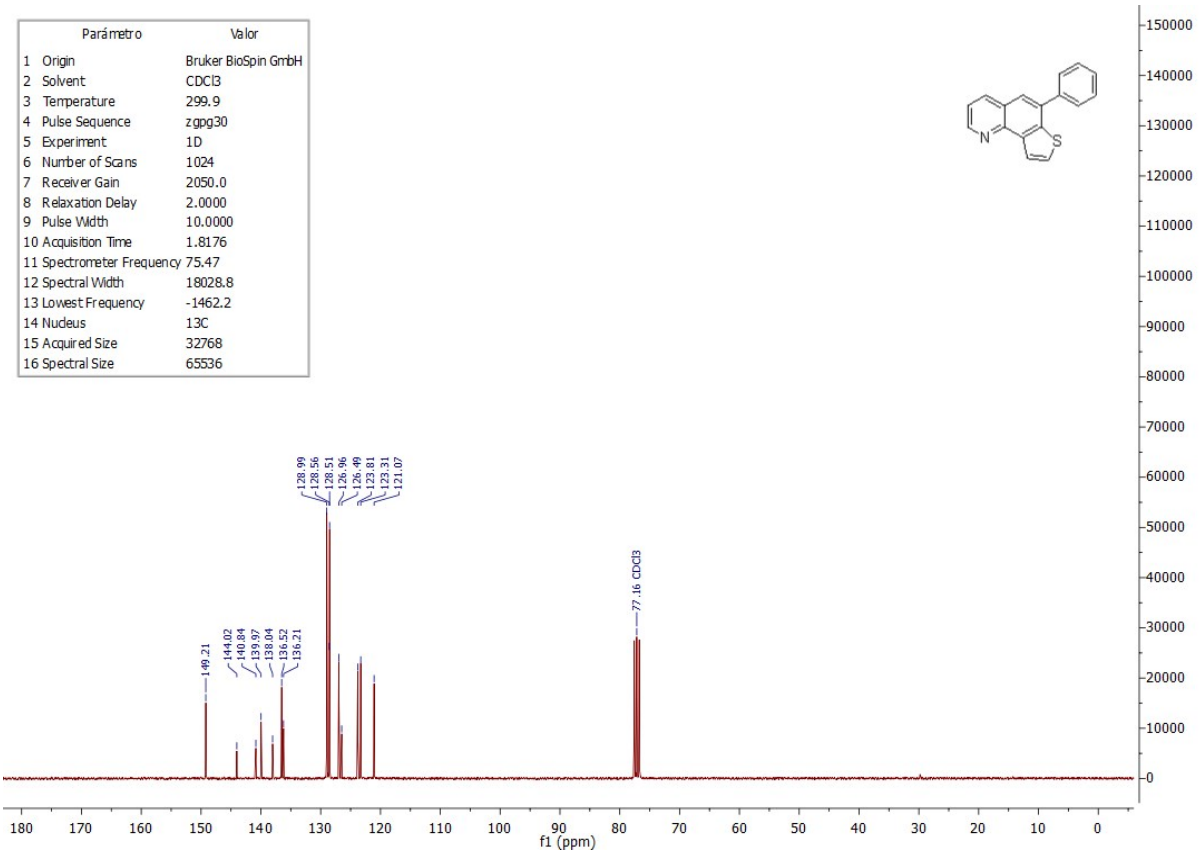


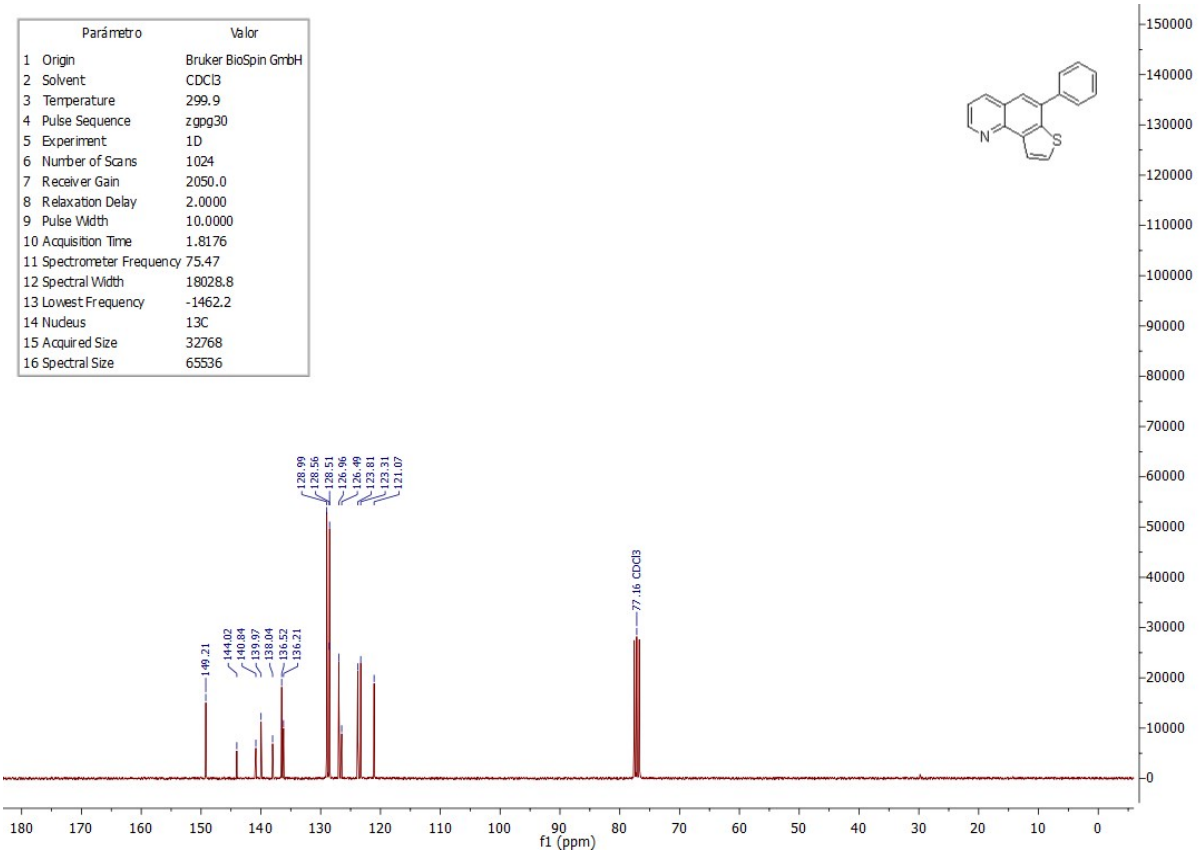
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1201.3
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536





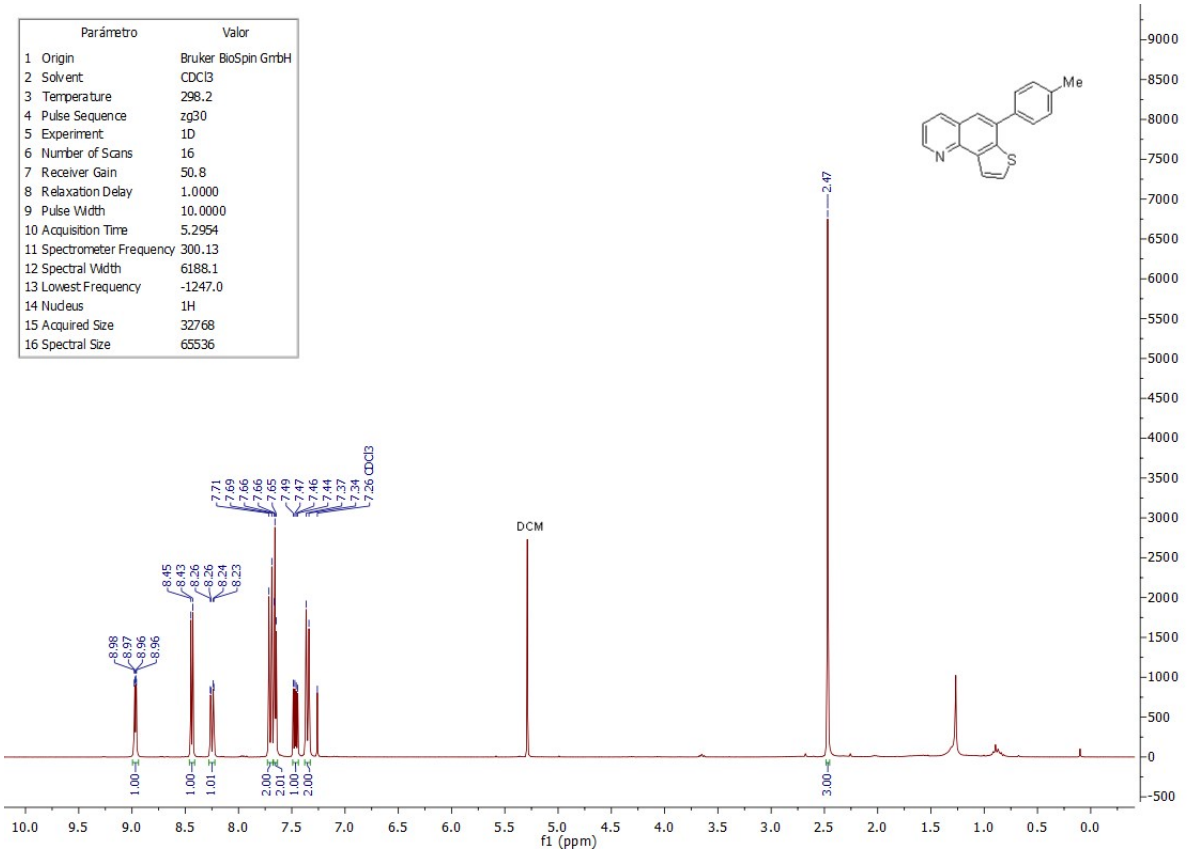
6-phenylthieno[2,3-*h*]quinoline **4a**



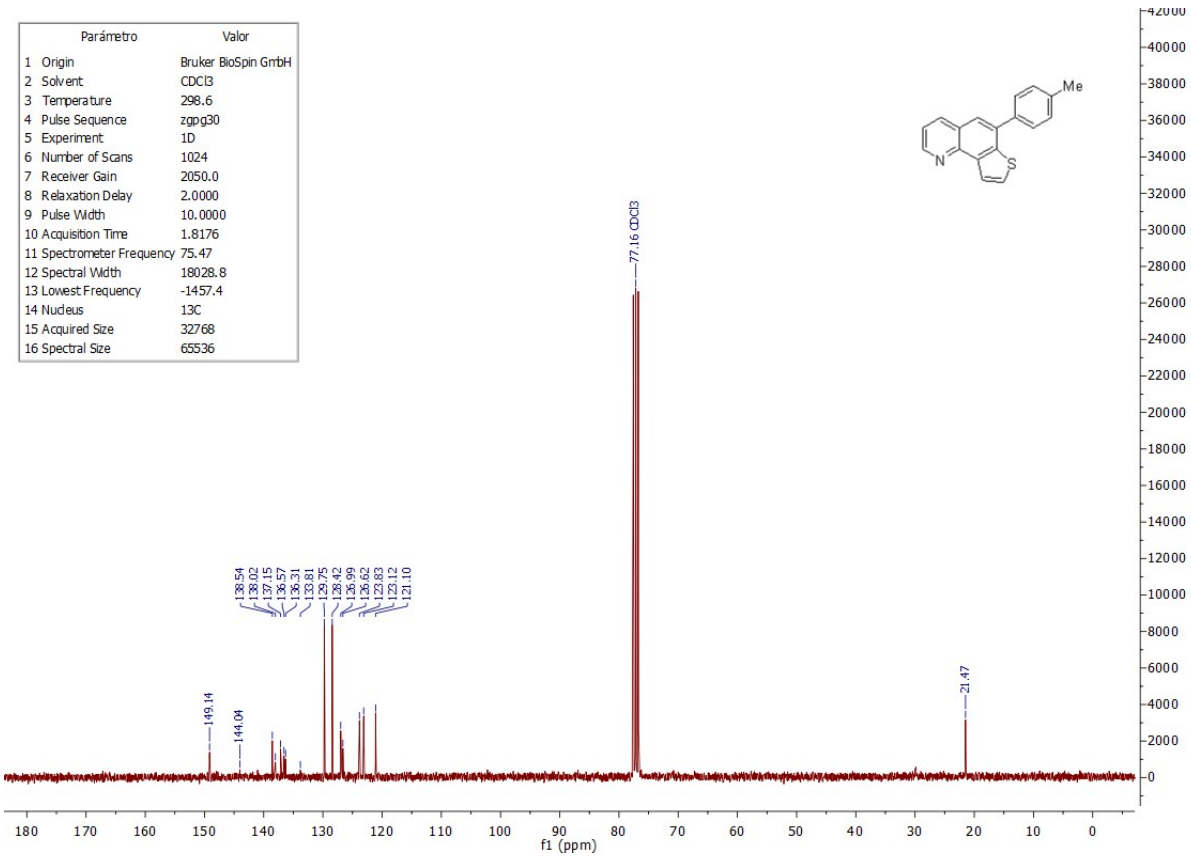


6-(*p*-tolyl)thieno[2,3-*h*]quinoline **4b**

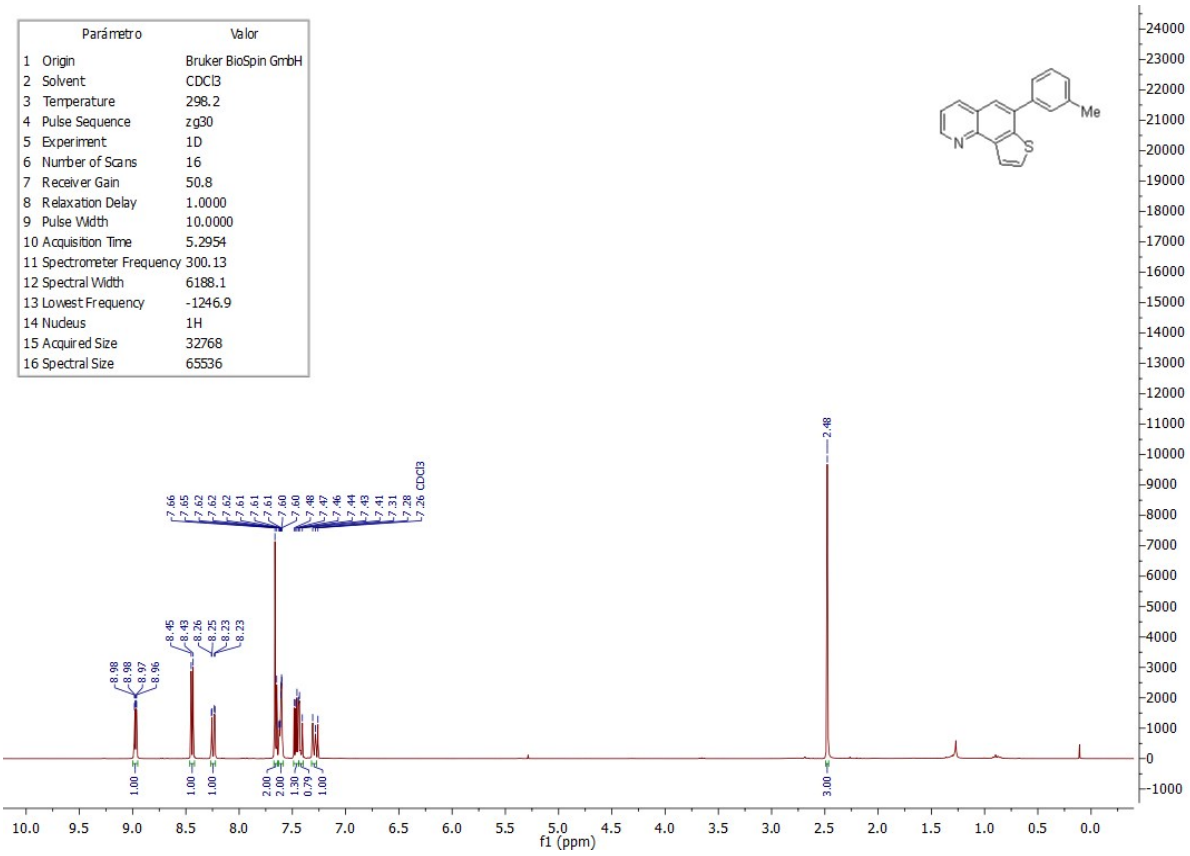
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	50.8
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1247.0
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

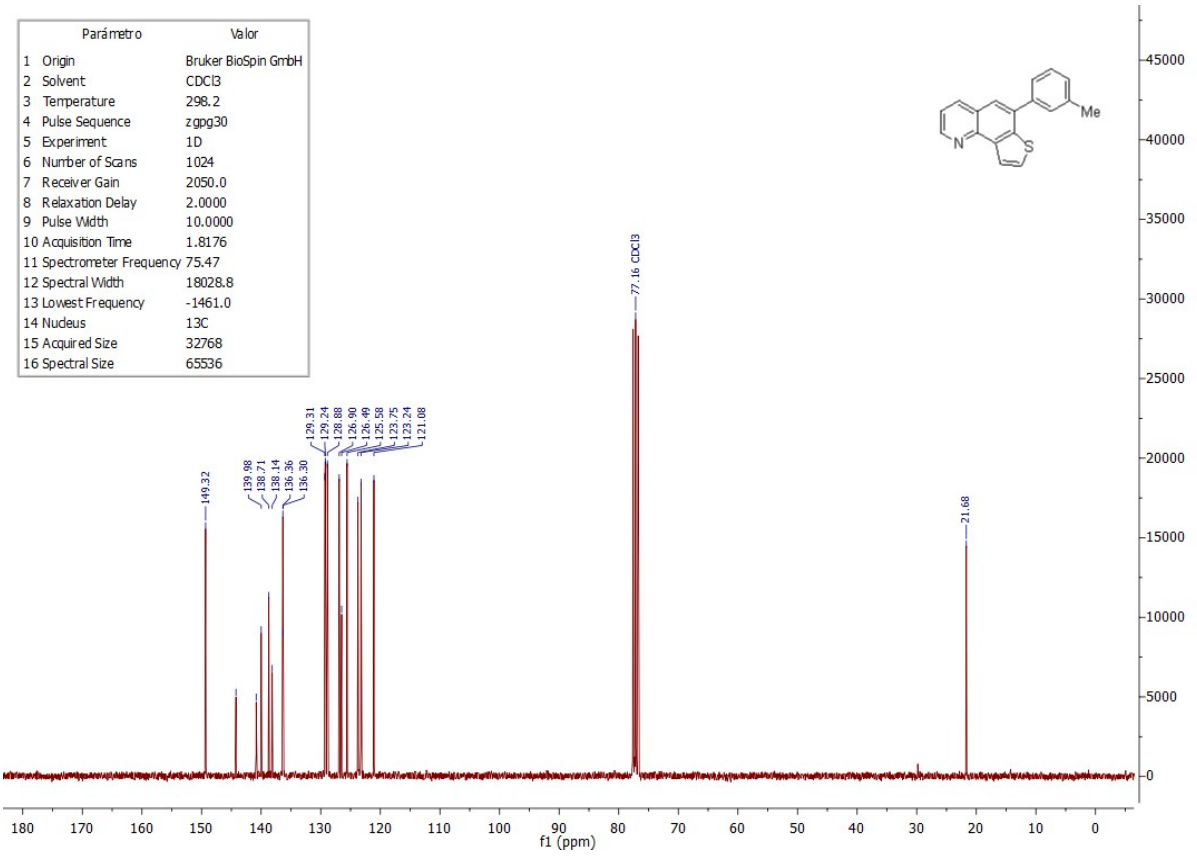


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.6
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1457.4
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

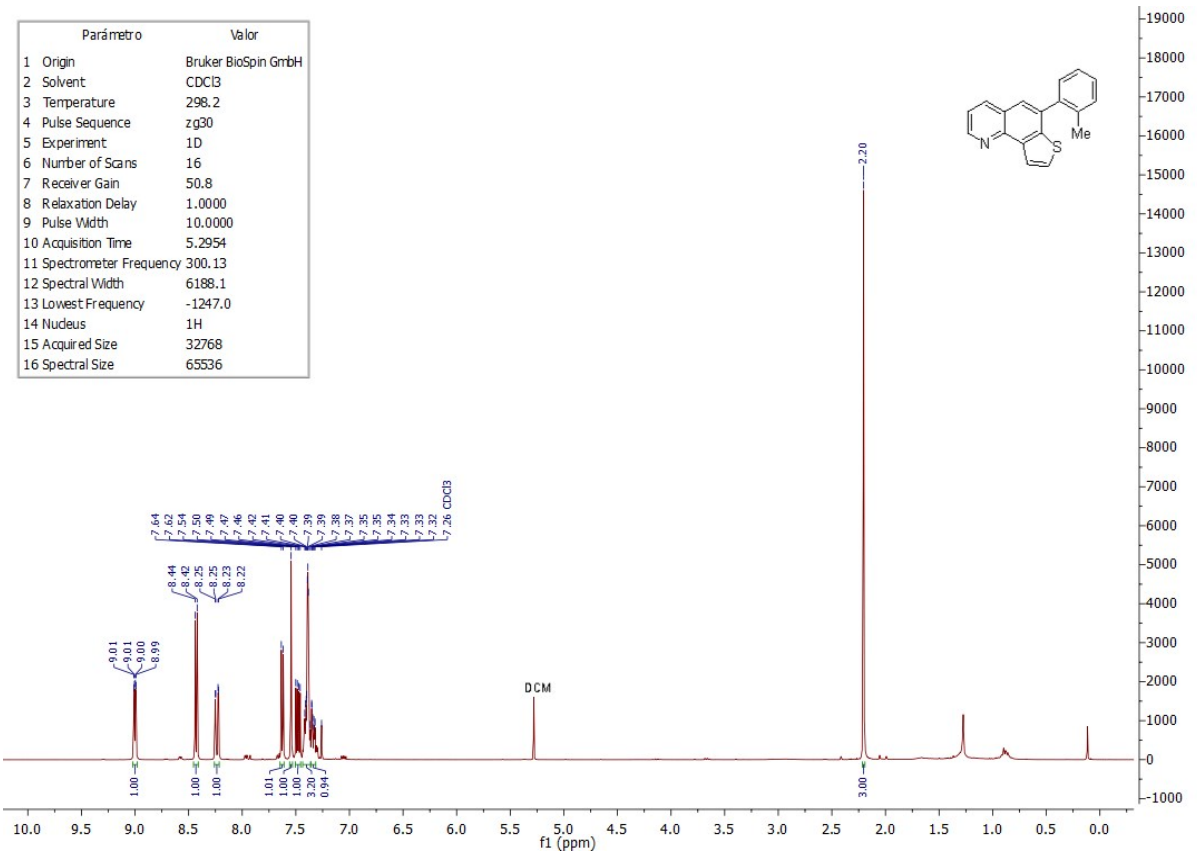


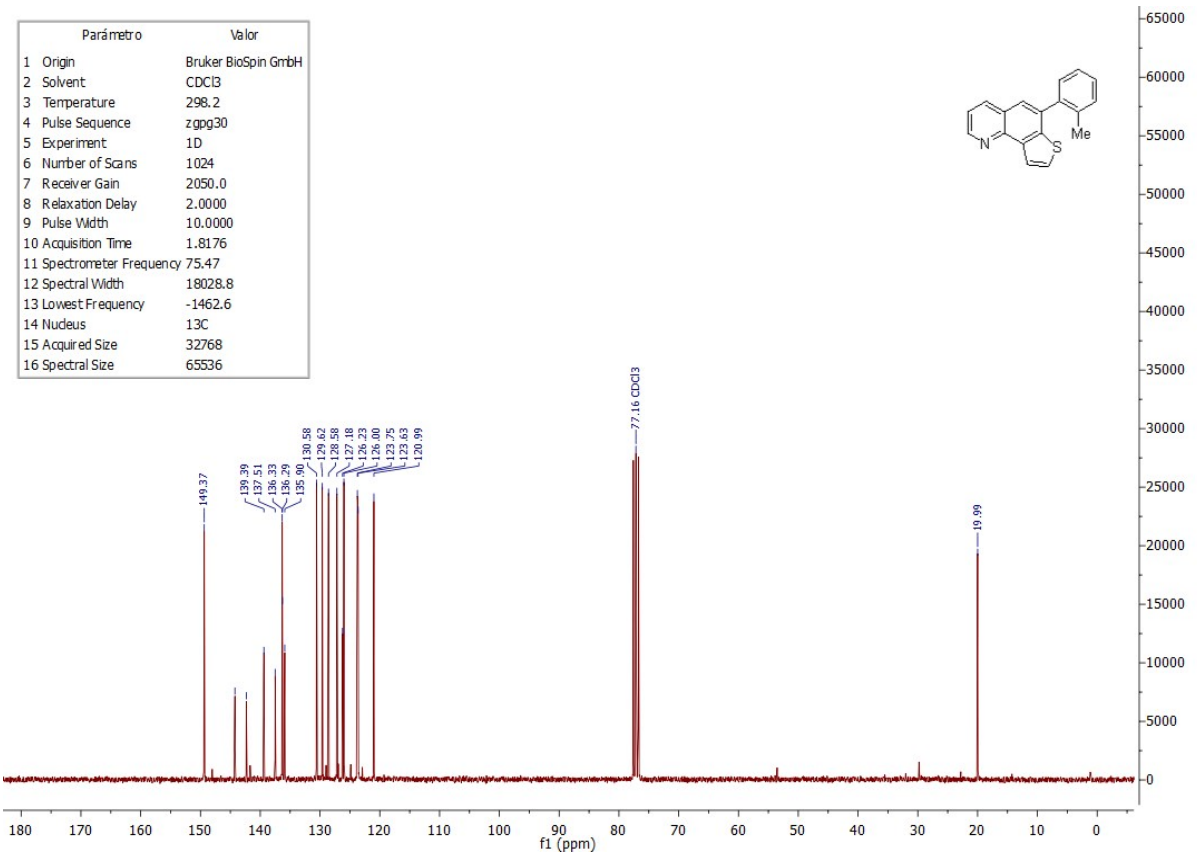
6-(*m*-tolyl)thieno[2,3-*h*]quinoline **4c**



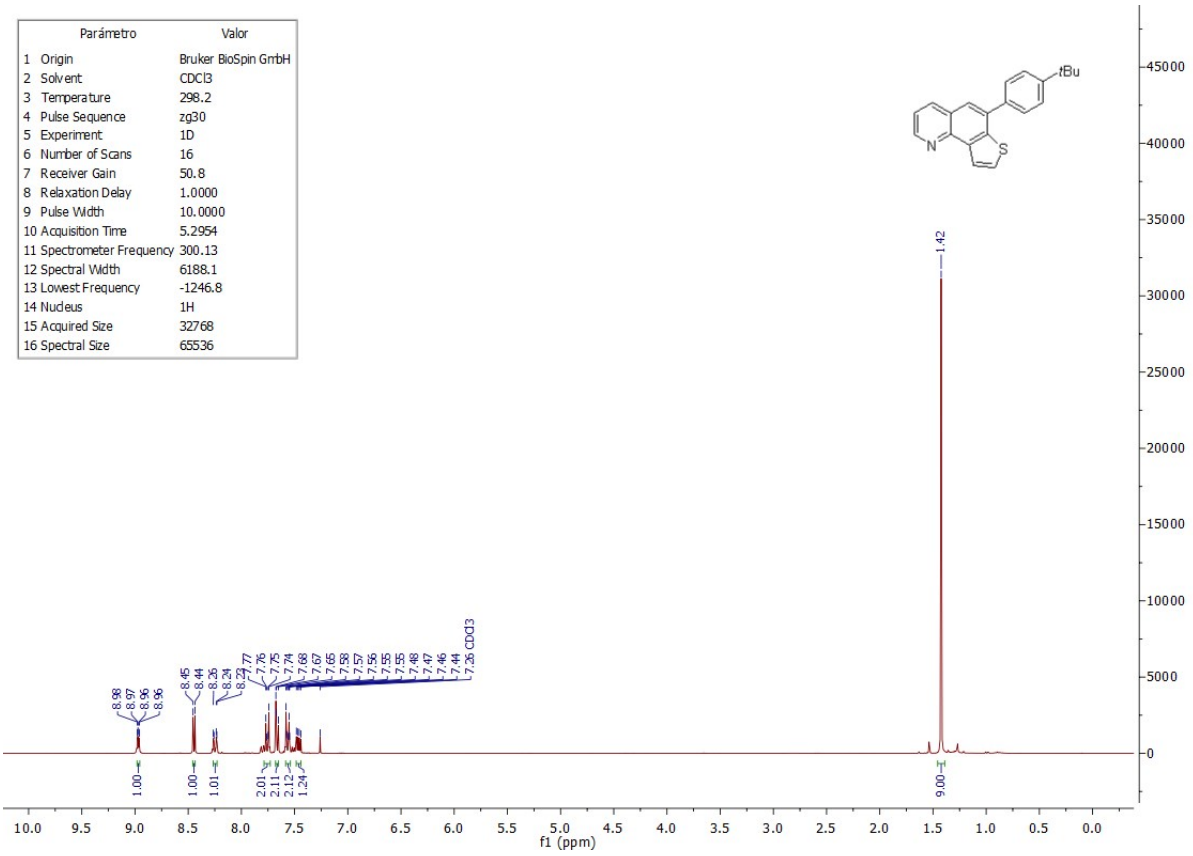


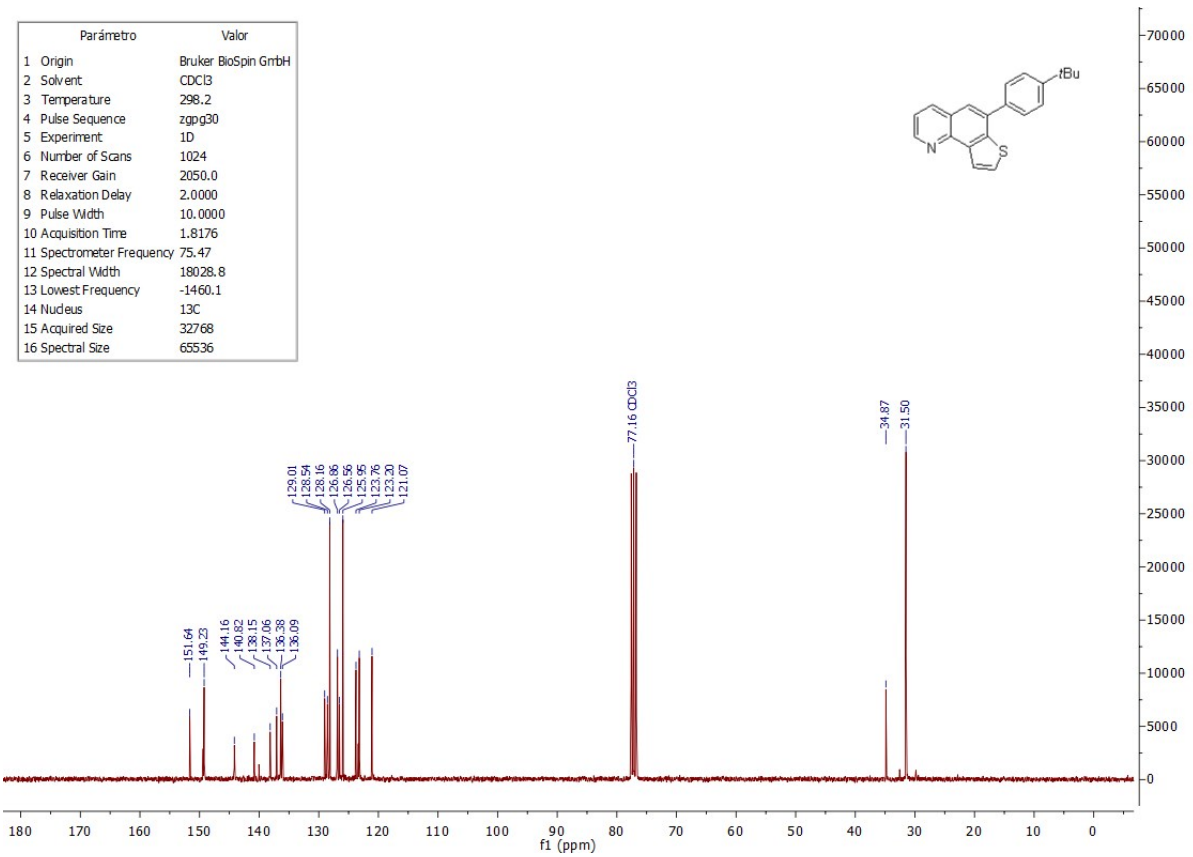
6-(*o*-tolyl)thieno[2,3-*h*]quinoline **4d**





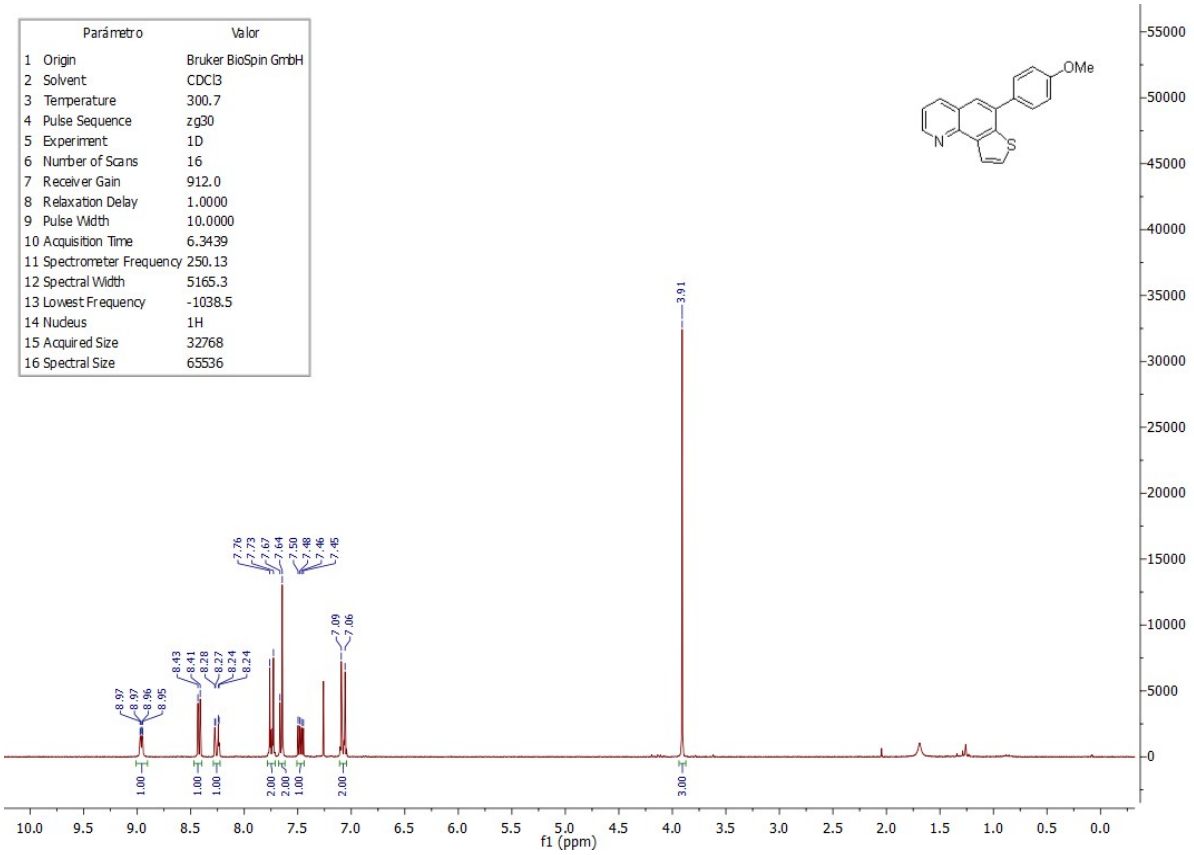
6-(4-(*tert*-butyl)phenyl)thieno[2,3-*h*]quinoline **4e**



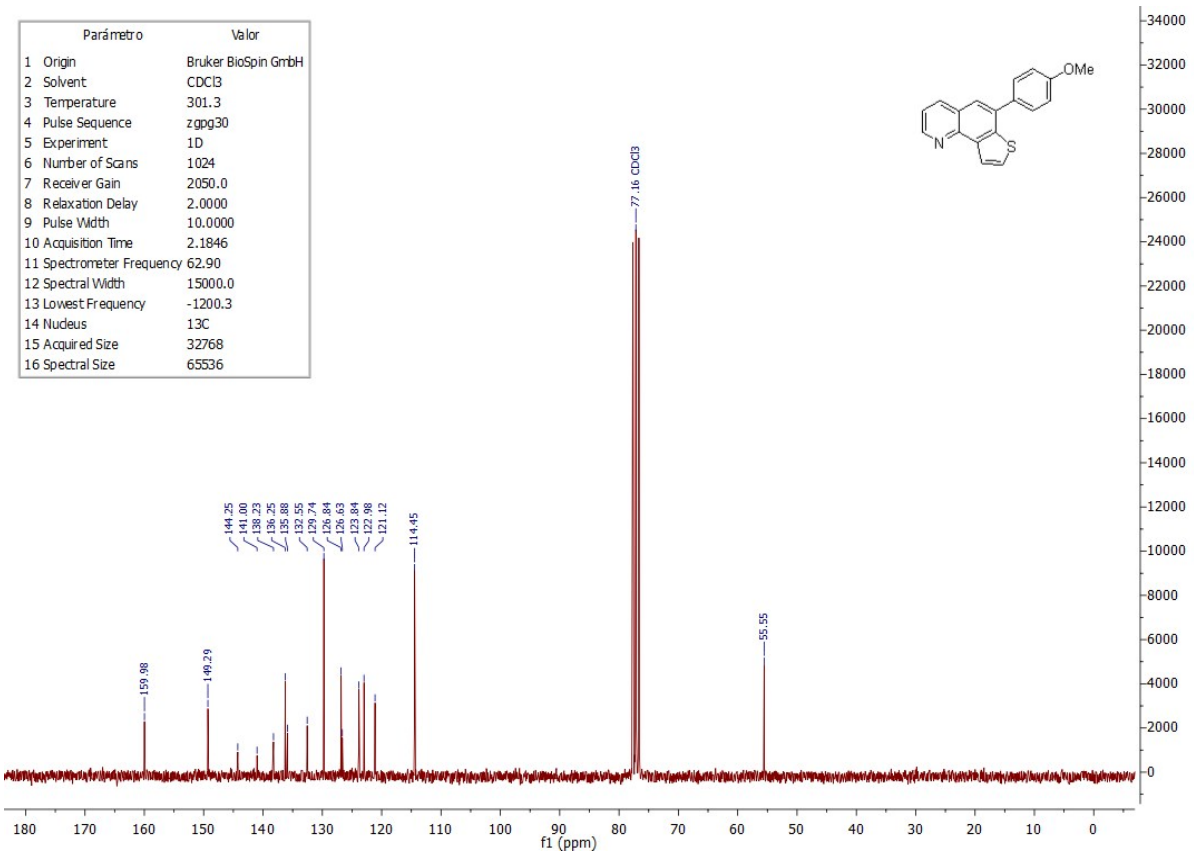


6-(4-methoxyphenyl)thieno[2,3-*h*]quinoline **4f**

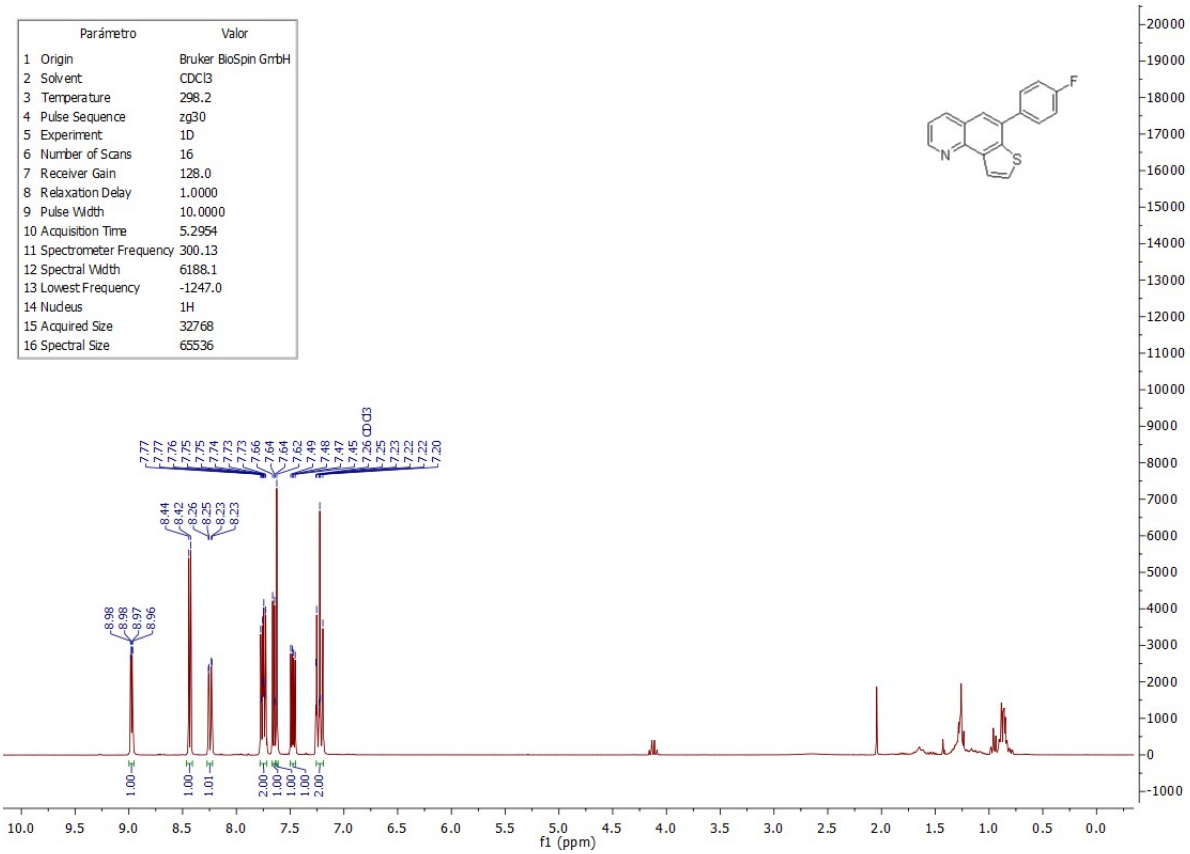
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	300.7
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	912.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.5
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

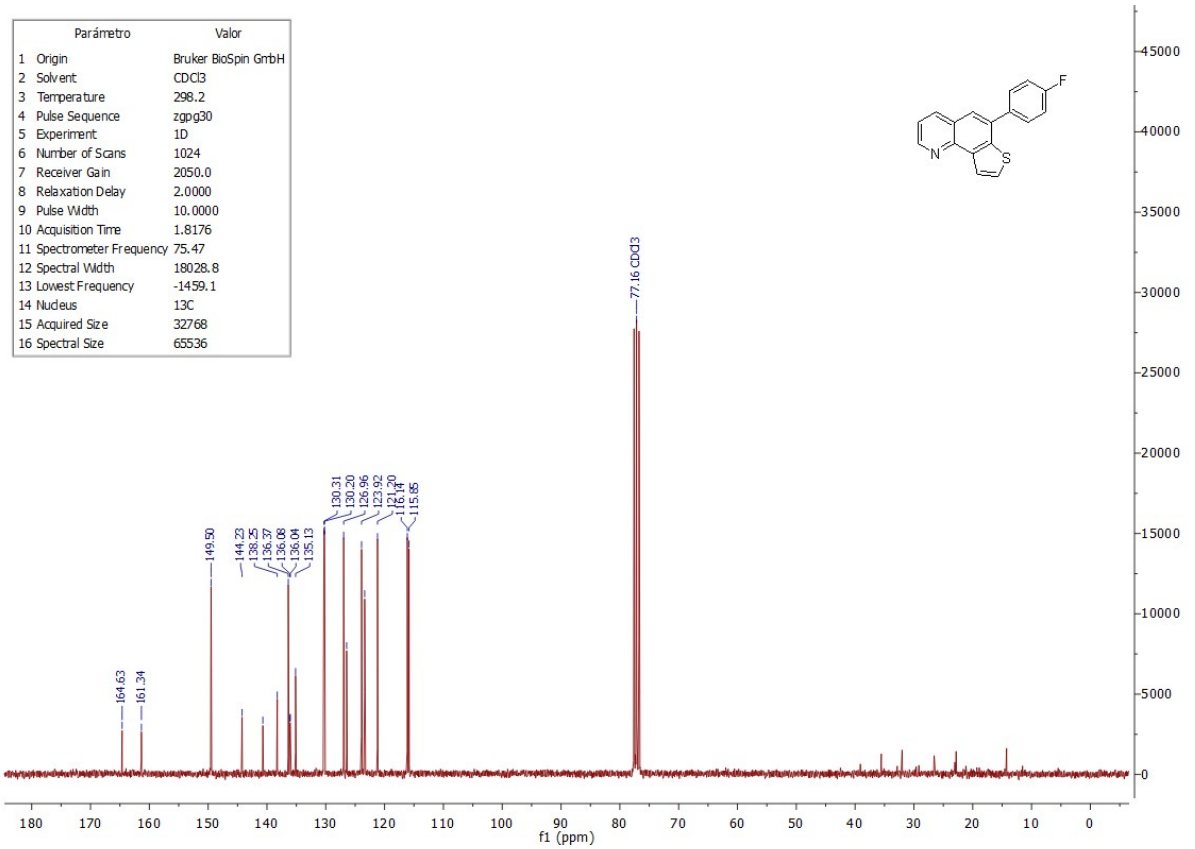


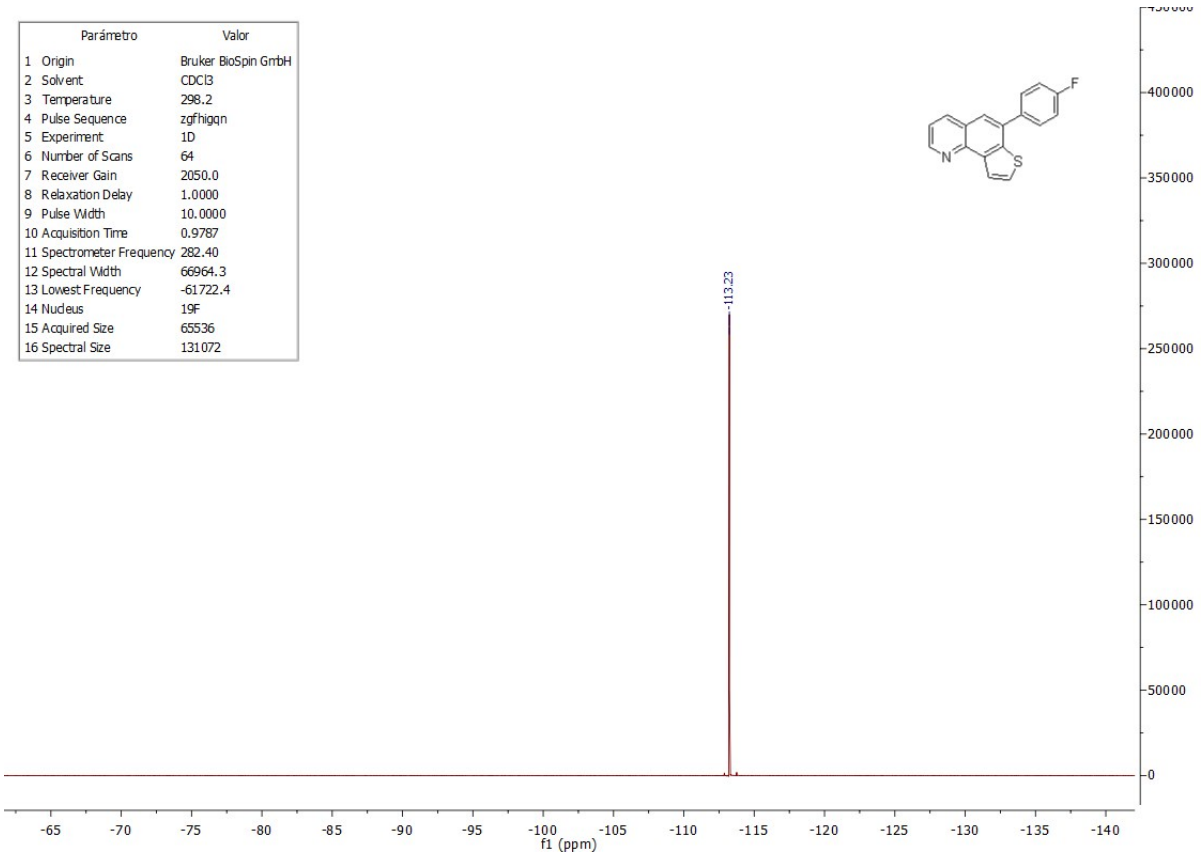
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	301.3
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1200.3
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536



6-(4-fluorophenyl)thieno[2,3-*h*]quinoline **4h**

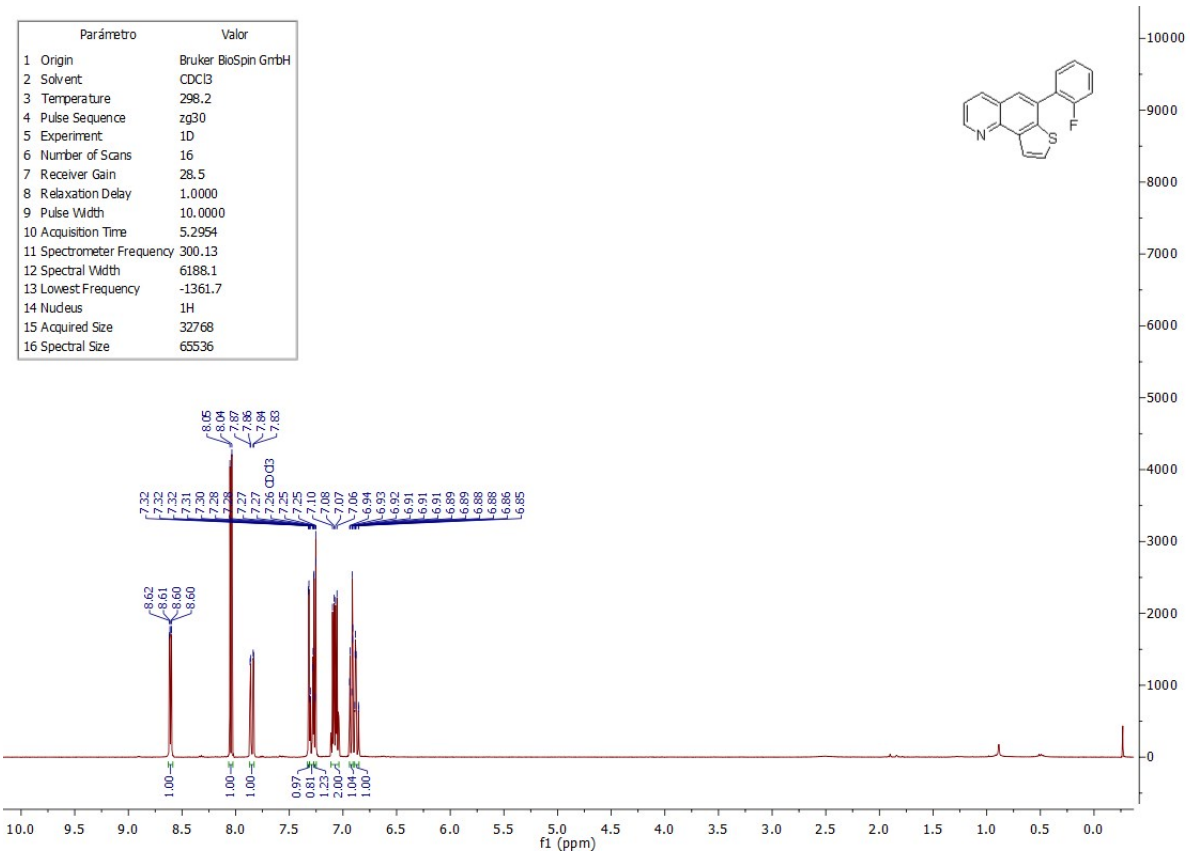




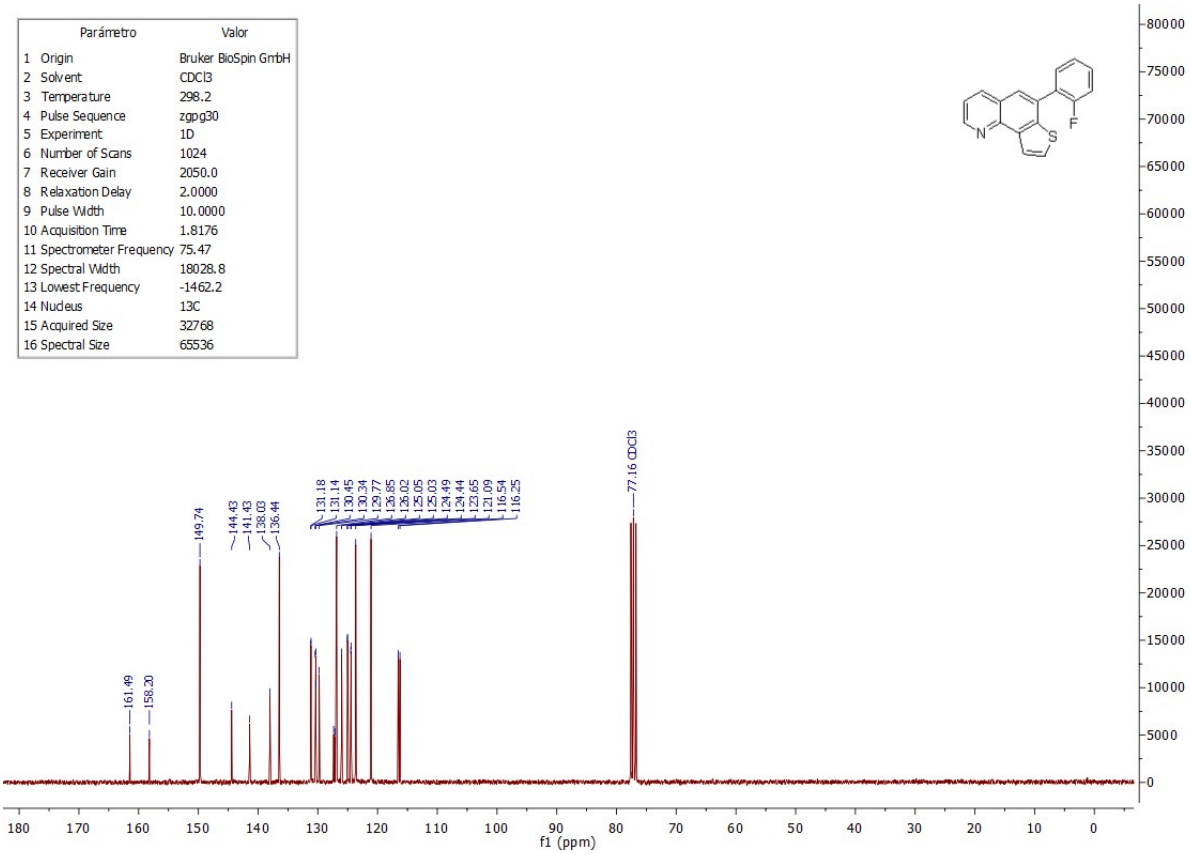


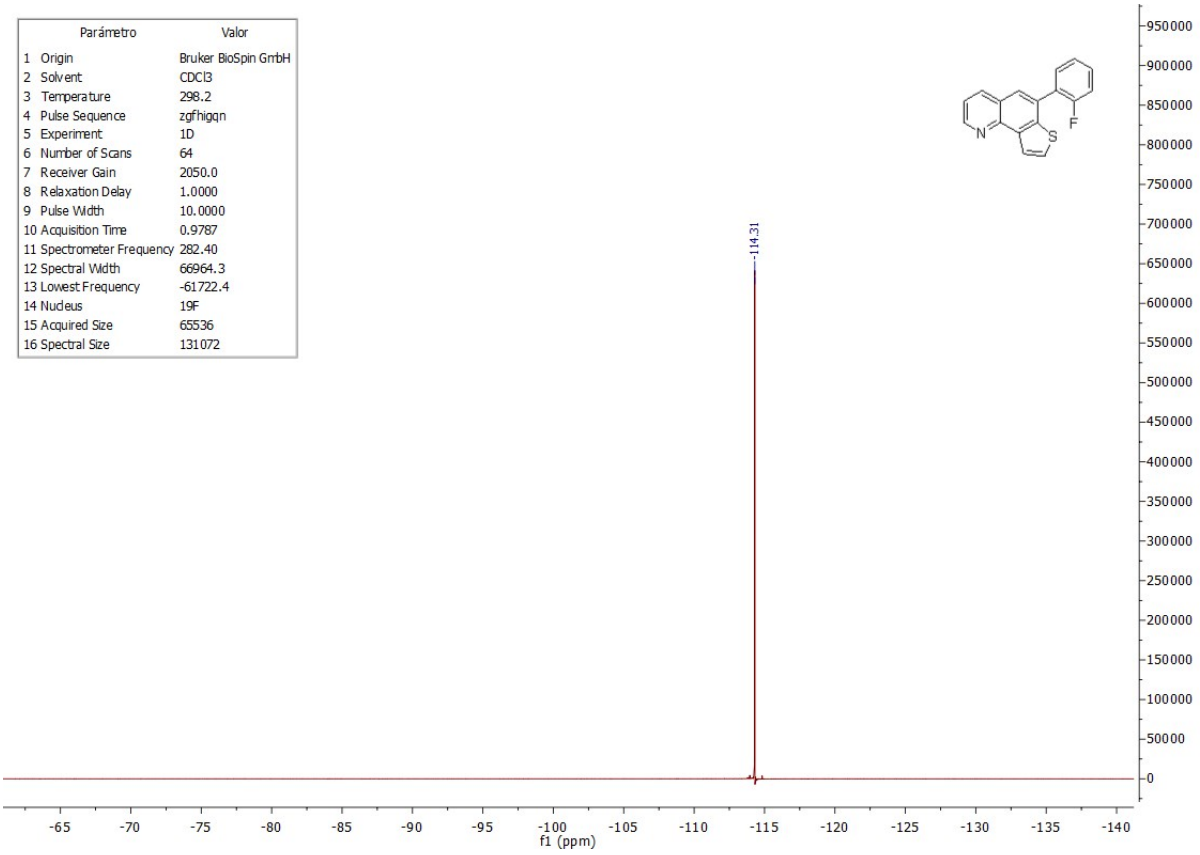
6-(2-fluorophenyl)thieno[2,3-*h*]quinoline **4i**

Parámetro	Valor
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	28.5
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	-1361.7
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

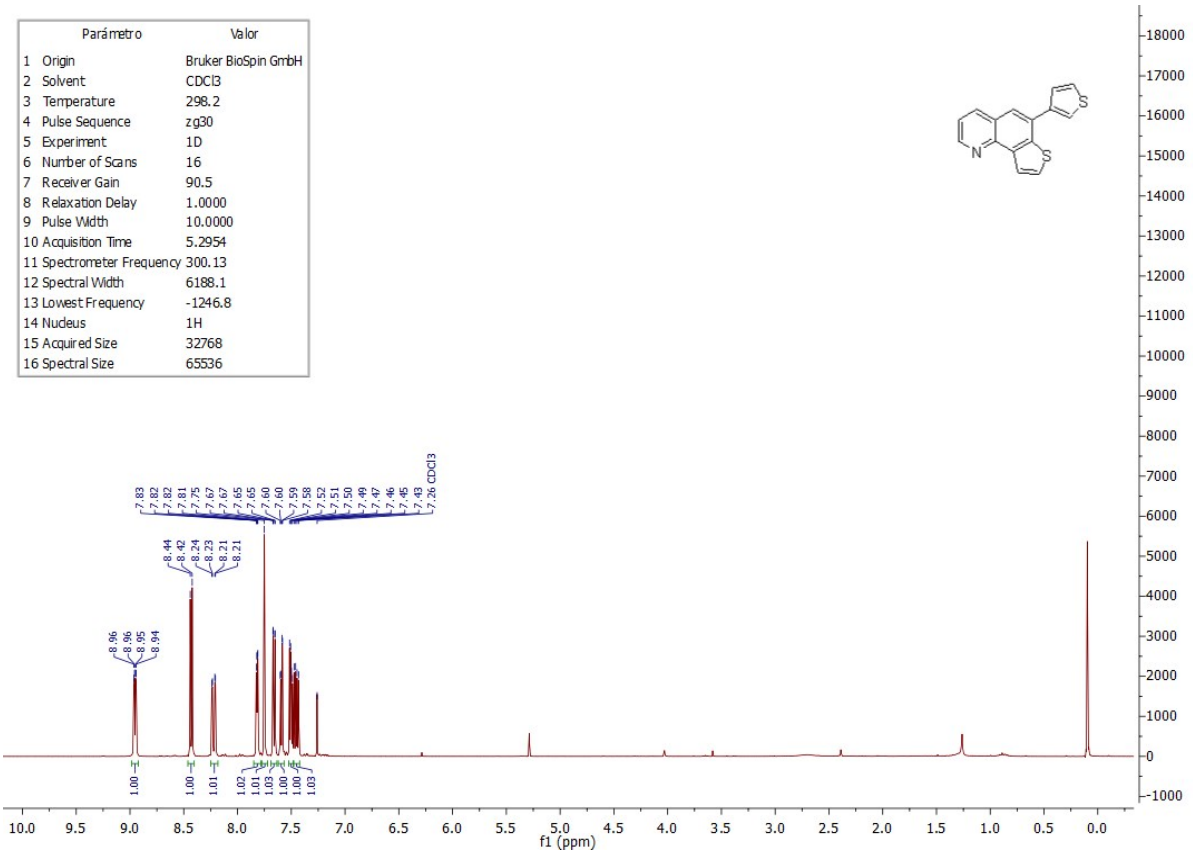


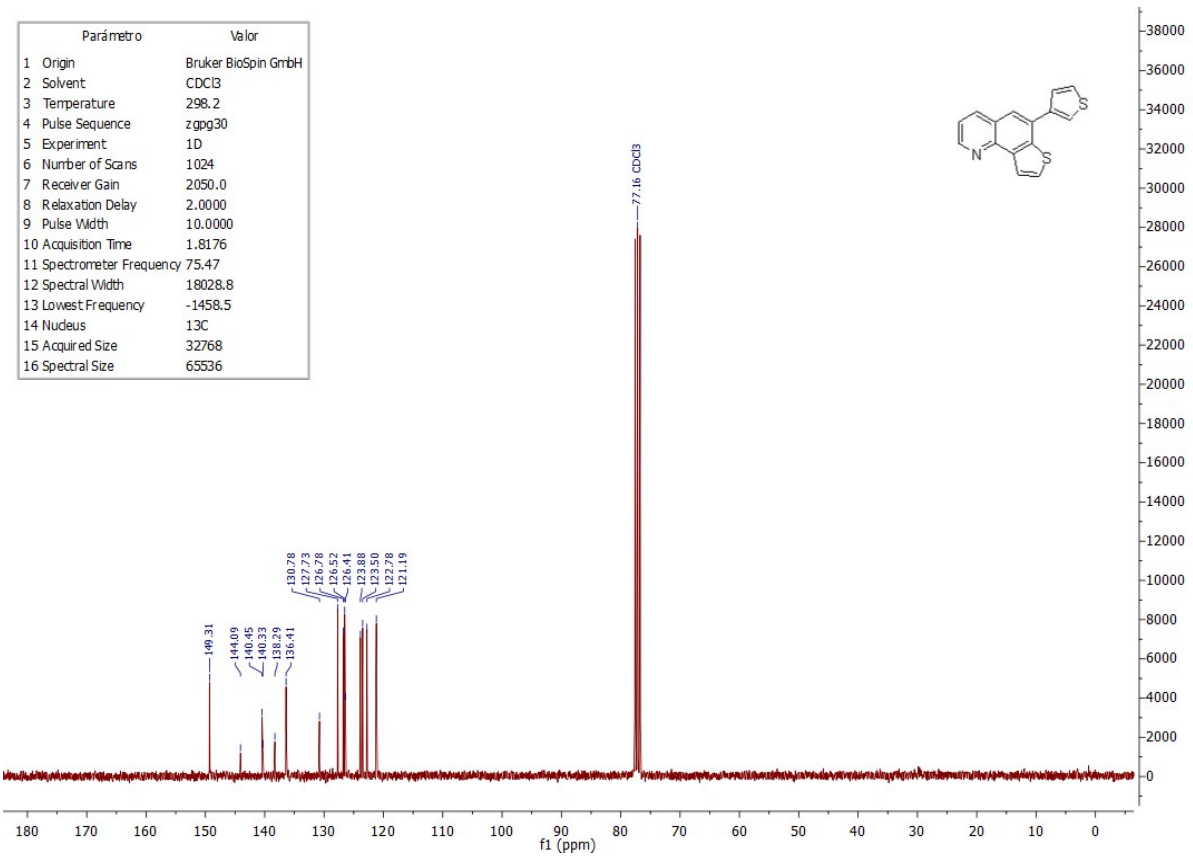
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1462.2
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536





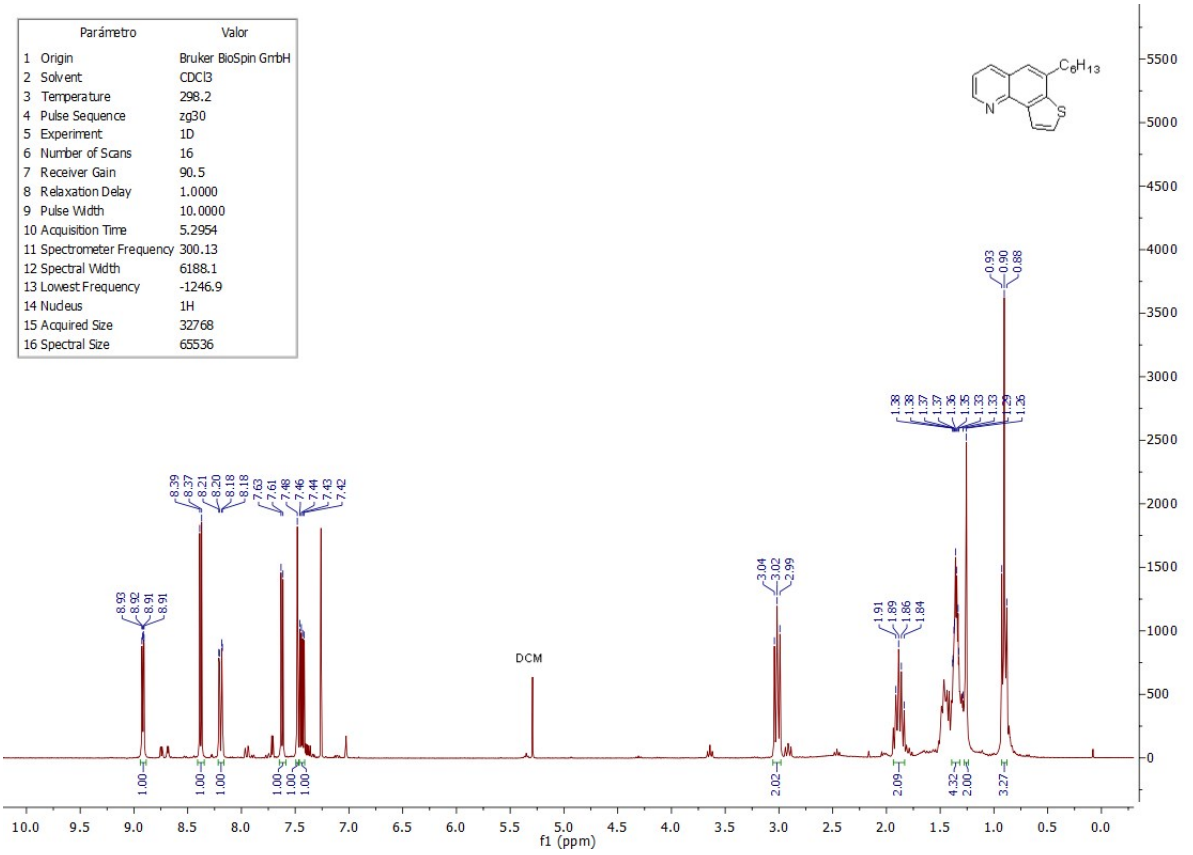
6-(thiophen-3-yl)thieno[2,3-*h*]quinoline **4k**



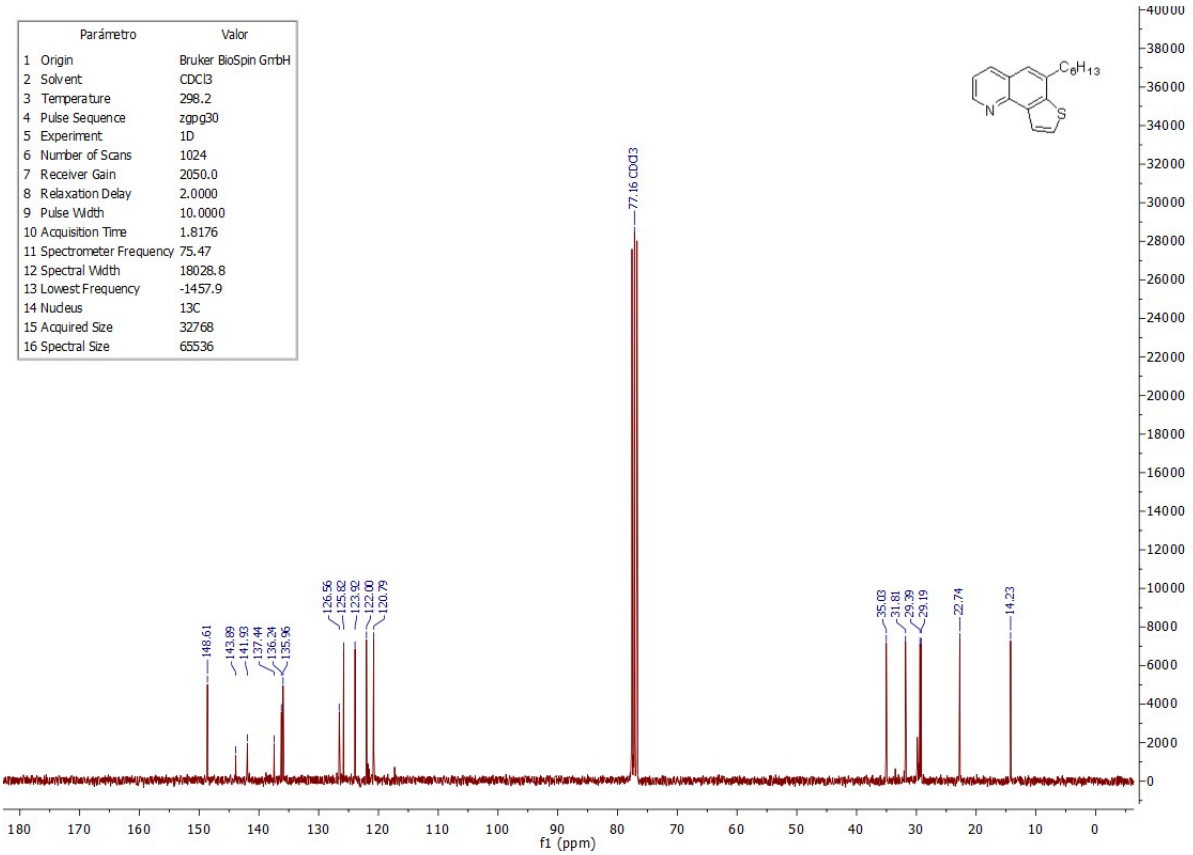


6-hexylthieno[2,3-*h*]quinoline **4l**

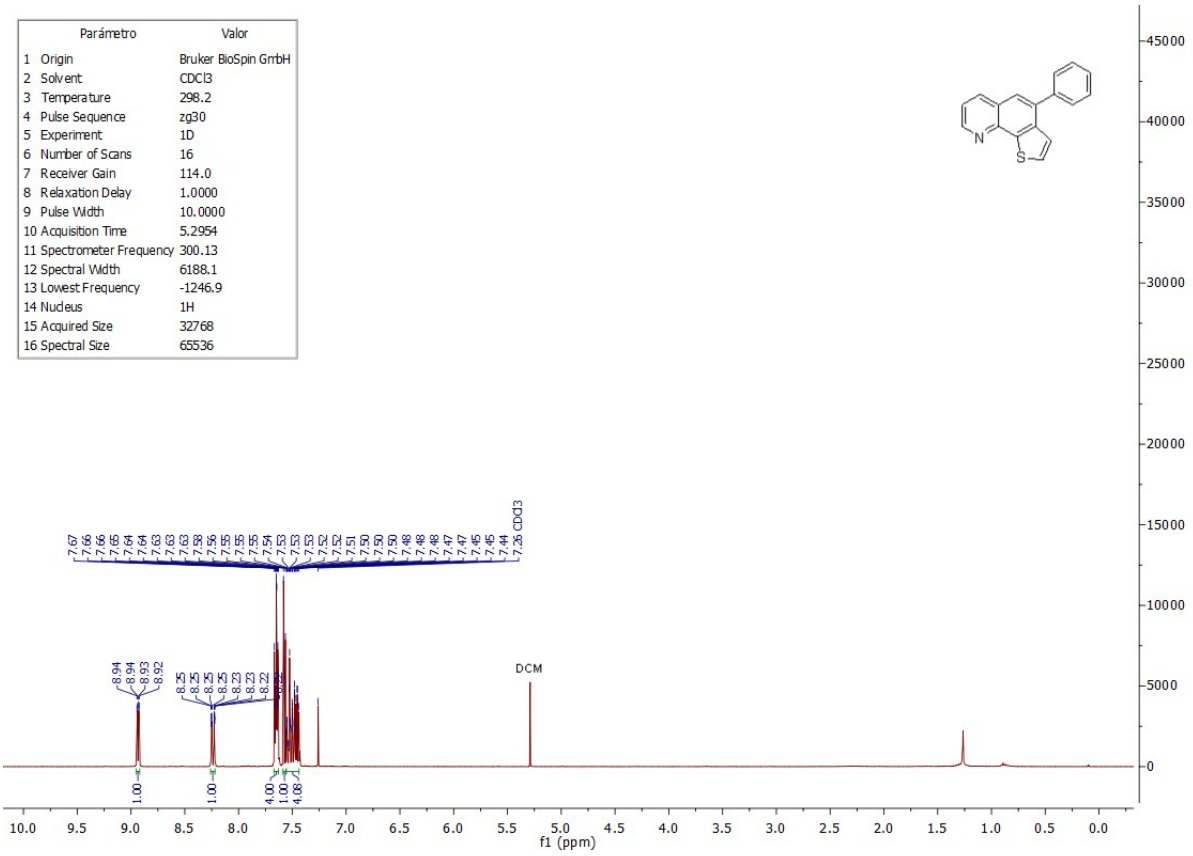
	Parámetro	Valor
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	298.2
4	Pulse Sequence	zg30
5	Experiment	1D
6	Number of Scans	16
7	Receiver Gain	90.5
8	Relaxation Delay	1.0000
9	Pulse Width	10.0000
10	Acquisition Time	5.2954
11	Spectrometer Frequency	300.13
12	Spectral Width	6188.1
13	Lowest Frequency	-1246.9
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

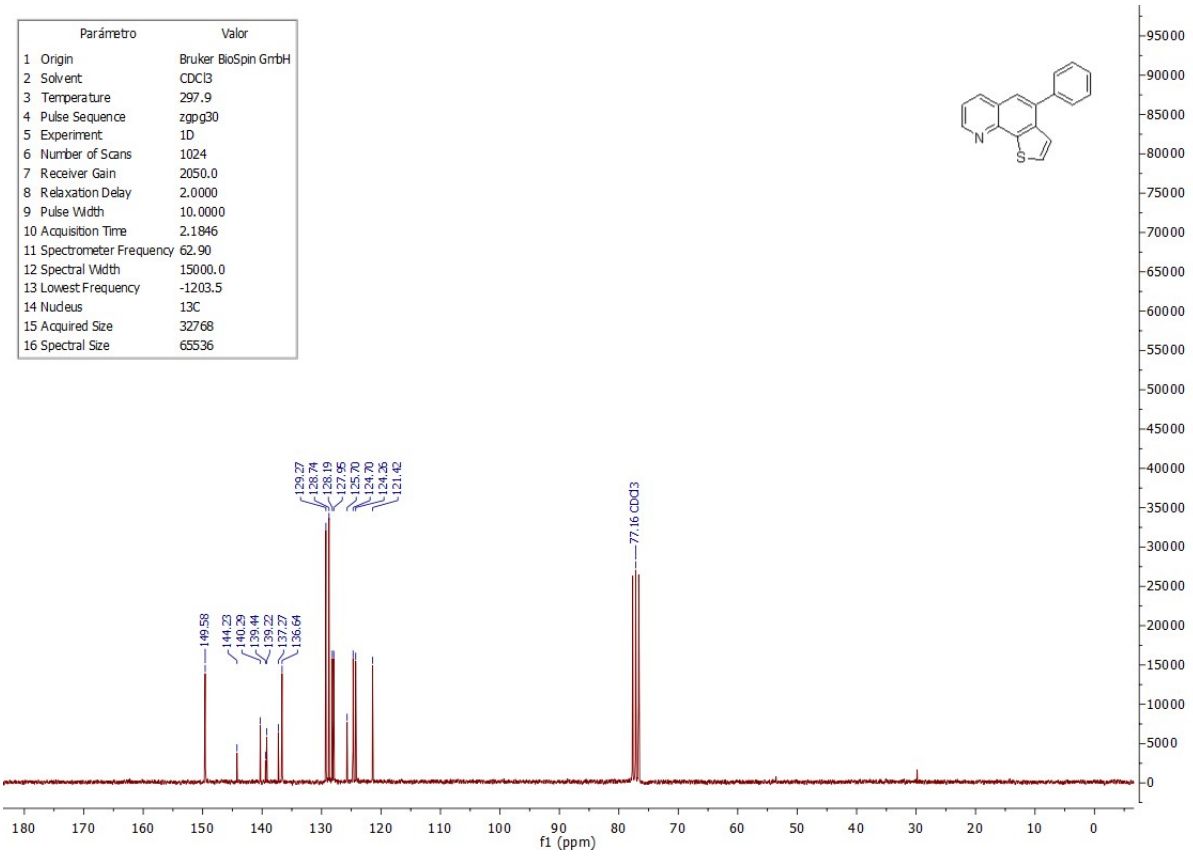


	Parámetro	Valor
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	298.2
4	Pulse Sequence	zgpg30
5	Experiment	1D
6	Number of Scans	1024
7	Receiver Gain	2050.0
8	Relaxation Delay	2.0000
9	Pulse Width	10.0000
10	Acquisition Time	1.8176
11	Spectrometer Frequency	75.47
12	Spectral Width	18028.8
13	Lowest Frequency	-1457.9
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

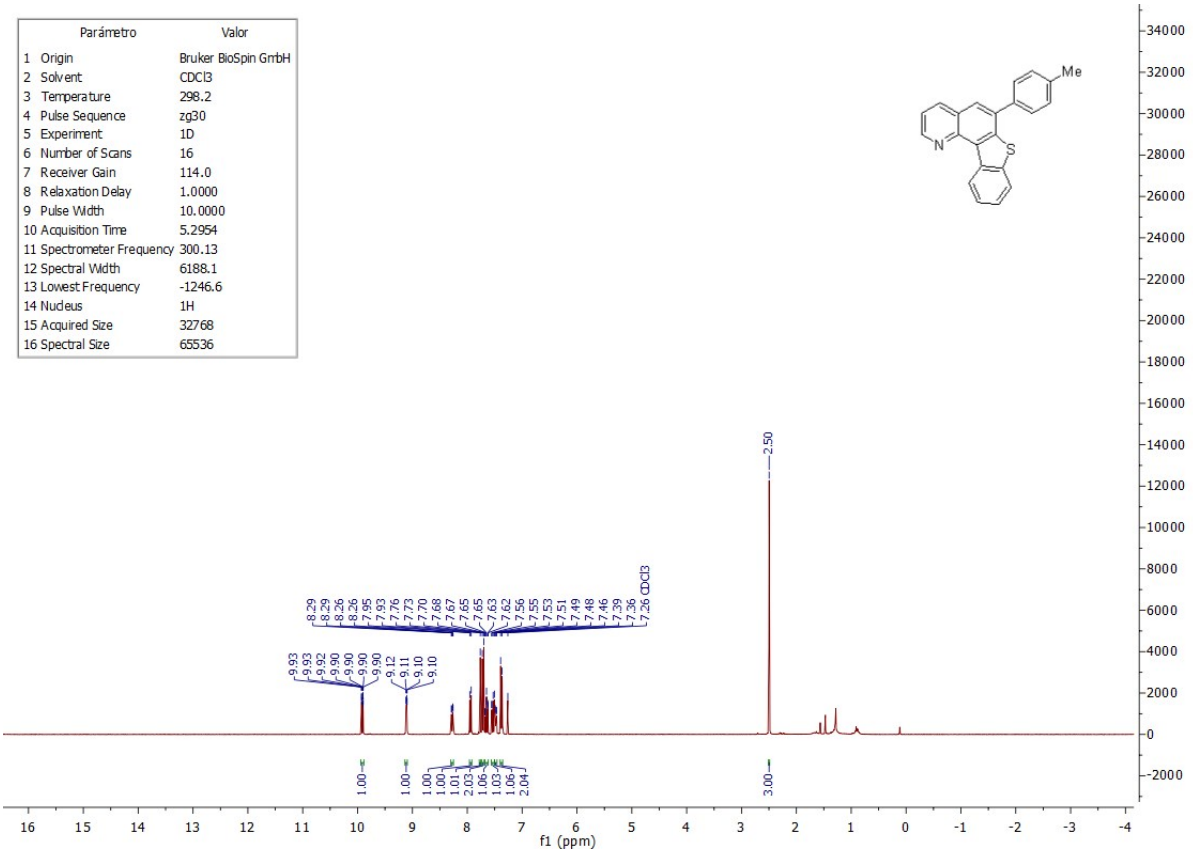


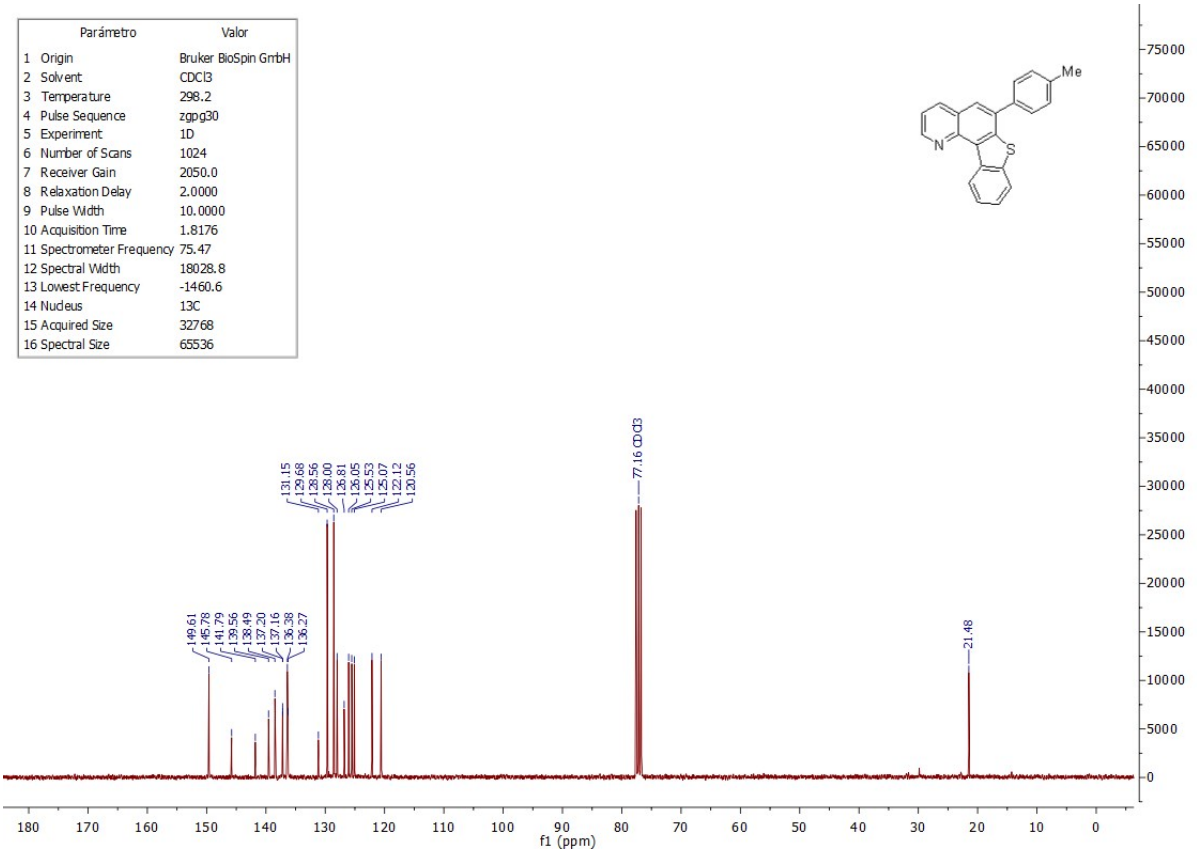
4-phenylthieno[3,2-*h*]quinoline **4m**



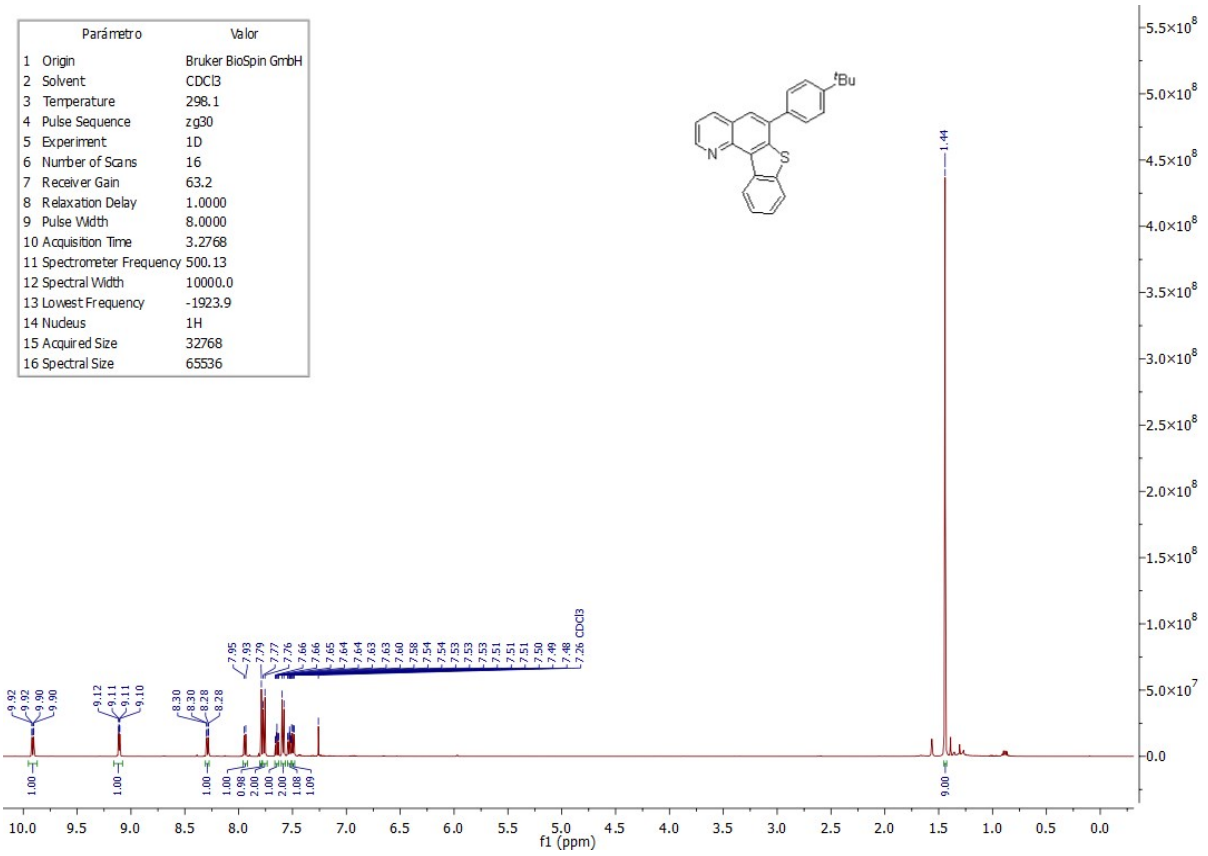


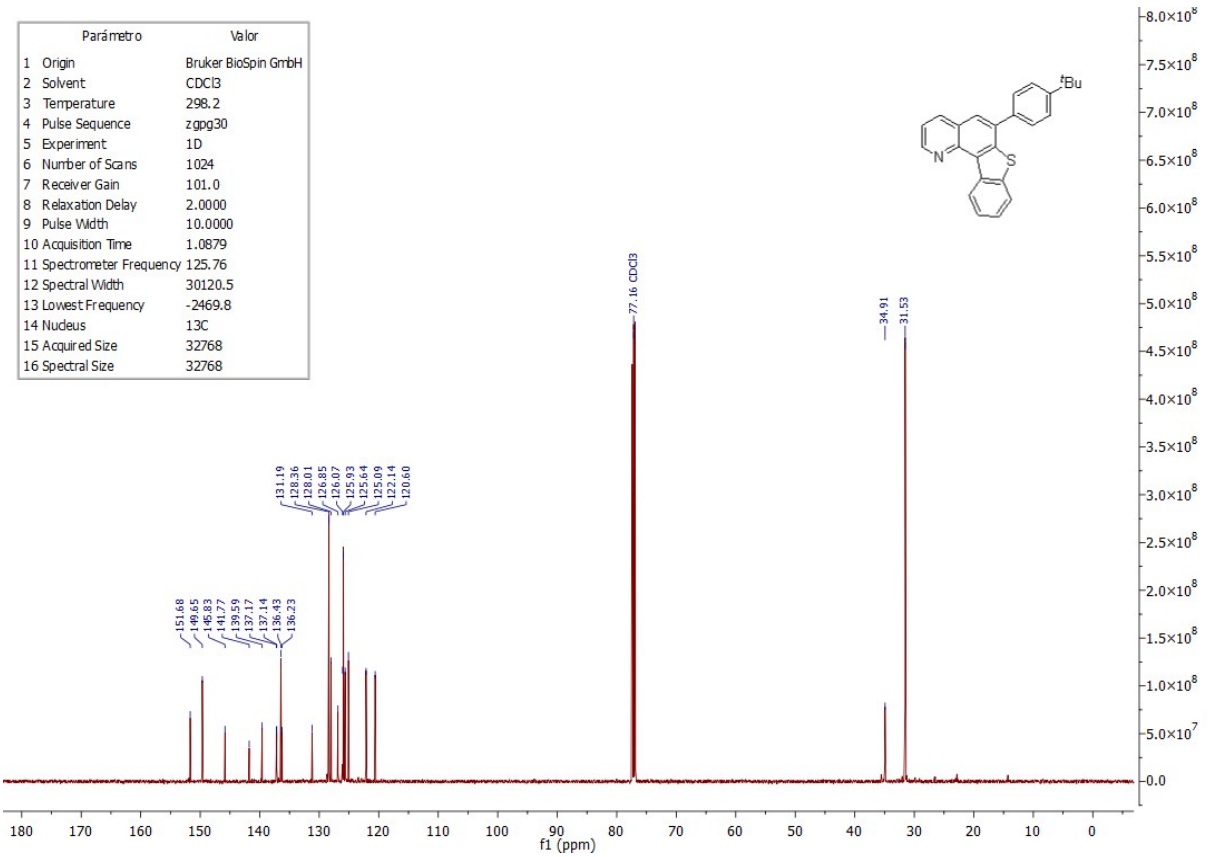
6-(*p*-tolyl)benzo[4,5]thieno[2,3-*h*]quinoline **4n**





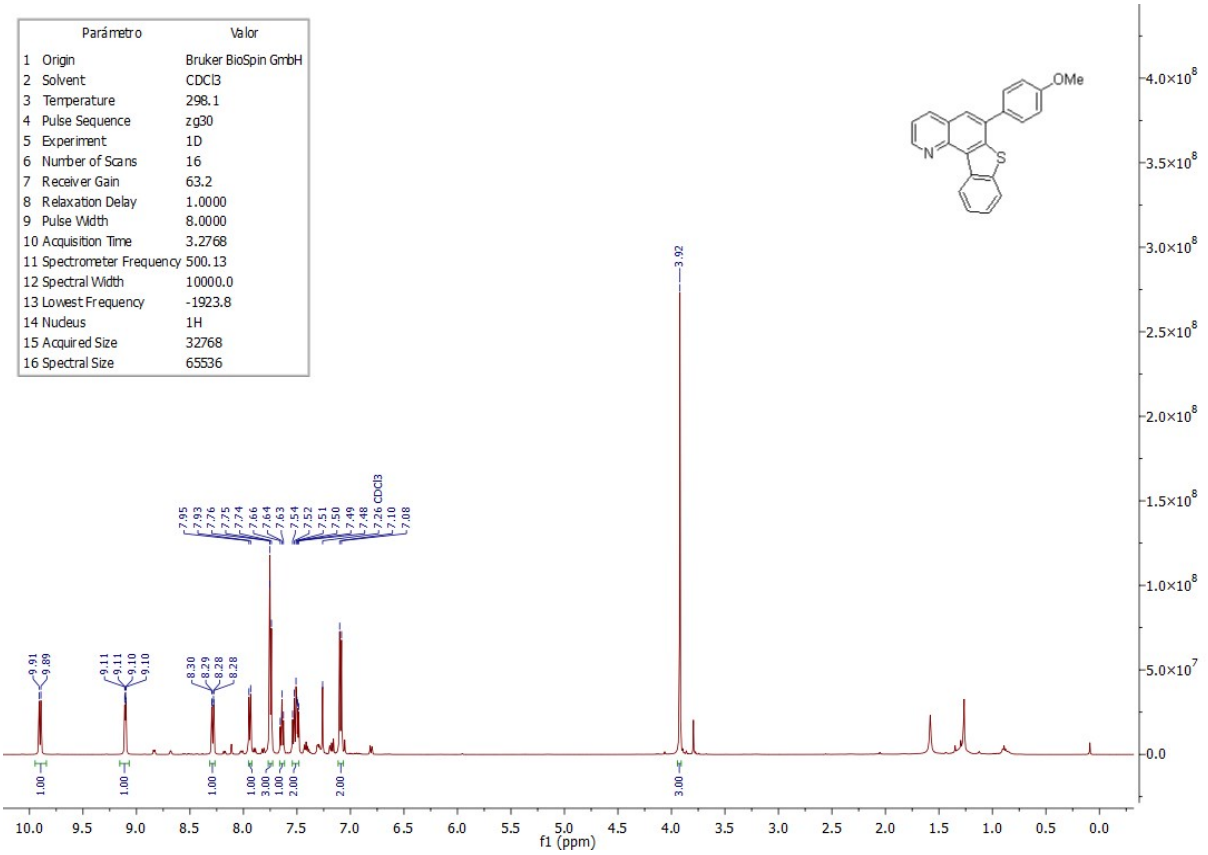
6-(4-(*tert*-butyl)phenyl)benzo[4,5]thieno[2,3-*h*]quinoline **4q**



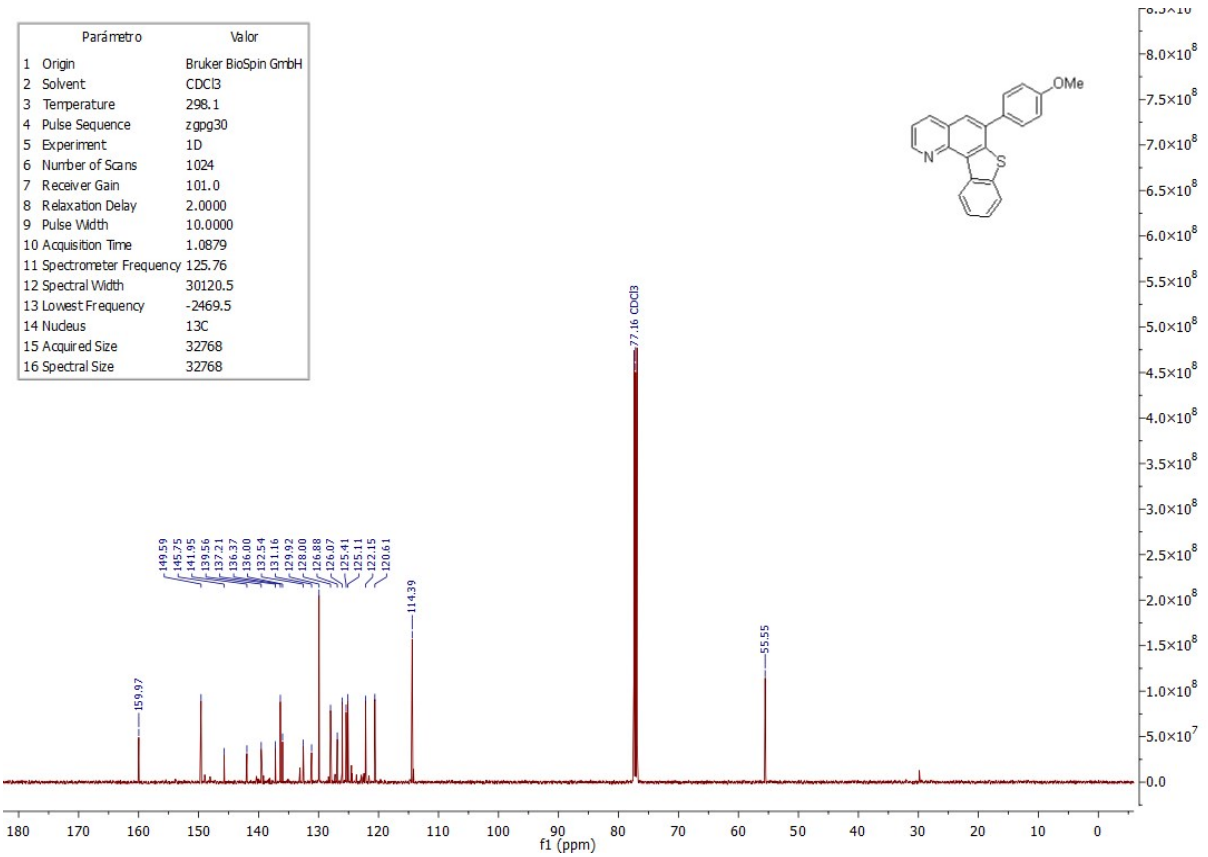


6-(4-methoxyphenyl)benzo[4,5]thieno[2,3-*h*]quinoline **4r**

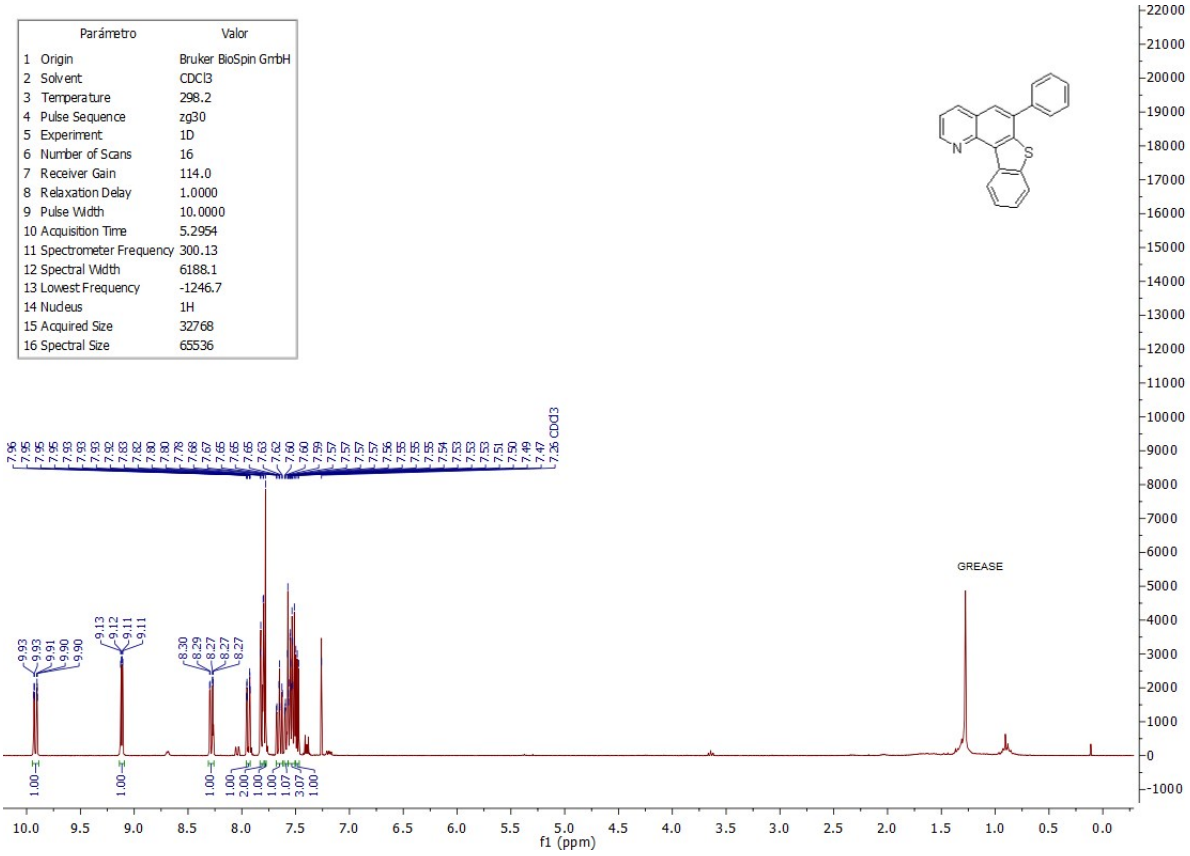
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	63.2
8 Relaxation Delay	1.0000
9 Pulse Width	8.0000
10 Acquisition Time	3.2768
11 Spectrometer Frequency	500.13
12 Spectral Width	10000.0
13 Lowest Frequency	-1923.8
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

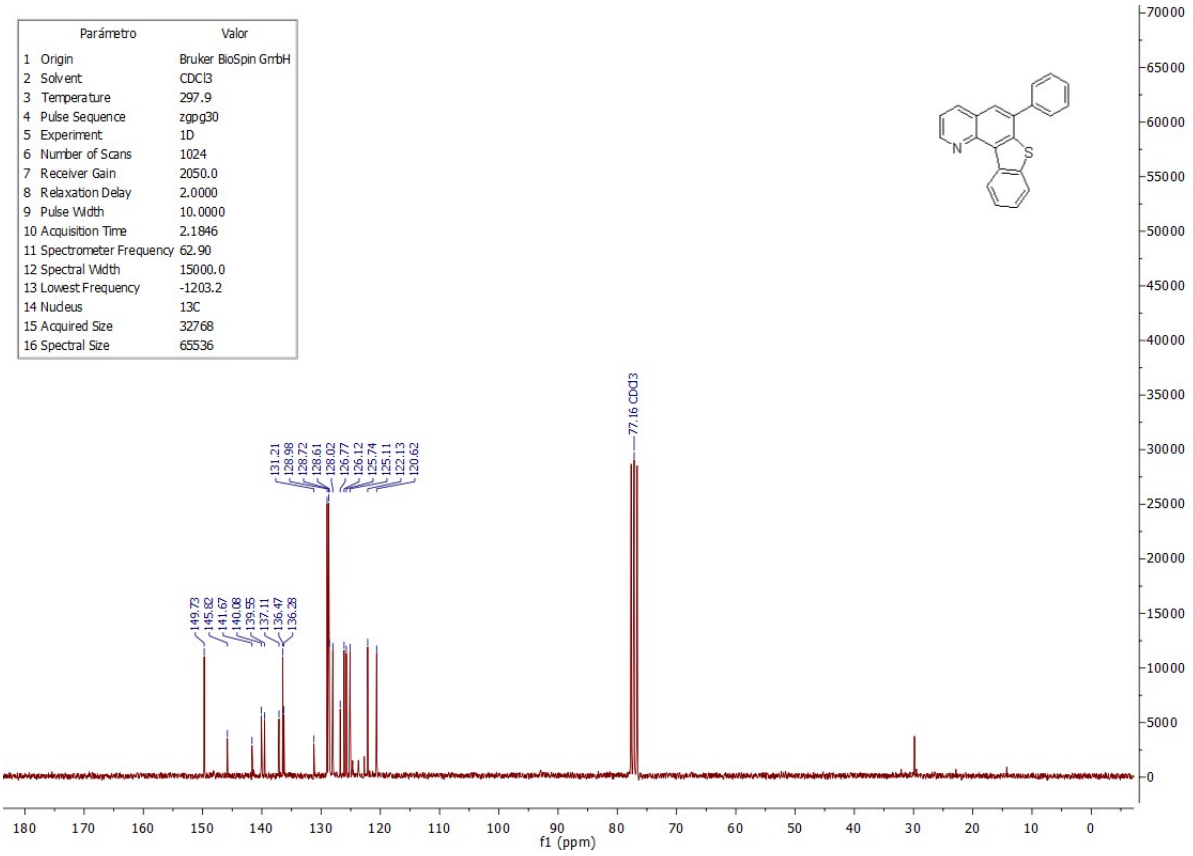


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	101.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.0879
11 Spectrometer Frequency	125.76
12 Spectral Width	30120.5
13 Lowest Frequency	-2469.5
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768

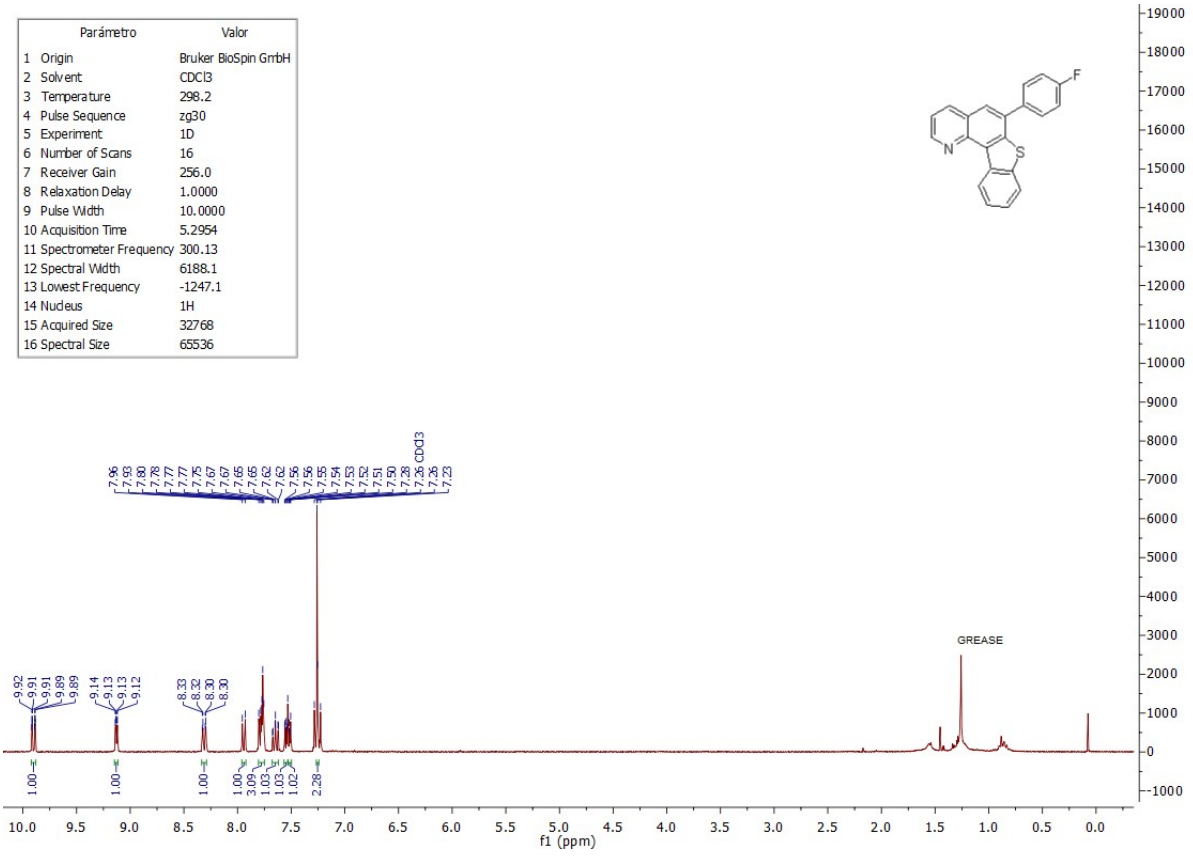


6-phenylbenzo[4,5]thieno[2,3-*h*]quinoline **4s**

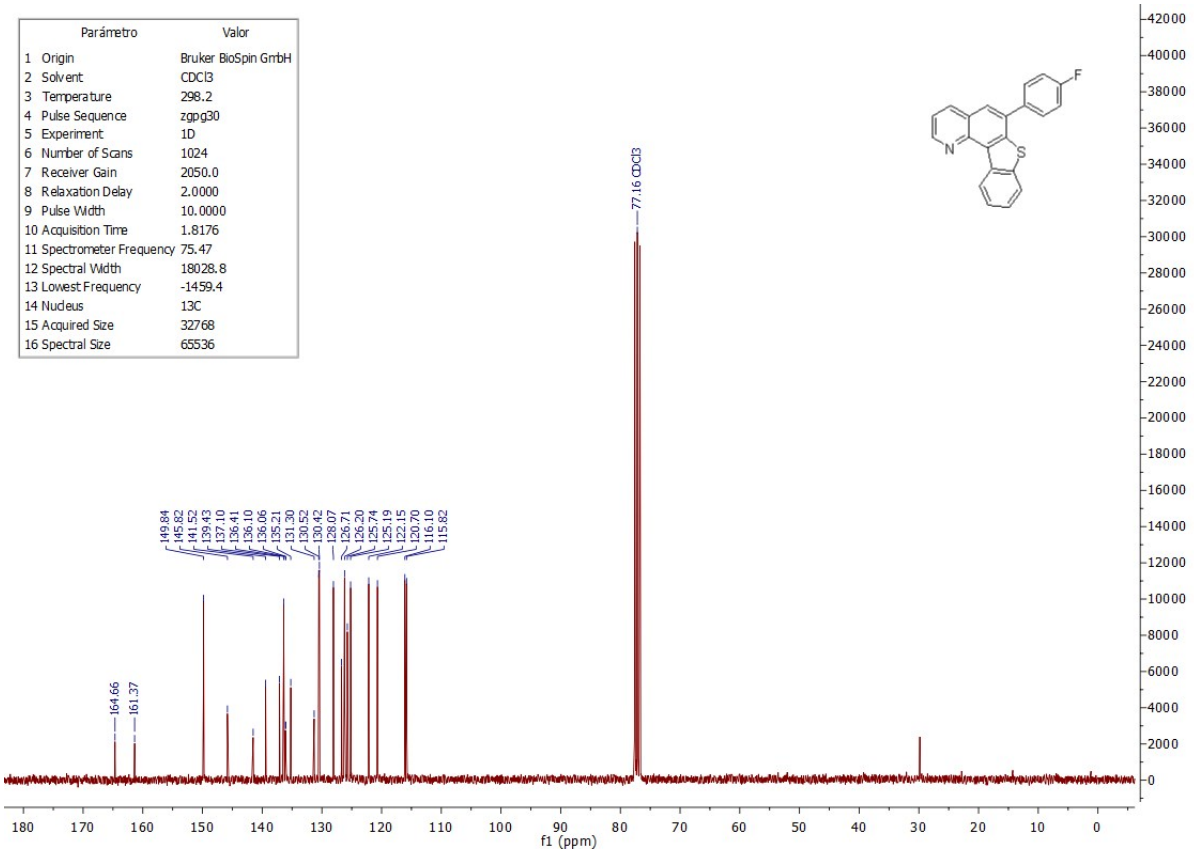




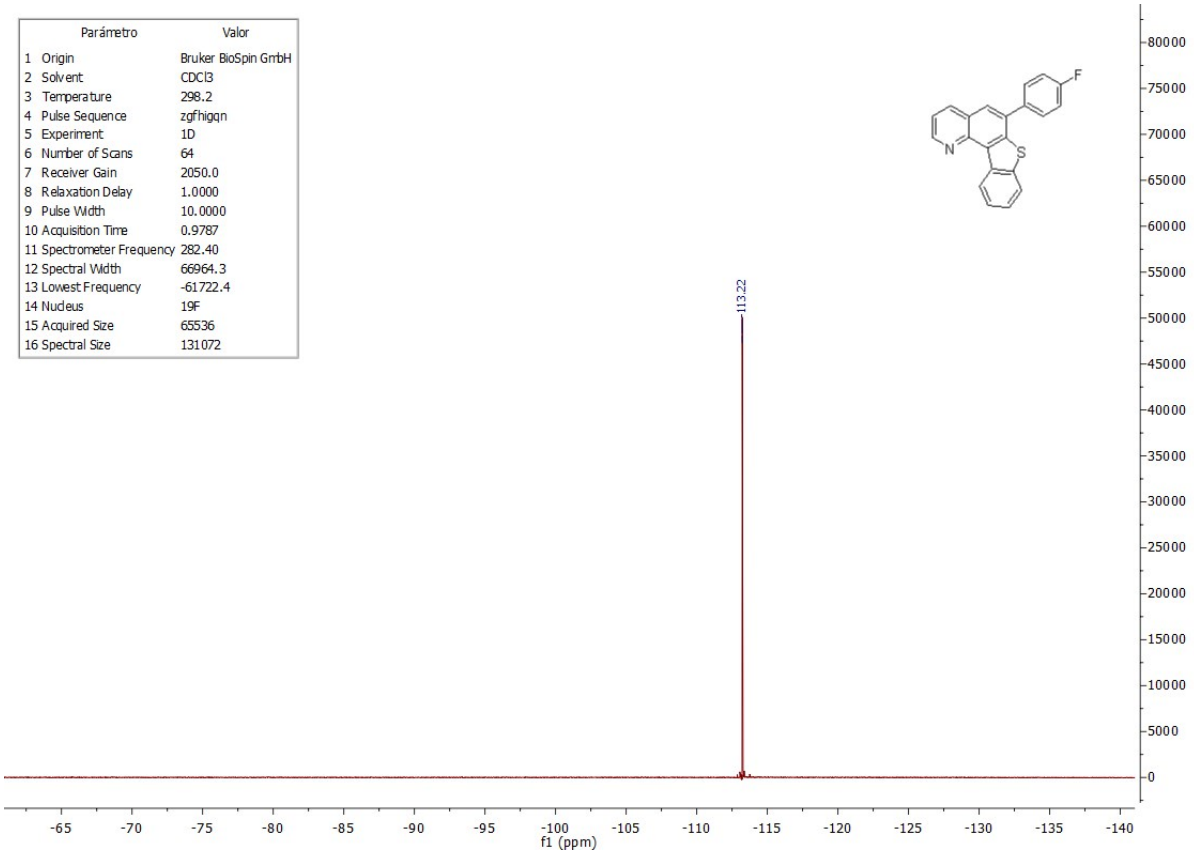
6-(4-fluorophenyl)benzo[4,5]thieno[2,3-*h*]quinoline **4t**



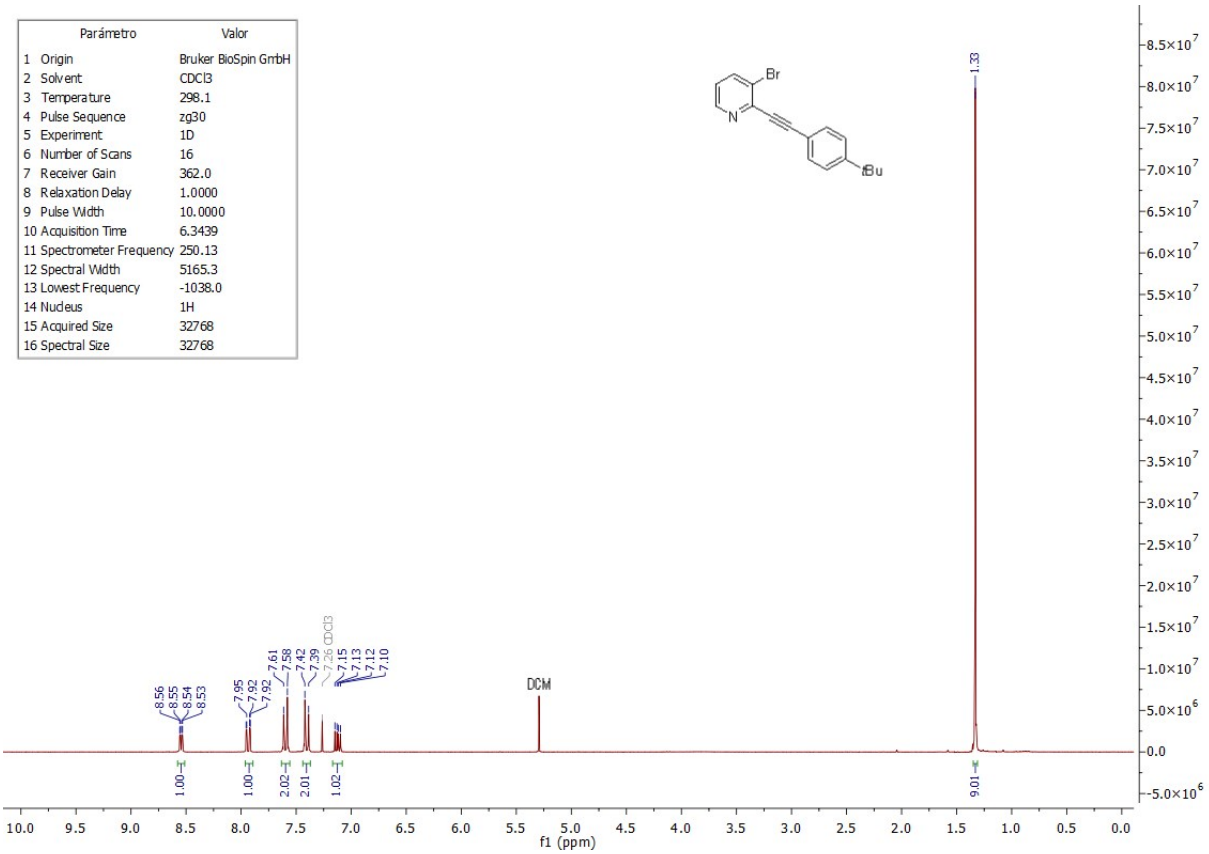
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1459.4
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

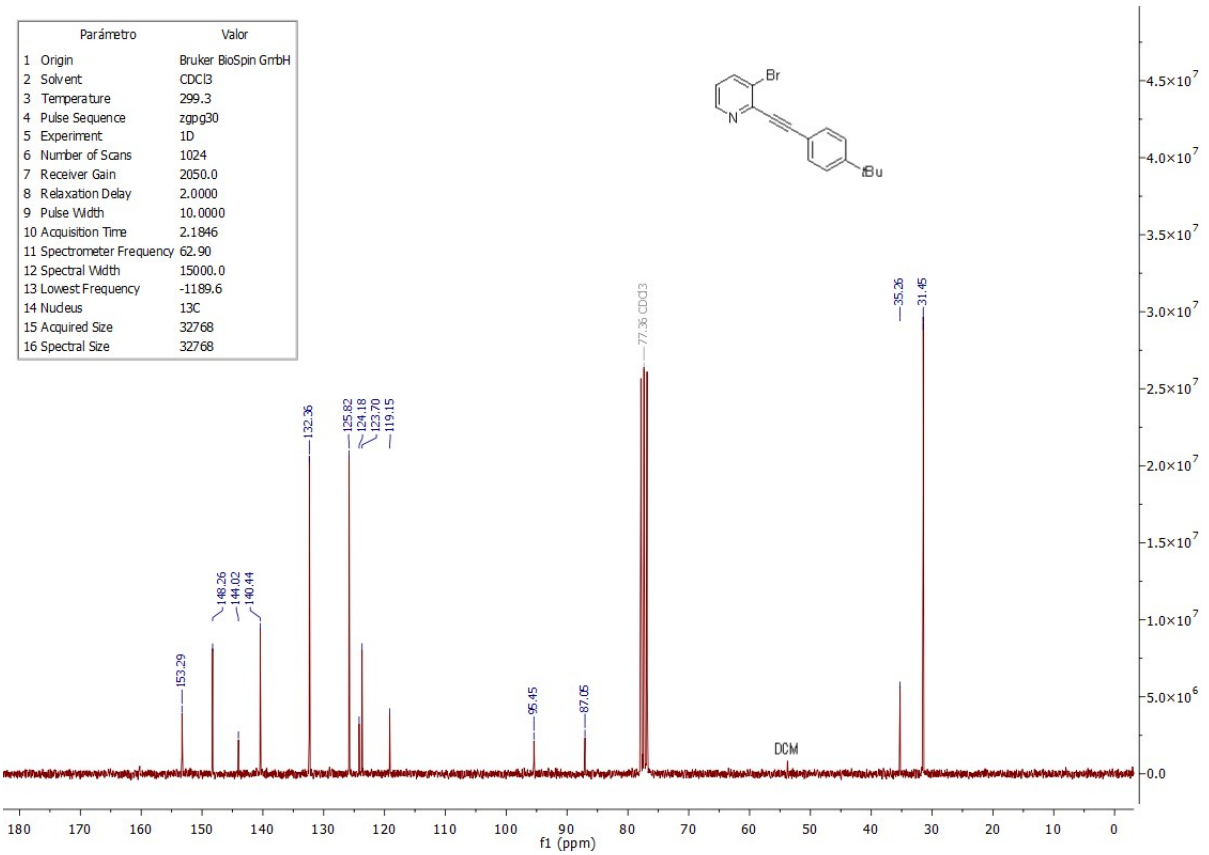


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgfhigqn
5 Experiment	1D
6 Number of Scans	64
7 Receiver Gain	2050.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	0.9787
11 Spectrometer Frequency	282.40
12 Spectral Width	66964.3
13 Lowest Frequency	-61722.4
14 Nucleus	19F
15 Acquired Size	65536
16 Spectral Size	131072

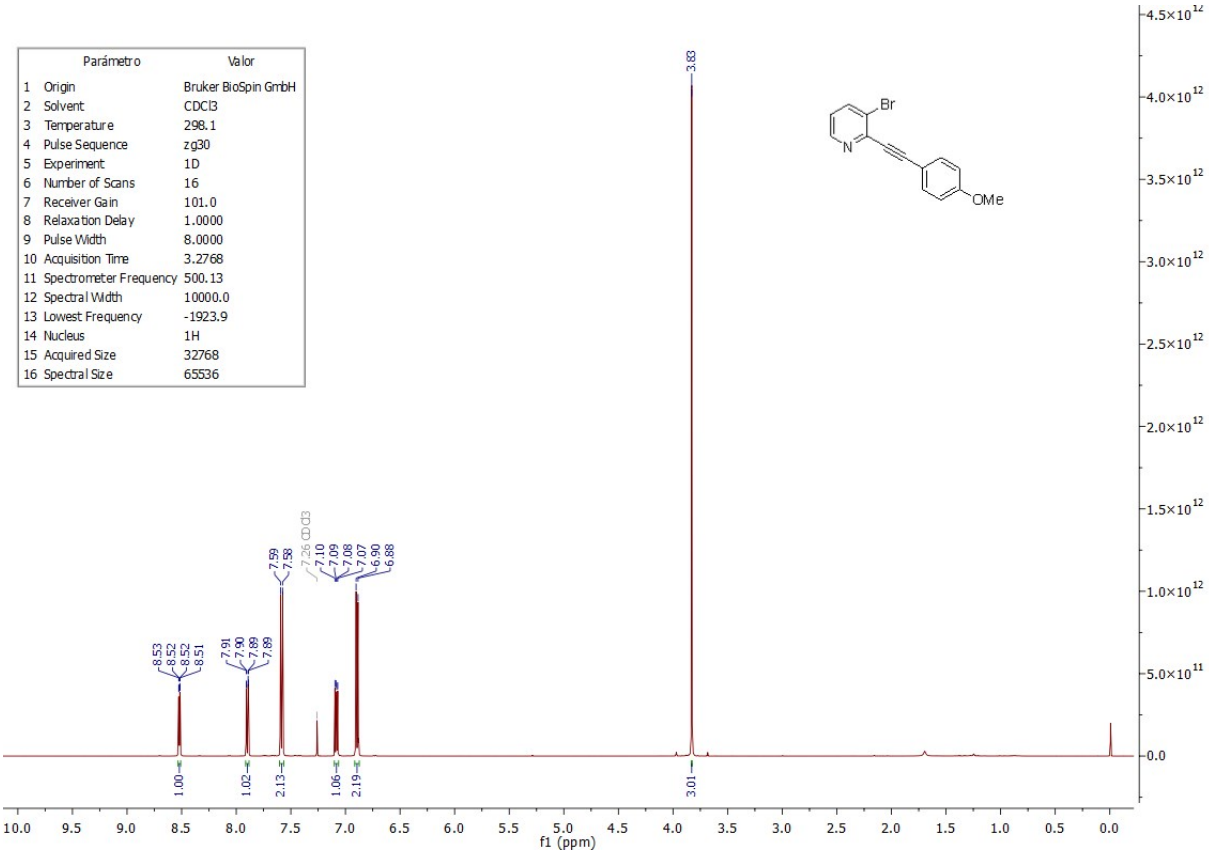


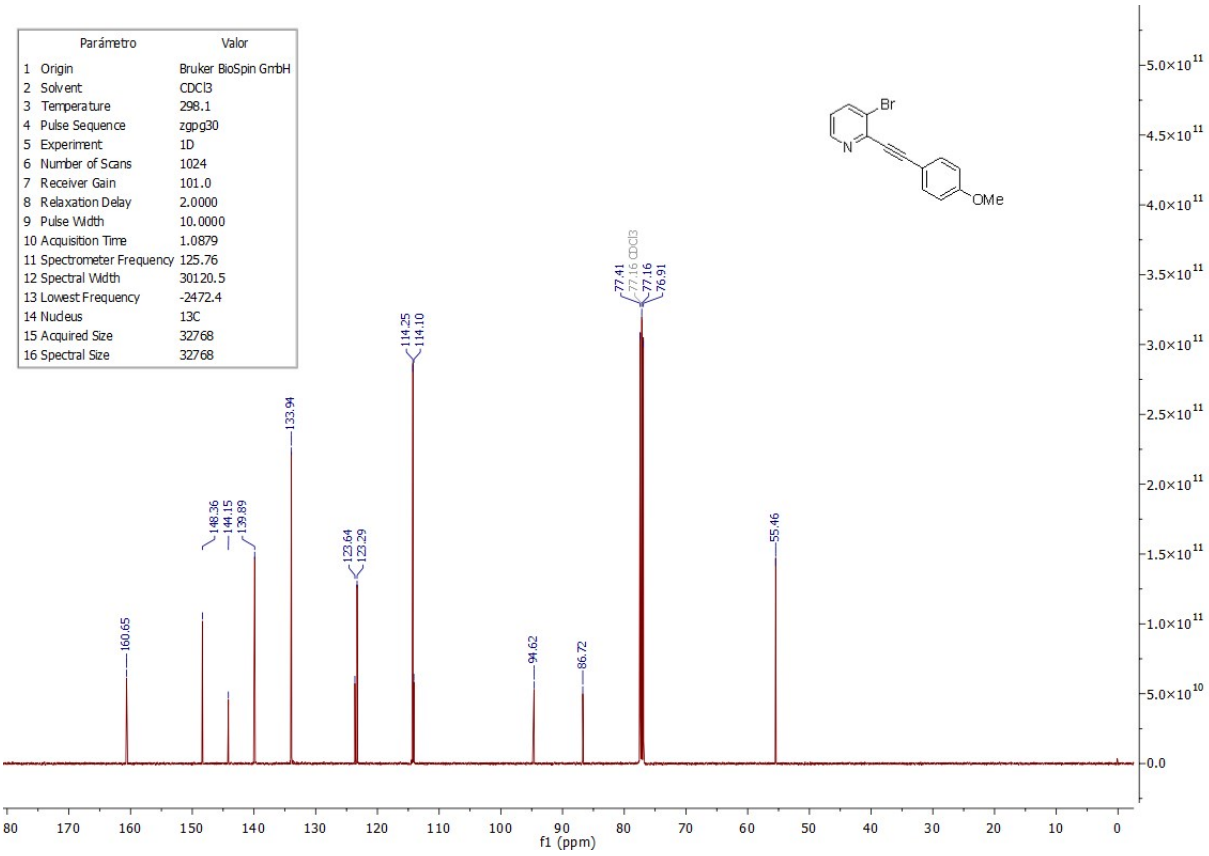
3-bromo-2-((4-(*tert*-butyl)phenyl)ethynyl)pyridine **5a**





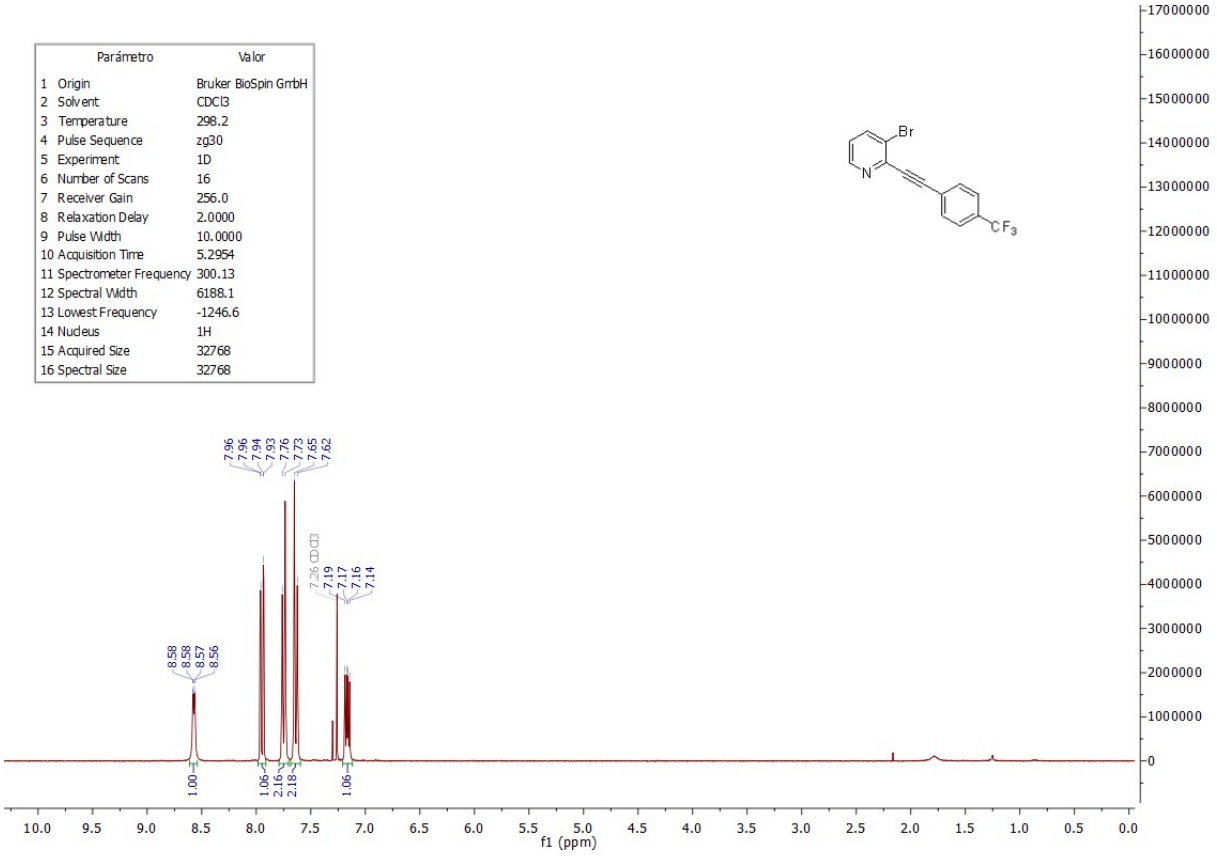
3-bromo-2-((4-methoxyphenyl)ethynyl)pyridine **5b**



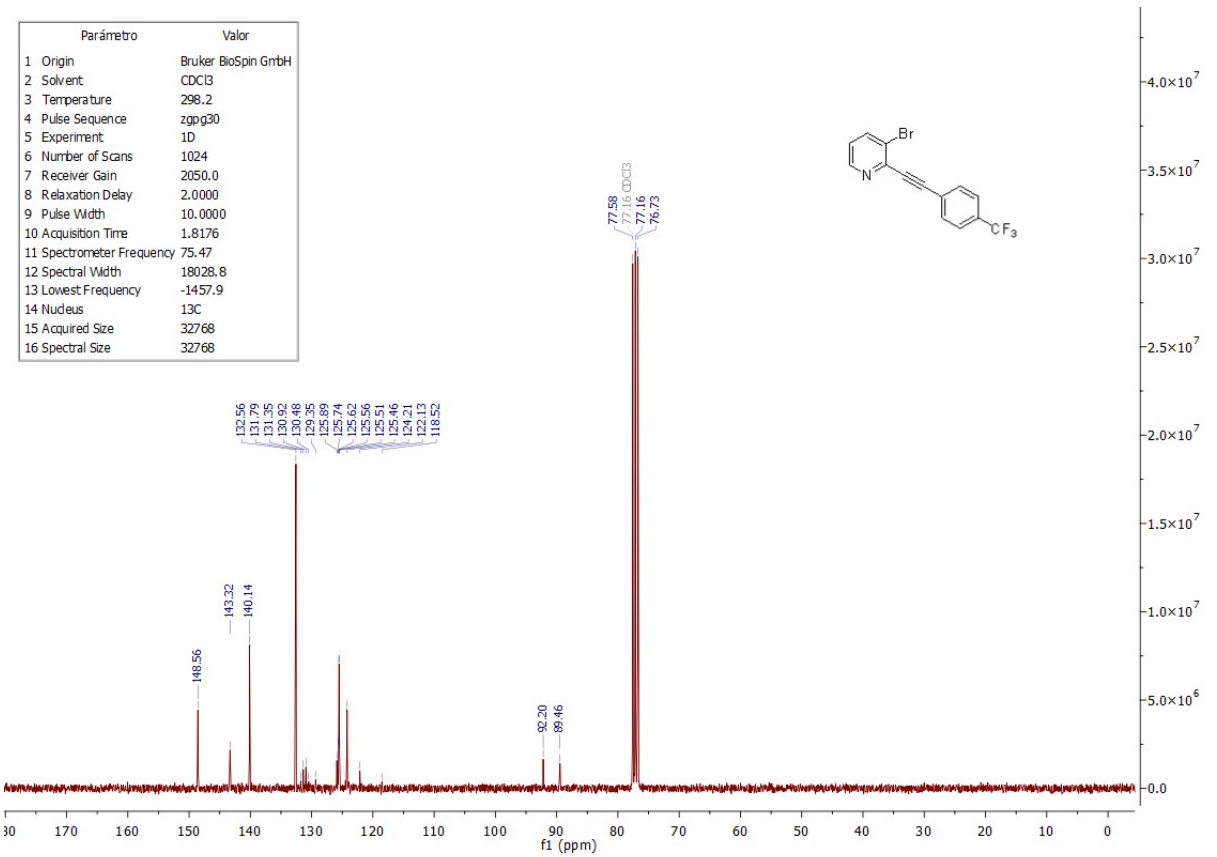


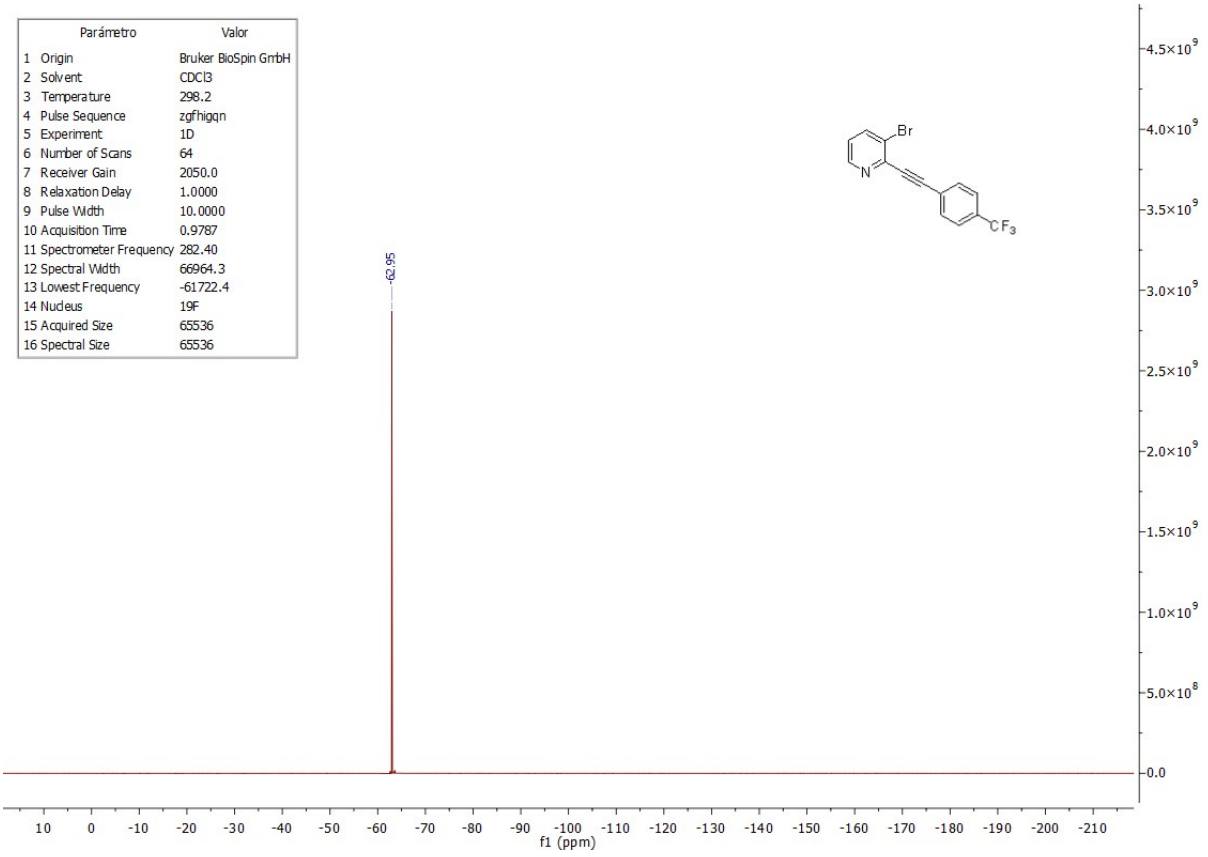
3-bromo-2-((4-(trifluoromethyl)phenyl)ethynyl)pyridine **5c**

Parâmetro	Valor
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	256.0
8 Relaxation Delay	2.0000
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	32768

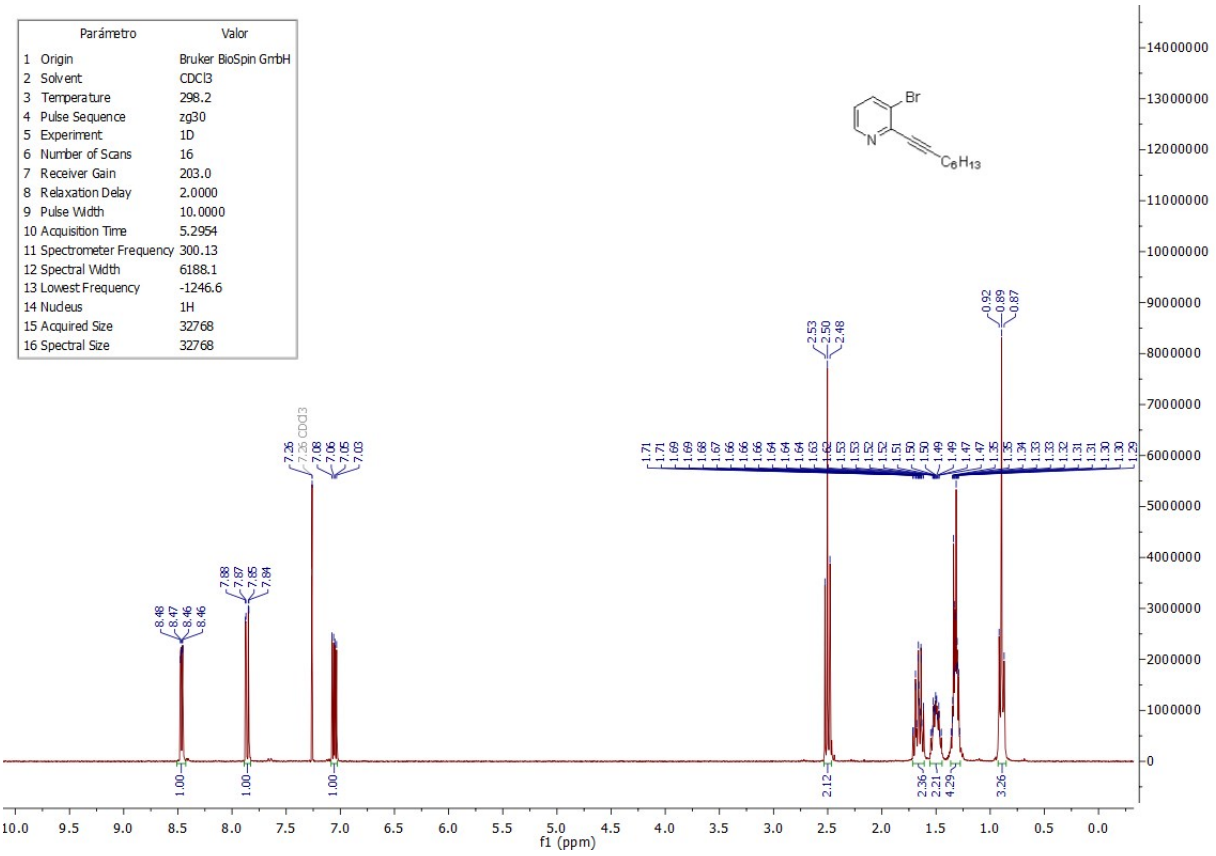


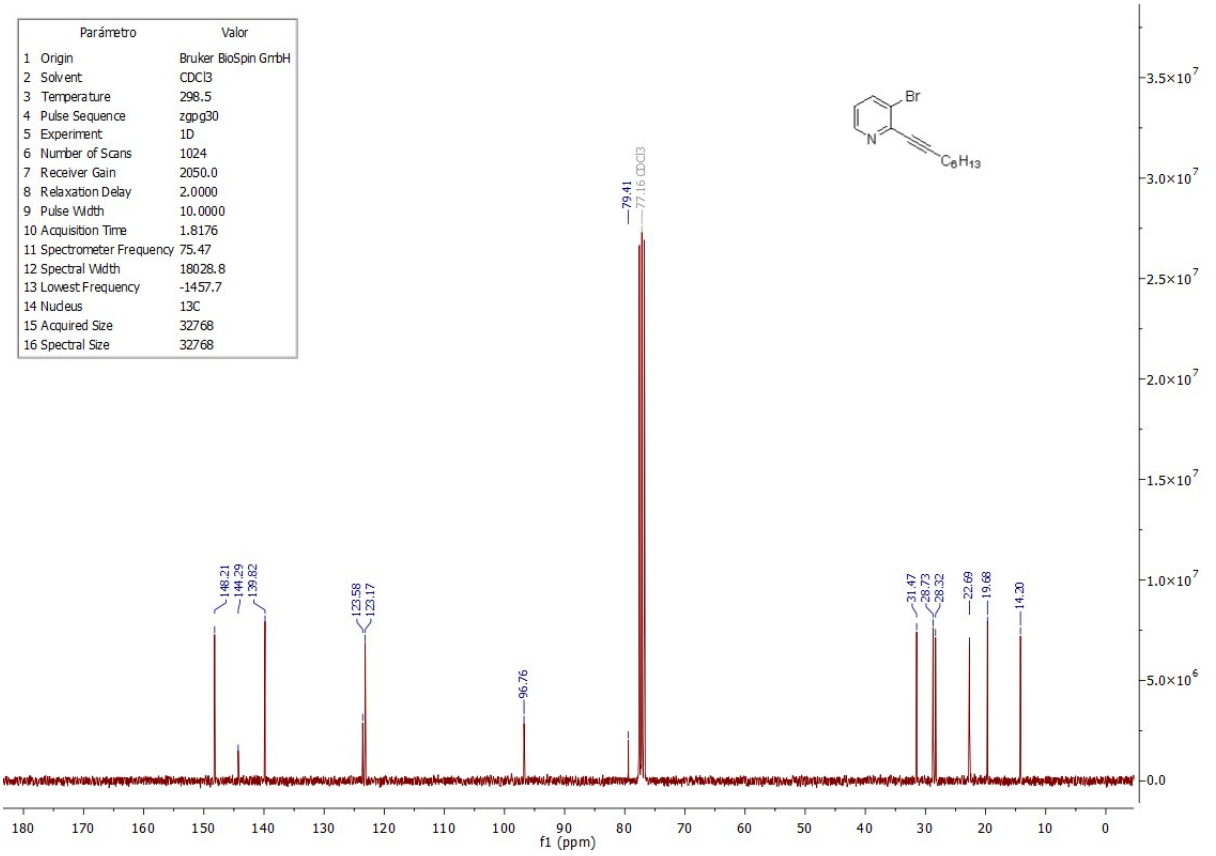
Parâmetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1457.9
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



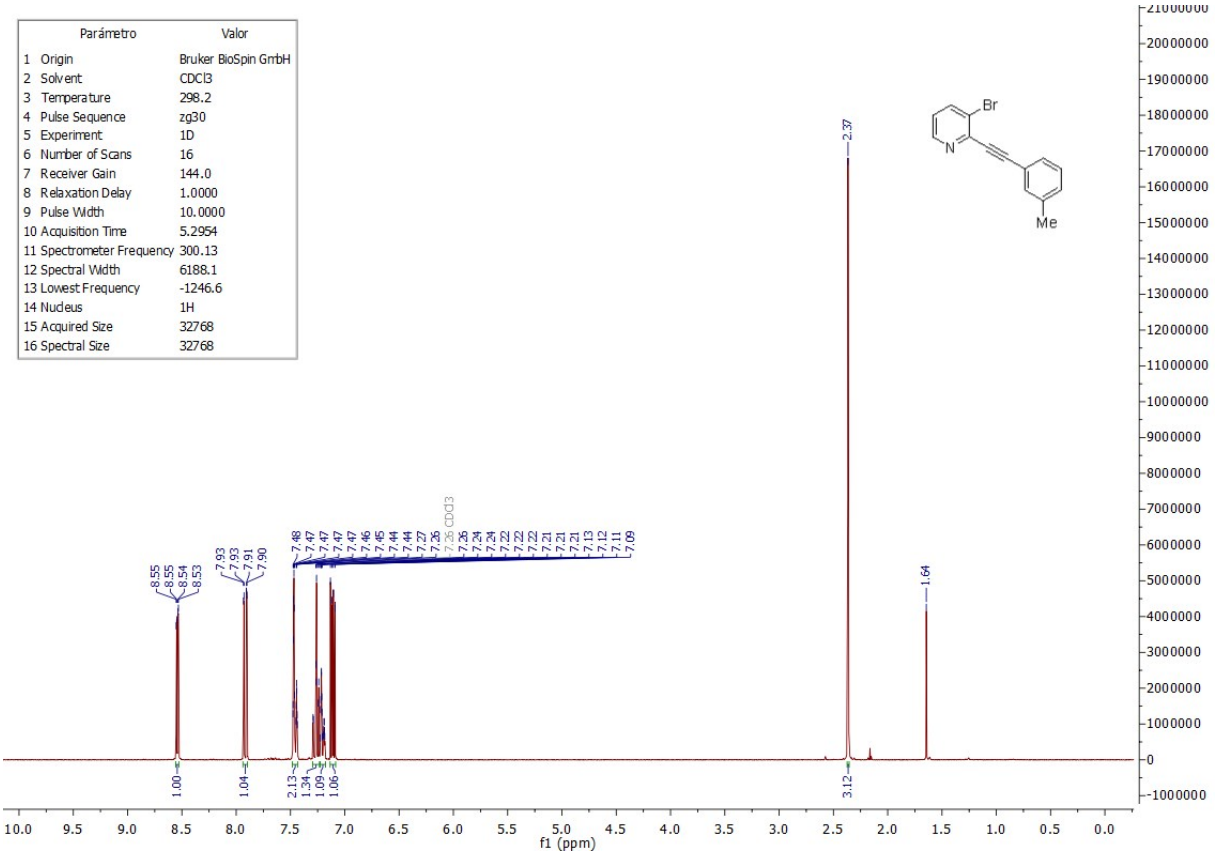


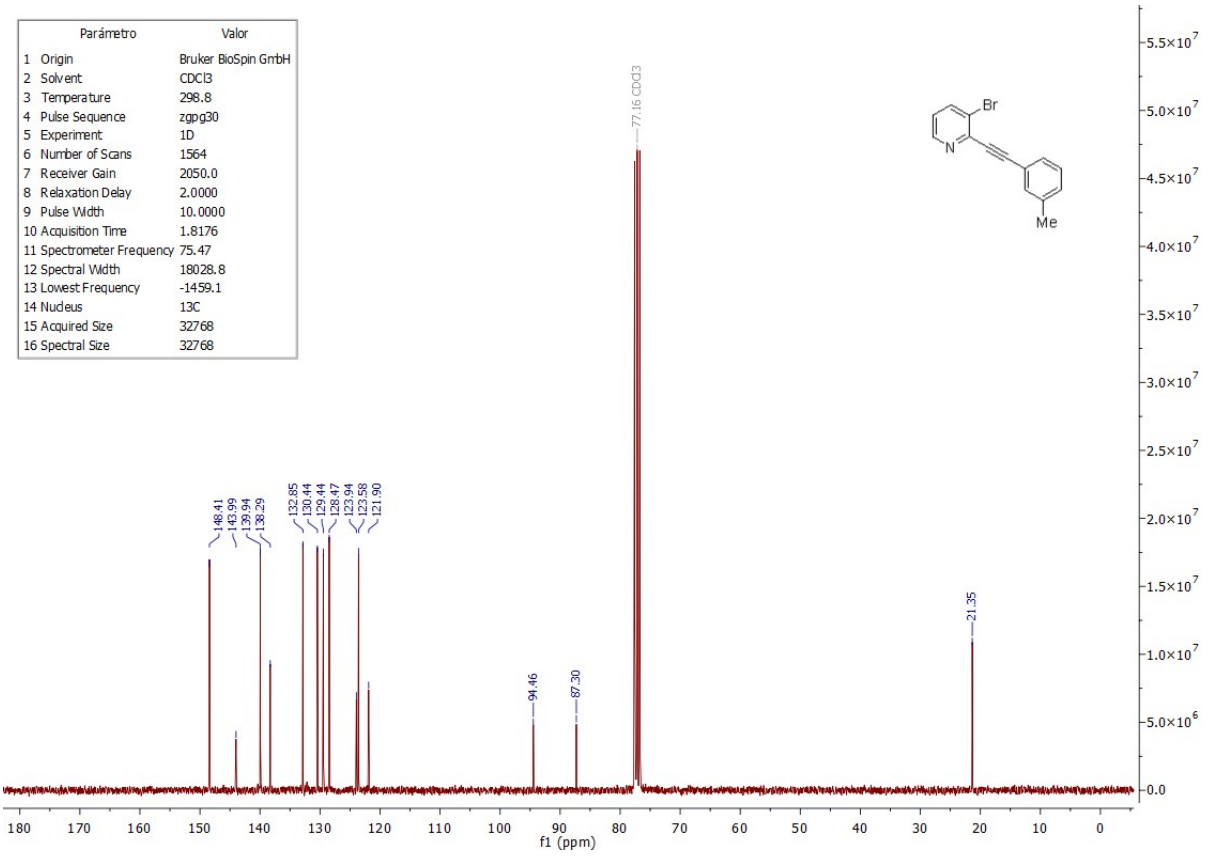
3-bromo-2-(oct-1-yn-1-yl)pyridine **5d**



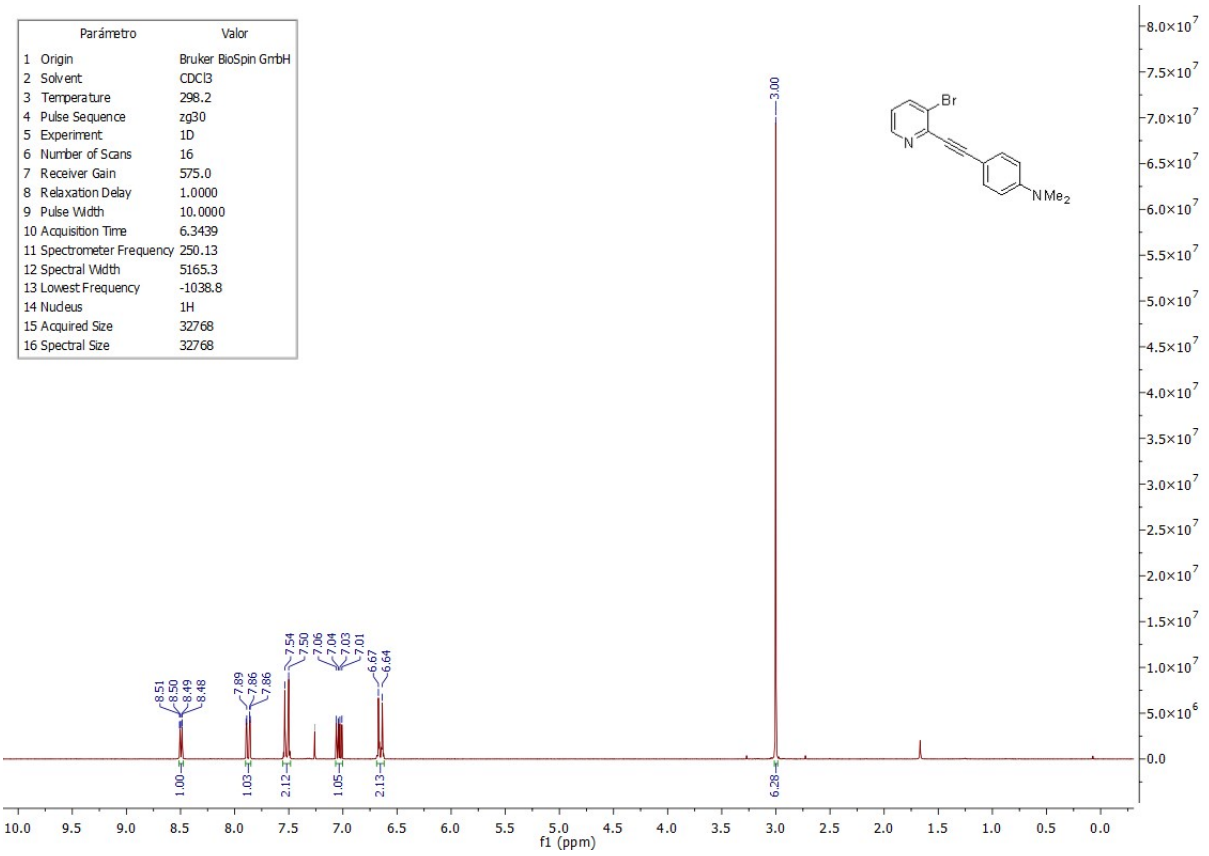


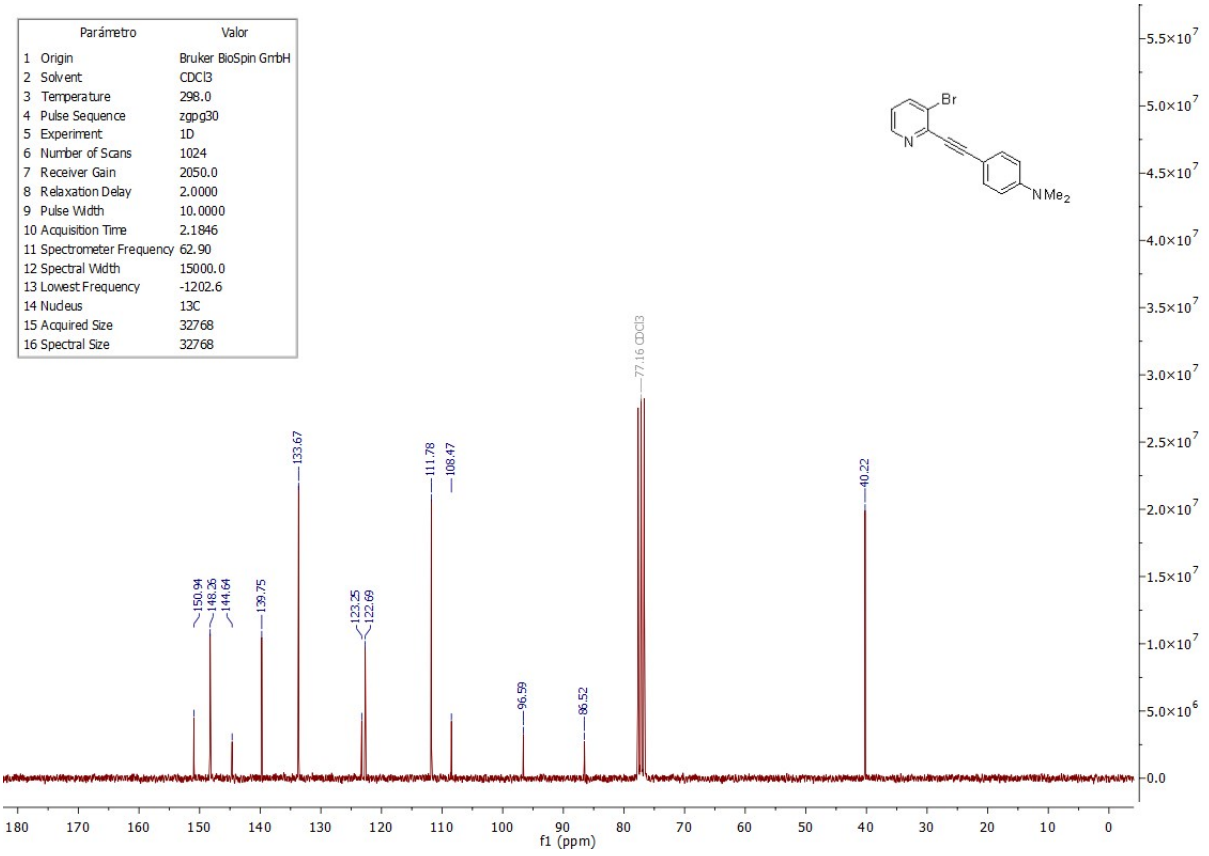
3-bromo-2-(*m*-tolylethynyl)pyridine **5e**


Parámetro Valor
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 144.0
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 32768
Br
N
Me
f1 (ppm)

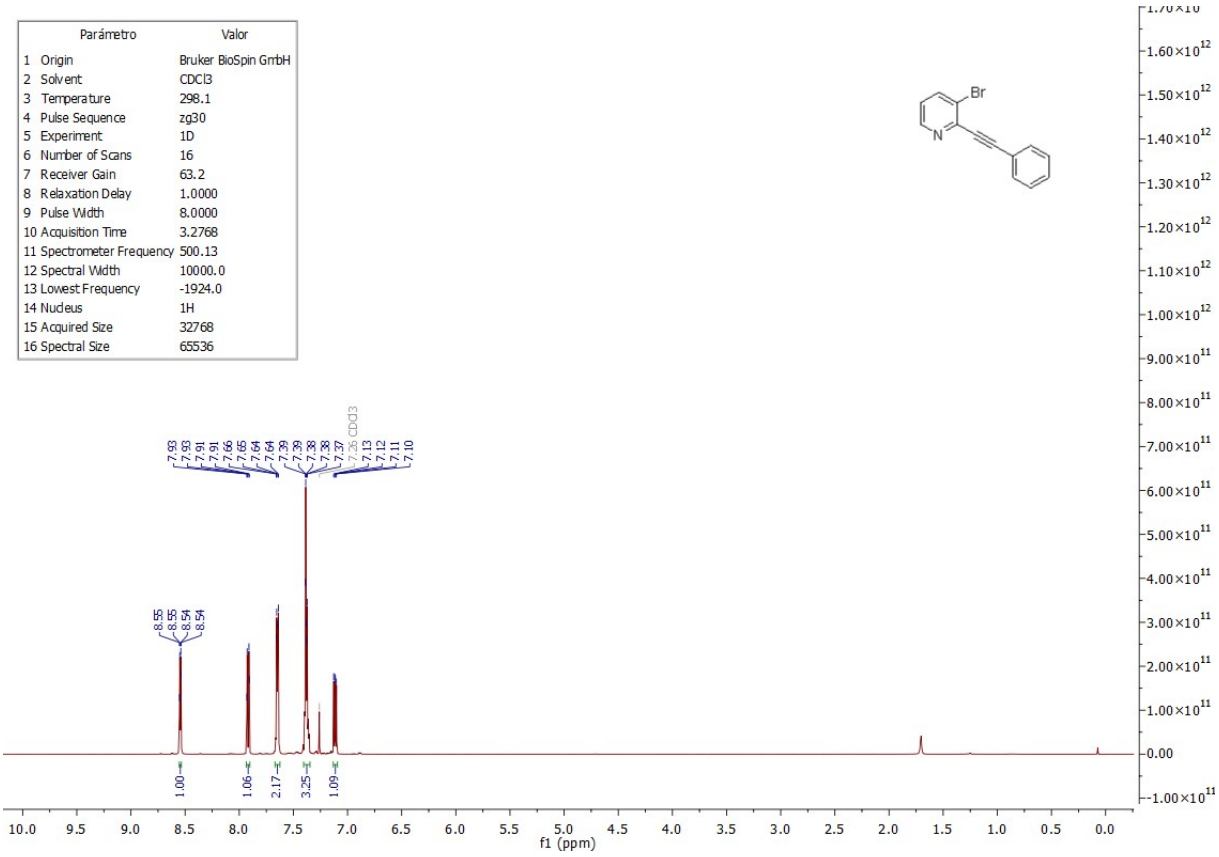


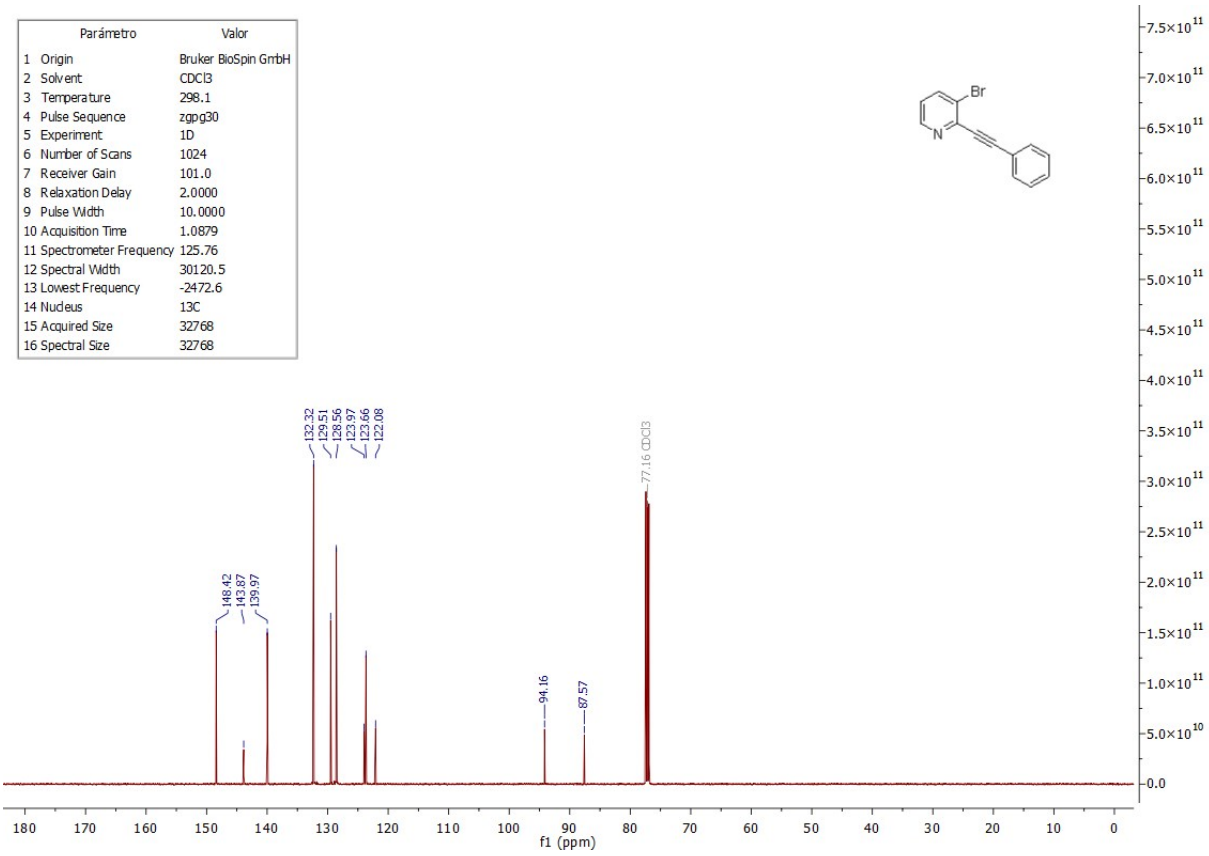
4-((3-bromopyridin-2-yl)ethynyl)-*N*,*N*-dimethylaniline **5f**


Parámetro Valor
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 575.0
8 Relaxation Delay 1.0000
9 Pulse Width 10.0000
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 32768
Br
N
NMe2
8.51
8.50
8.49
8.48
7.89
7.86
7.86
7.54
7.50
7.06
7.04
7.03
7.01
6.67
6.64
3.00
1.00
1.03
2.12
1.05
2.13
6.28
f1 (ppm)

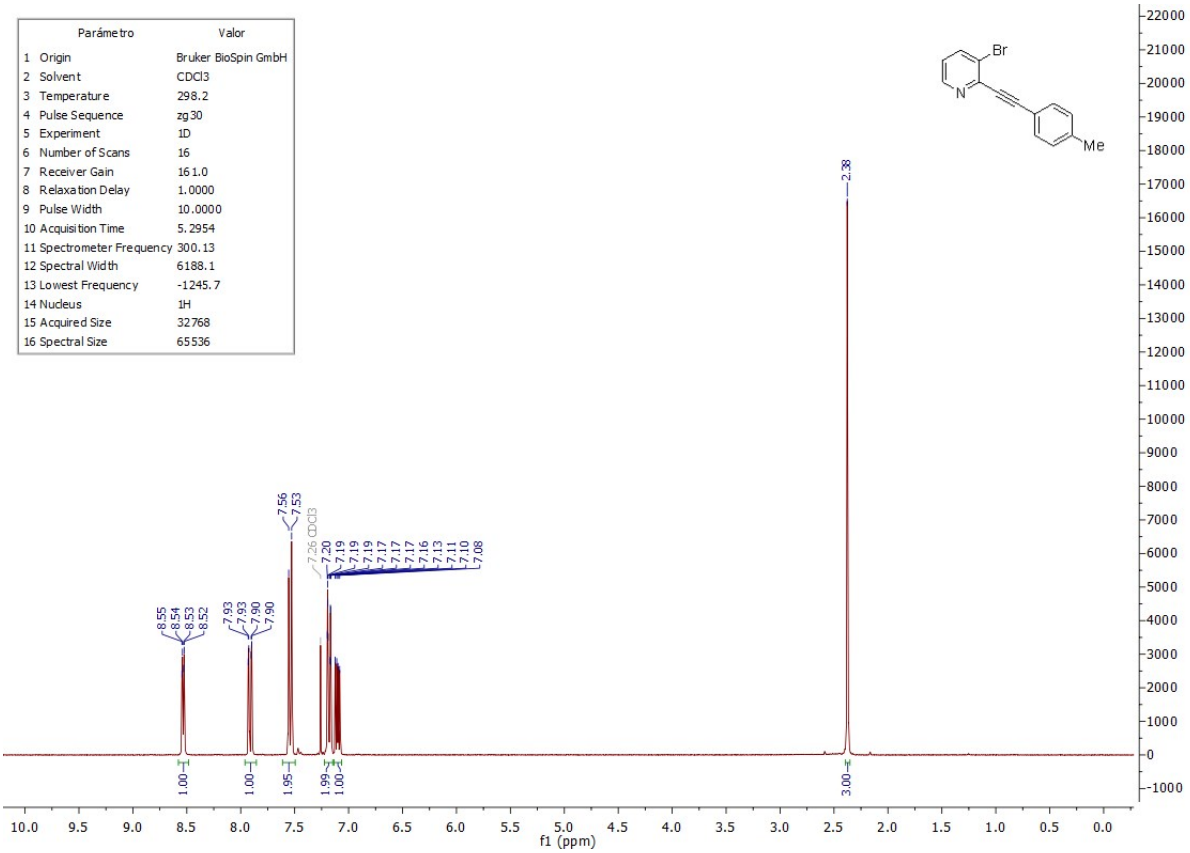

Parámetro Valor
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Pulse Sequence zgpg30
5 Experiment 1D
6 Number of Scans 1024
7 Receiver Gain 2050.0
8 Relaxation Delay 2.0000
9 Pulse Width 10.0000
10 Acquisition Time 2.1846
11 Spectrometer Frequency 62.90
12 Spectral Width 15000.0
13 Lowest Frequency -1202.6
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 32768
Br
N
NMe2
150.94
148.26
144.64
139.75
133.67
123.25
122.69
111.78
108.47
96.59
86.52
77.16 CDCl3
40.22
f1 (ppm)

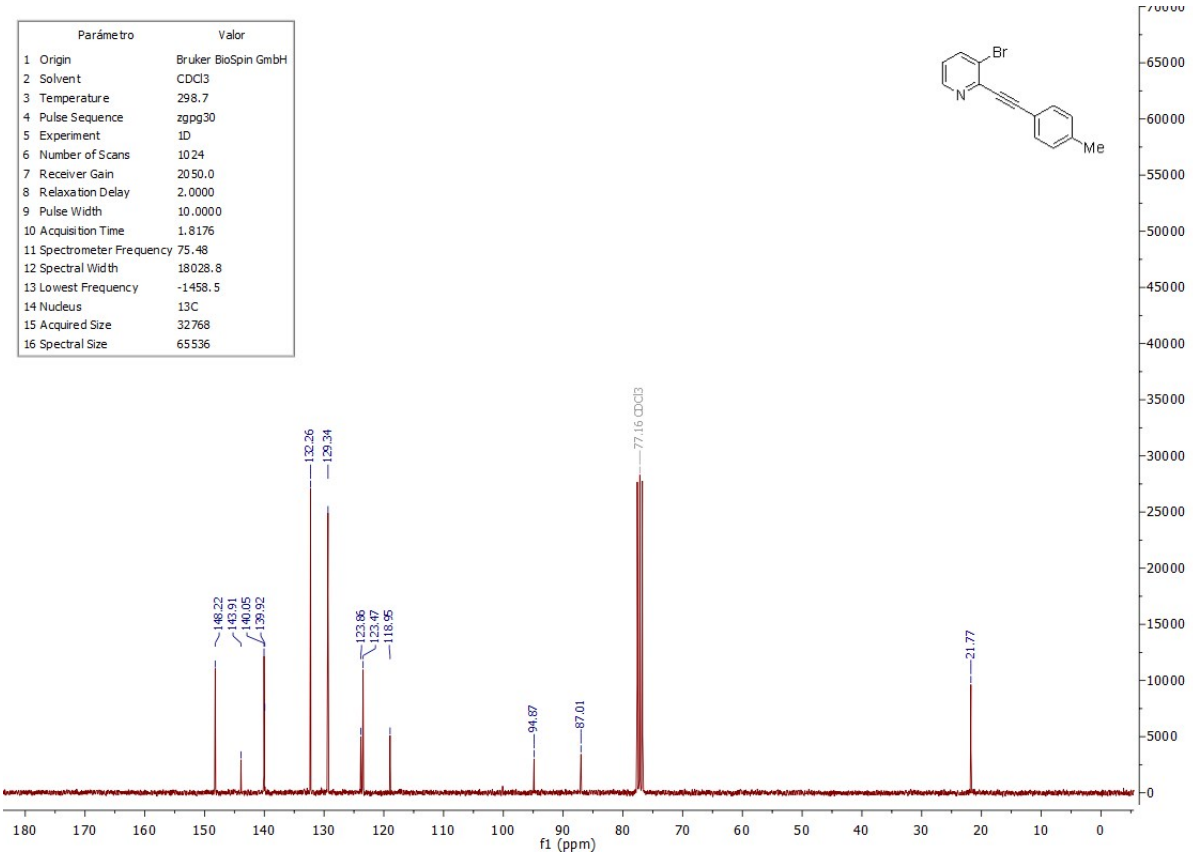
3-bromo-2-(phenylethynyl)pyridine **5g**





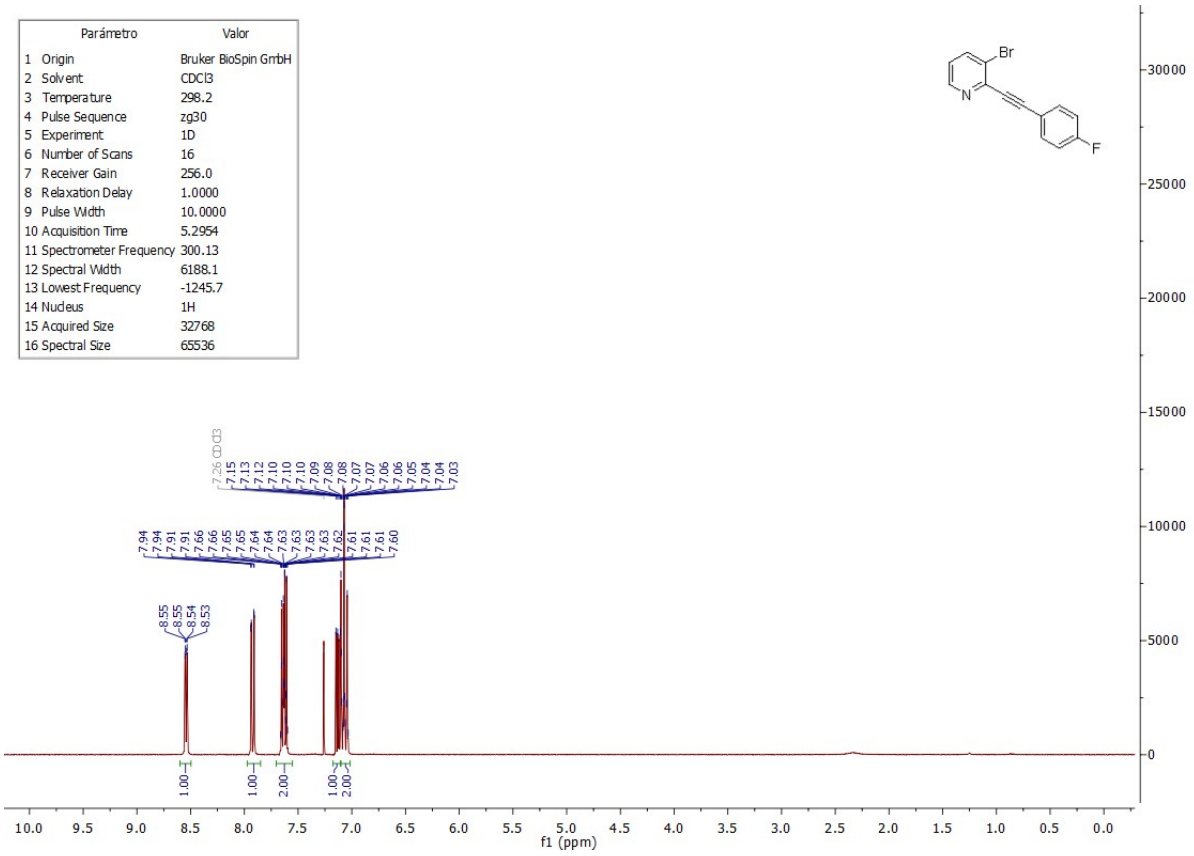
3-bromo-2-(*p*-tolylethynyl)pyridine **5h**



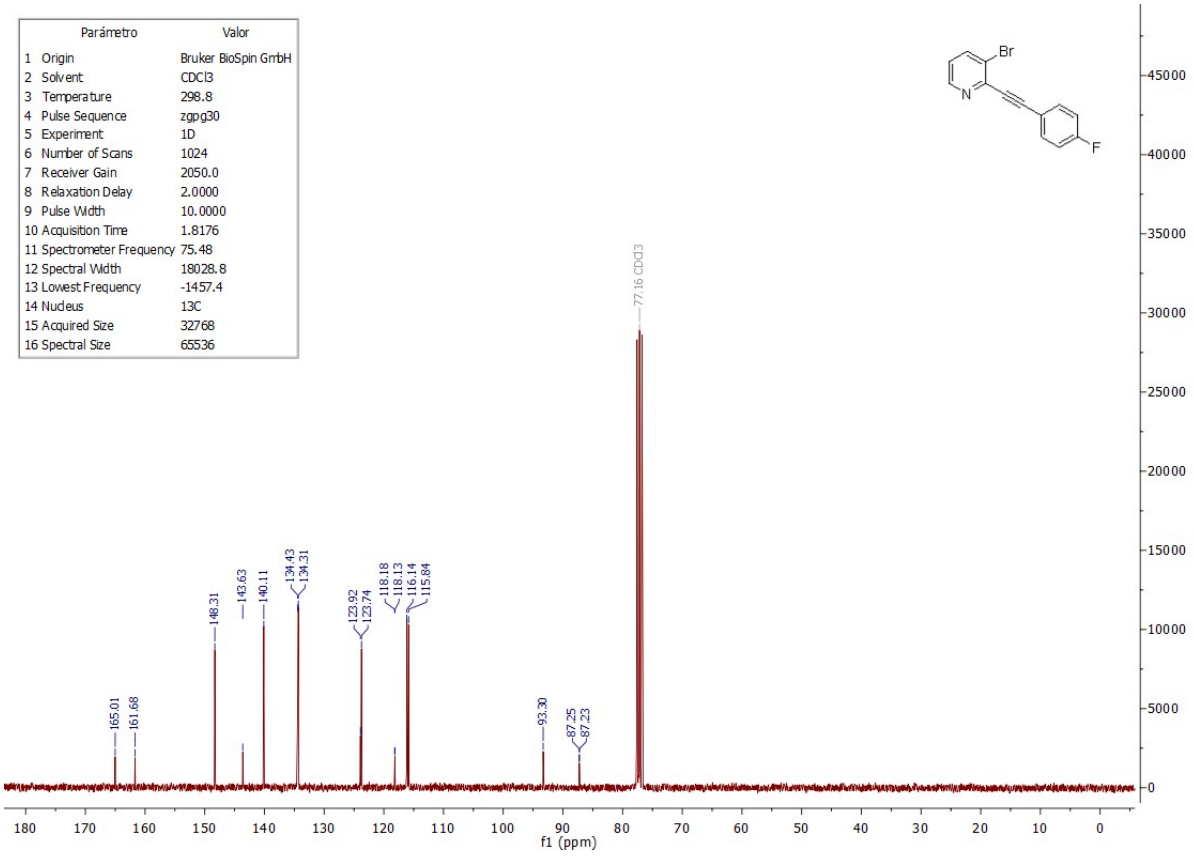


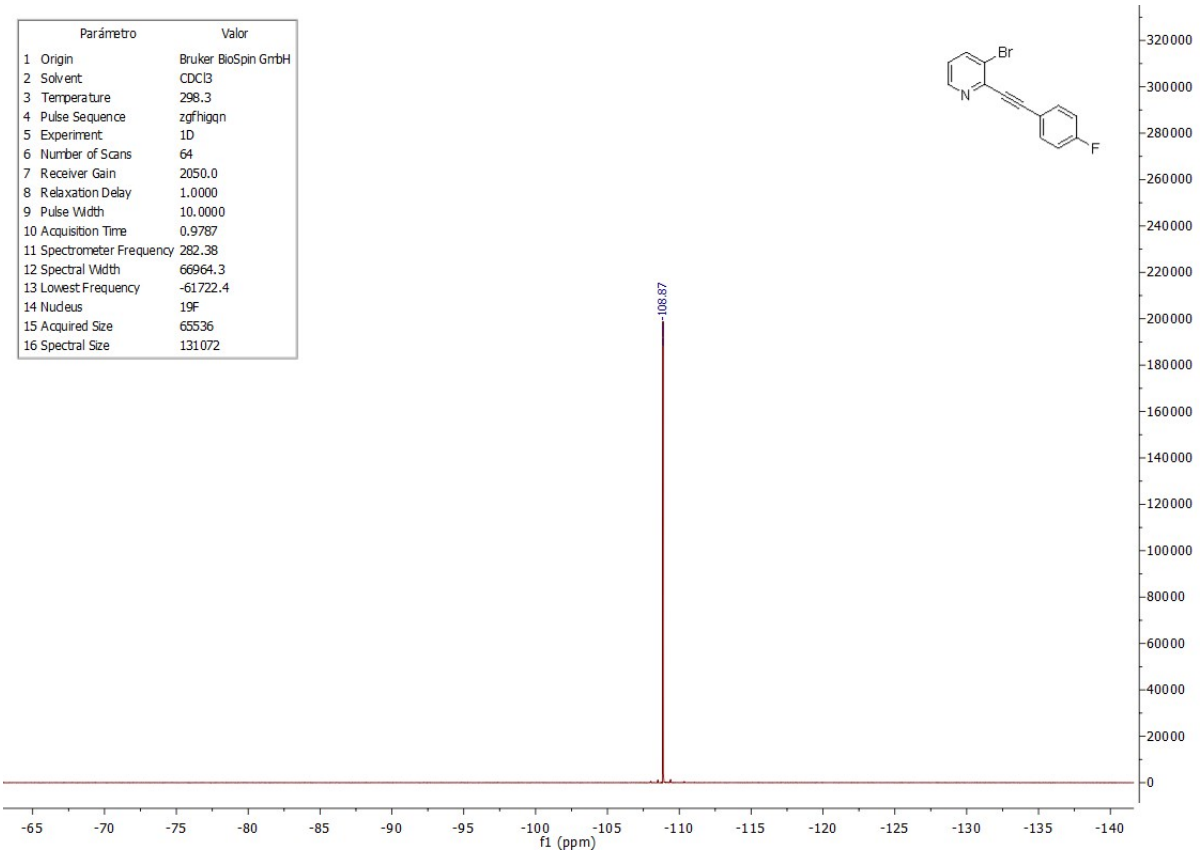
3-bromo-2-((4-fluorophenyl)ethynyl)pyridine **5i**

Parámetro	Valor
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	256.0
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	-1245.7
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

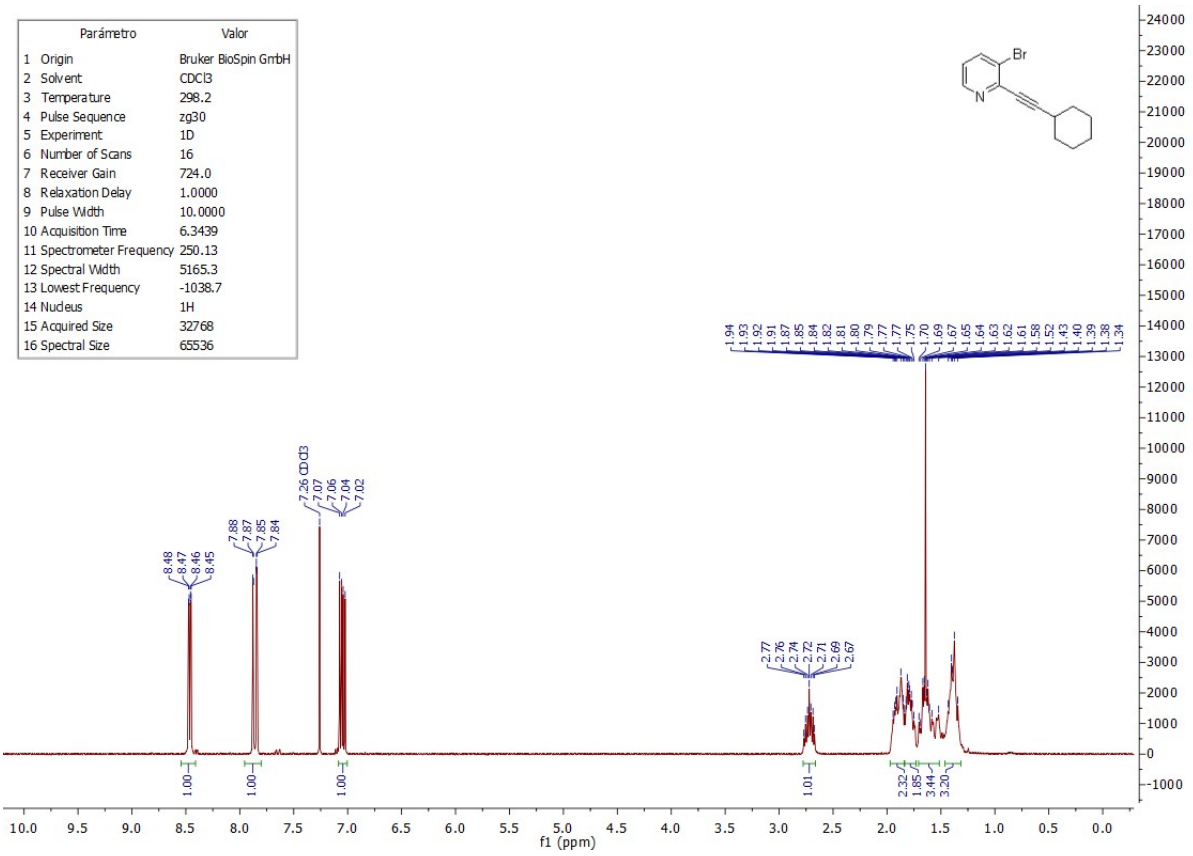


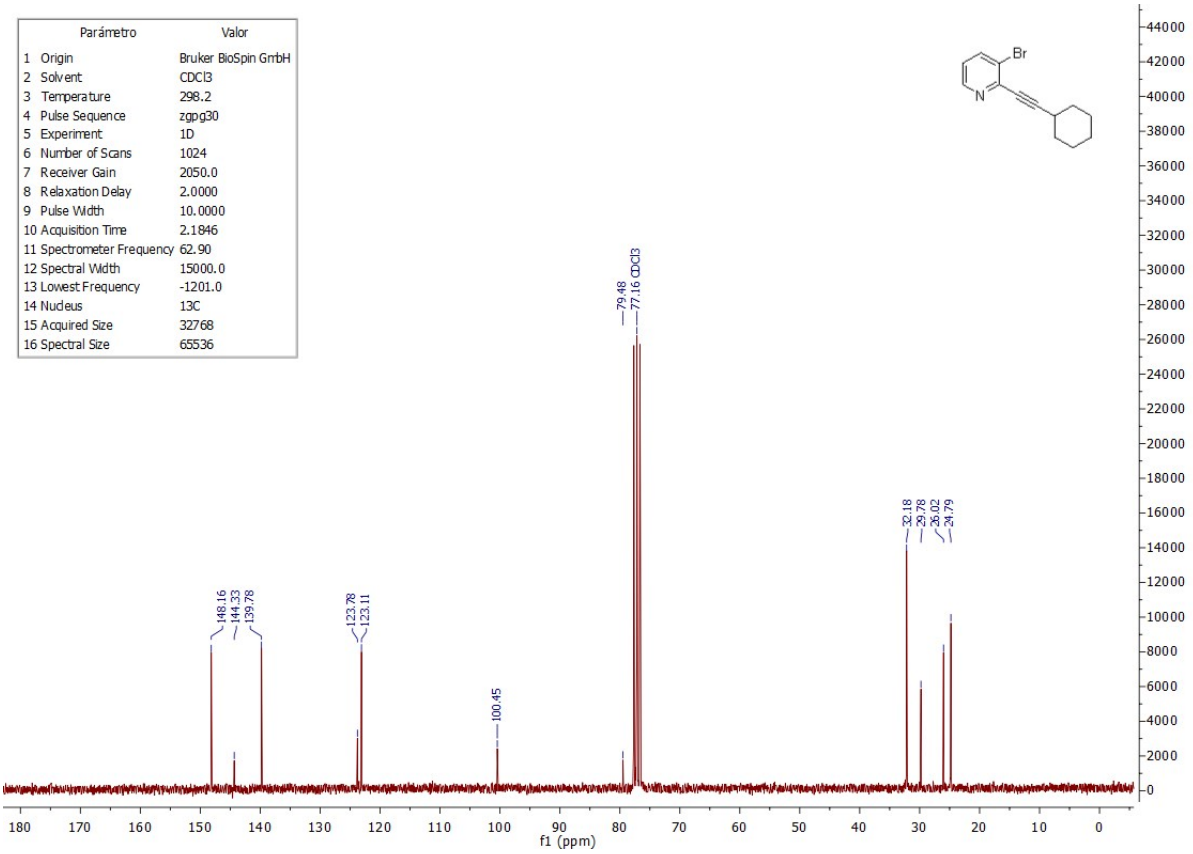
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.8
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.48
12 Spectral Width	18028.8
13 Lowest Frequency	-1457.4
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536





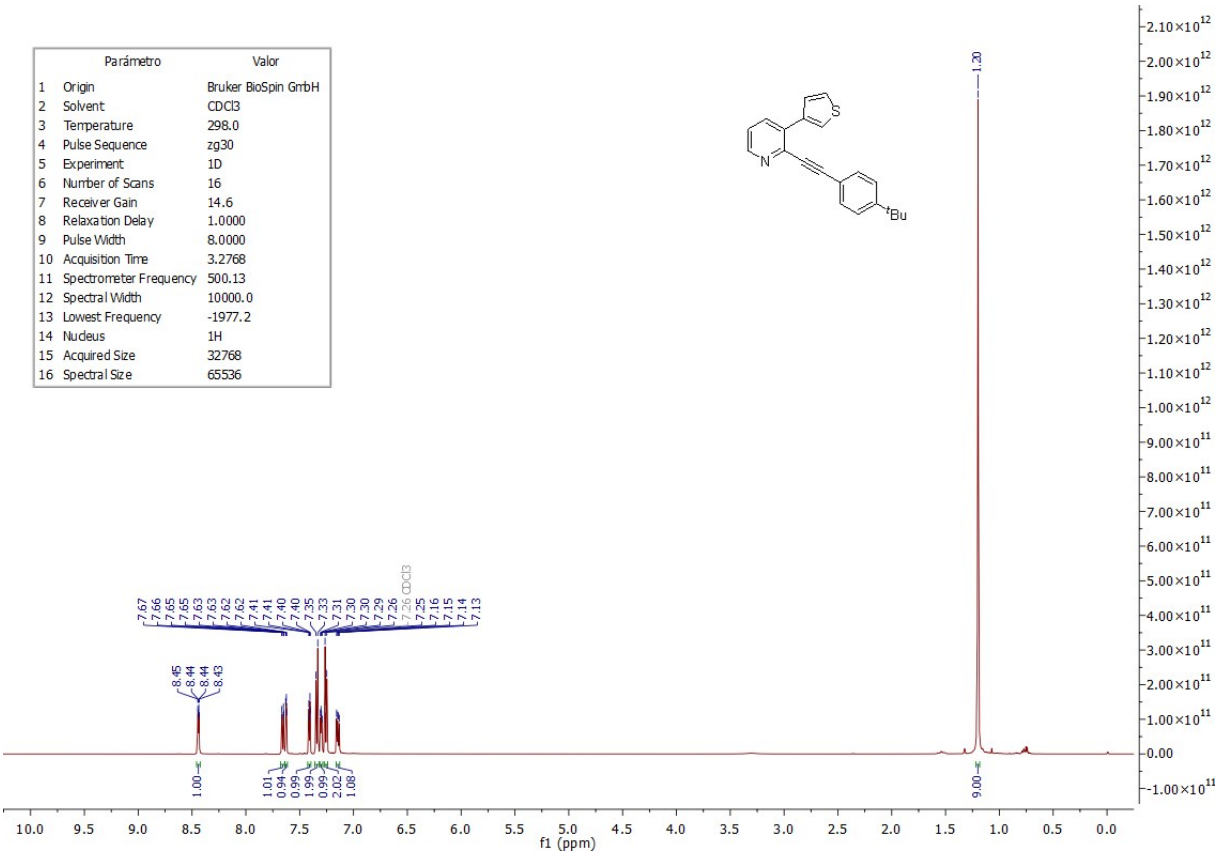
3-bromo-2-(cyclohexylethynyl)pyridine **5j**



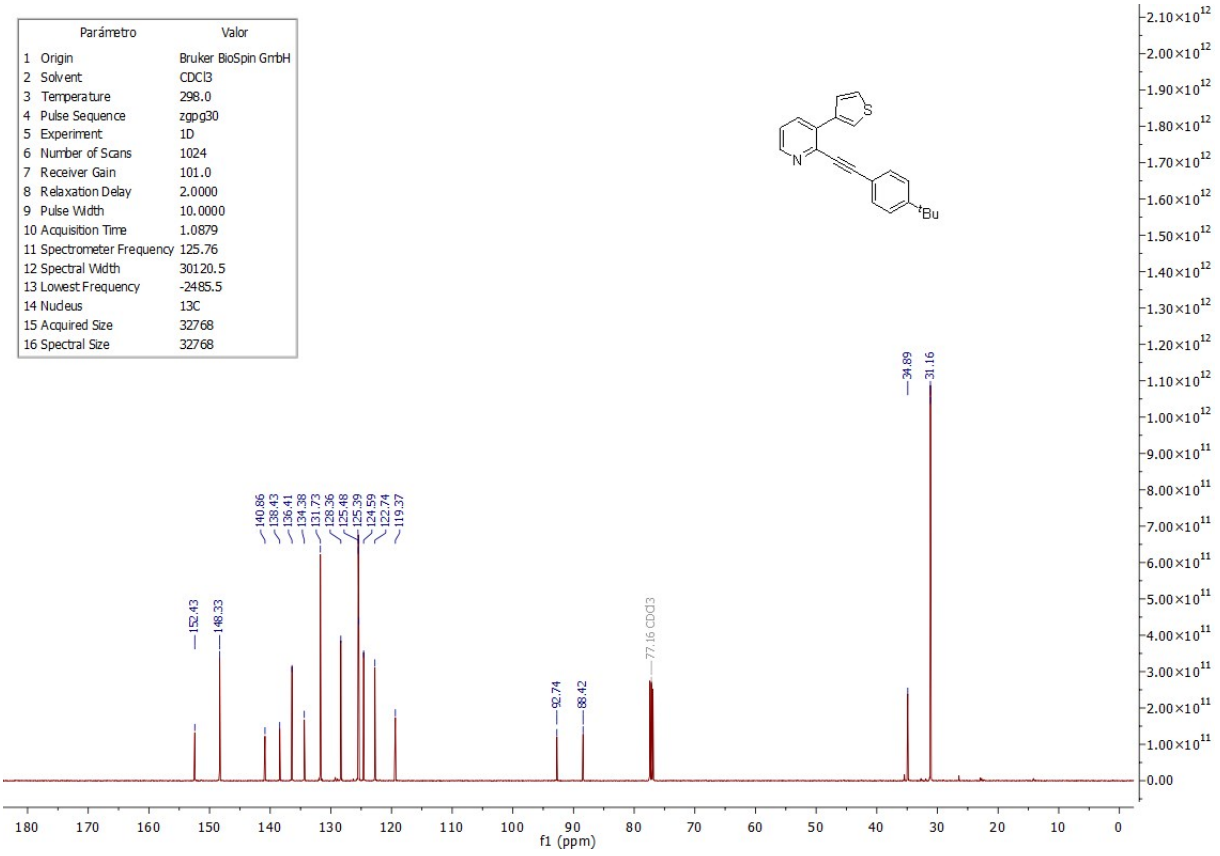


2-((4-(*tert*-butyl)phenyl)ethynyl)-3-(thiophen-3-yl)pyridine **6a**

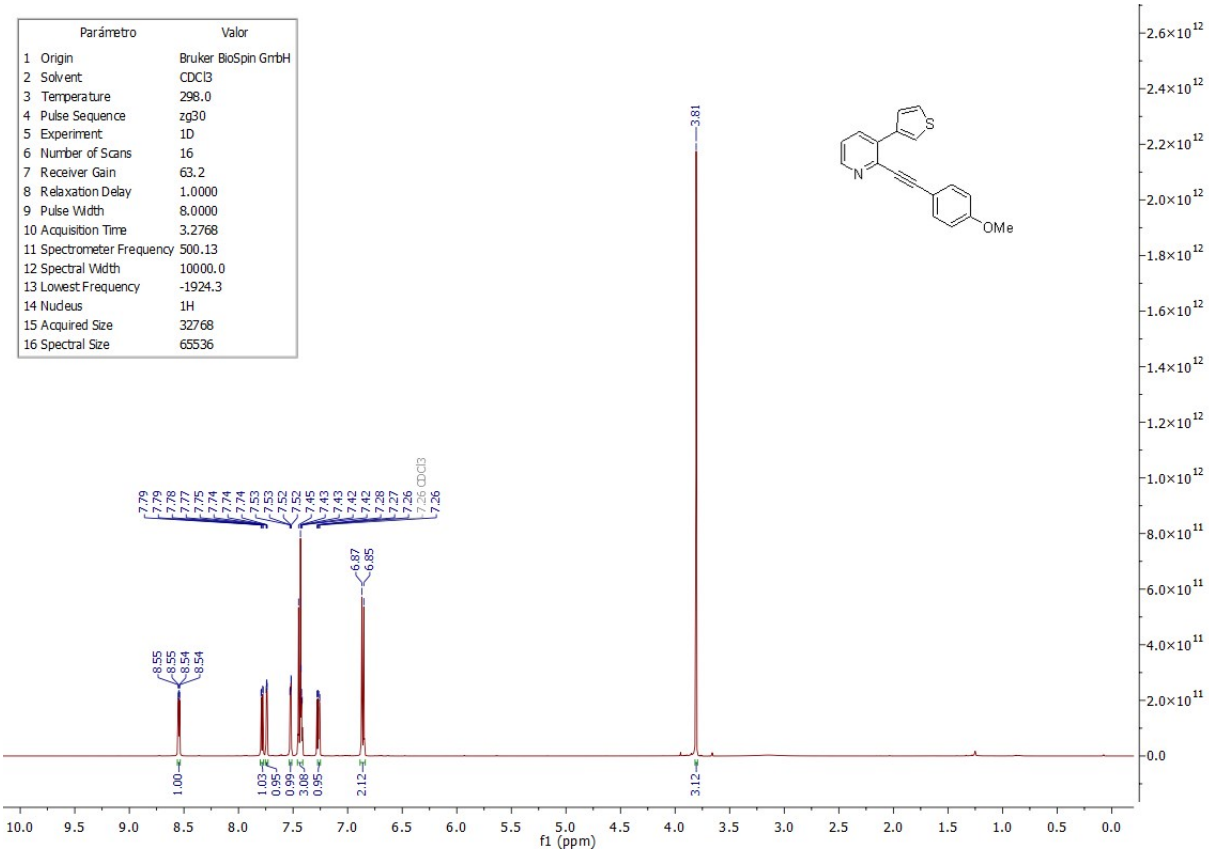
	Parámetro	Valor
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	298.0
4	Pulse Sequence	zg30
5	Experiment	1D
6	Number of Scans	16
7	Receiver Gain	14.6
8	Relaxation Delay	1.0000
9	Pulse Width	8.0000
10	Acquisition Time	3.2768
11	Spectrometer Frequency	500.13
12	Spectral Width	10000.0
13	Lowest Frequency	-1977.2
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

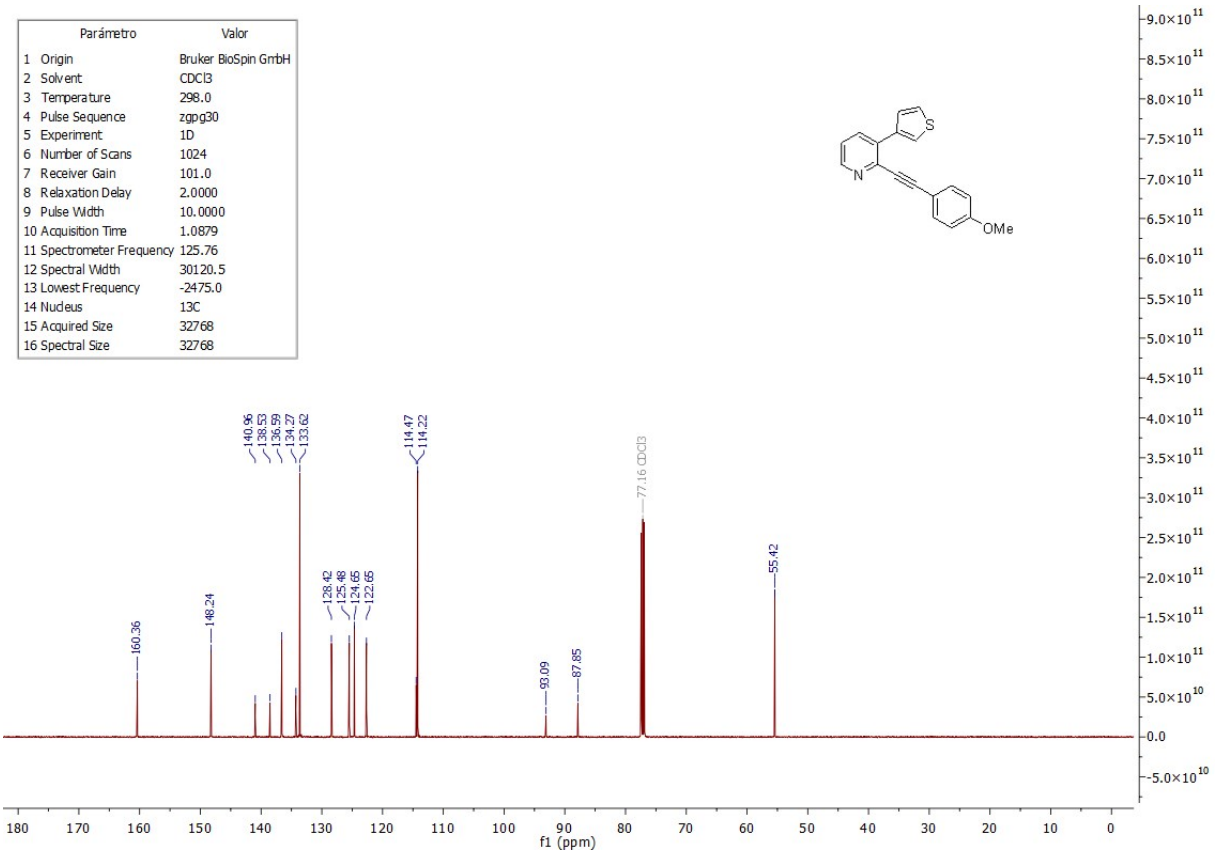


	Parámetro	Valor
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	298.0
4	Pulse Sequence	zgpg30
5	Experiment	1D
6	Number of Scans	1024
7	Receiver Gain	101.0
8	Relaxation Delay	2.0000
9	Pulse Width	10.0000
10	Acquisition Time	1.0879
11	Spectrometer Frequency	125.76
12	Spectral Width	30120.5
13	Lowest Frequency	-2485.5
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	32768

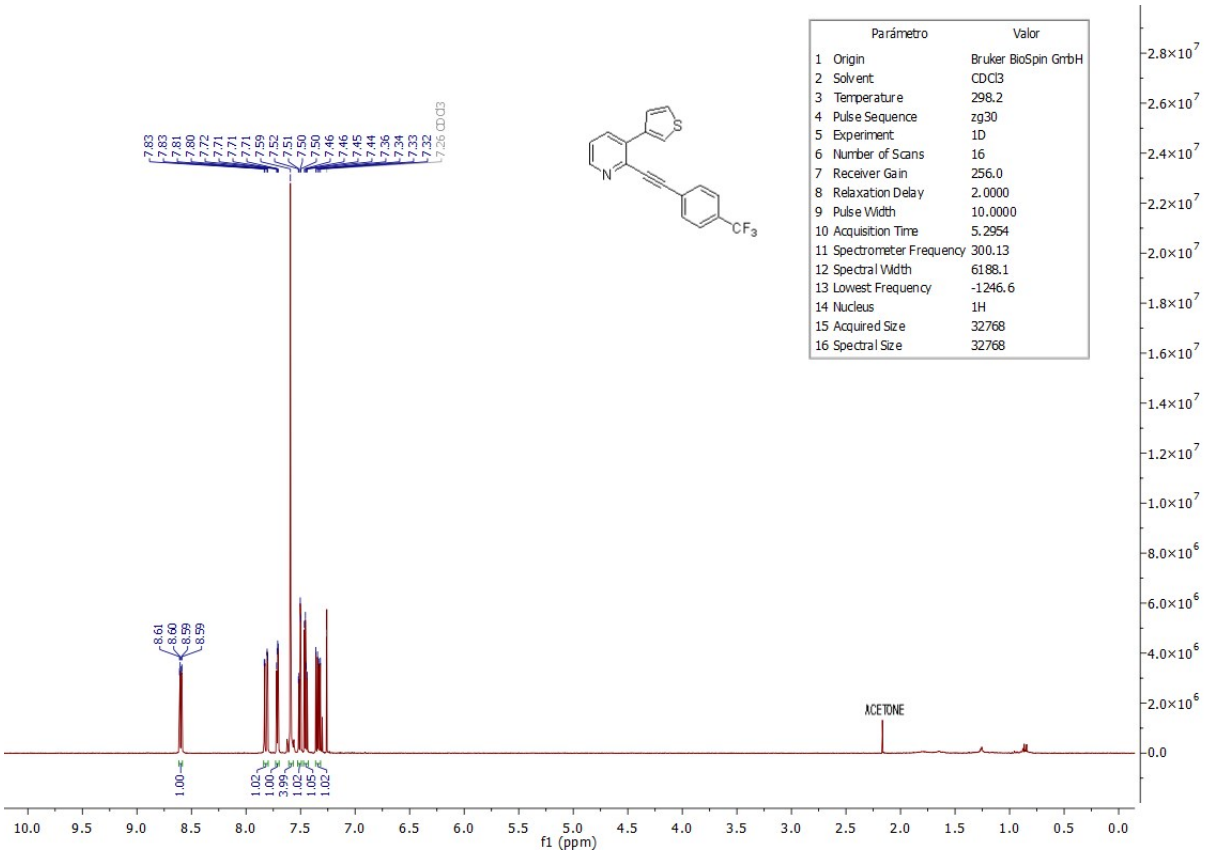


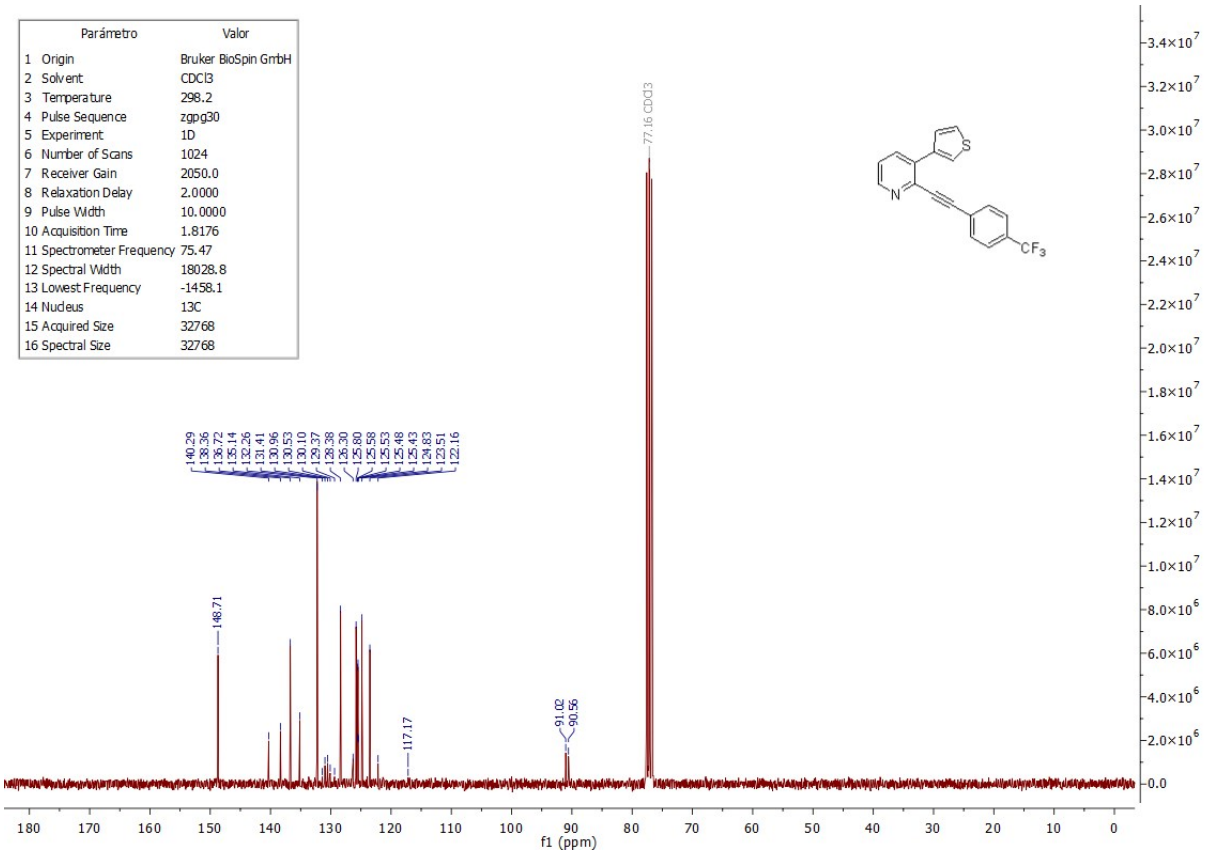
2-((4-methoxyphenyl)ethynyl)-3-(thiophen-3-yl)pyridine **6b**

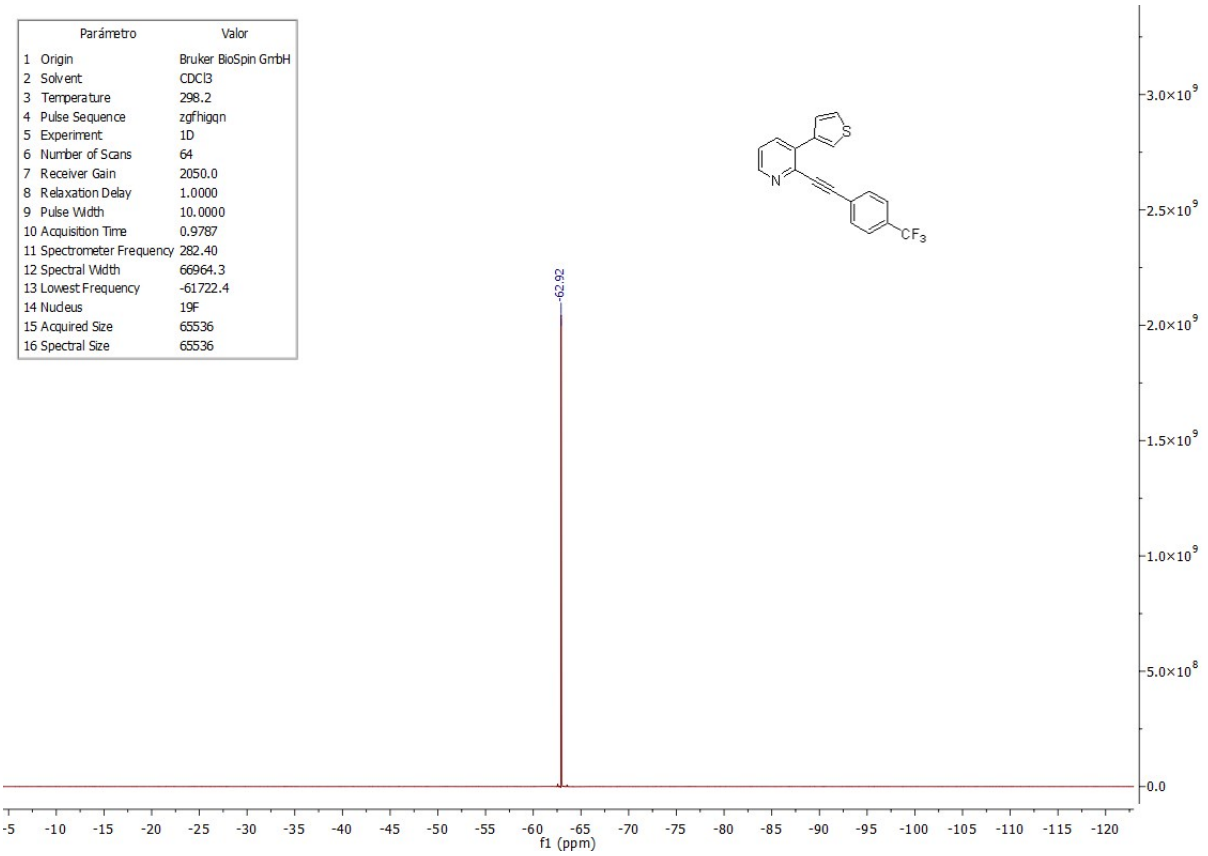




3-(thiophen-3-yl)-2-((4-(trifluoromethyl)phenyl)ethynyl)pyridine **6c**

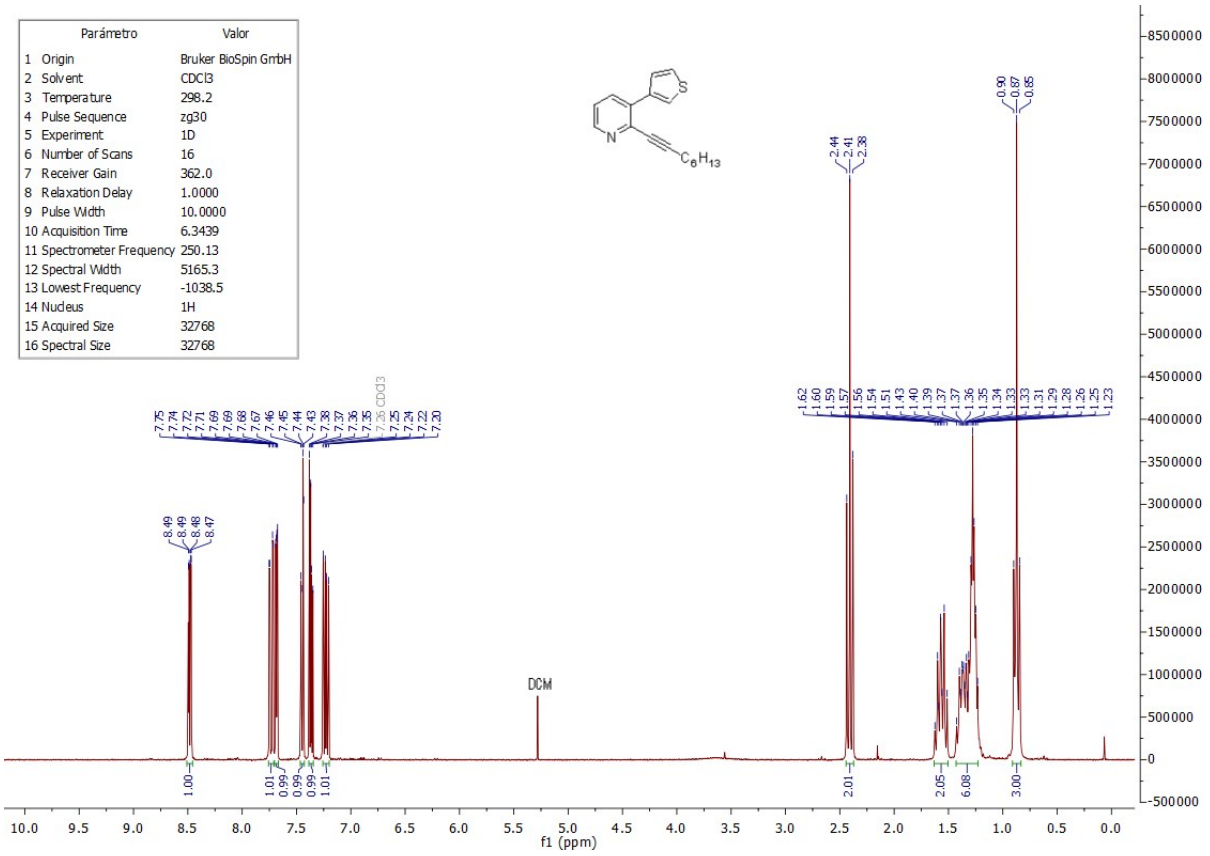

Parámetro Valor
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Pulse Sequence zg30
5 Experiment 1D
6 Number of Scans 16
7 Receiver Gain 256.0
8 Relaxation Delay 2.0000
9 Pulse Width 10.0000
10 Acquisition Time 5.2954
11 Spectrometer Frequency 300.13
12 Spectral Width 6188.1
13 Lowest Frequency -1246.6
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 32768
7.83 7.83 7.81 7.80 7.72 7.71 7.71 7.59 7.52 7.51 7.50 7.50 7.46 7.46 7.45 7.44 7.36 7.34 7.33 7.32
7.26 CDCl3
8.61 8.60 8.59 8.59
ACETONE
1.00 1.02 1.00 3.99 1.02 1.05 1.02
S N CF3
f1 (ppm)

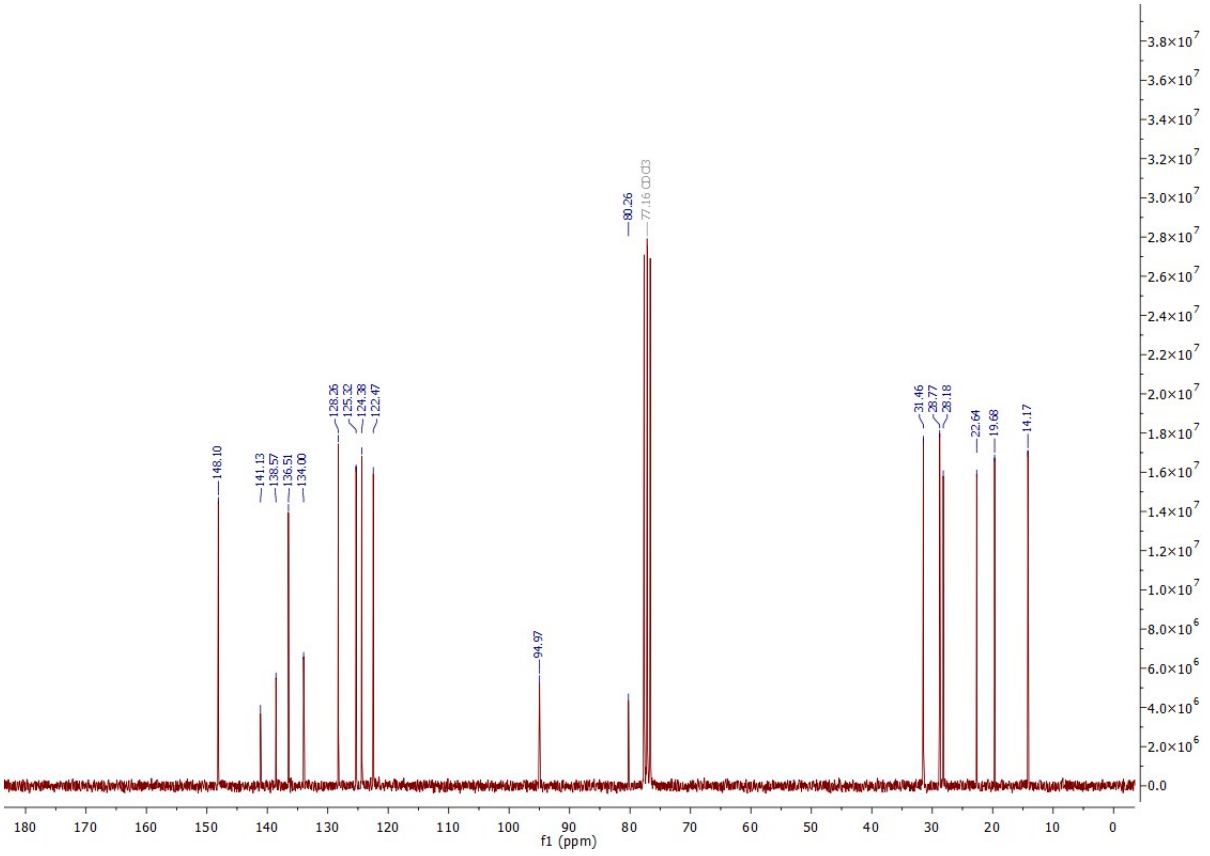

Parámetro Valor
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.2
4 Pulse Sequence zgpg30
5 Experiment 1D
6 Number of Scans 1024
7 Receiver Gain 2050.0
8 Relaxation Delay 2.0000
9 Pulse Width 10.0000
10 Acquisition Time 1.8176
11 Spectrometer Frequency 75.47
12 Spectral Width 18028.8
13 Lowest Frequency -1458.1
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 32768
140.29 138.36 136.72 135.14 132.26 131.41 130.96 130.53 130.10 129.37 128.38 126.30 125.80 125.58 125.53 125.48 125.43 124.83 123.51 122.16
77.16 CDCl3
148.71
117.17
91.02 90.56
S N CF3
f1 (ppm)



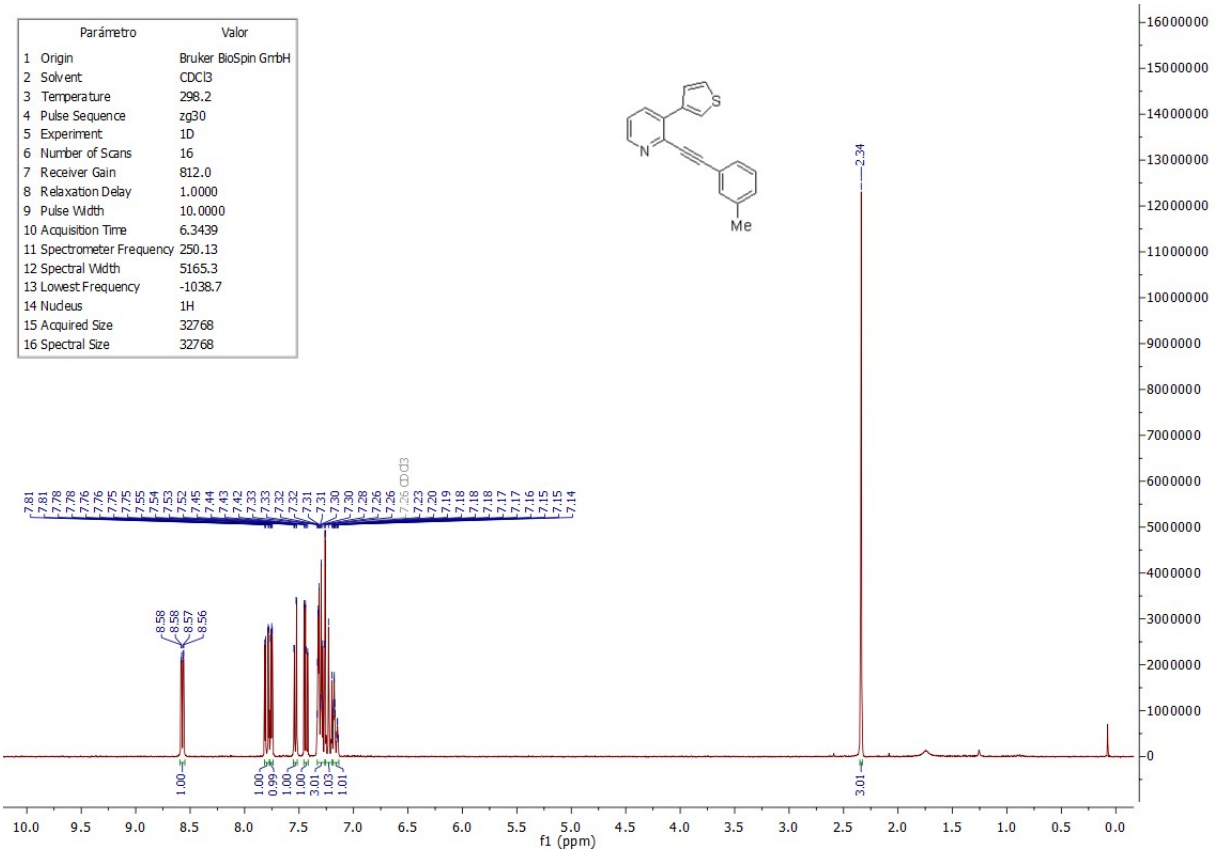
2-(oct-1-yn-1-yl)-3-(thiophen-3-yl)pyridine **6d**

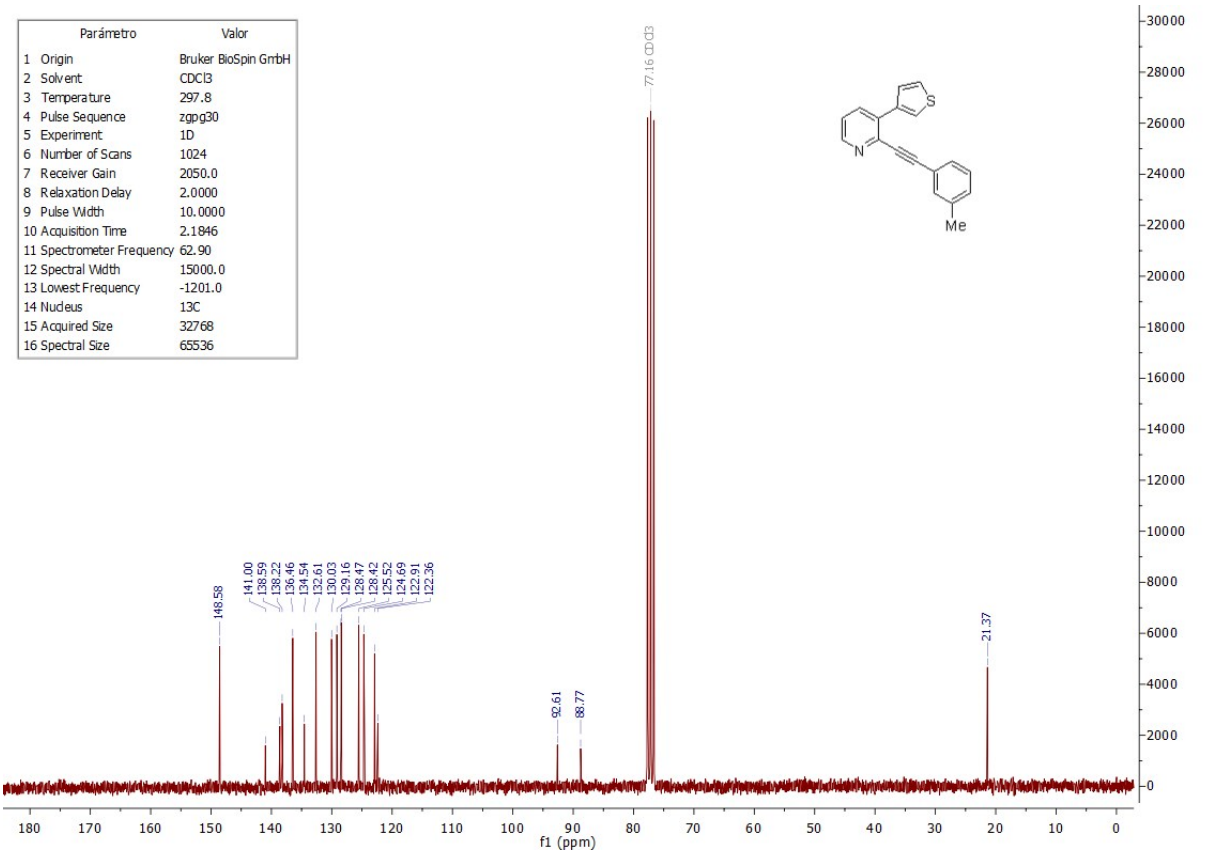
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	362.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.5
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768



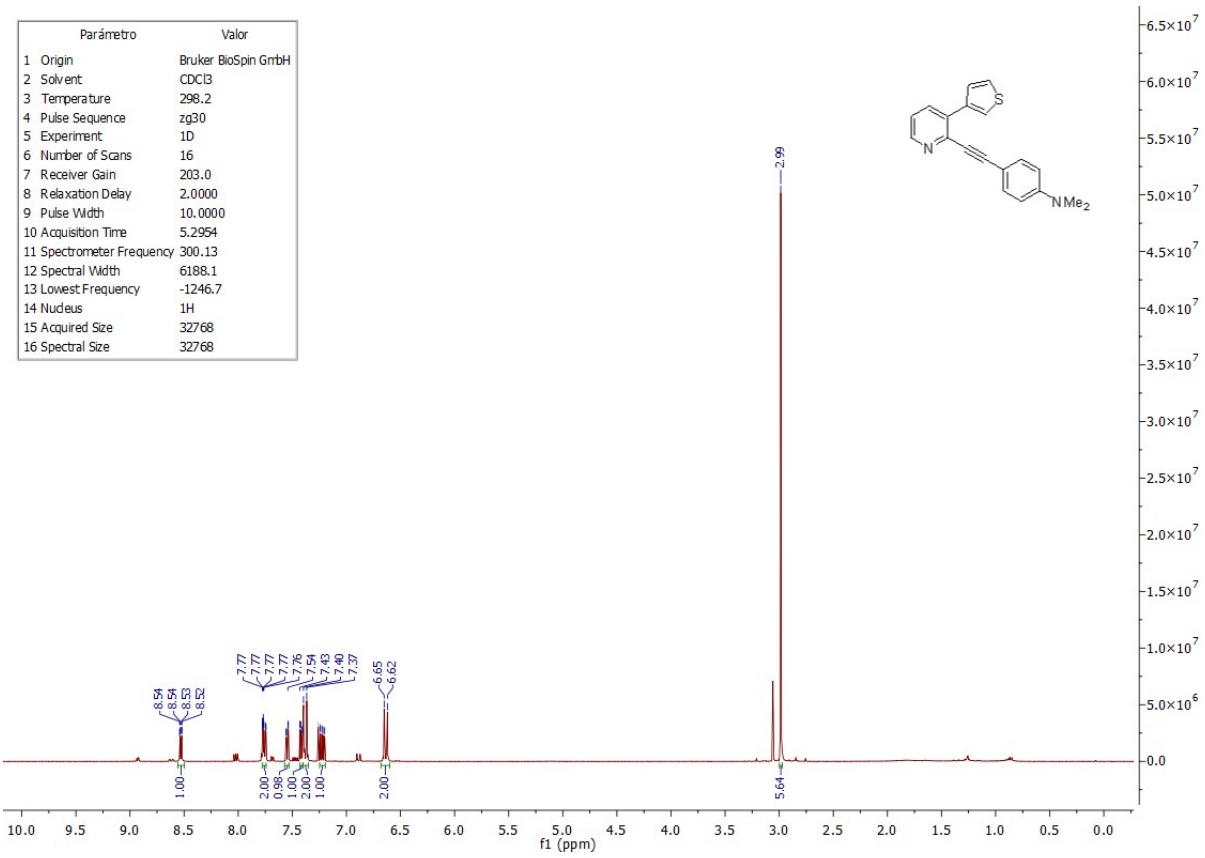


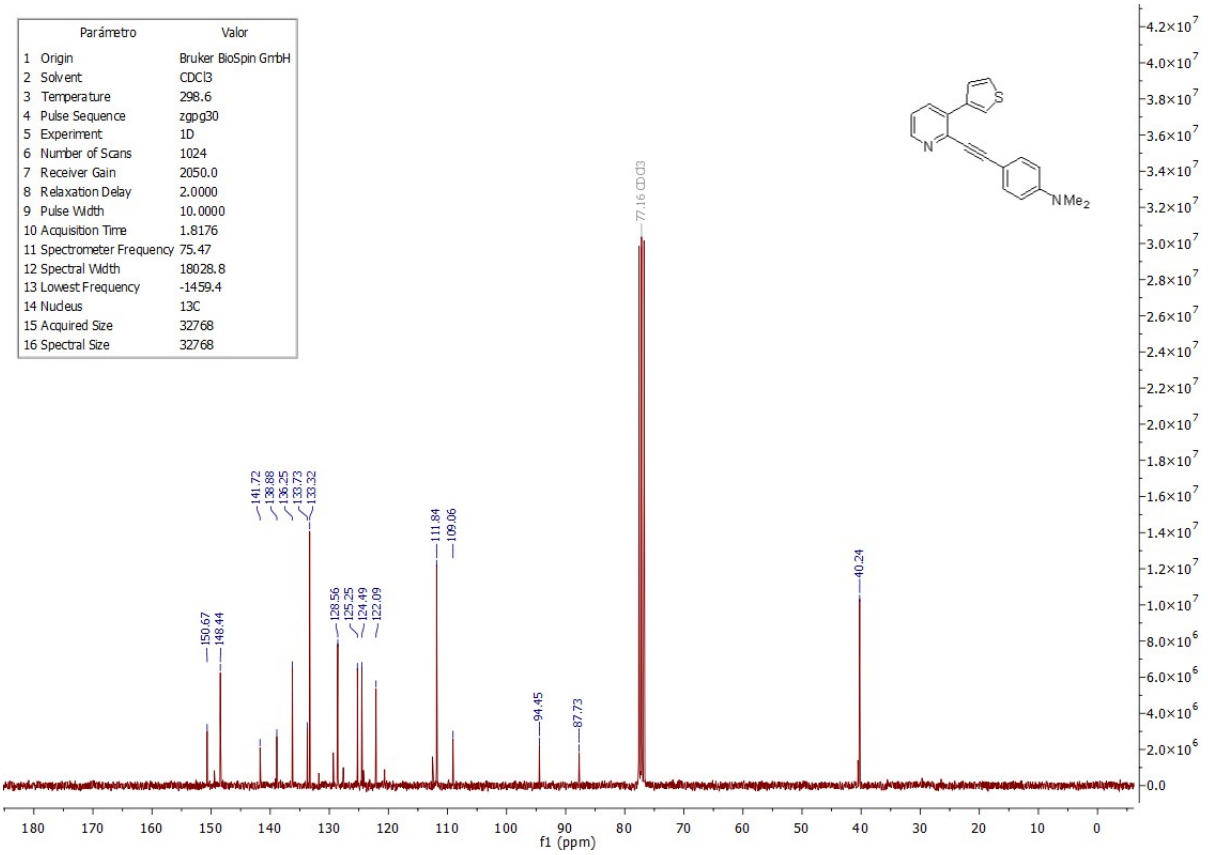
3-(thiophen-3-yl)-2-(*m*-tolylethynyl)pyridine **6e**





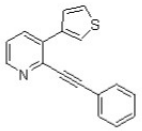
N,*N*-dimethyl-4-((3-(thiophen-3-yl)pyridin-2-yl)ethynyl)aniline **6f**

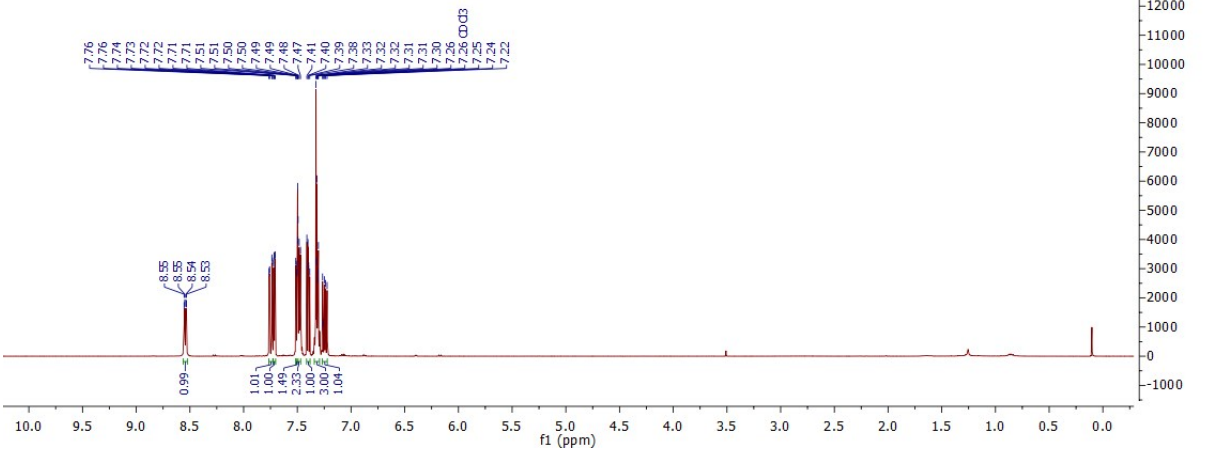




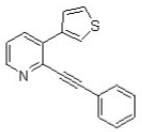
2-(phenylethynyl)-3-(thiophen-3-yl)pyridine **6g**

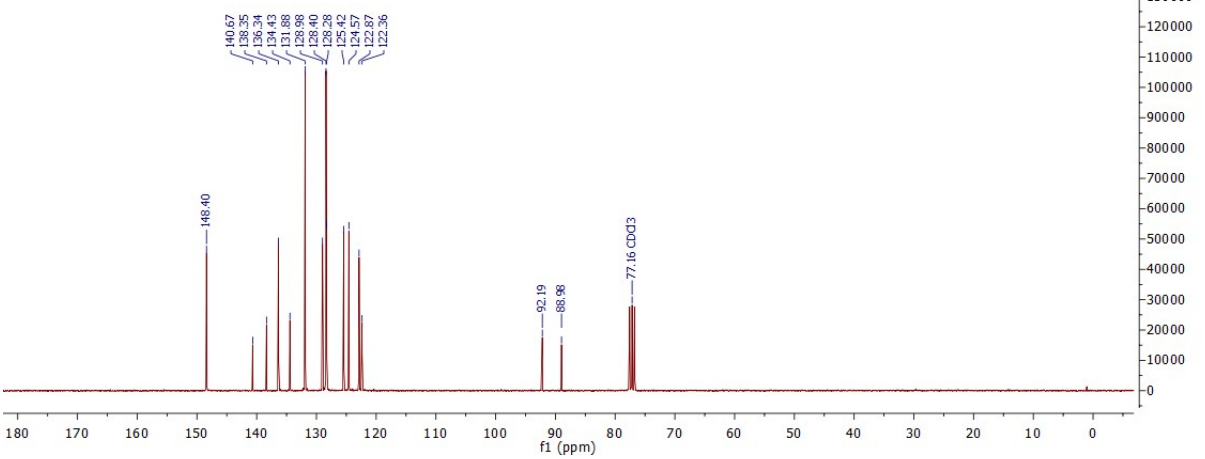
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	22.6
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1247.0
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536



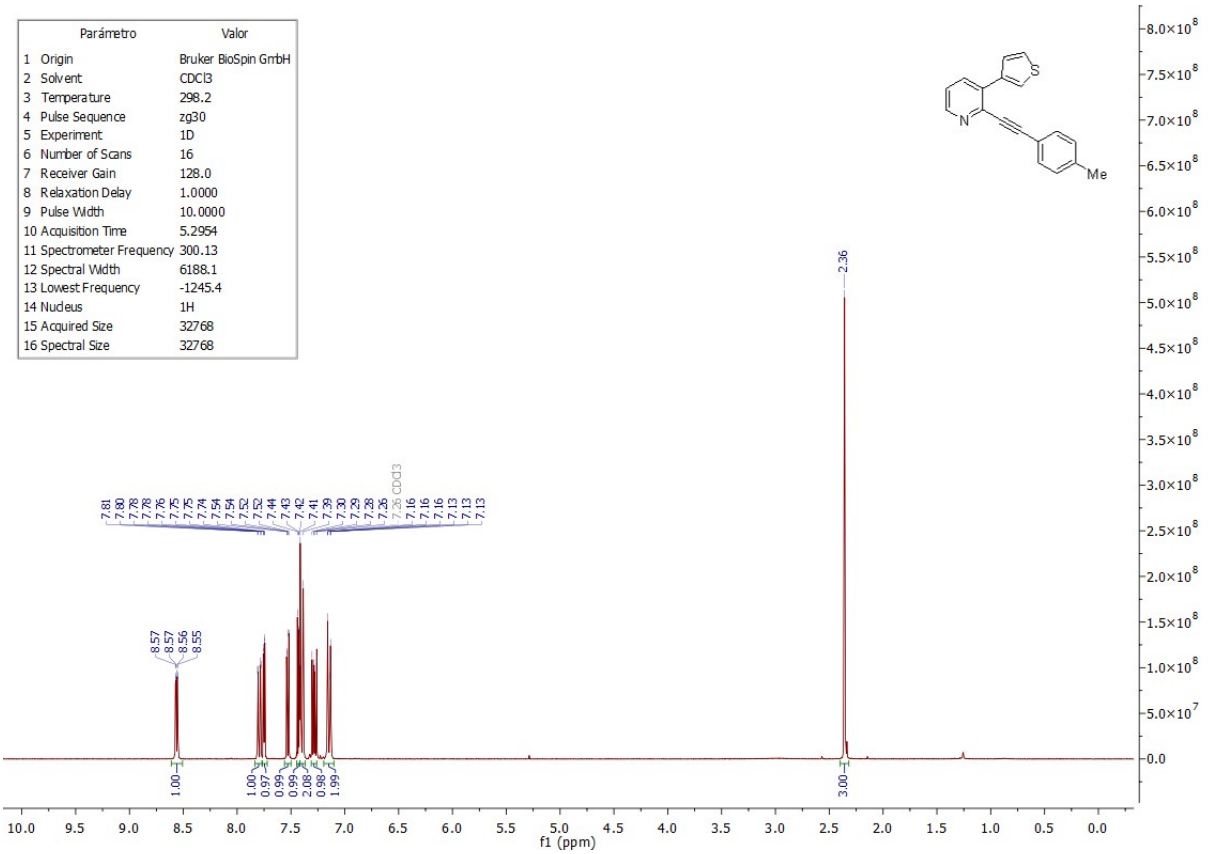


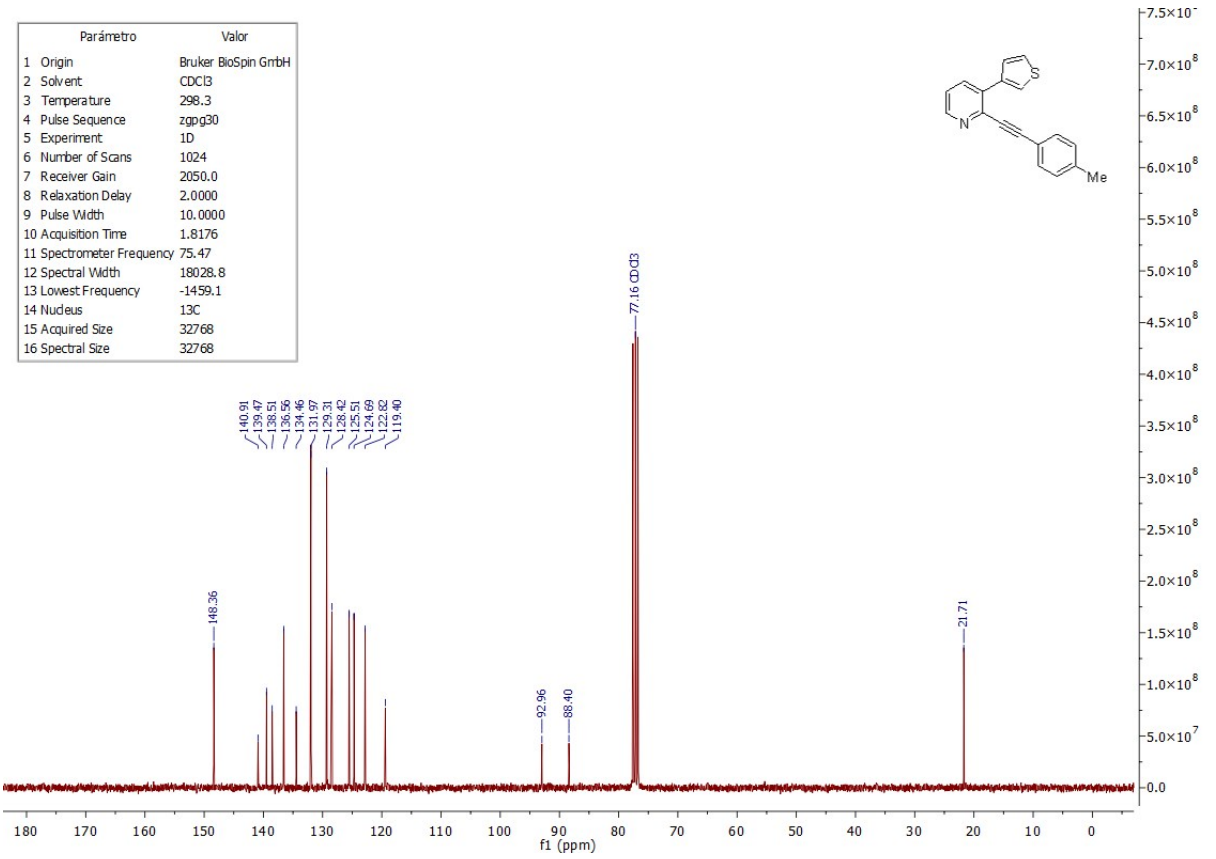
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1470.6
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536



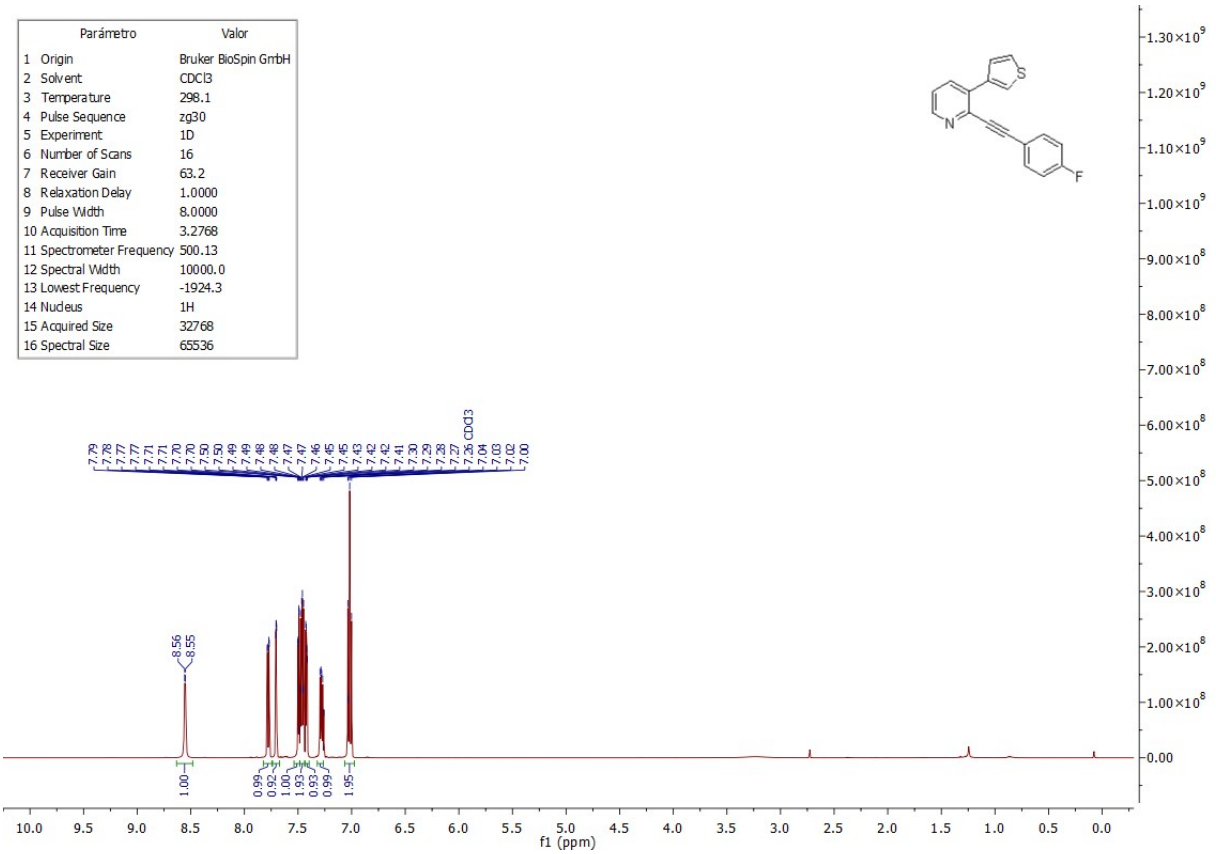


3-(thiophen-3-yl)-2-(*p*-tolylethynyl)pyridine **6h**

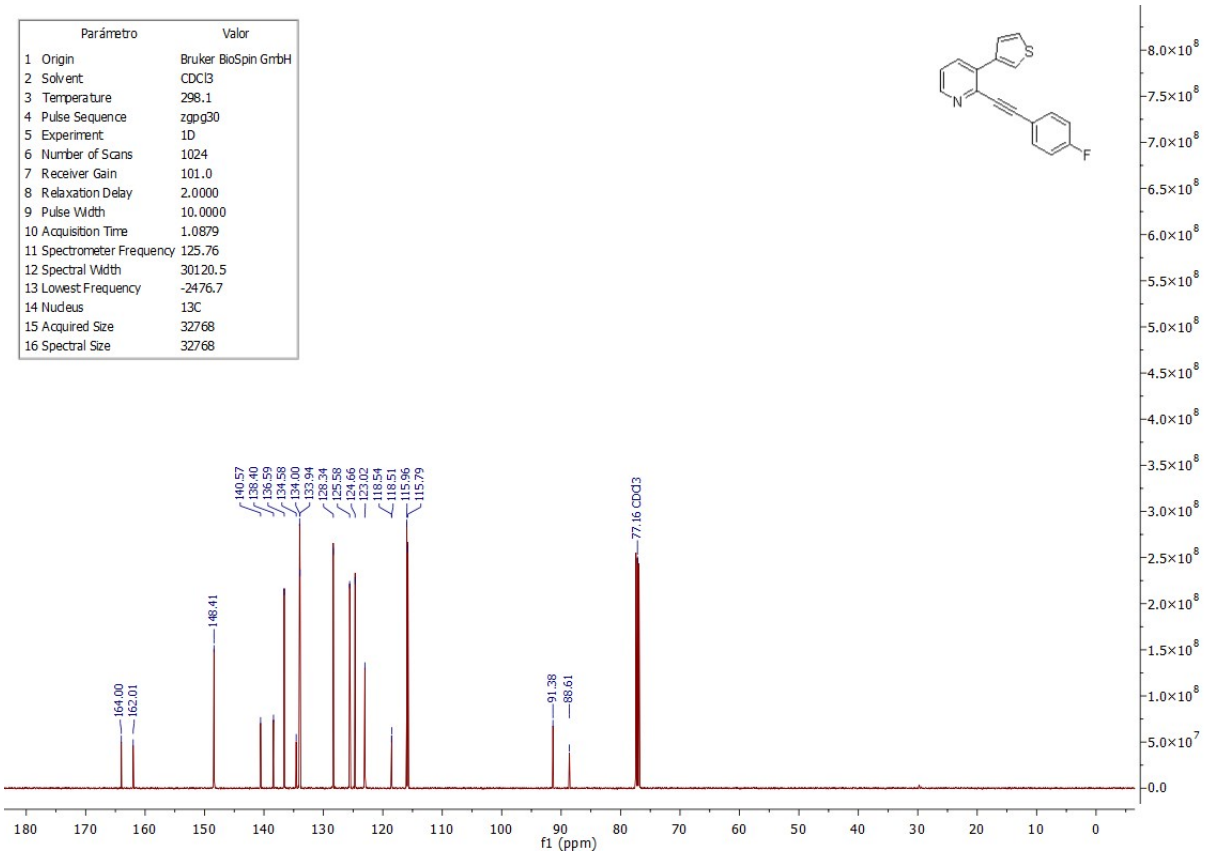




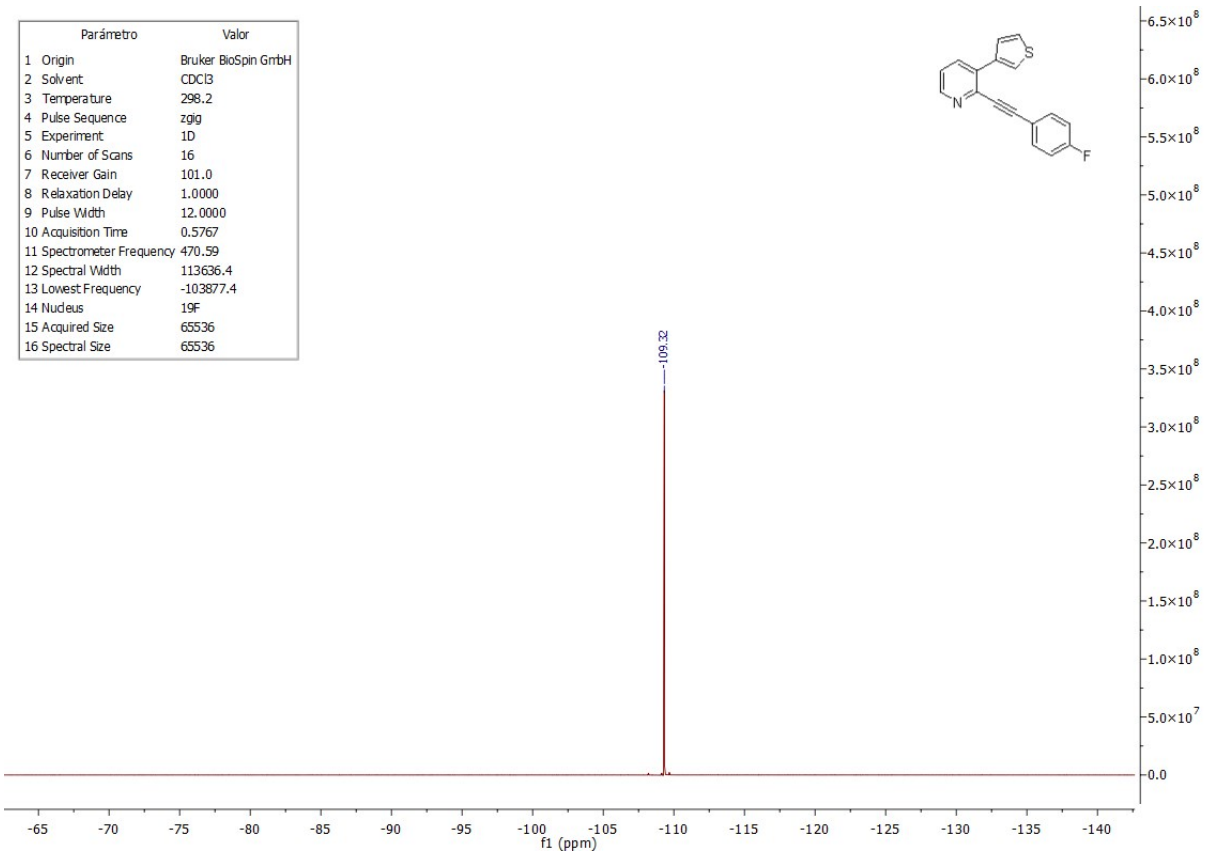
2-((4-fluorophenyl)ethynyl)-3-(thiophen-3-yl)pyridine **6i**



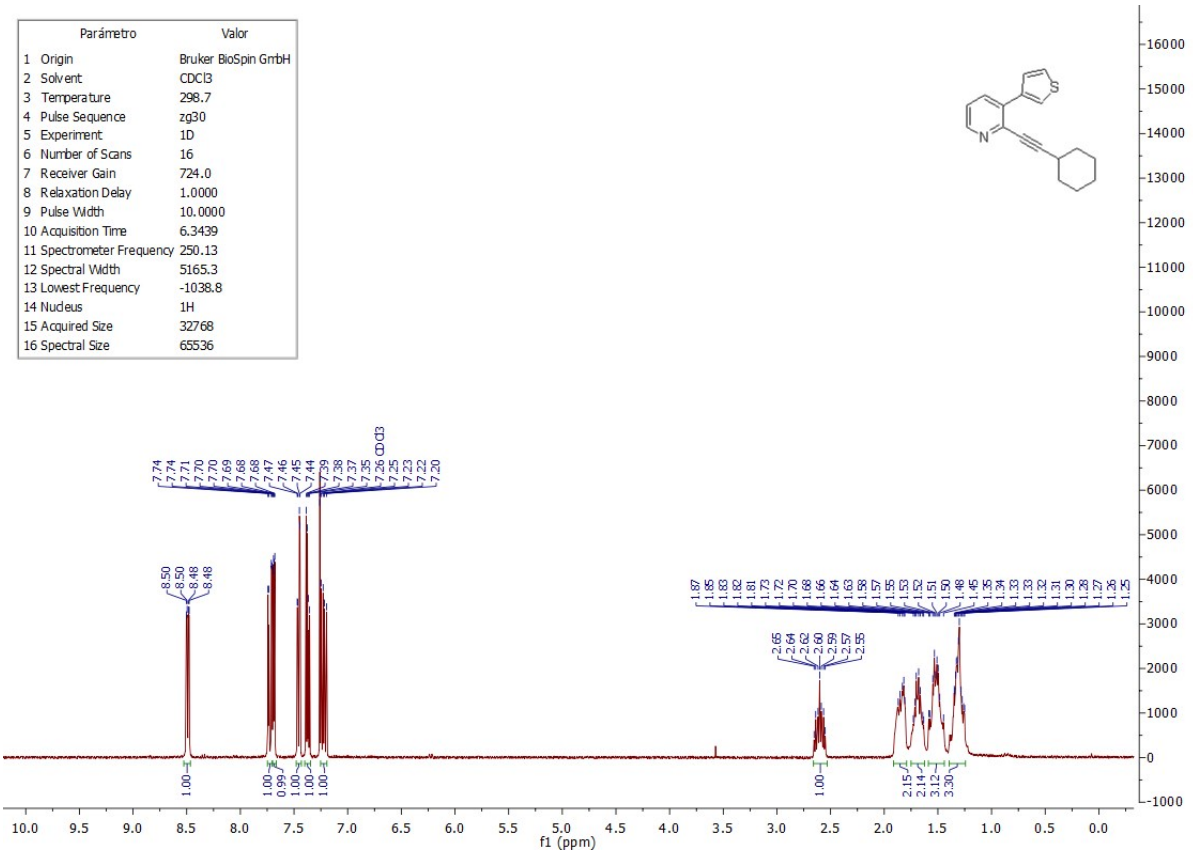
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	101.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.0879
11 Spectrometer Frequency	125.76
12 Spectral Width	30120.5
13 Lowest Frequency	-2476.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768

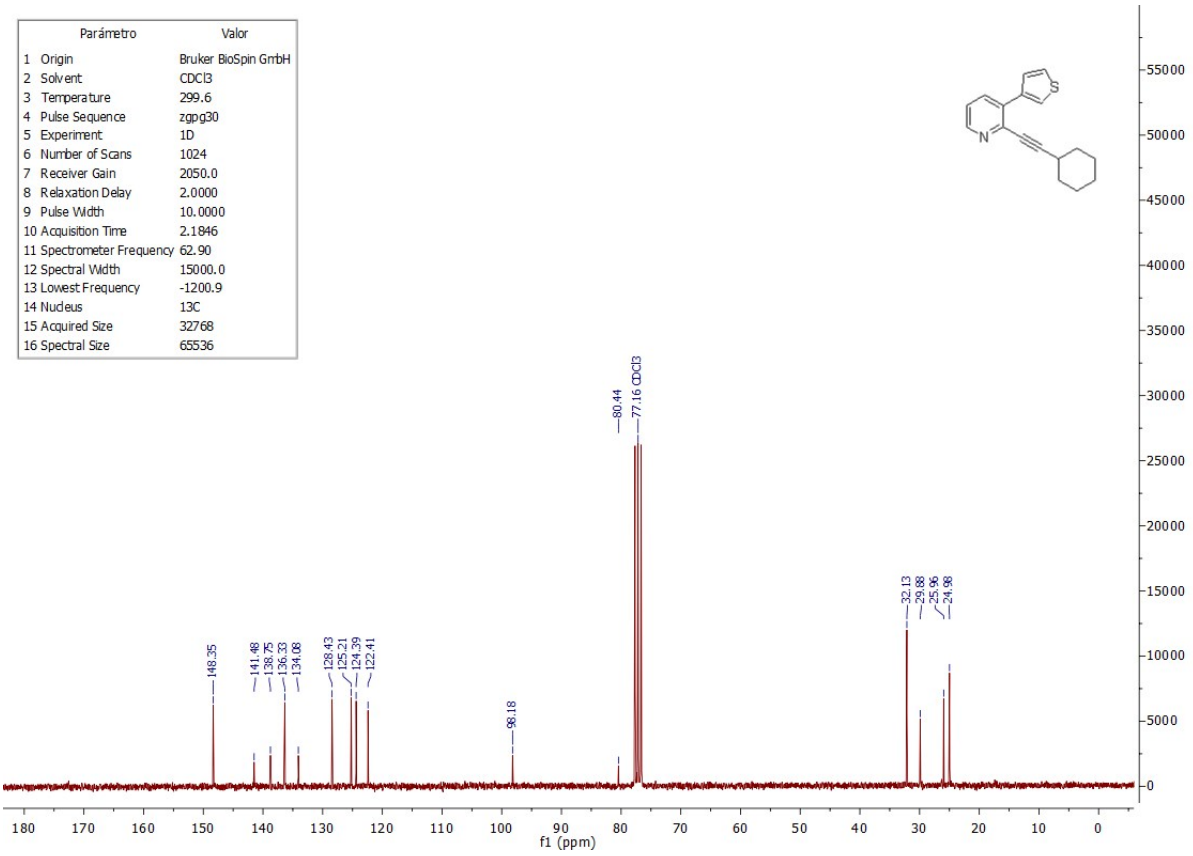


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgig
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	101.0
8 Relaxation Delay	1.0000
9 Pulse Width	12.0000
10 Acquisition Time	0.5767
11 Spectrometer Frequency	470.59
12 Spectral Width	113636.4
13 Lowest Frequency	-103877.4
14 Nucleus	19F
15 Acquired Size	65536
16 Spectral Size	65536



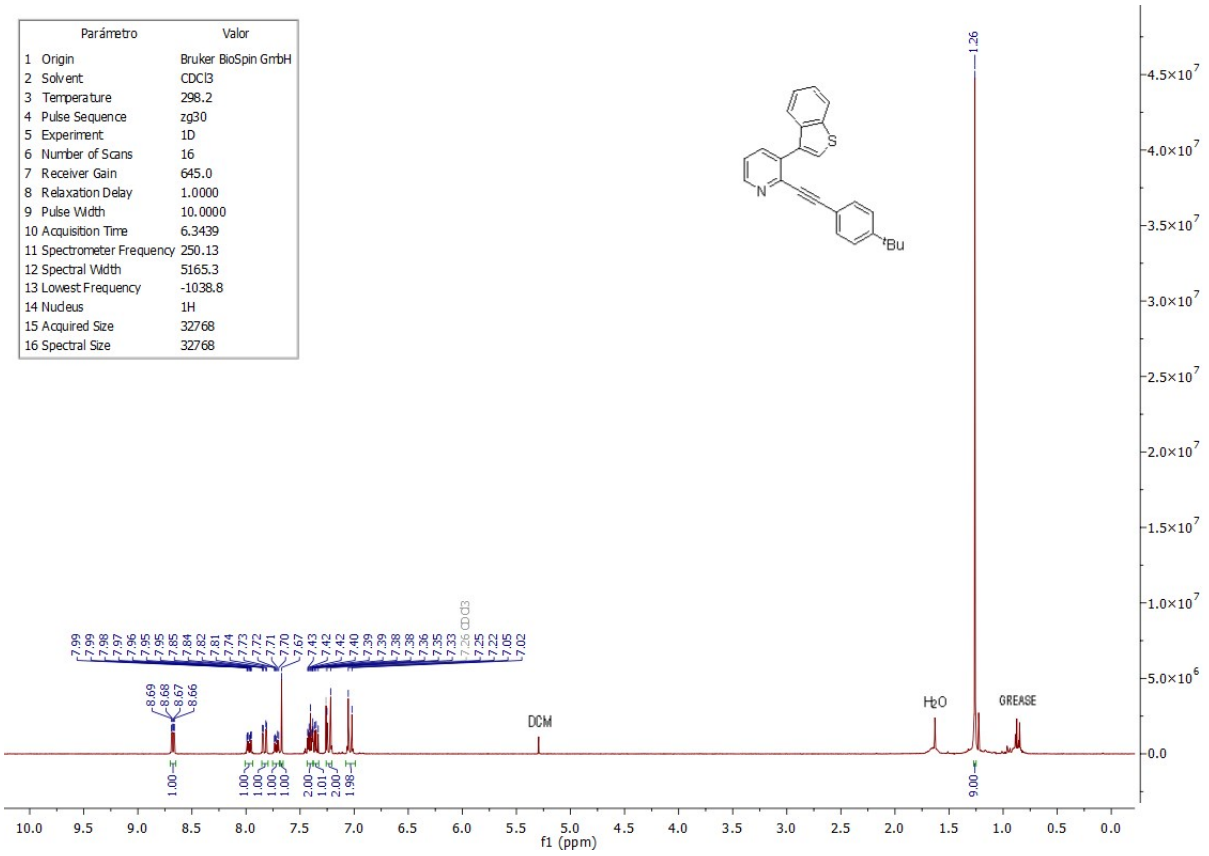
2-(cyclohexylethynyl)-3-(thiophen-3-yl)pyridine **6j**



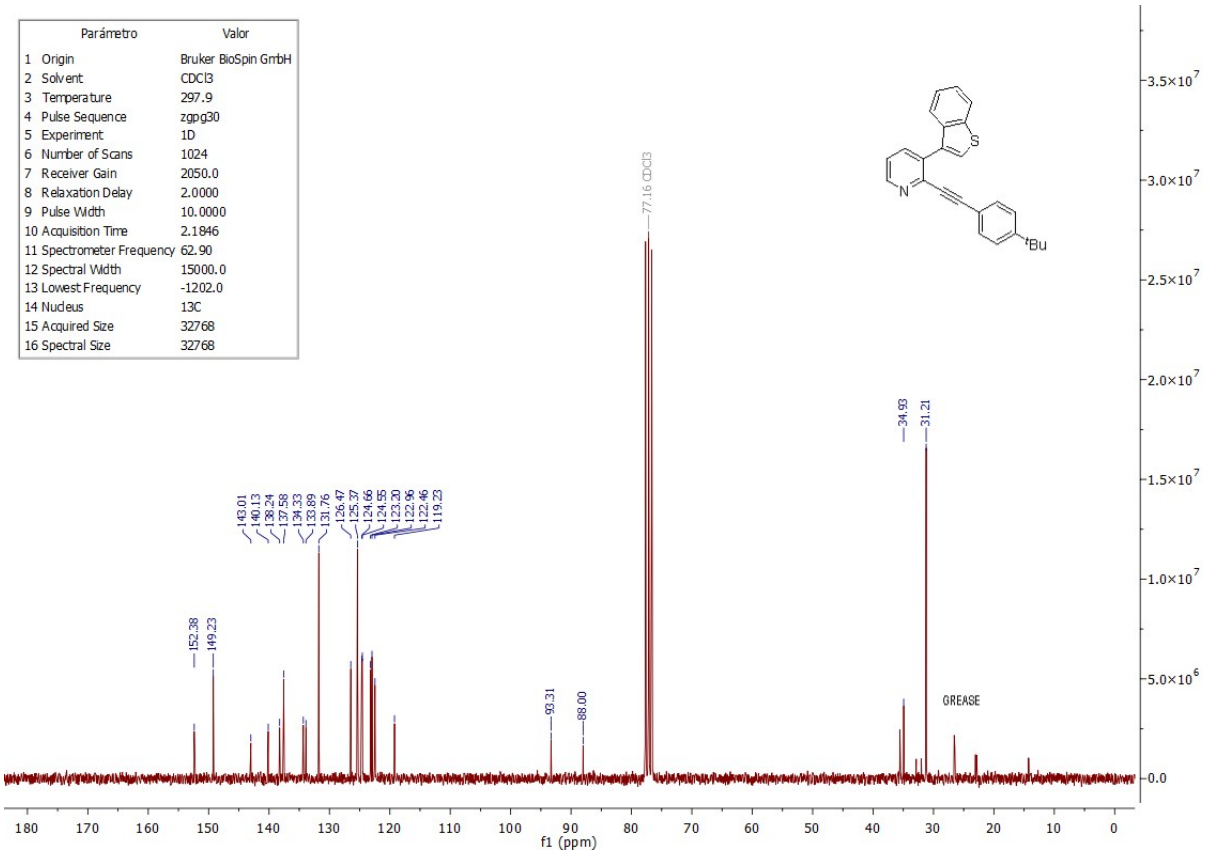


3-(benzo[*b*]thiophen-3-yl)-2-((4-(*tert*-butyl)phenyl)ethynyl)pyridine **6k**

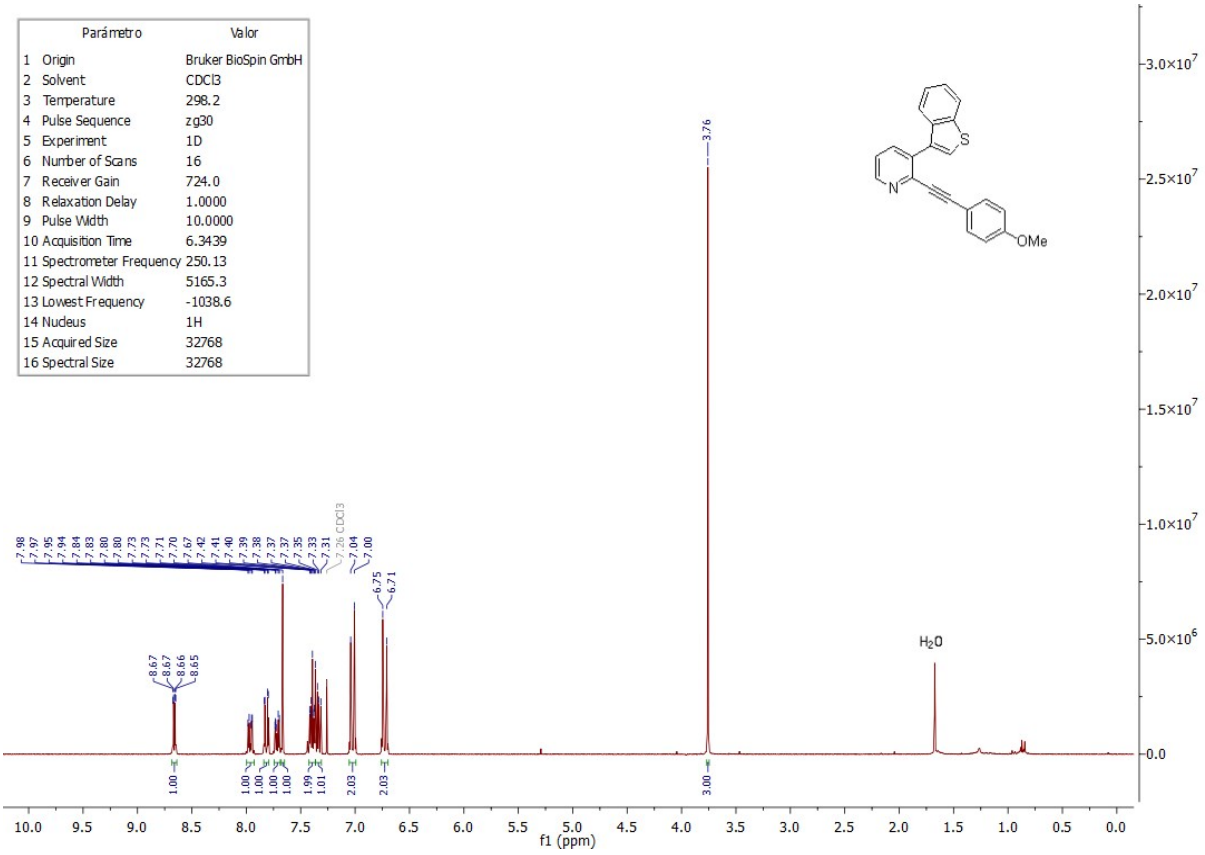
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	645.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.8
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768

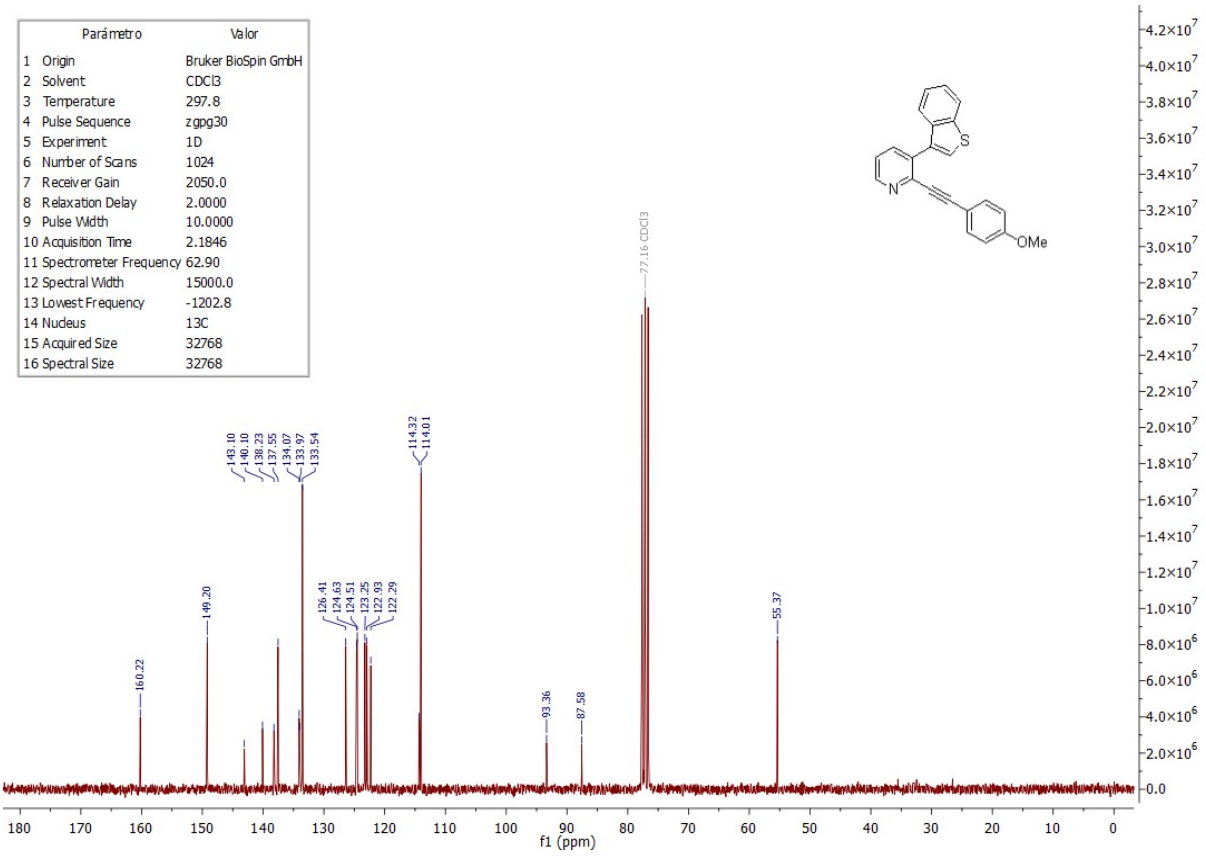


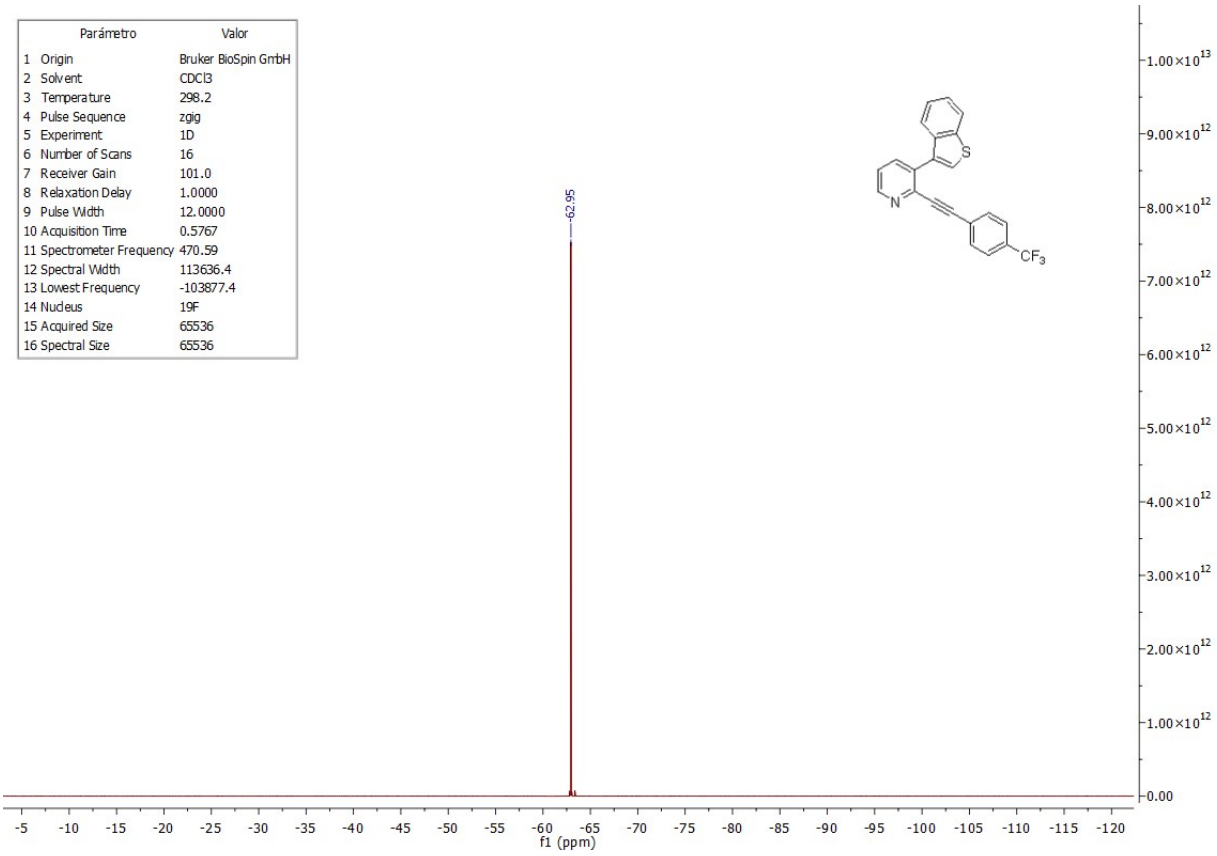
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.9
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1202.0
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



3-(benzo[*b*]thiophen-3-yl)-2-((4-methoxyphenyl)ethynyl)pyridine **6l**

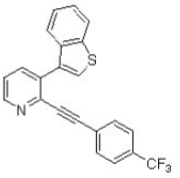


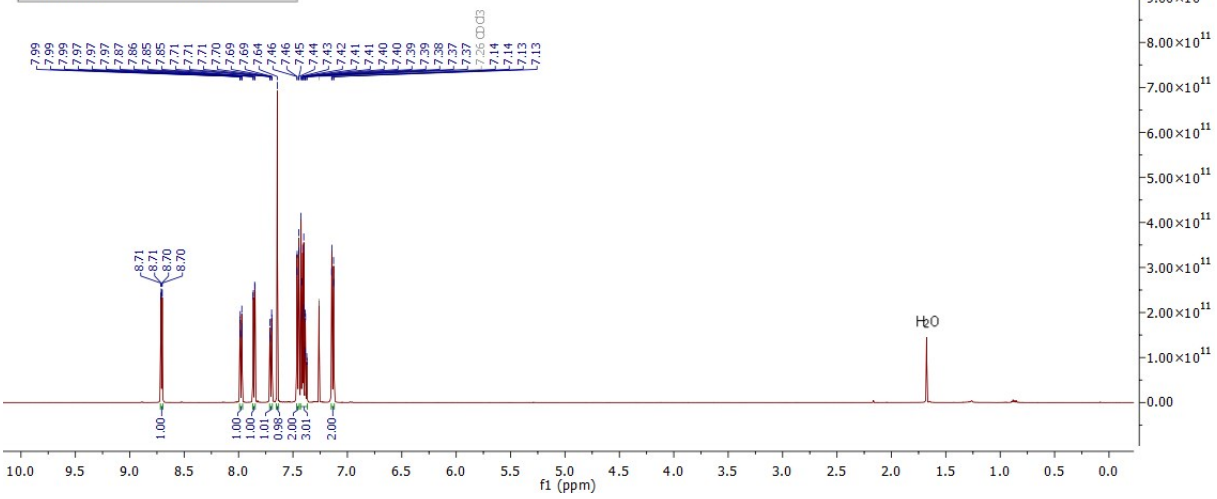

Parámetro Valor
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 297.8
4 Pulse Sequence zgpg30
5 Experiment 1D
6 Number of Scans 1024
7 Receiver Gain 2050.0
8 Relaxation Delay 2.0000
9 Pulse Width 10.0000
10 Acquisition Time 2.1846
11 Spectrometer Frequency 62.90
12 Spectral Width 15000.0
13 Lowest Frequency -1202.8
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 32768
S
N
OMe
160.22
149.20
143.10
140.10
138.23
137.55
134.07
133.97
133.54
126.41
124.63
124.51
123.25
122.93
122.29
114.32
114.01
93.36
87.58
77.16 CDCl3
55.37
f1 (ppm)



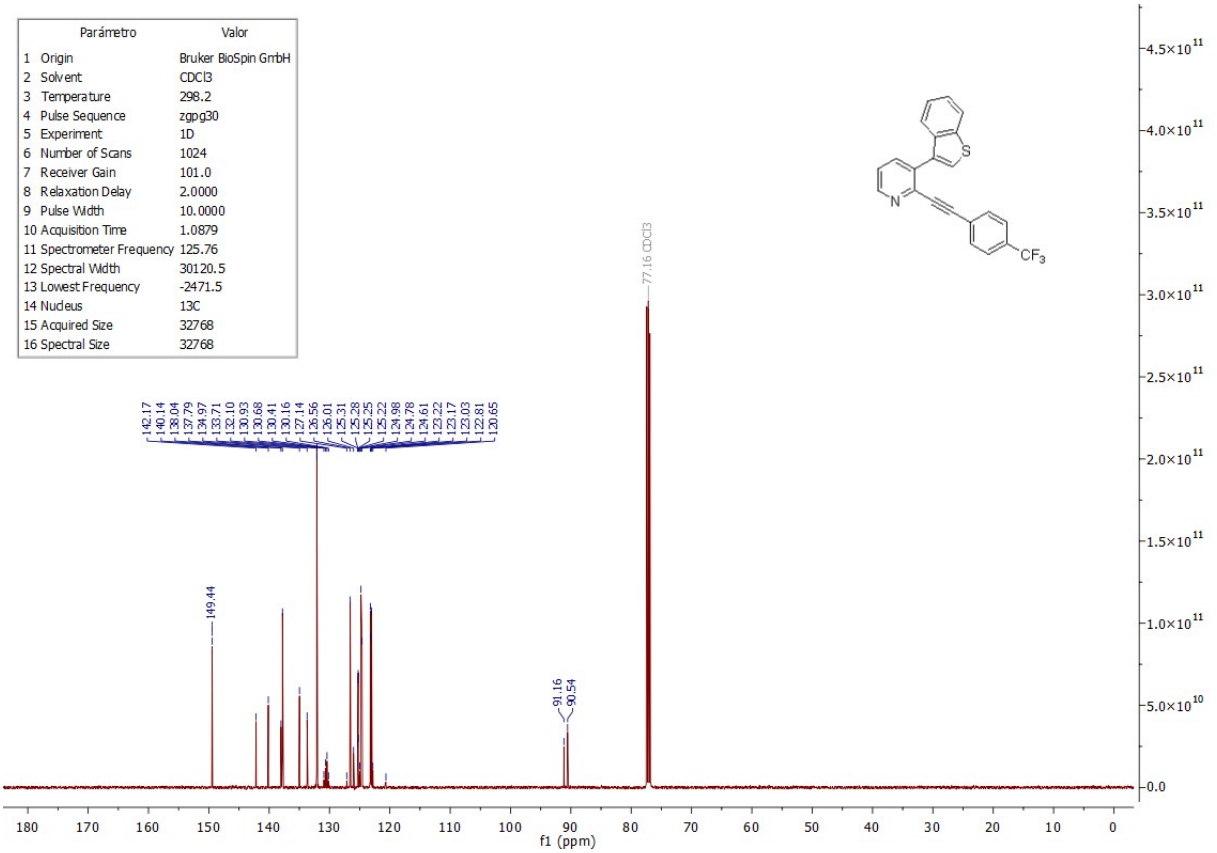
3-(benzo[*b*]thiophen-3-yl)-2-((4-(trifluoromethyl)phenyl)ethynyl)pyridine **6m**

Parámetro	Valor
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	63.2
8 Relaxation Delay	1.0000
9 Pulse Width	8.0000
10 Acquisition Time	3.2768
11 Spectrometer Frequency	500.13
12 Spectral Width	10000.0
13 Lowest Frequency	-1924.3
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536



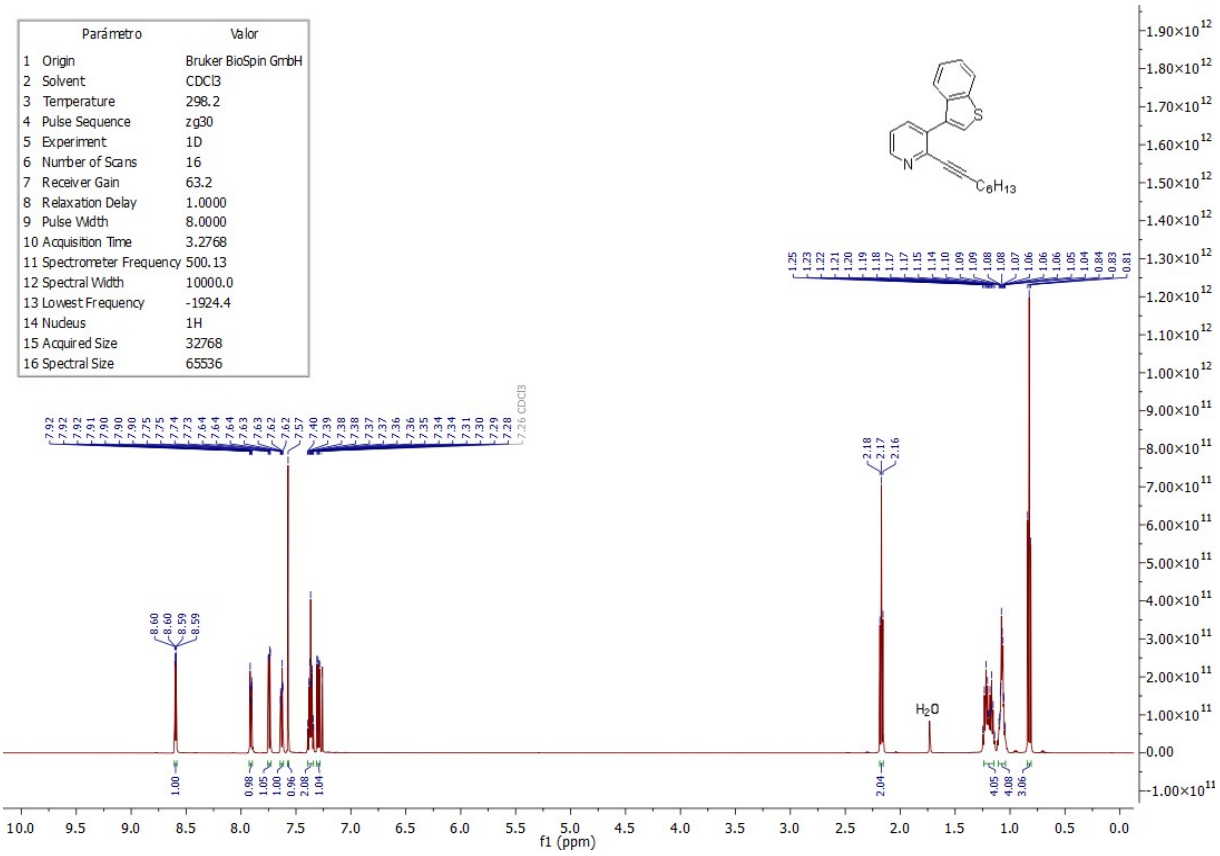


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	101.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.0879
11 Spectrometer Frequency	125.76
12 Spectral Width	30120.5
13 Lowest Frequency	-2471.5
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768

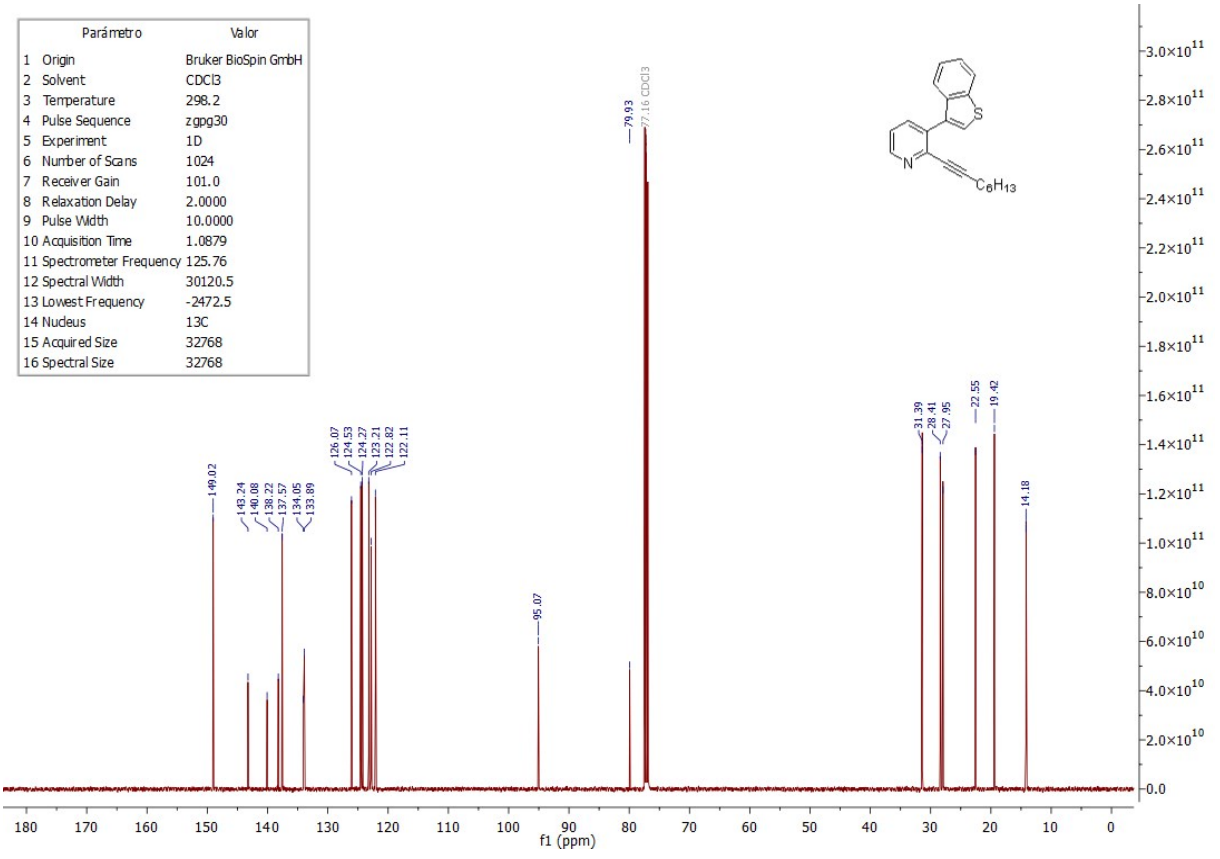


3-(benzo[*b*]thiophen-3-yl)-2-(oct-1-yn-1-yl)pyridine **6n**

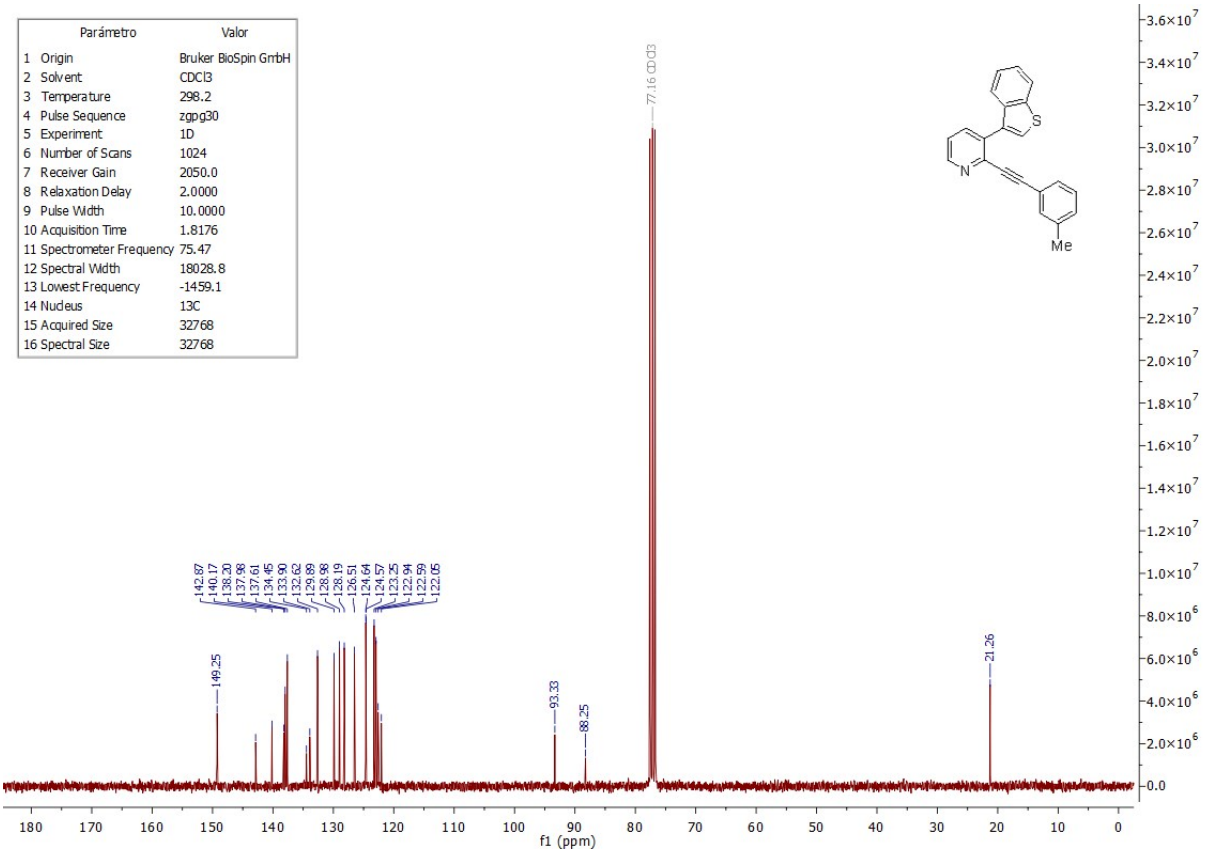
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	63.2
8 Relaxation Delay	1.0000
9 Pulse Width	8.0000
10 Acquisition Time	3.2768
11 Spectrometer Frequency	500.13
12 Spectral Width	10000.0
13 Lowest Frequency	-1924.4
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

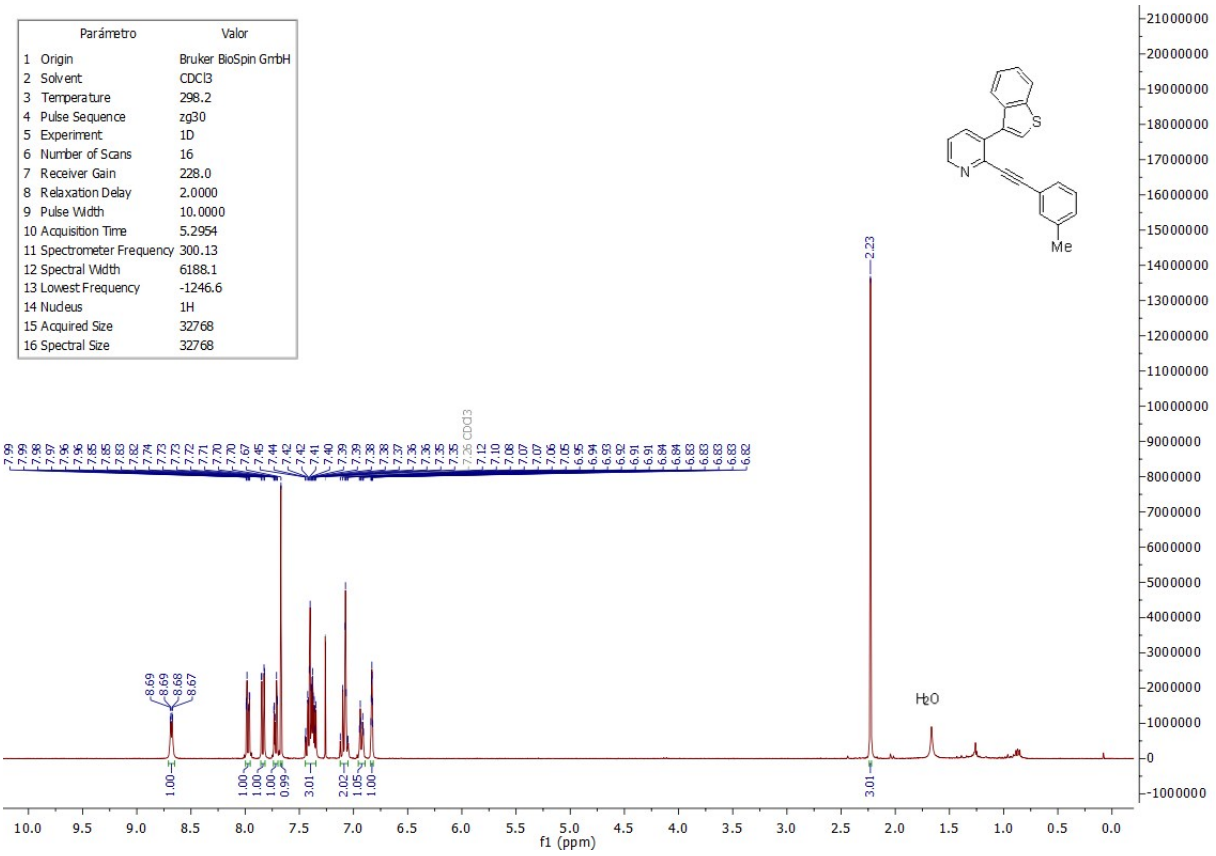


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	101.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.0879
11 Spectrometer Frequency	125.76
12 Spectral Width	30120.5
13 Lowest Frequency	-2472.5
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768

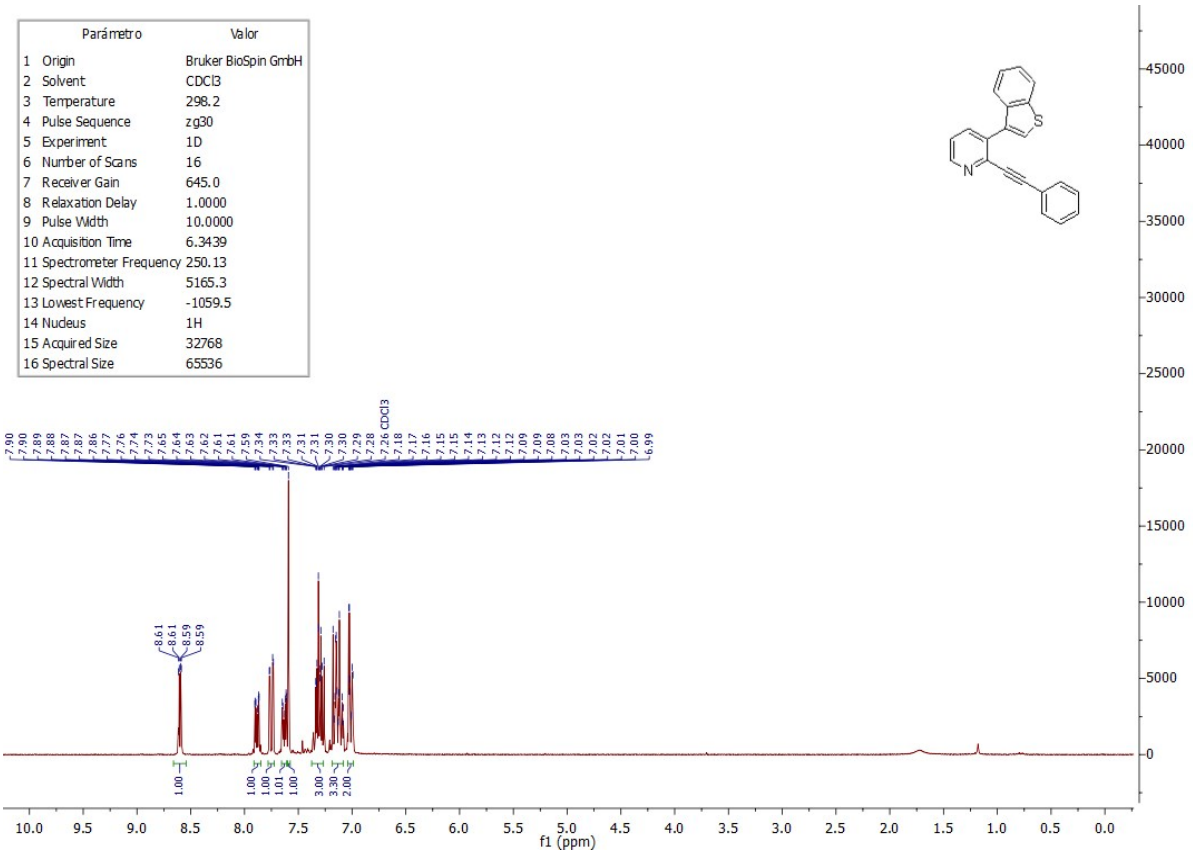


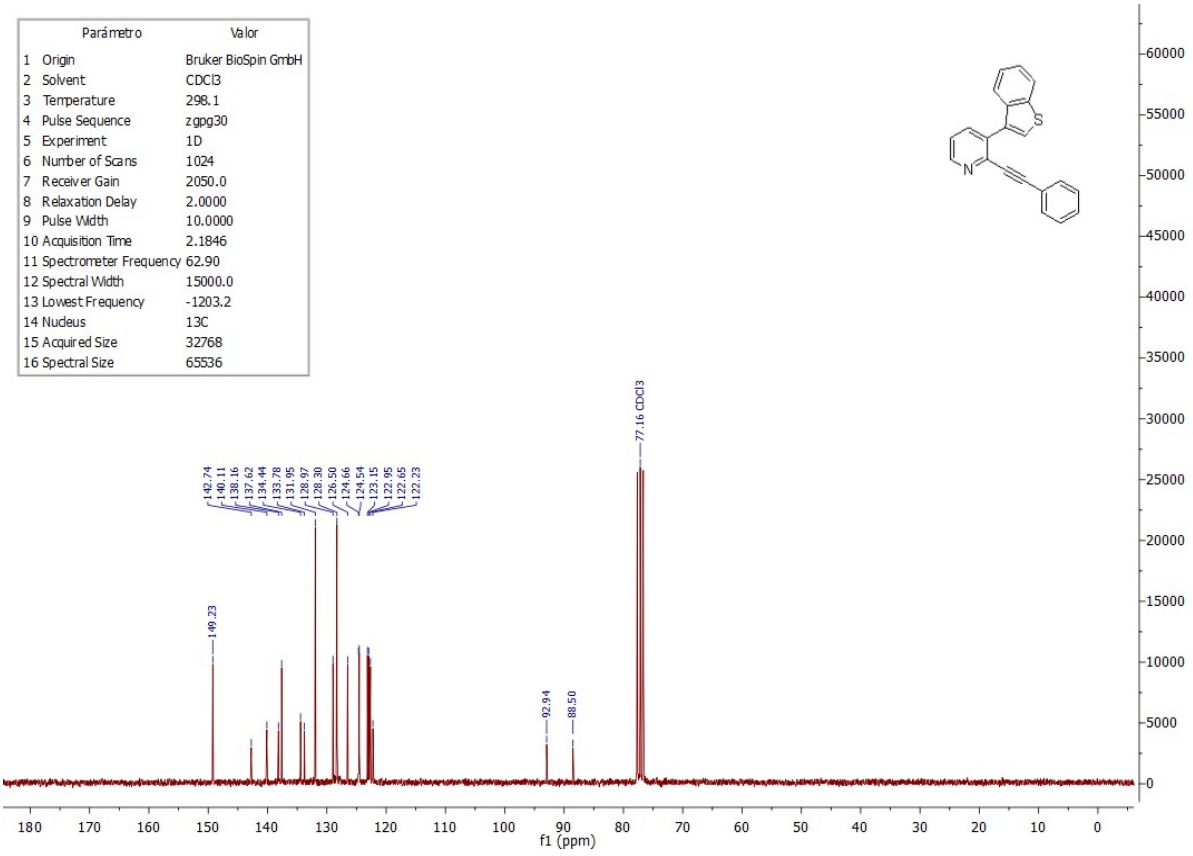
3-(benzo[*b*]thiophen-3-yl)-2-(*m*-tolylethynyl)pyridine **6o**





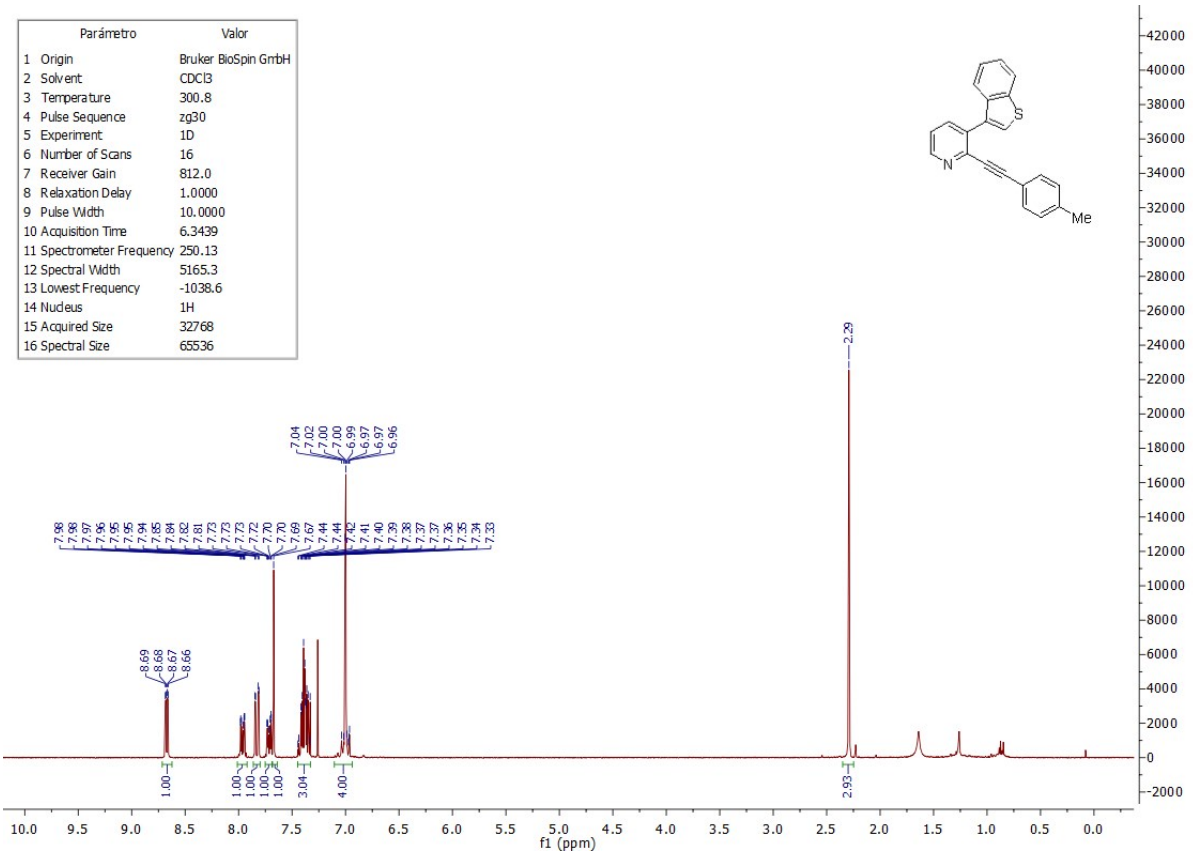
3-(benzo[*b*]thiophen-3-yl)-2-(phenylethynyl)pyridine **6p**



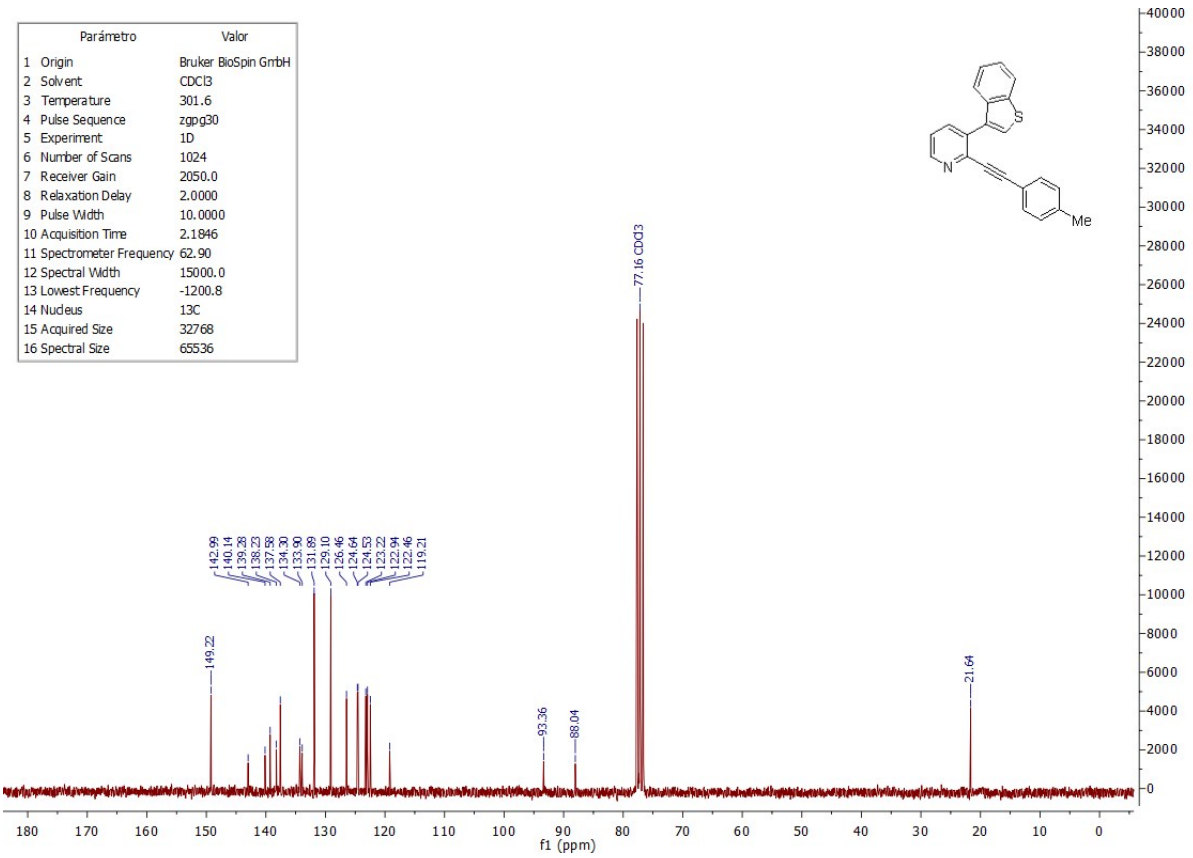


3-(benzo[*b*]thiophen-3-yl)-2-(*p*-tolylethynyl)pyridine **6q**

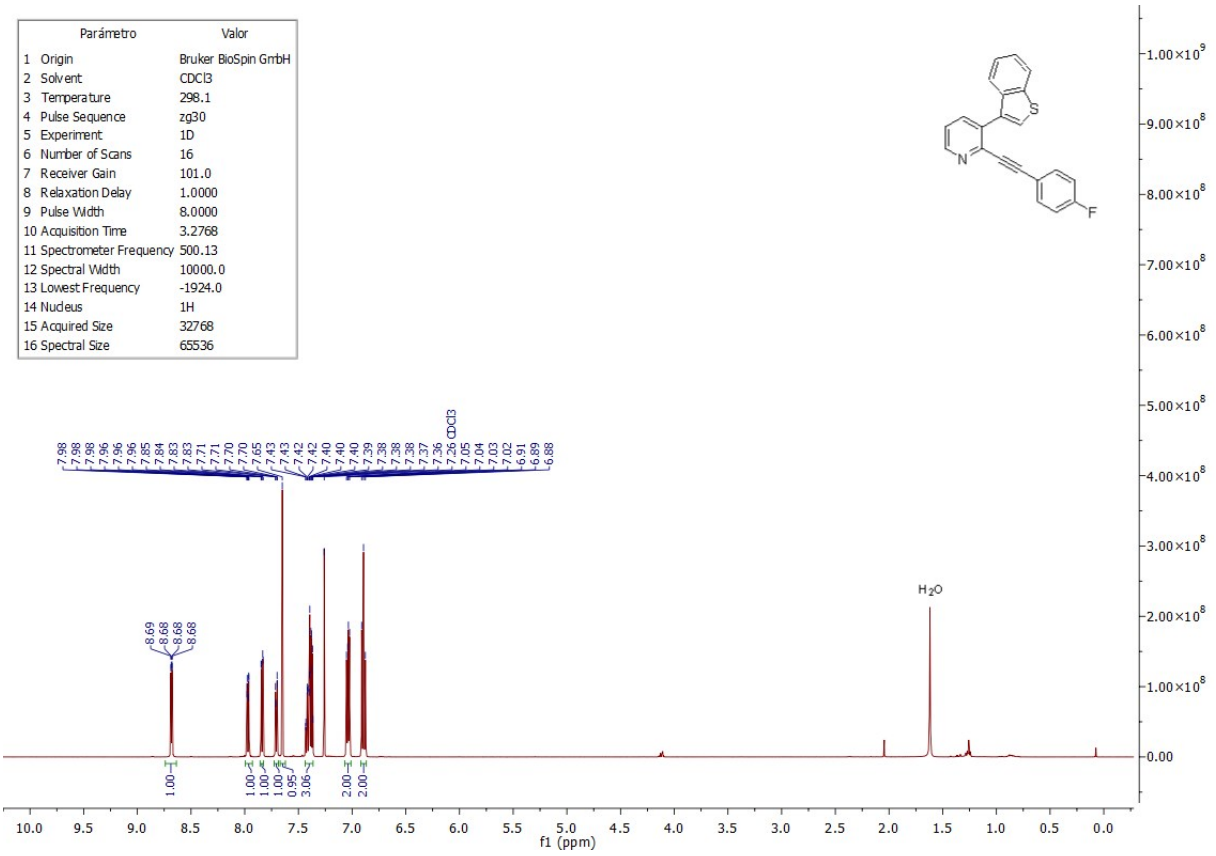
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	300.8
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	812.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.6
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536



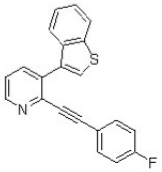
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	301.6
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1200.8
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

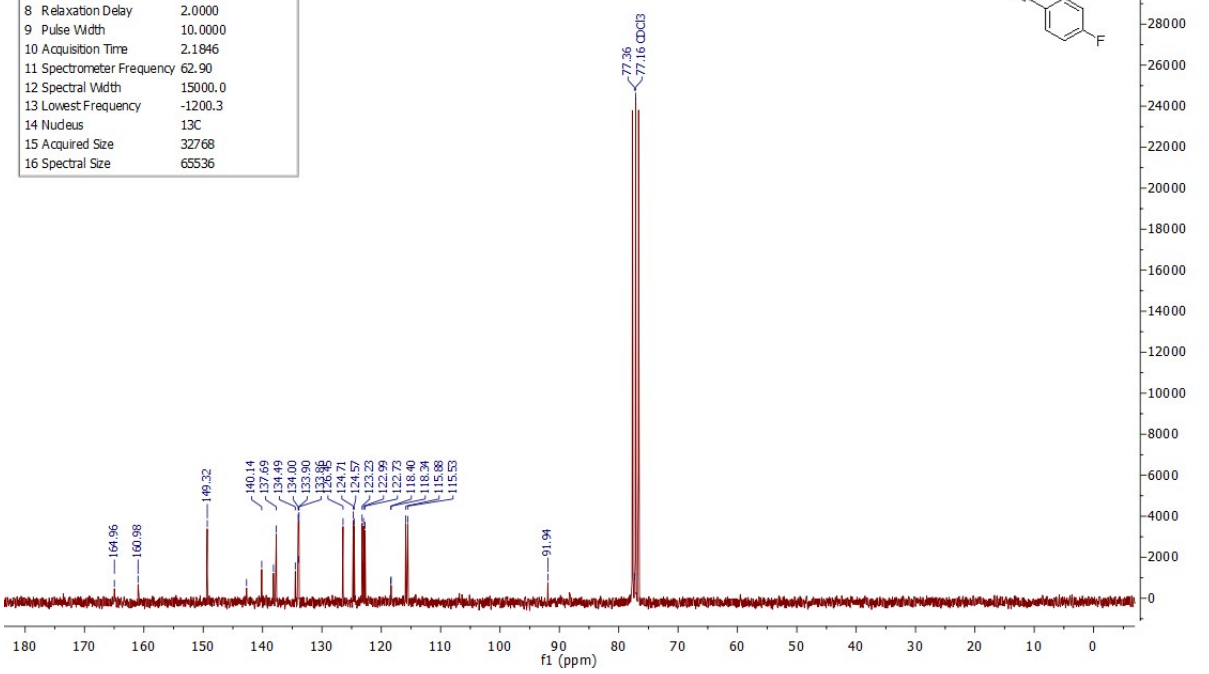


3-(benzo[*b*]thiophen-3-yl)-2-((4-fluorophenyl)ethynyl)pyridine **6r**

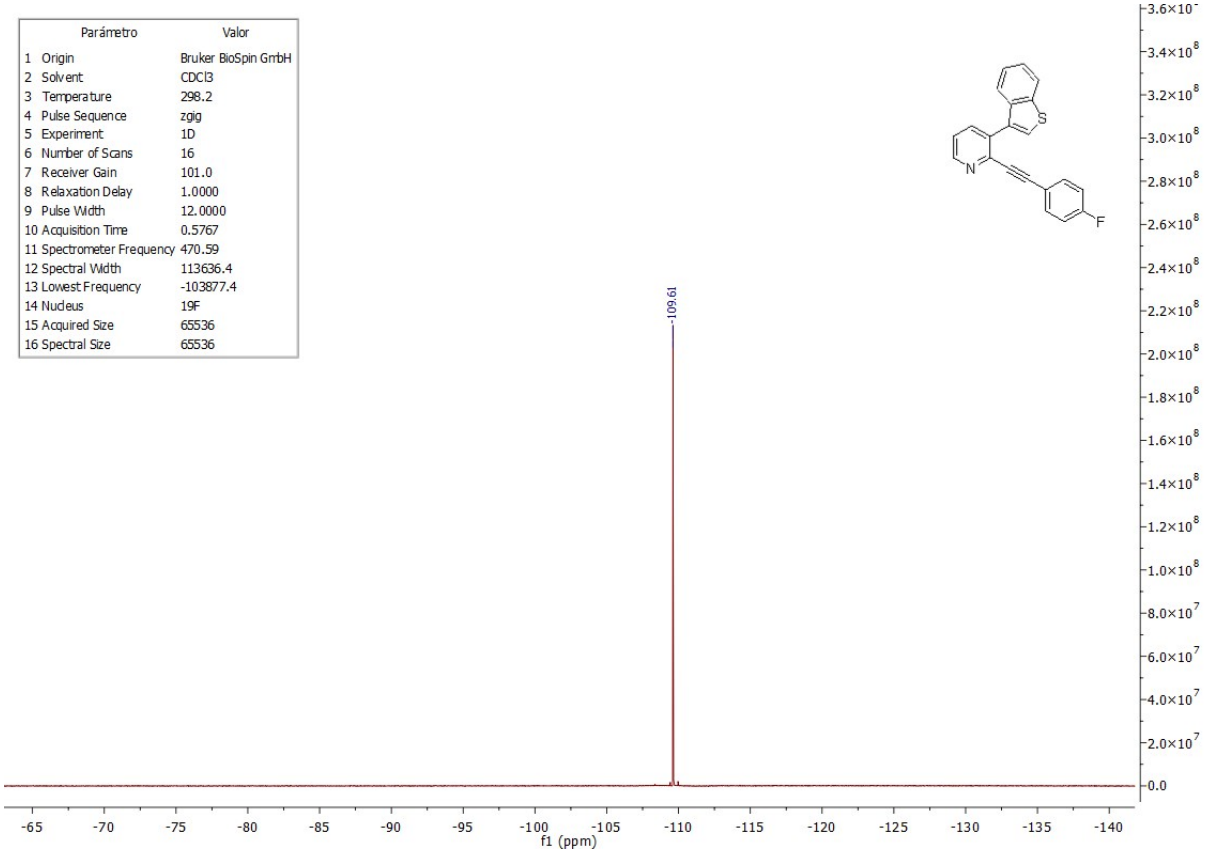


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	301.1
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1200.3
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536

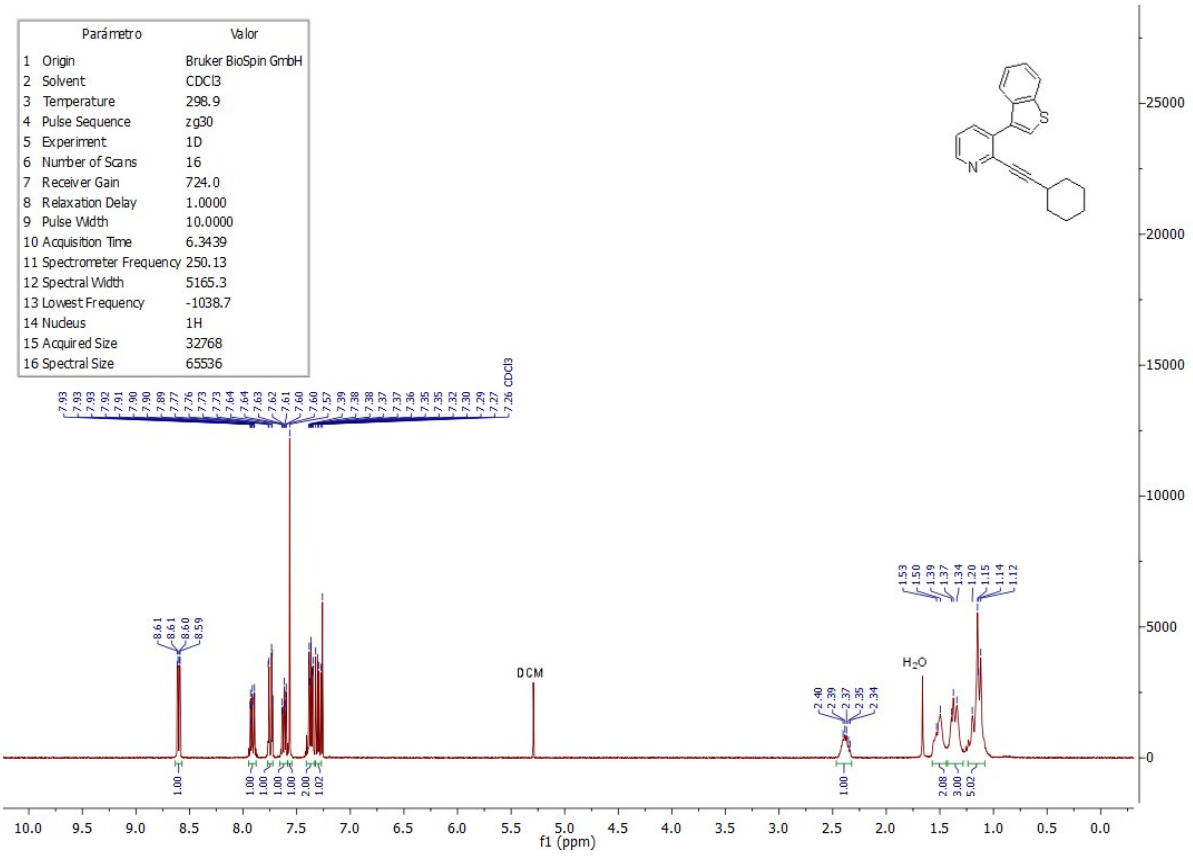


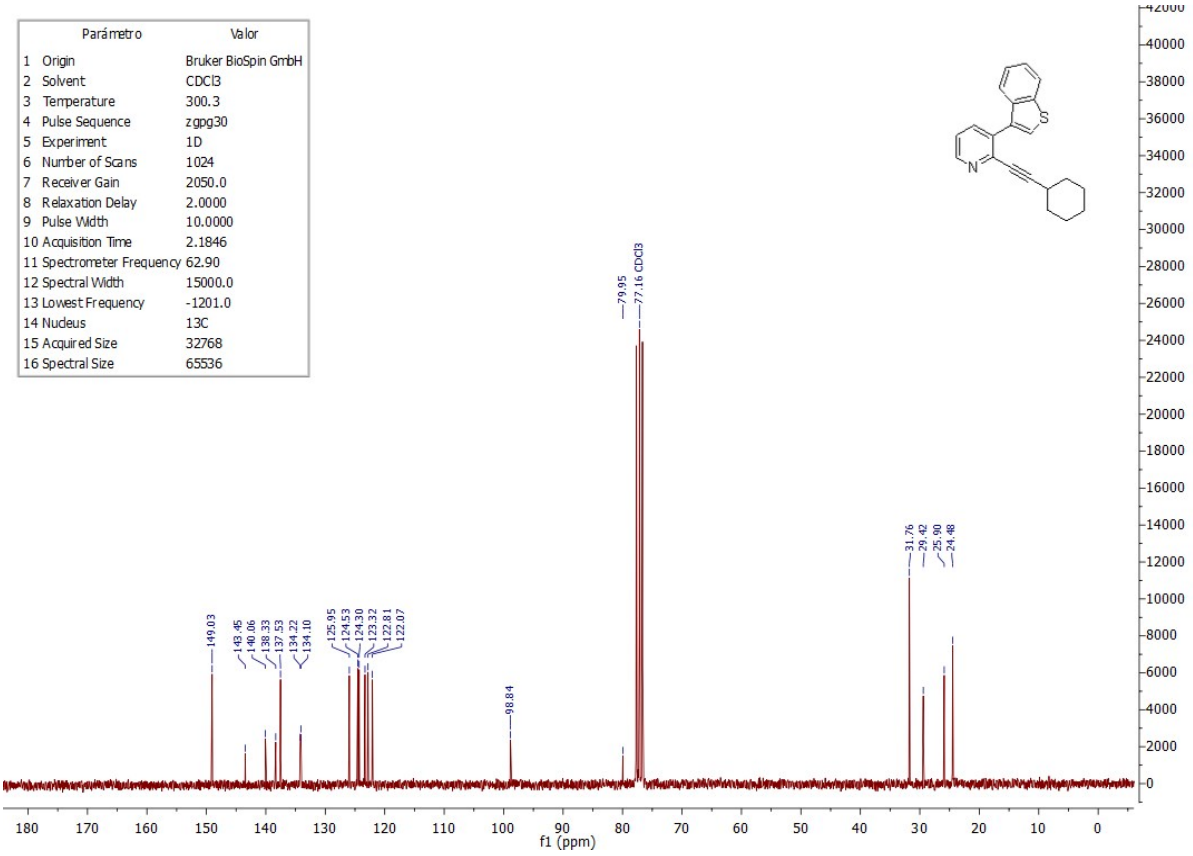


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgig
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	101.0
8 Relaxation Delay	1.0000
9 Pulse Width	12.0000
10 Acquisition Time	0.5767
11 Spectrometer Frequency	470.59
12 Spectral Width	113636.4
13 Lowest Frequency	-103877.4
14 Nucleus	19F
15 Acquired Size	65536
16 Spectral Size	65536



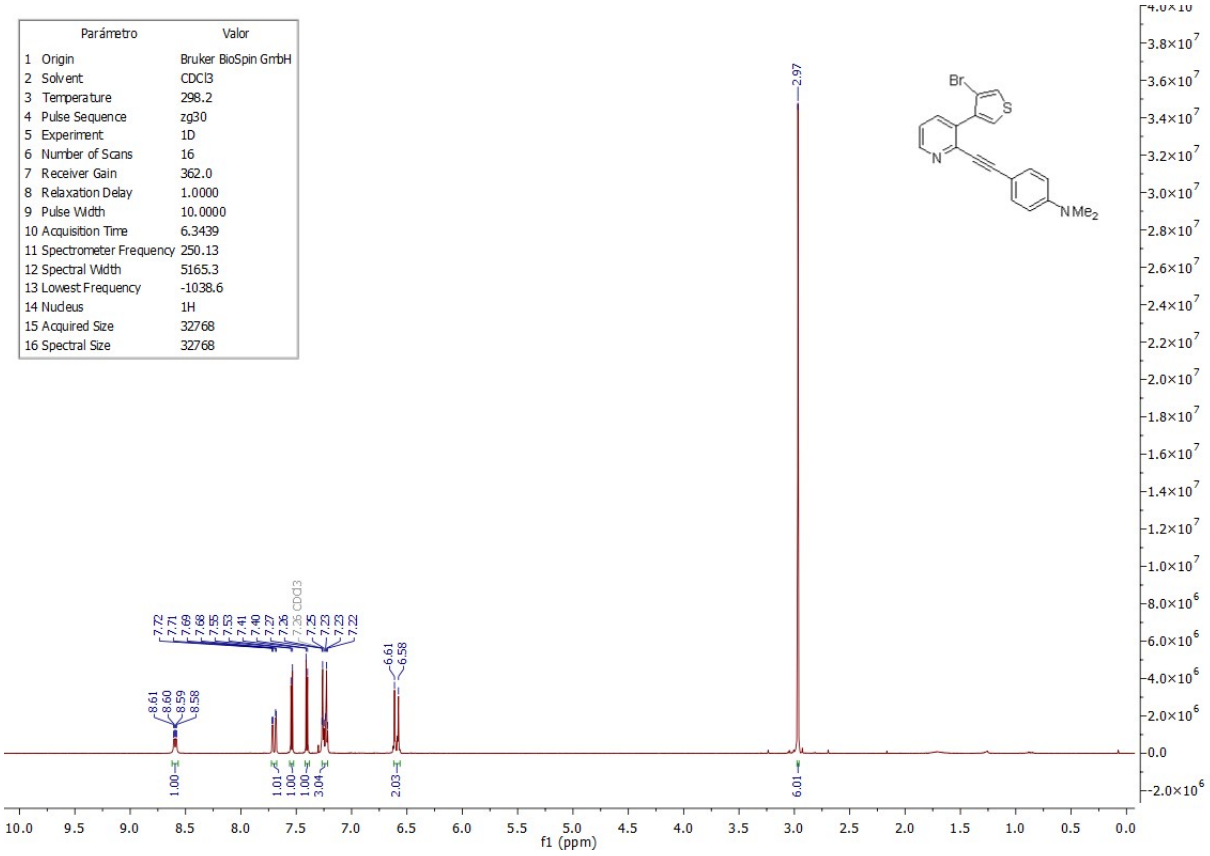
3-(benzo[*b*]thiophen-3-yl)-2-(cyclohexylethynyl)pyridine **6s**



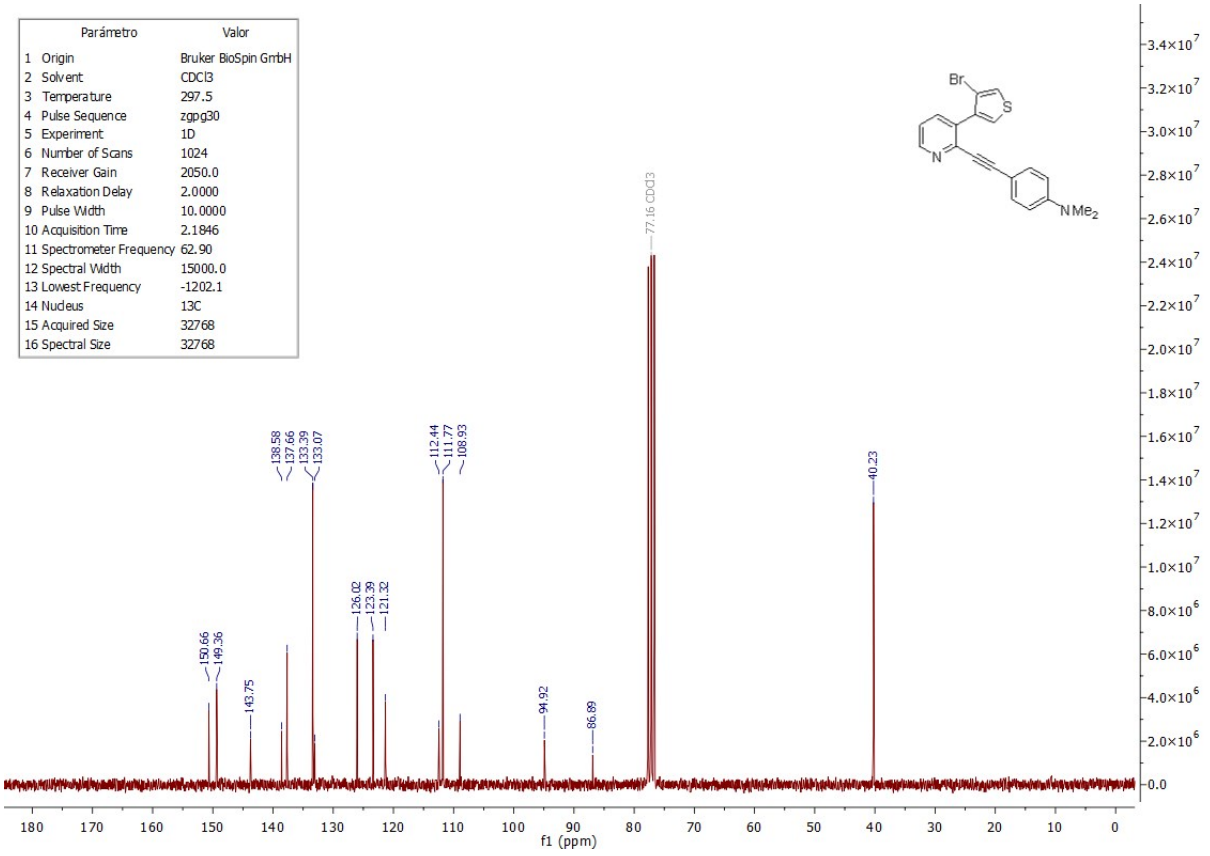


4-((3-(4-bromothiophen-3-yl)pyridin-2-yl)ethynyl)-*N*,*N*-dimethylaniline **6t**

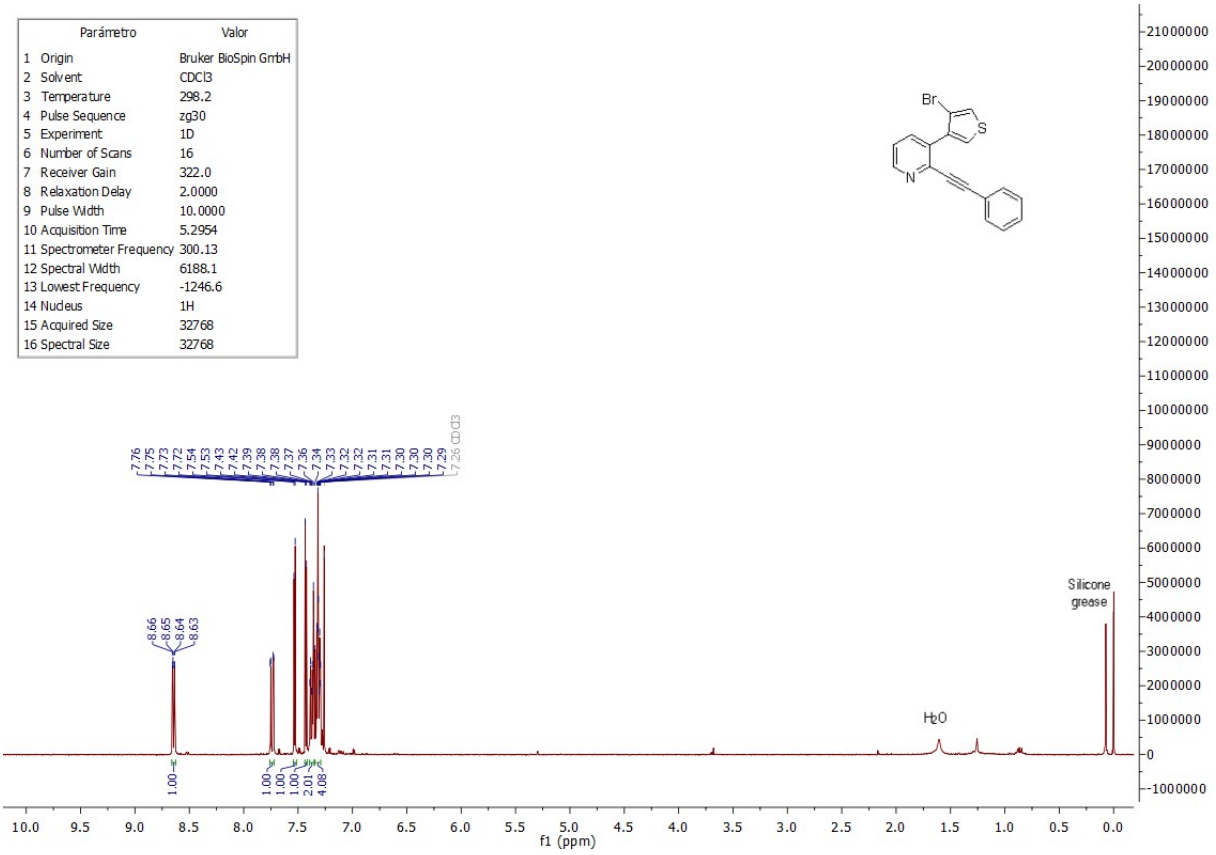
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	362.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.6
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768

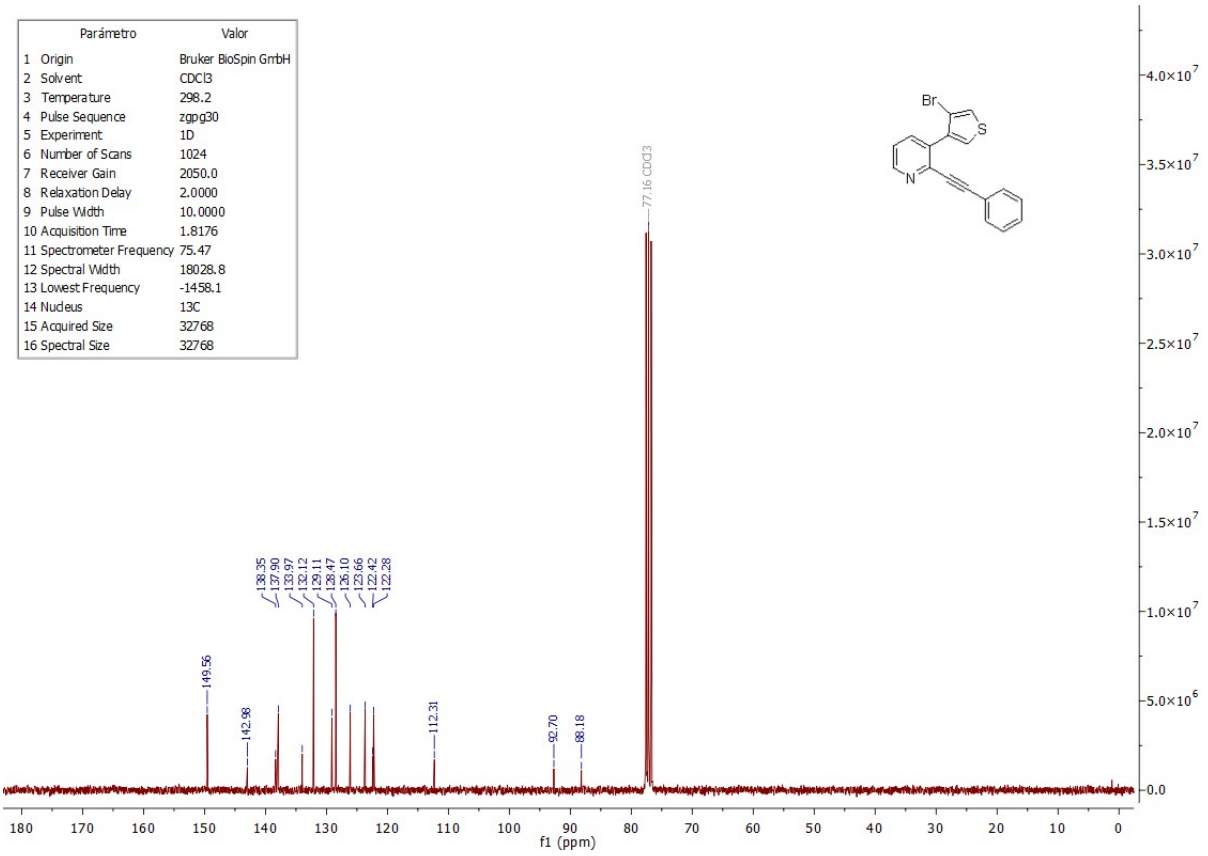


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.5
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1202.1
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



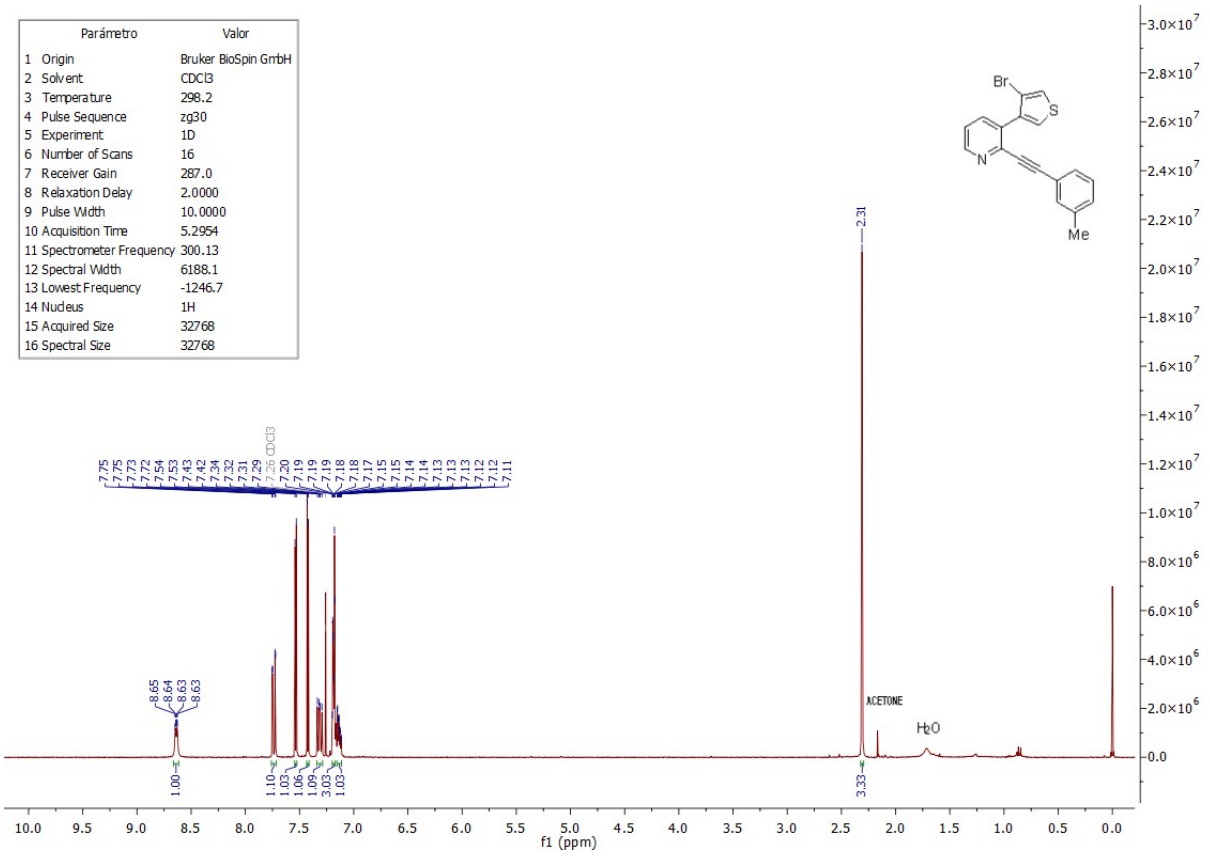
3-(4-bromothiophen-3-yl)-2-(phenylethynyl)pyridine **6u**



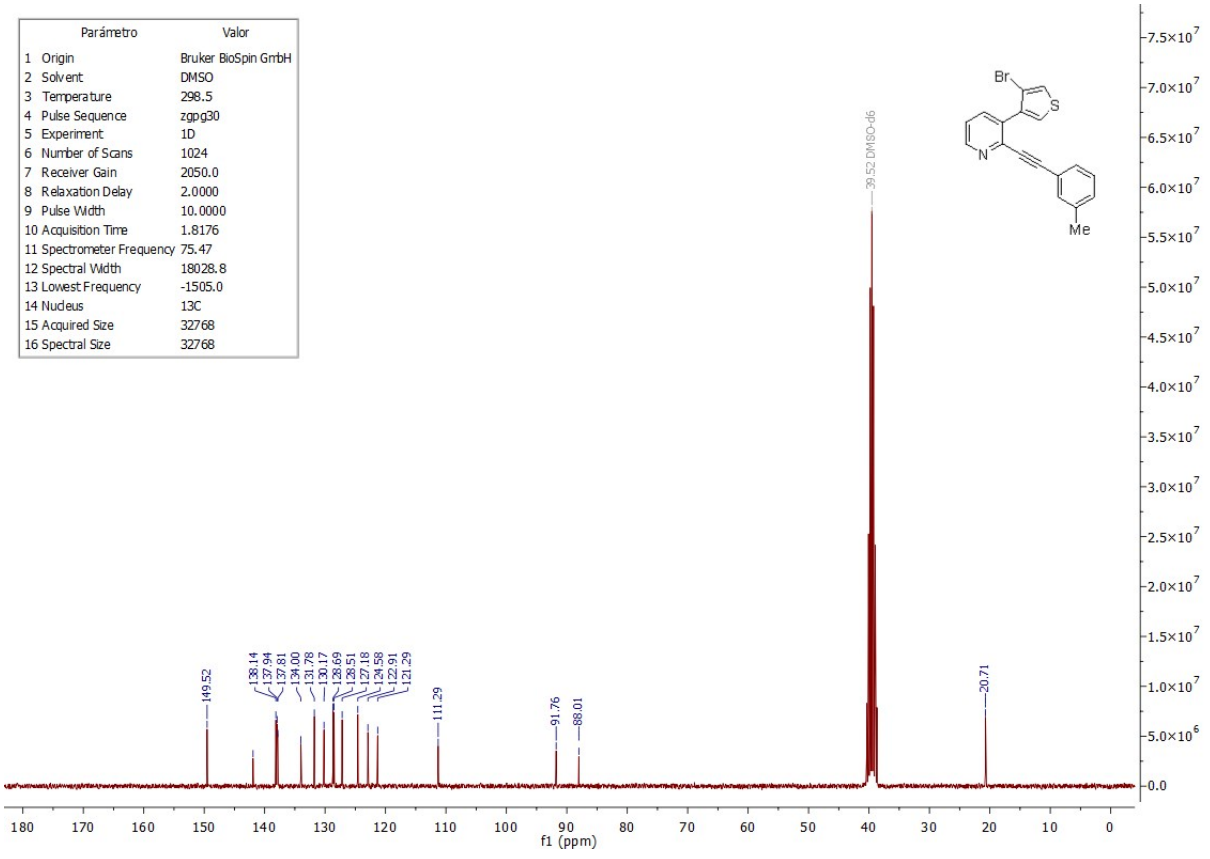


3-(4-bromothiophen-3-yl)-2-(*m*-tolylethynyl)pyridine **6v**

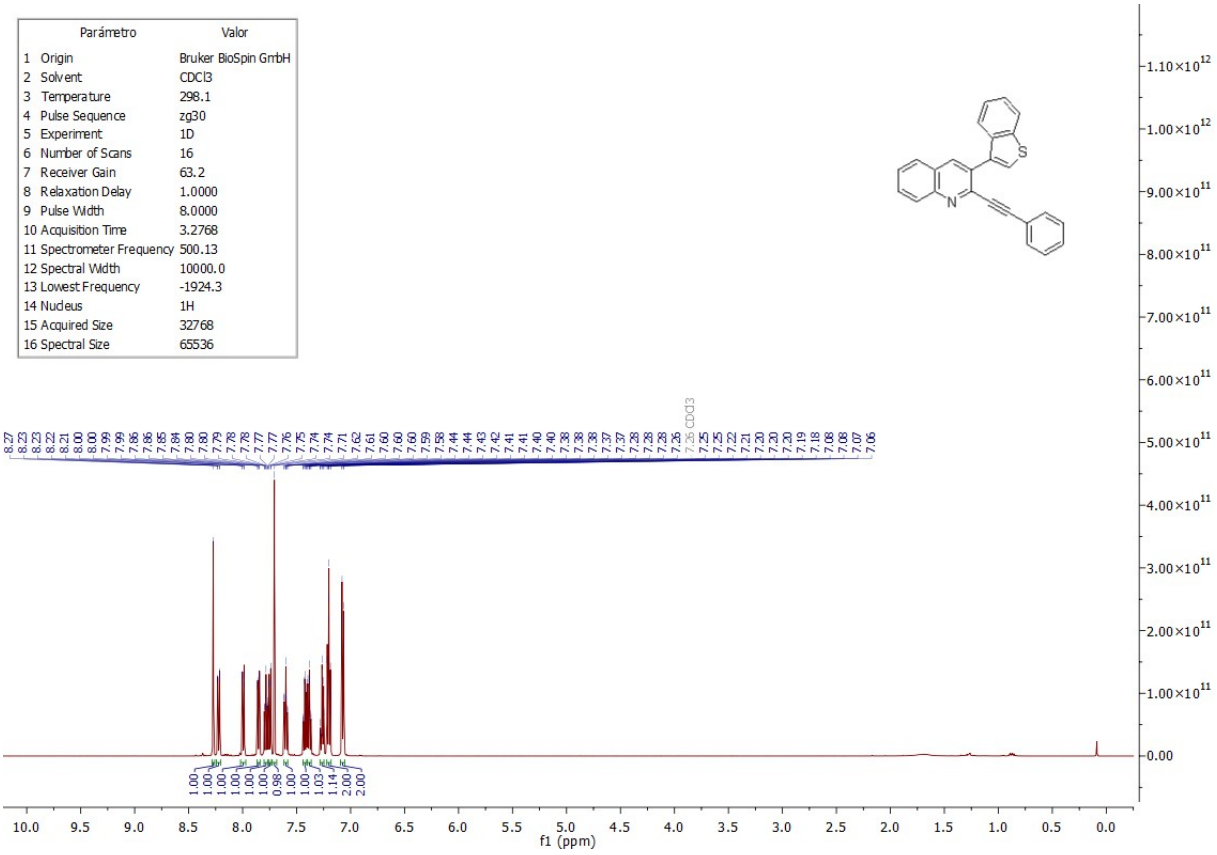
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	287.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1246.7
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768

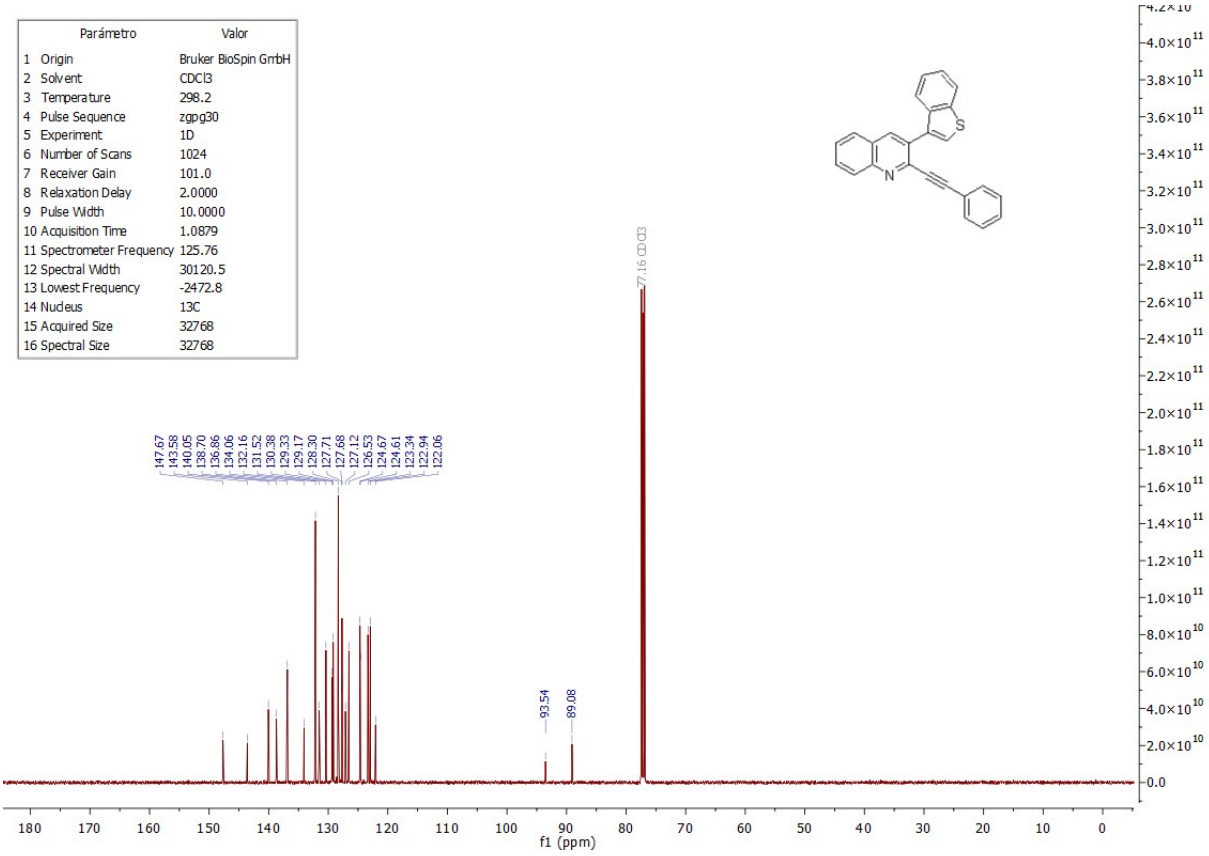


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	DMSO
3 Temperature	298.5
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1505.0
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



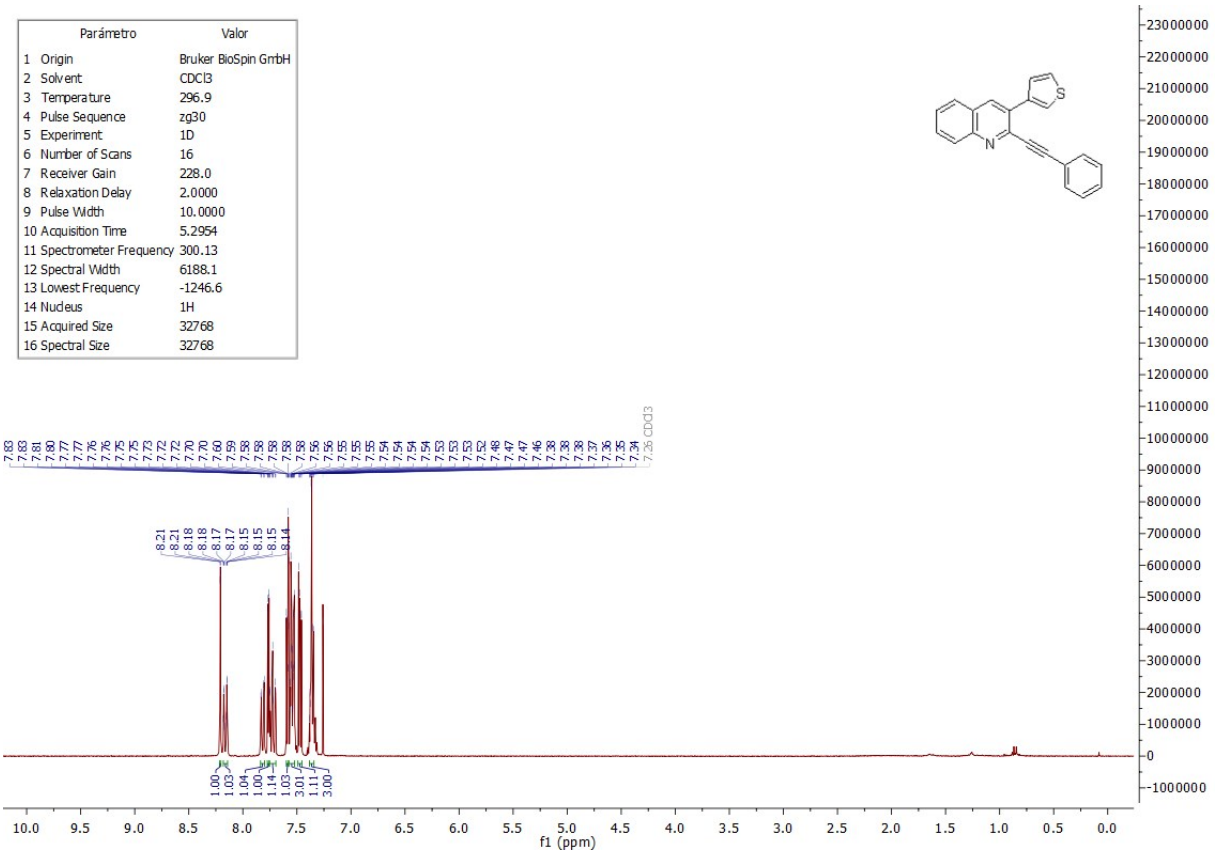
3-(benzo*[b]*thiophen-3-yl)-2-(phenylethynyl)quinoline **6w**



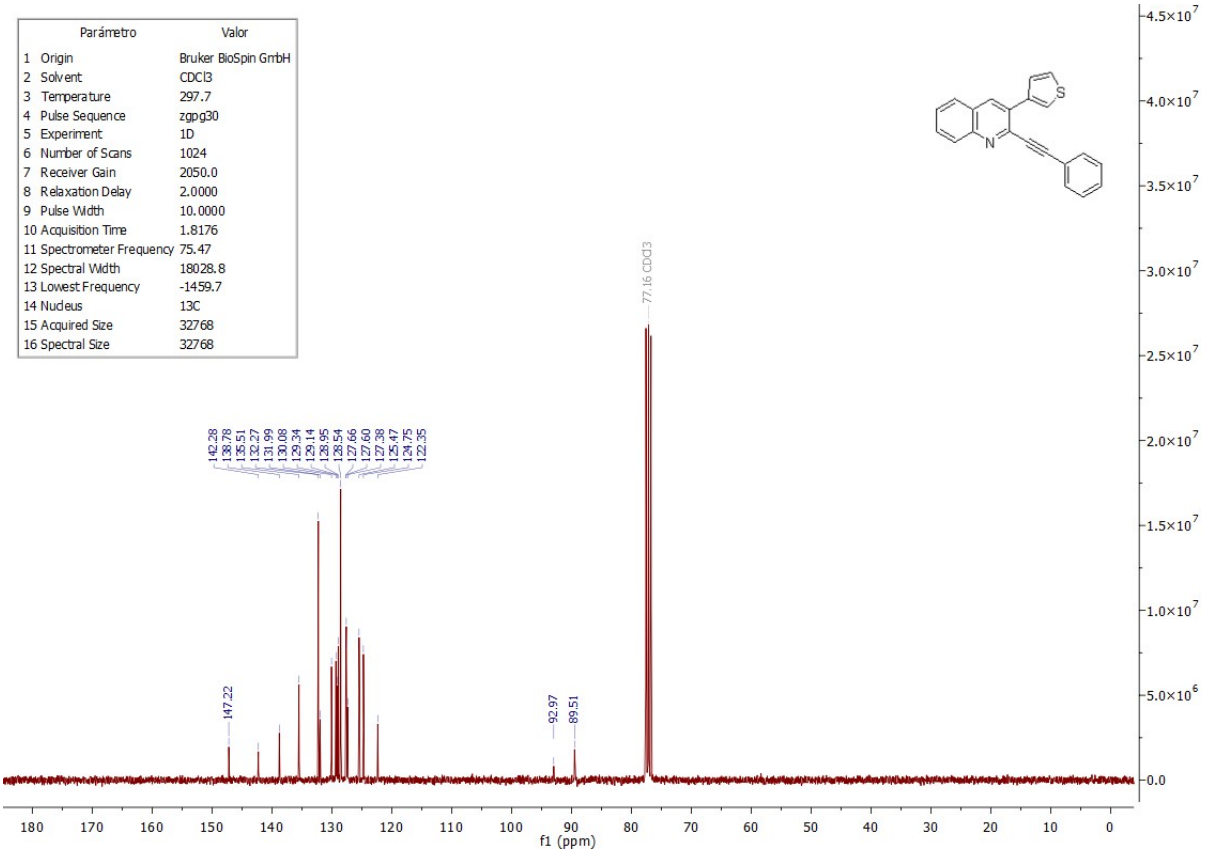


2-(phenylethynyl)-3-(thiophen-3-yl)quinoline **6x**

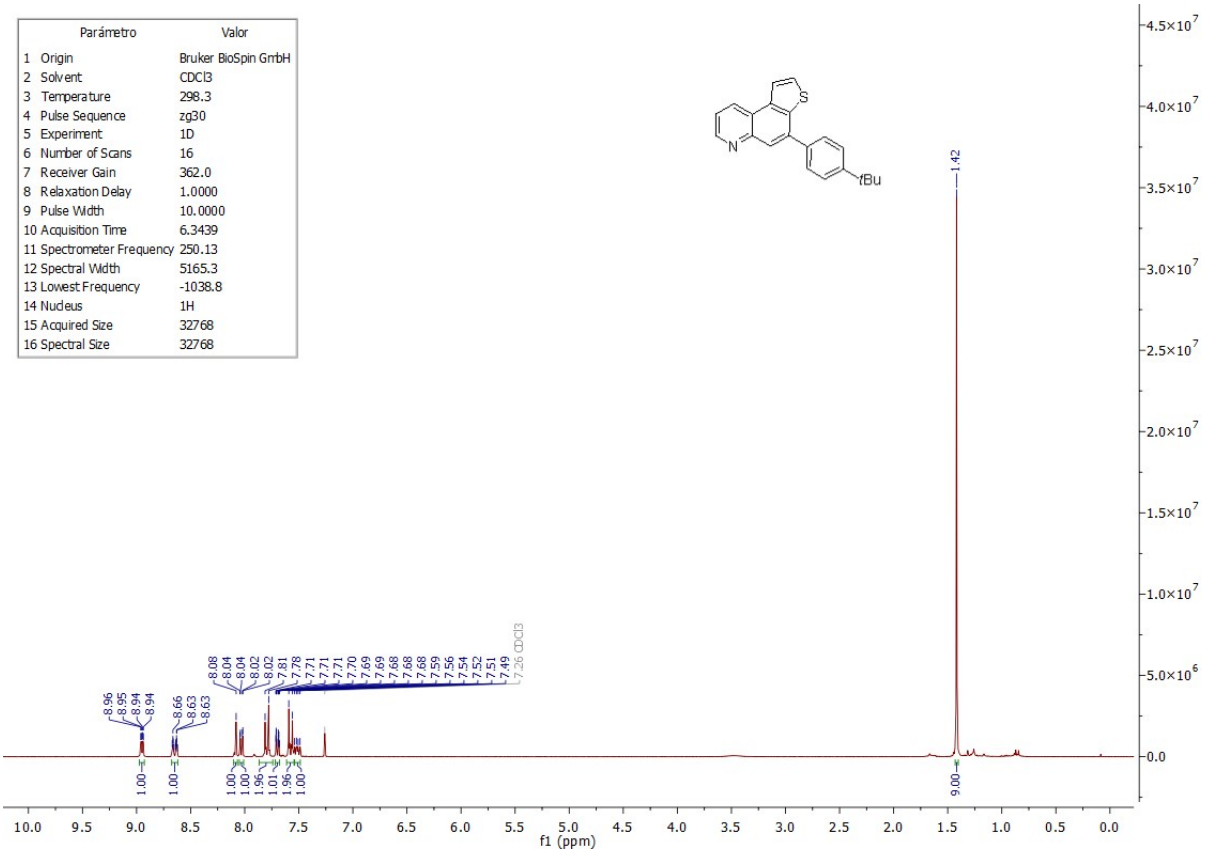
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.9
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	228.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1246.6
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768

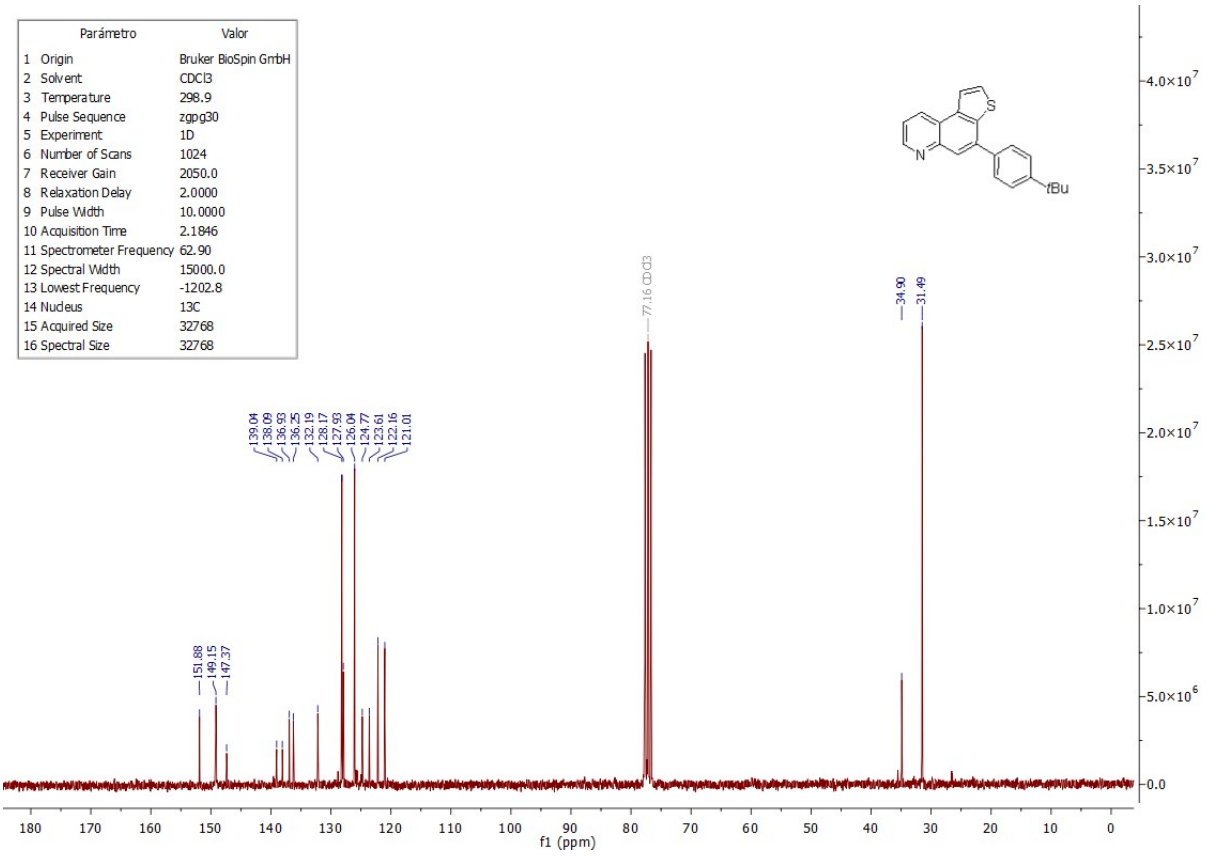


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.7
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1459.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



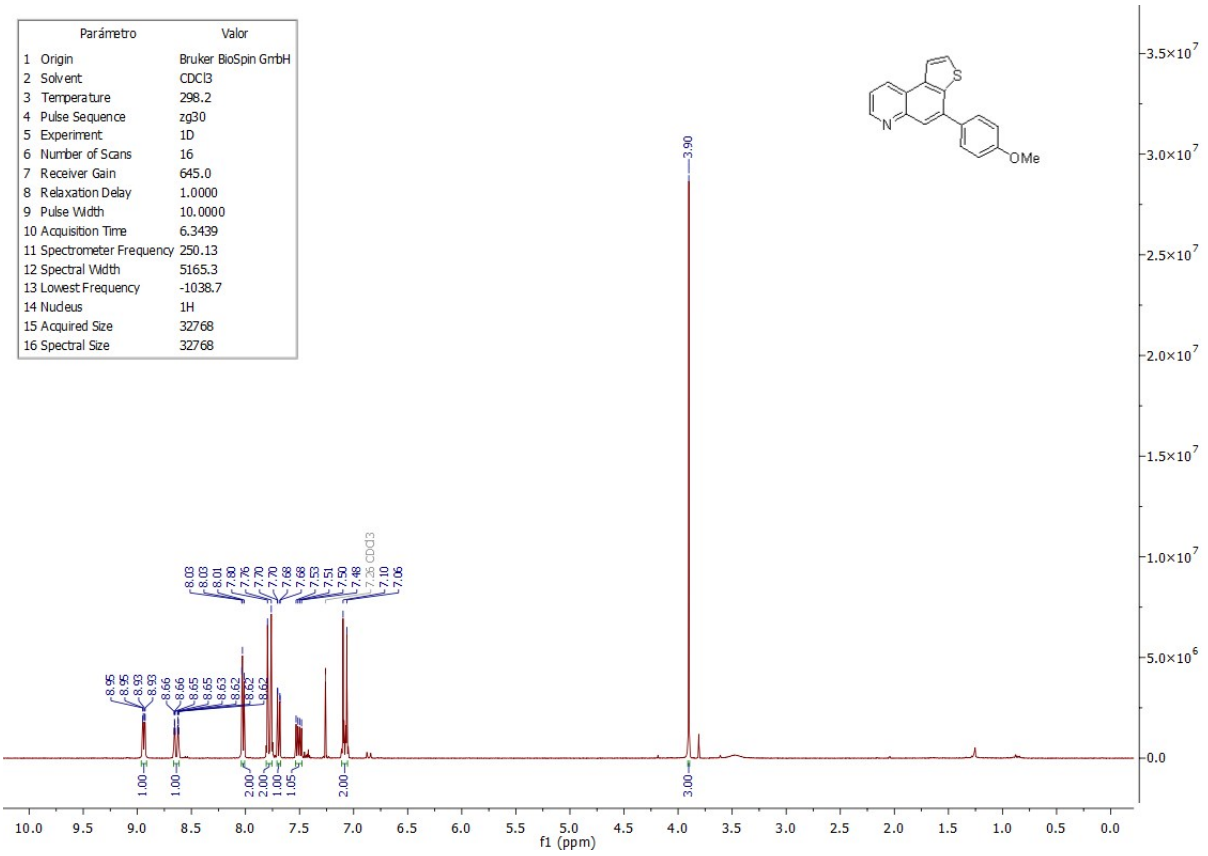
4-(4-(*tert*-butyl)phenyl)thieno[3,2-*f*]quinoline **7a**



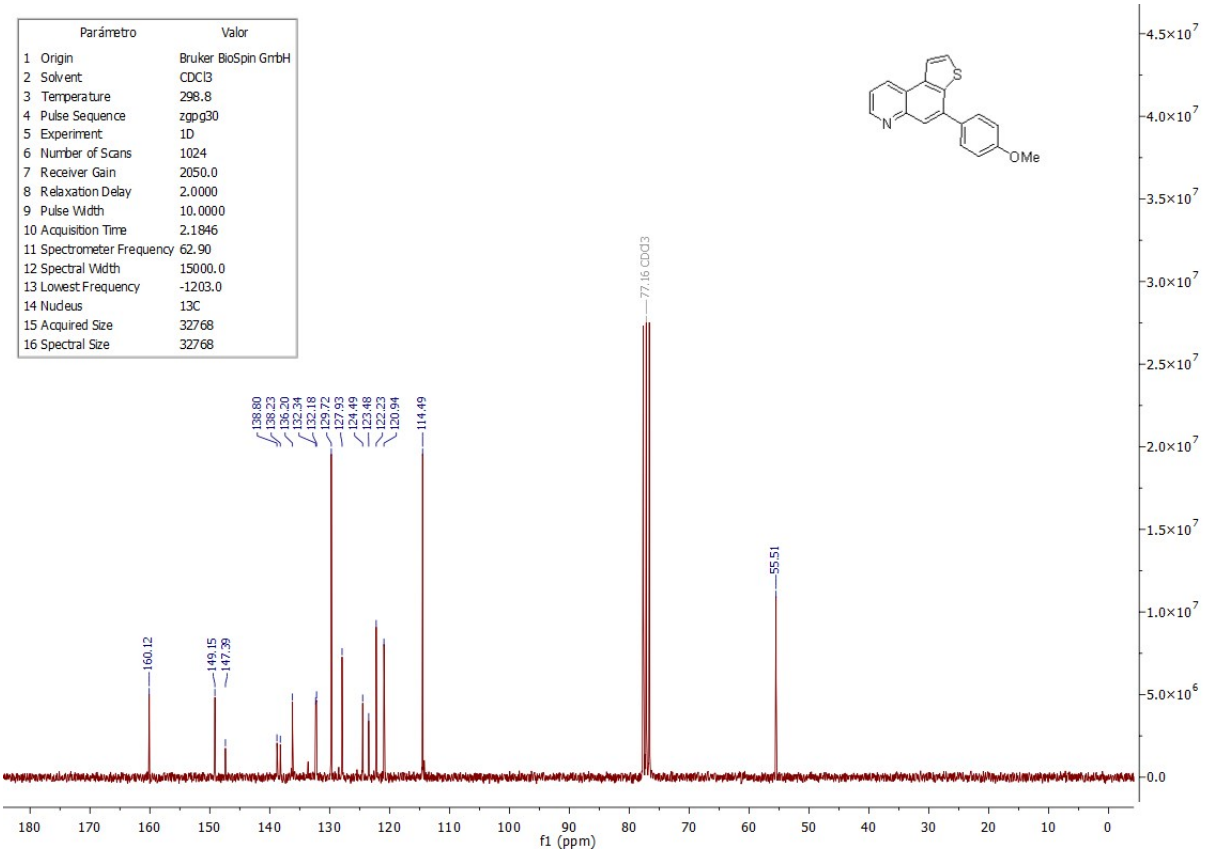


4-(4-methoxyphenyl)thieno[3,2-*f*]quinoline **7b**

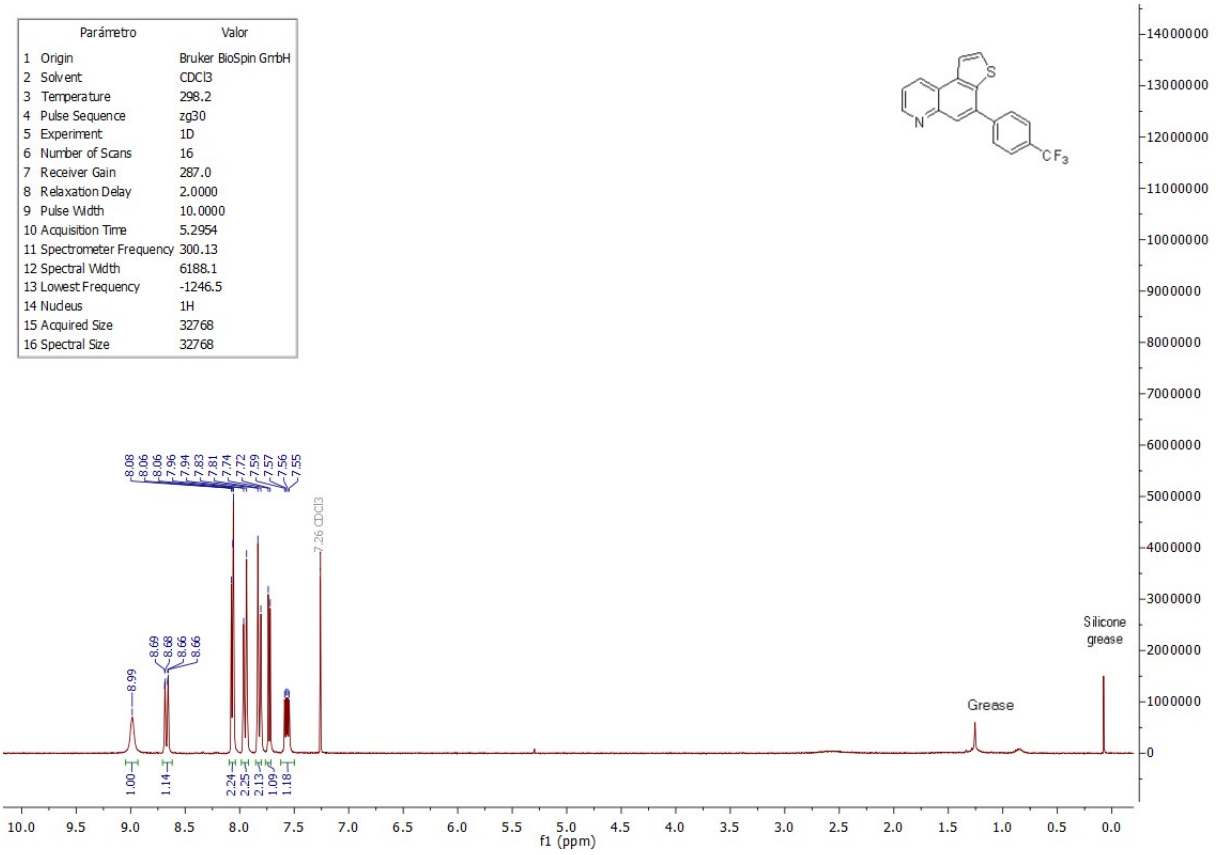
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	645.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.7
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768



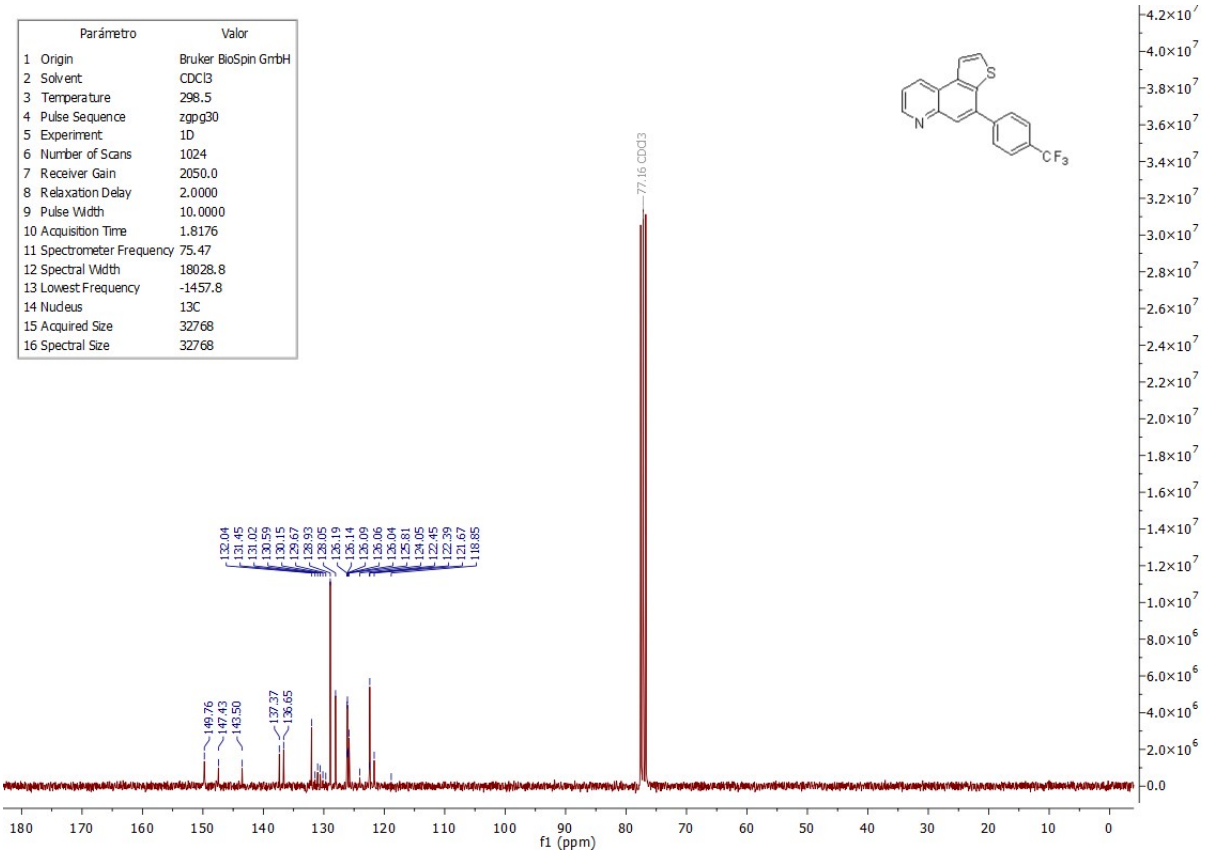
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.8
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1203.0
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



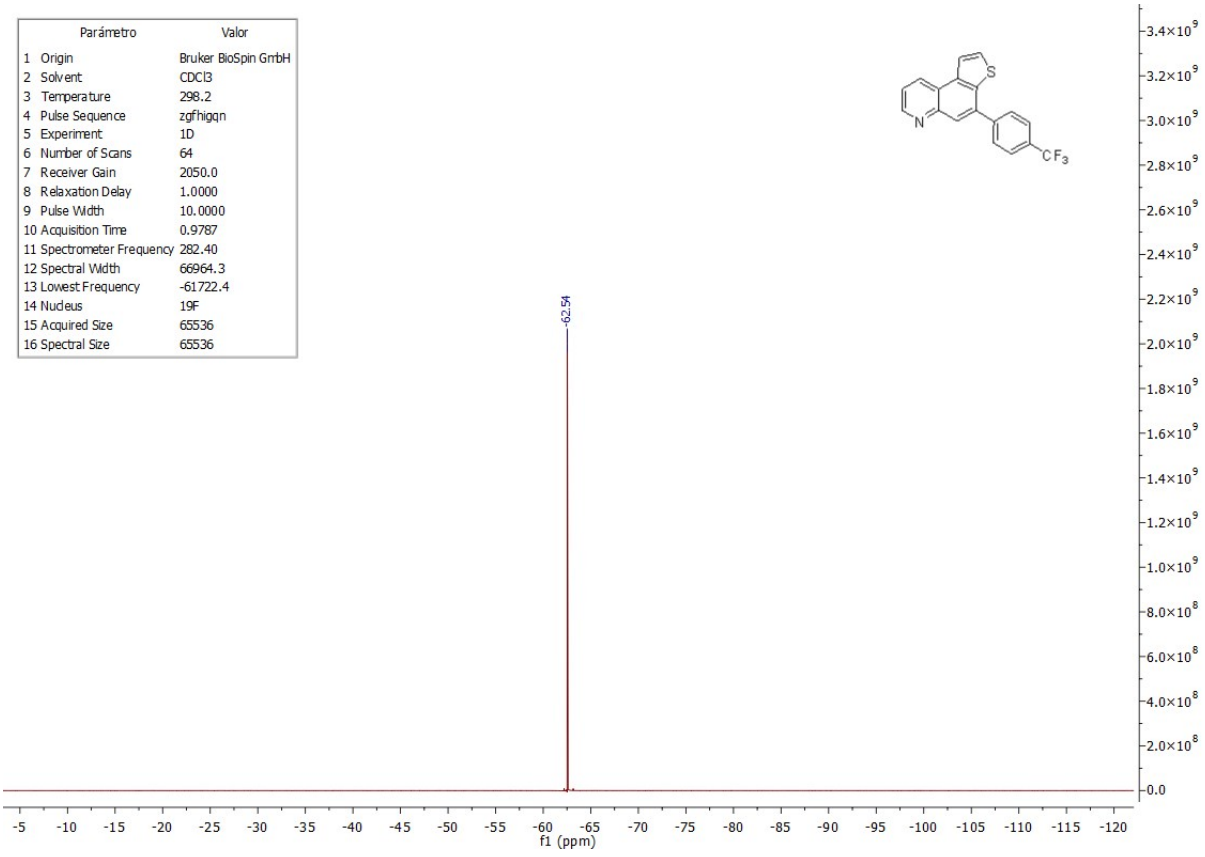
4-(4-(trifluoromethyl)phenyl)thieno[3,2-*f*]quinoline **7c**



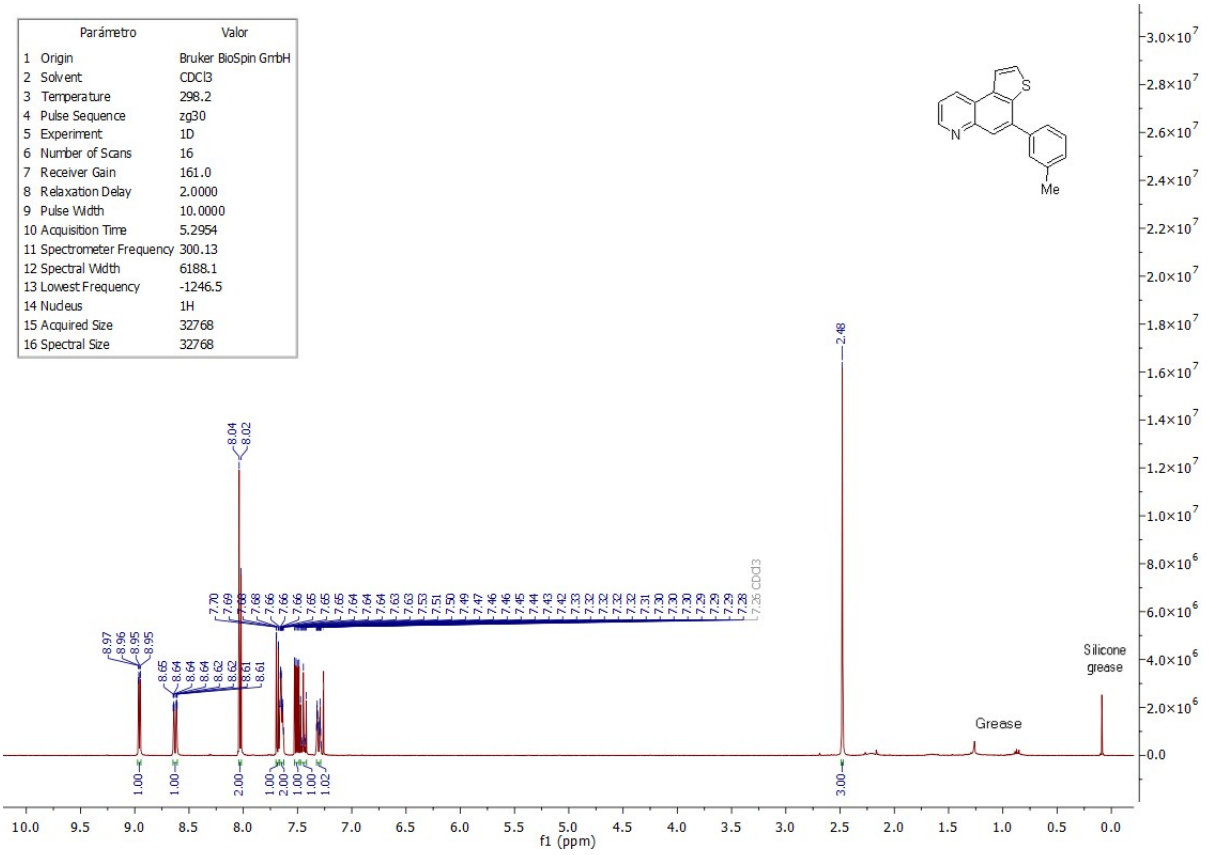
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.5
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1457.8
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768

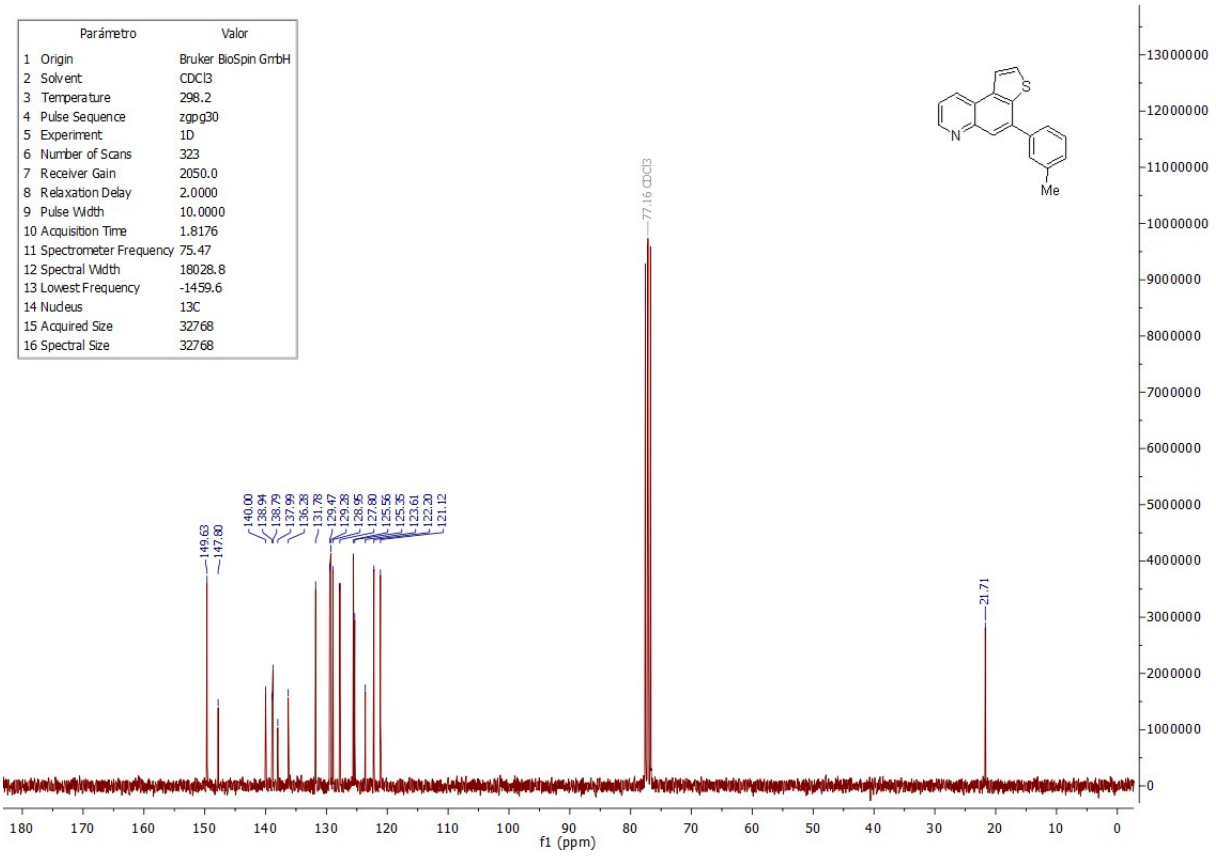


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgfhigqn
5 Experiment	1D
6 Number of Scans	64
7 Receiver Gain	2050.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	0.9787
11 Spectrometer Frequency	282.40
12 Spectral Width	66964.3
13 Lowest Frequency	-61722.4
14 Nucleus	19F
15 Acquired Size	65536
16 Spectral Size	65536

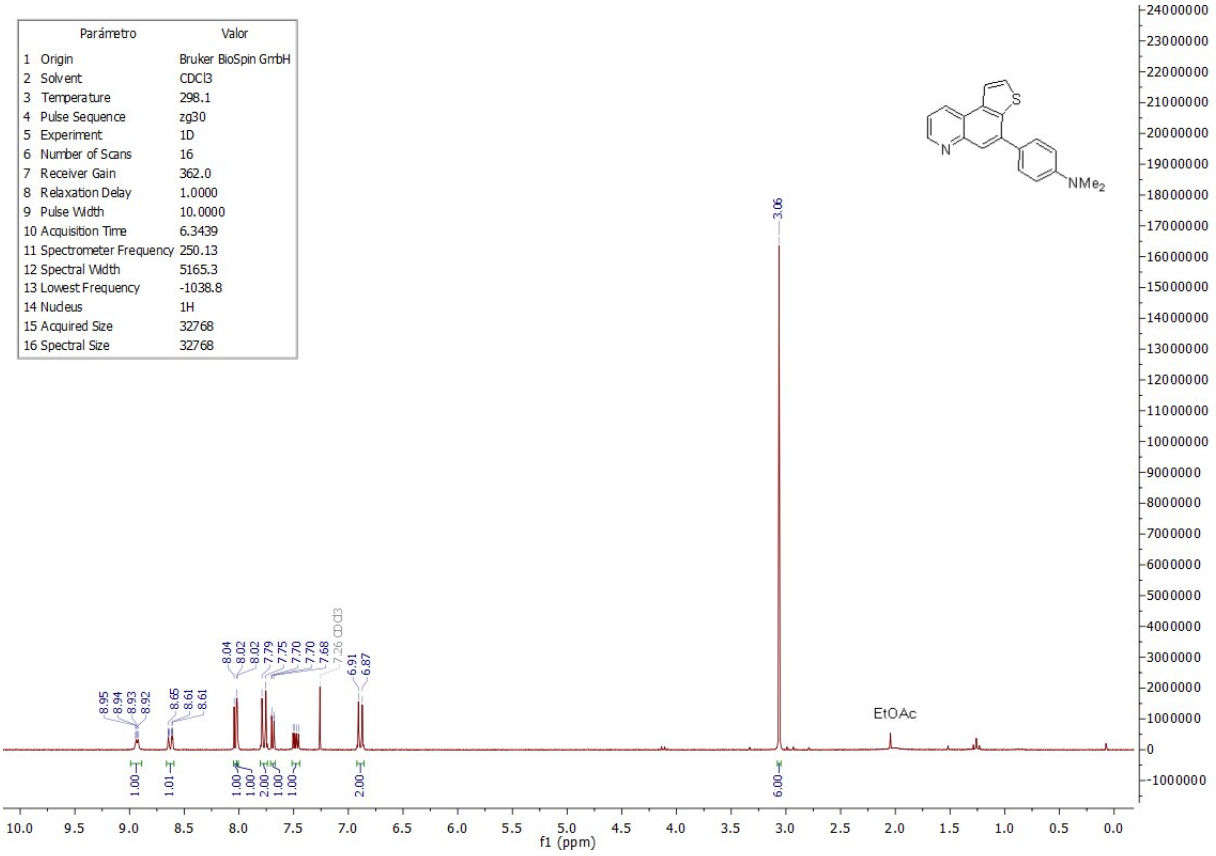


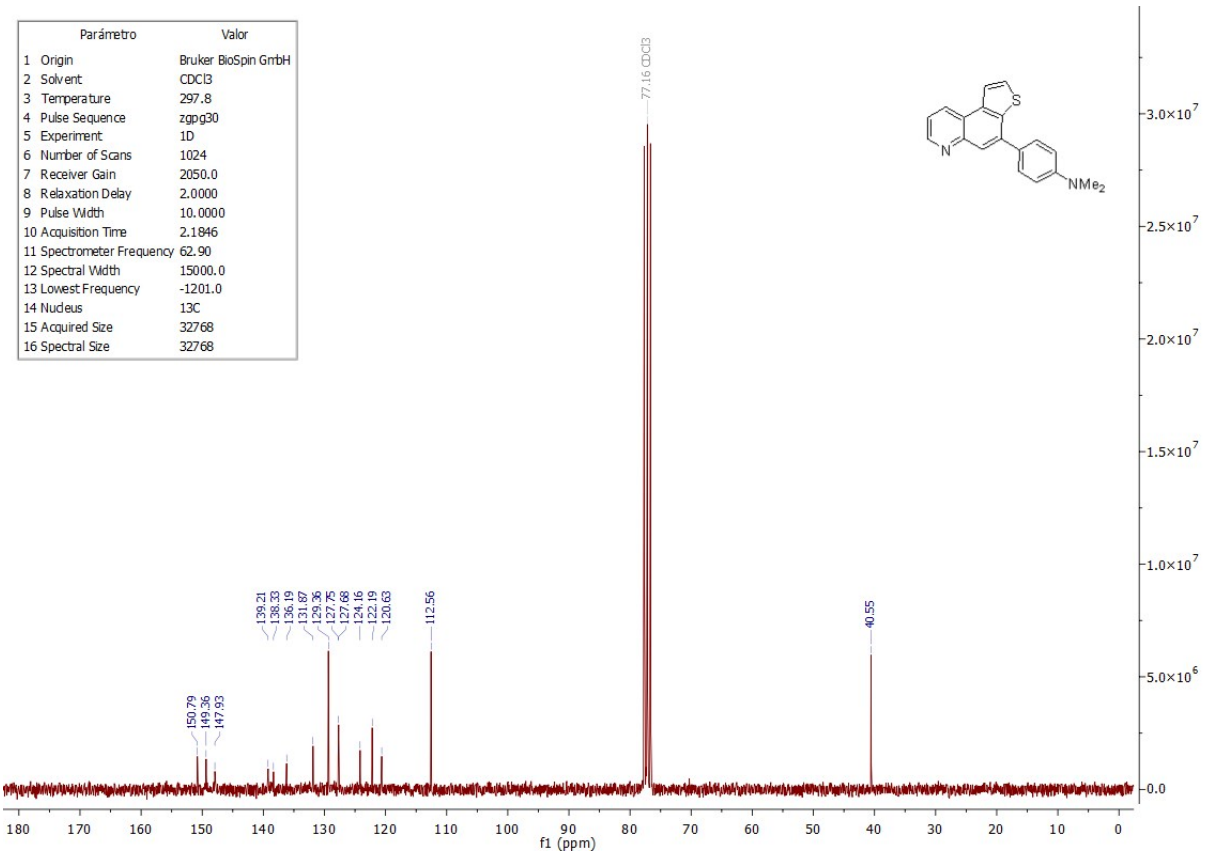
4-(*m*-tolyl)thieno[3,2-*f*]quinoline **7e**





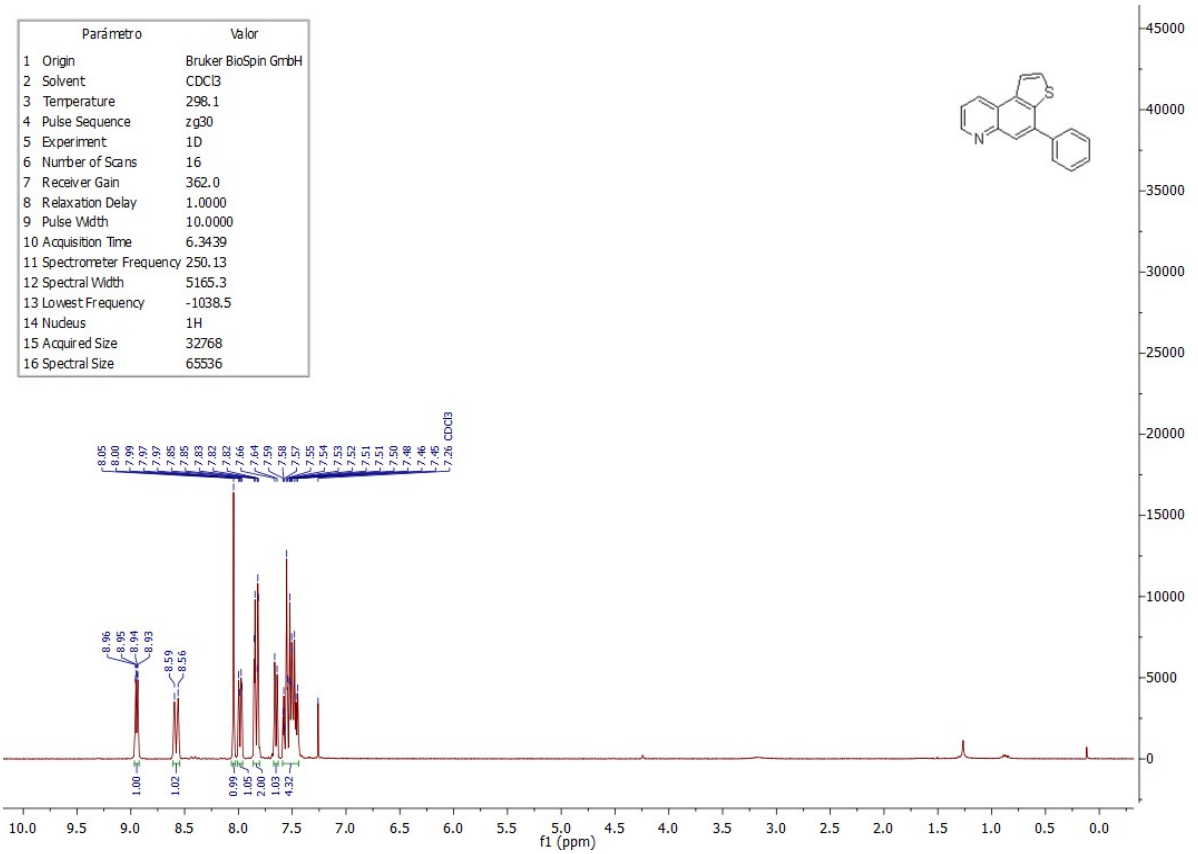
N,*N*-dimethyl-4-(thieno[3,2-*f*]quinolin-4-yl)aniline **7f**



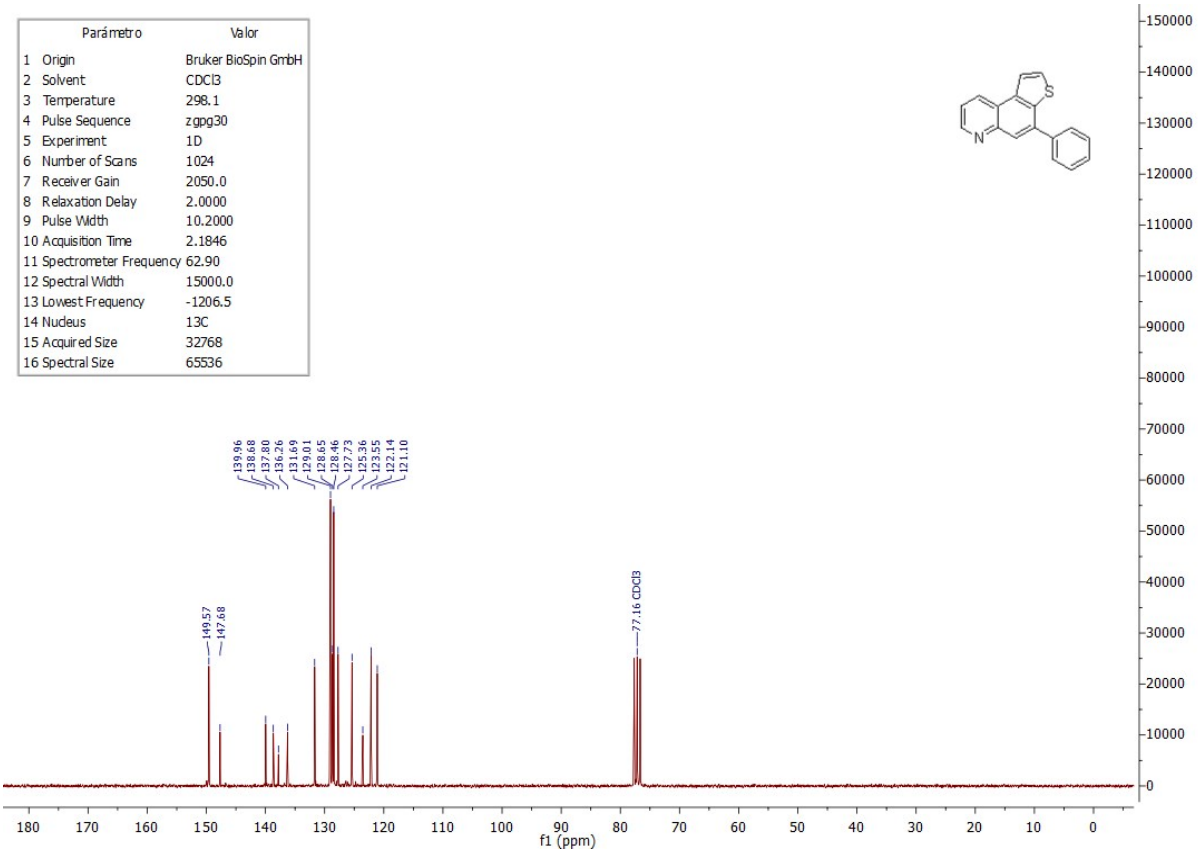


4-phenylthieno[3,2-*f*]quinoline **7g**

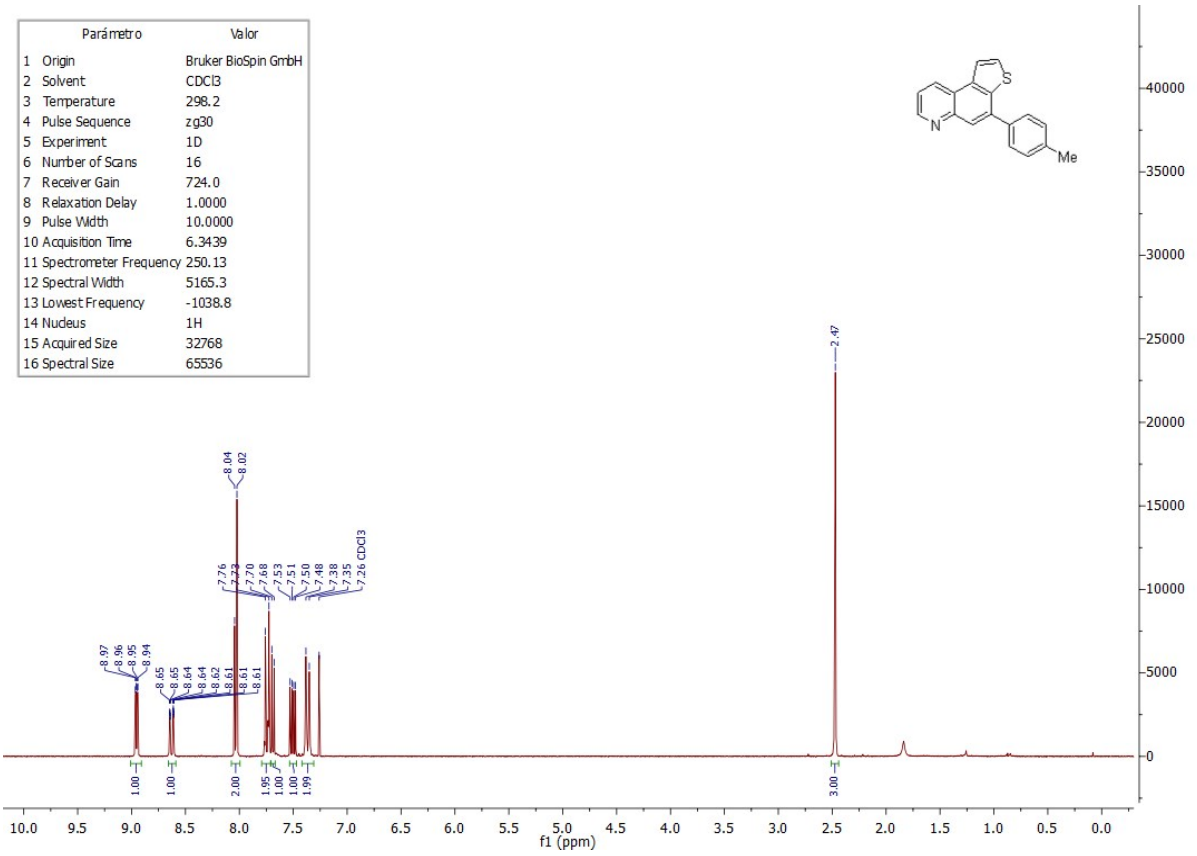
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	362.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.5
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536

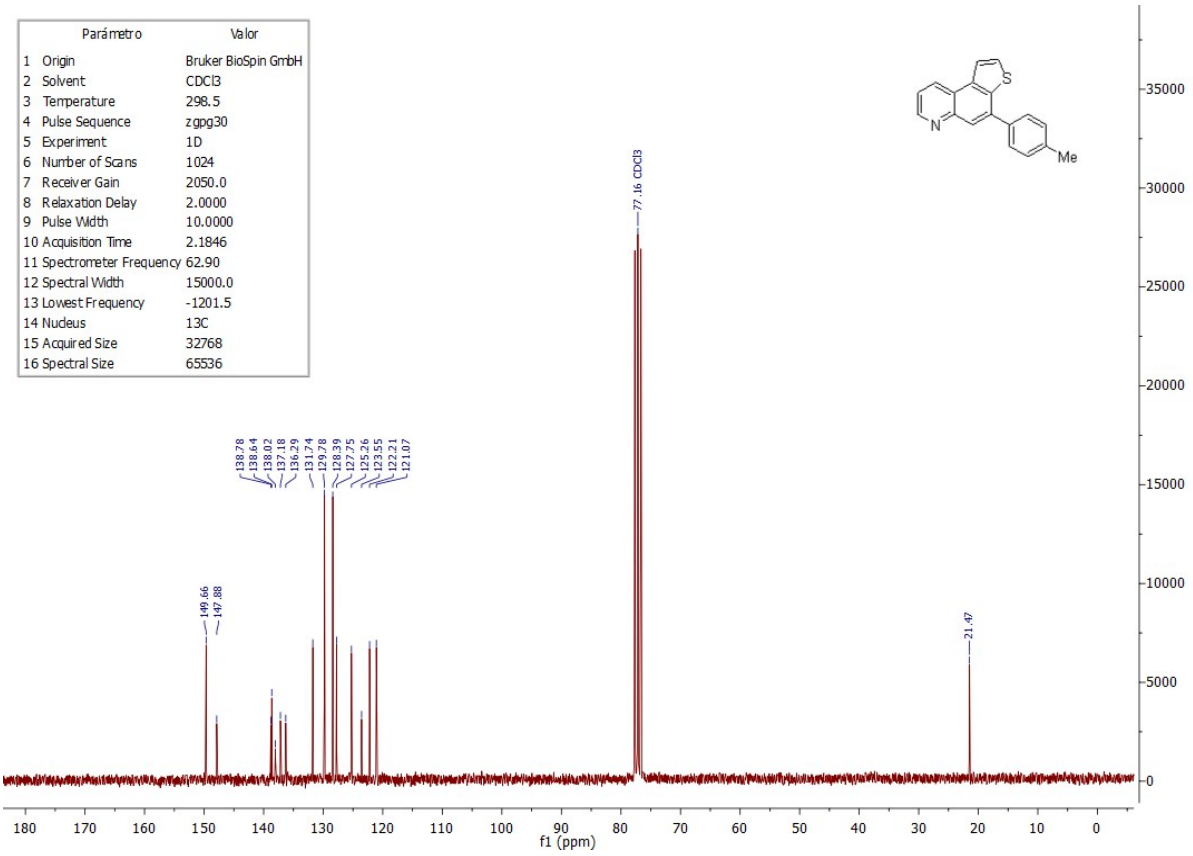


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.2000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1206.5
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	65536



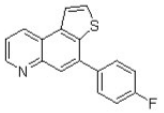
4-(*p*-tolyl)thieno[3,2-*f*]quinoline **7h**

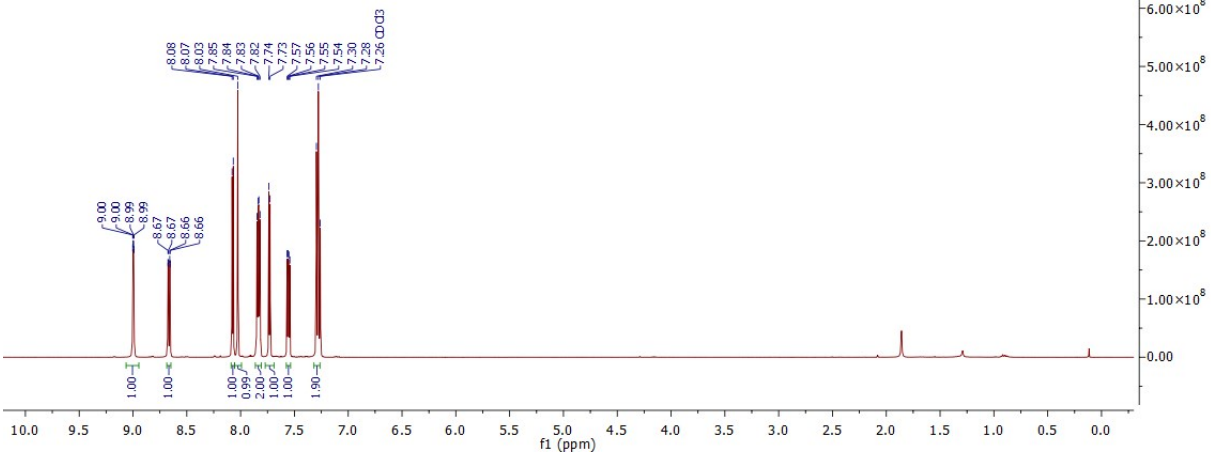




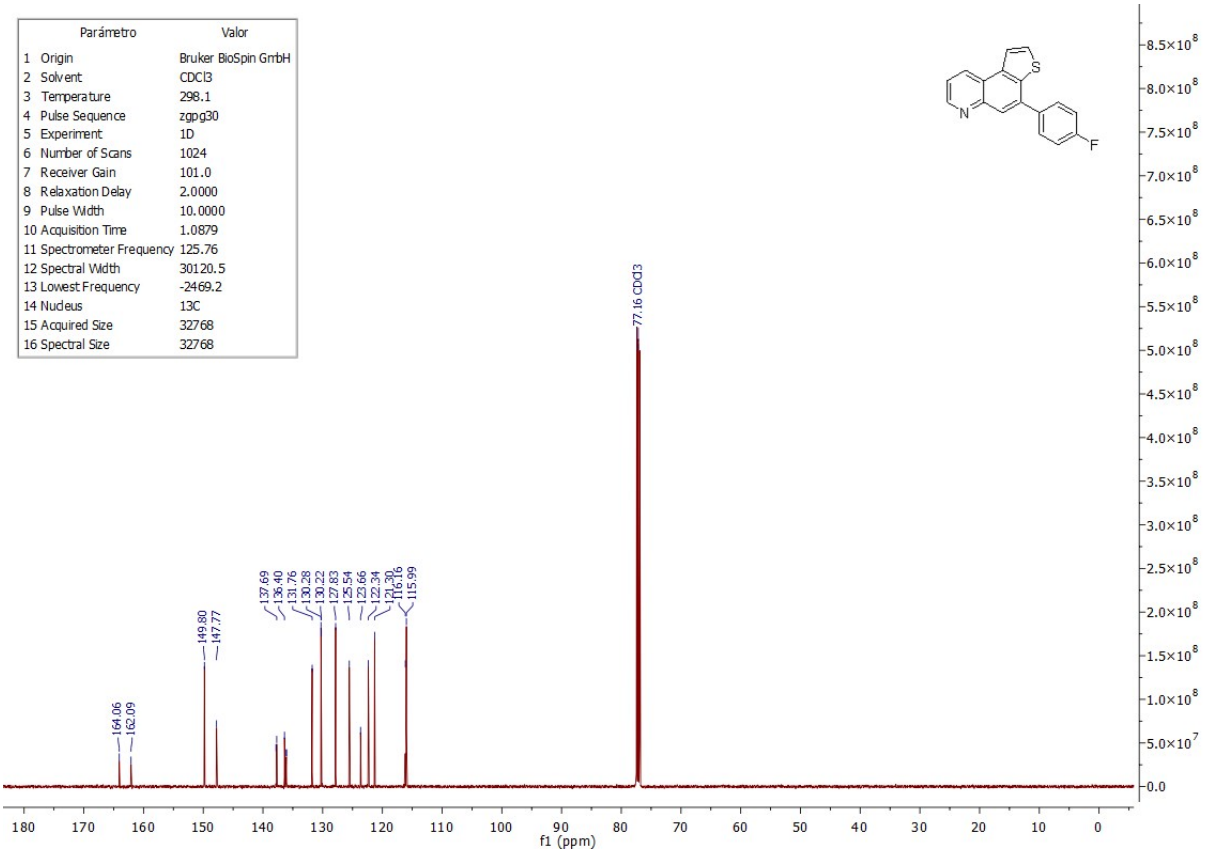
4-(4-fluorophenyl)thieno[3,2-*f*]quinoline **7i**

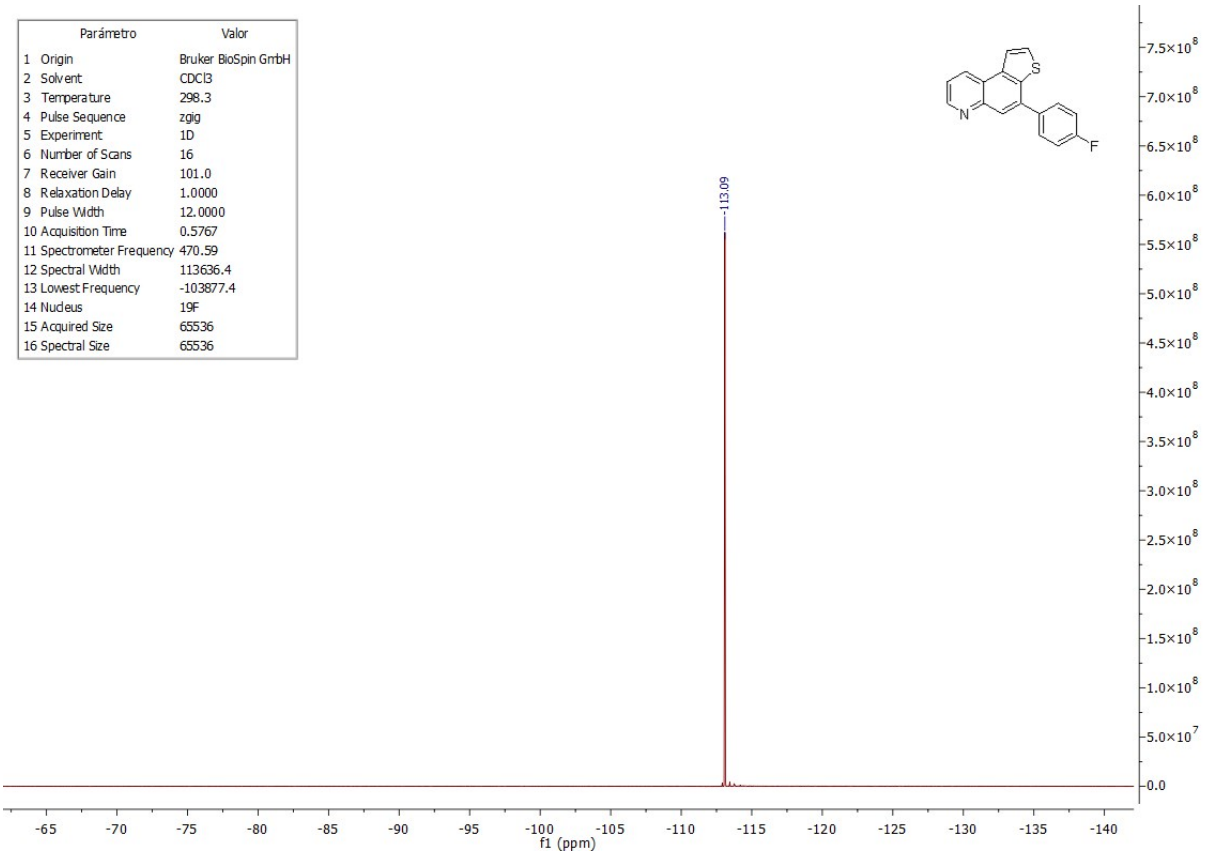
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	101.0
8 Relaxation Delay	1.0000
9 Pulse Width	8.0000
10 Acquisition Time	3.2768
11 Spectrometer Frequency	500.13
12 Spectral Width	10000.0
13 Lowest Frequency	-1906.0
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536





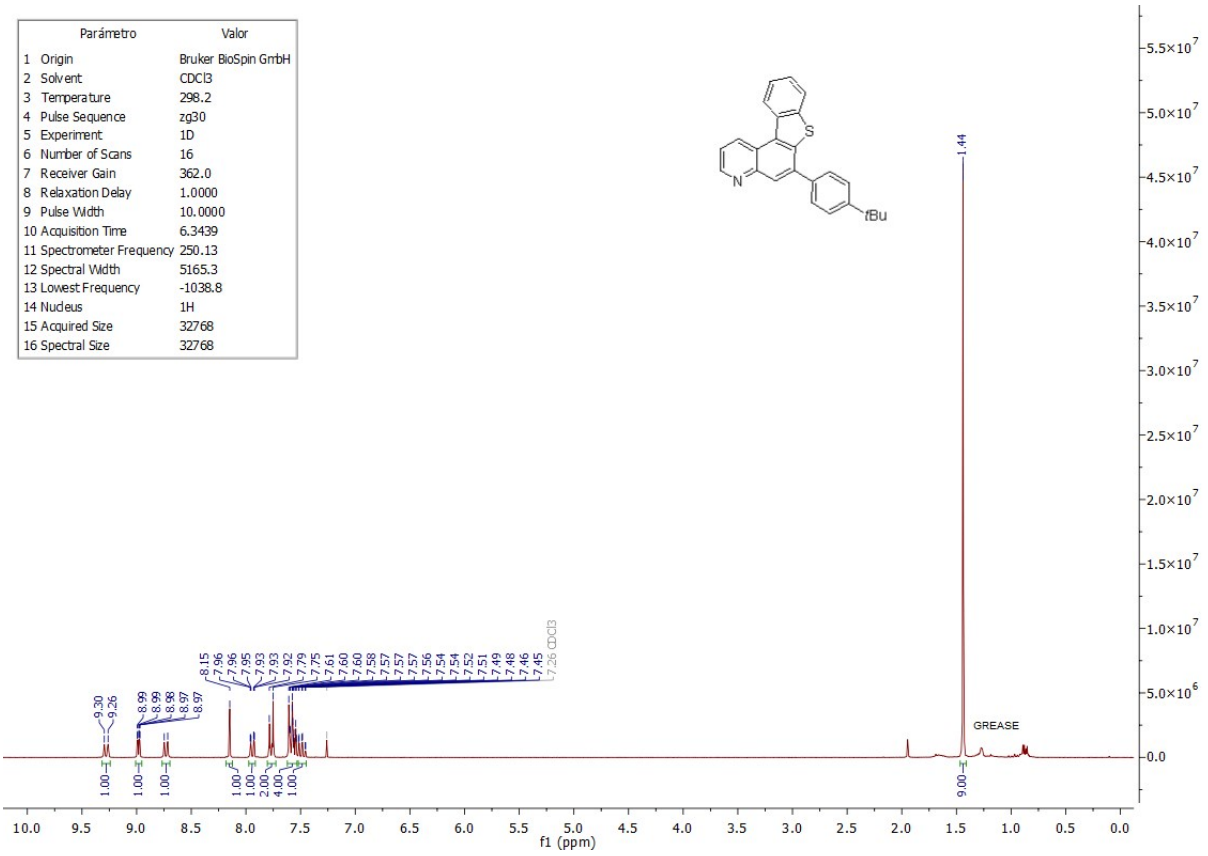
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	101.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.0879
11 Spectrometer Frequency	125.76
12 Spectral Width	30120.5
13 Lowest Frequency	-2469.2
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



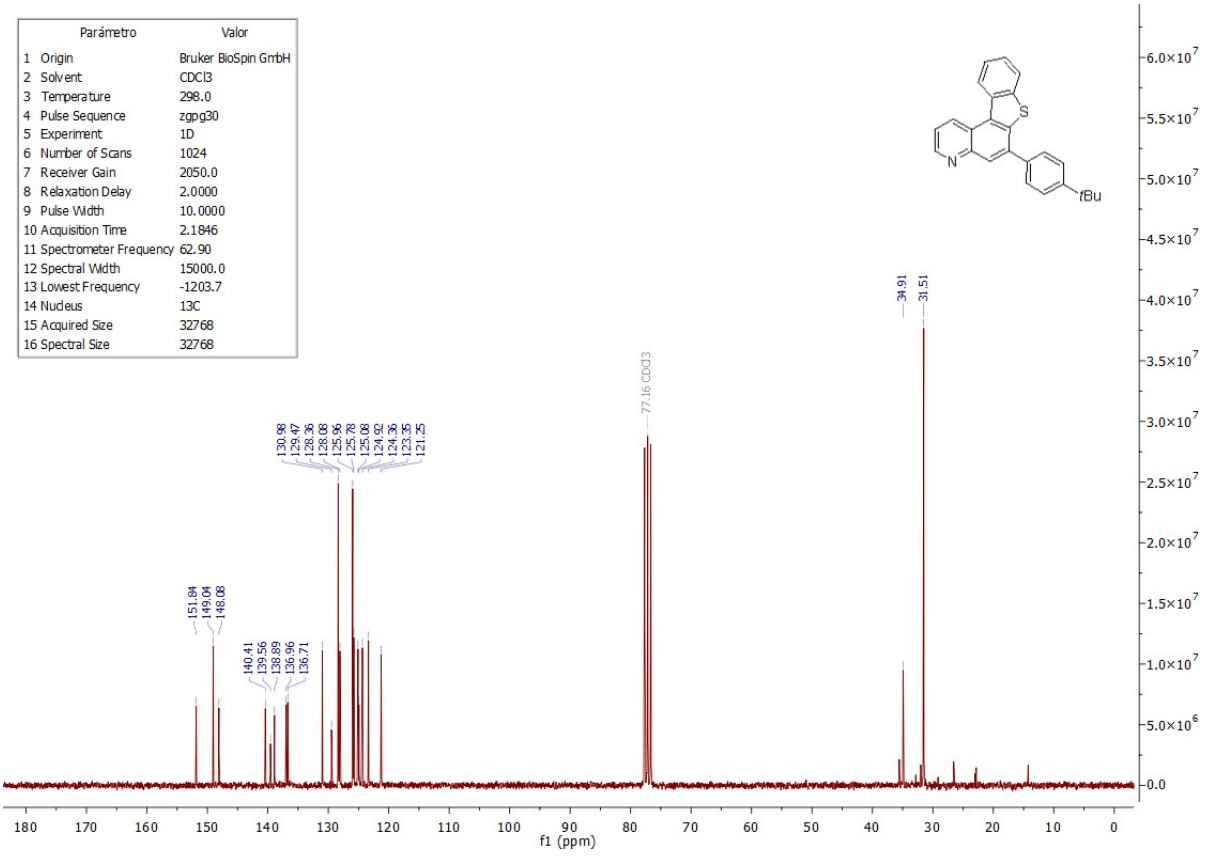


6-(4-(*tert*-butyl)phenyl)benzo[4,5]thieno[3,2-*f*]quinoline **7k**

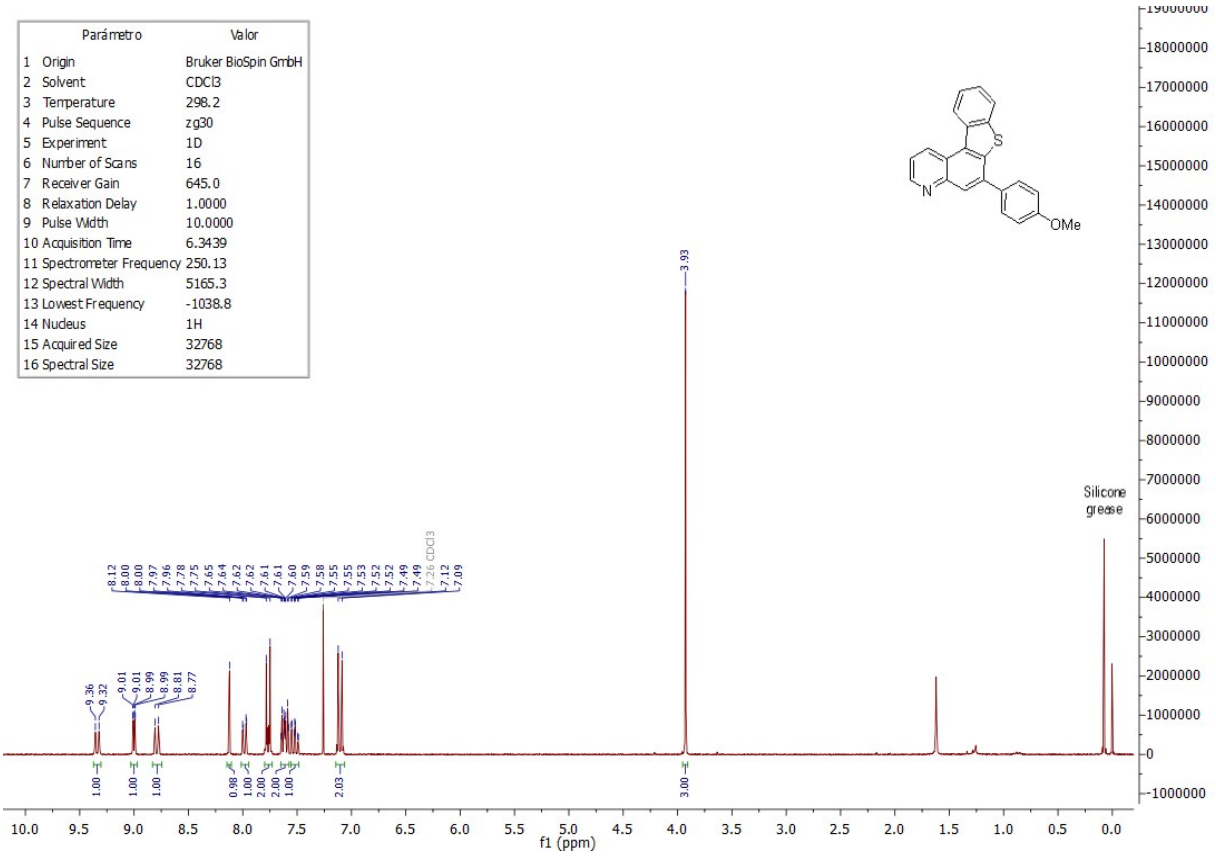
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	362.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.8
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768

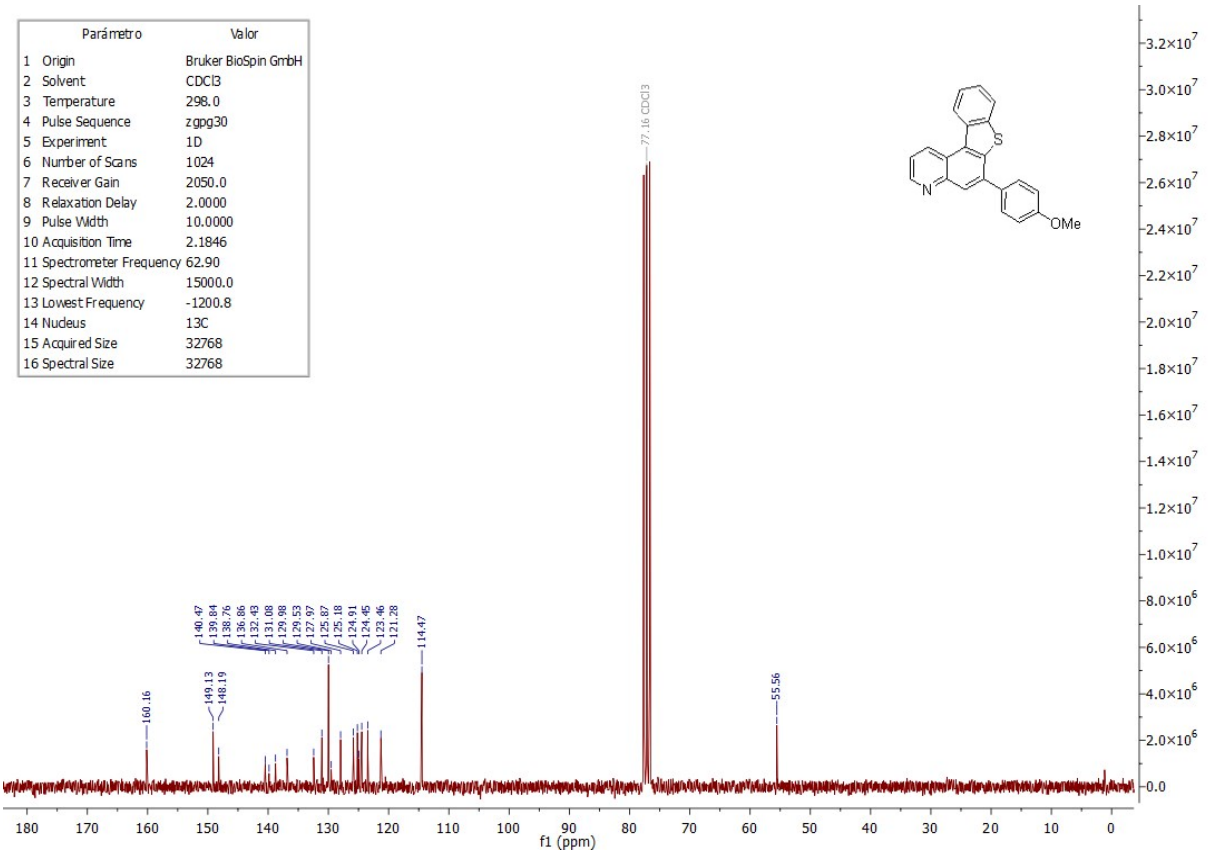


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1203.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



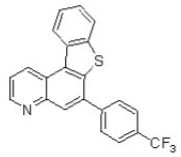
6-(4-methoxyphenyl)benzo[4,5]thieno[3,2-*f*]quinoline **7l**

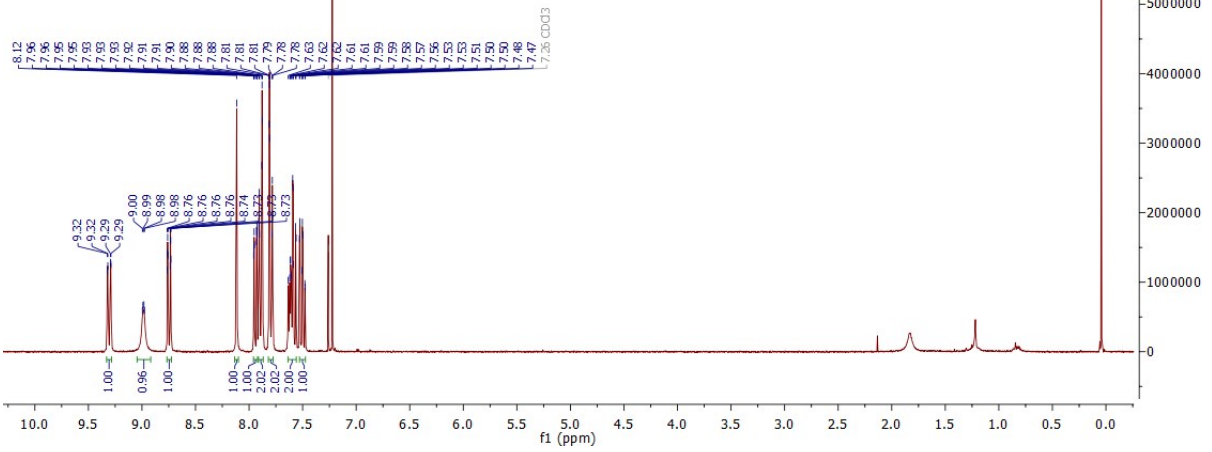




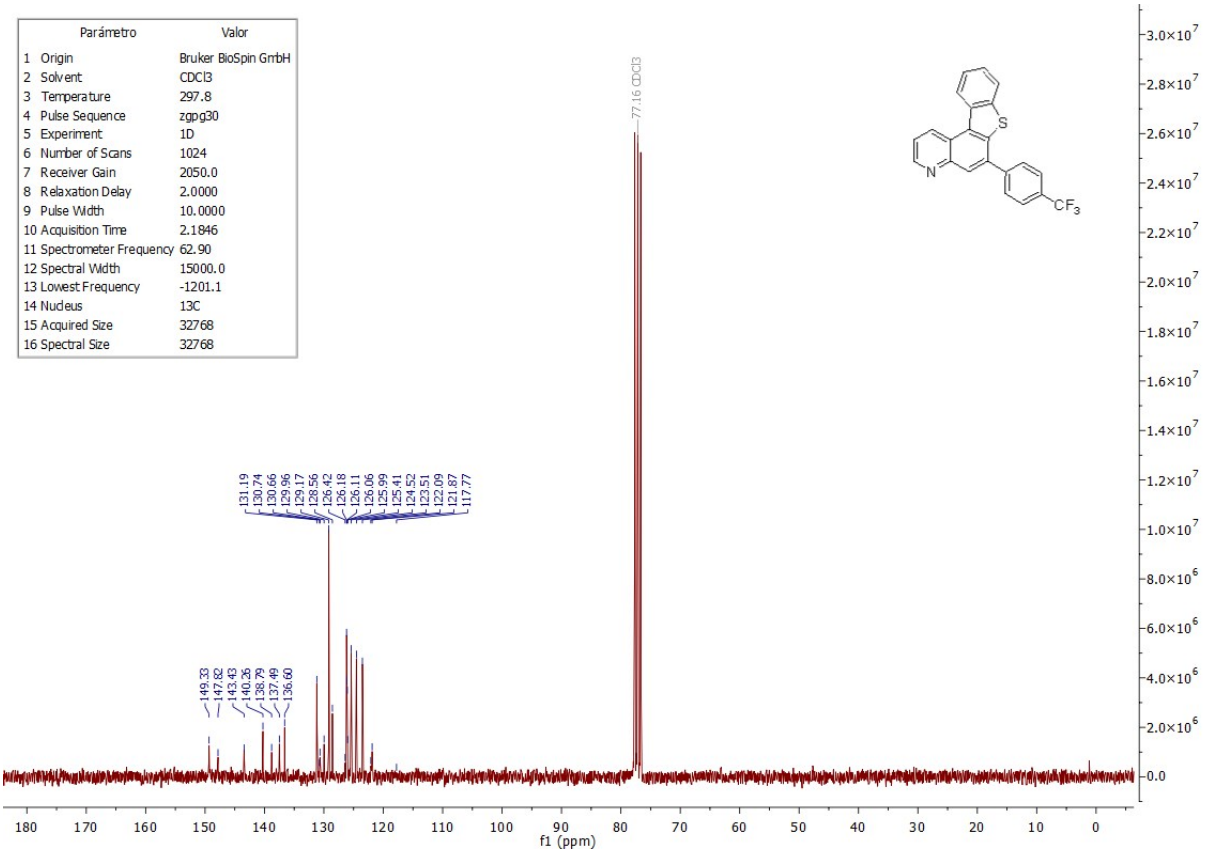
6-(4-(trifluoromethyl)phenyl)benzo[4,5]thieno[3,2-*f*]quinoline **7m**

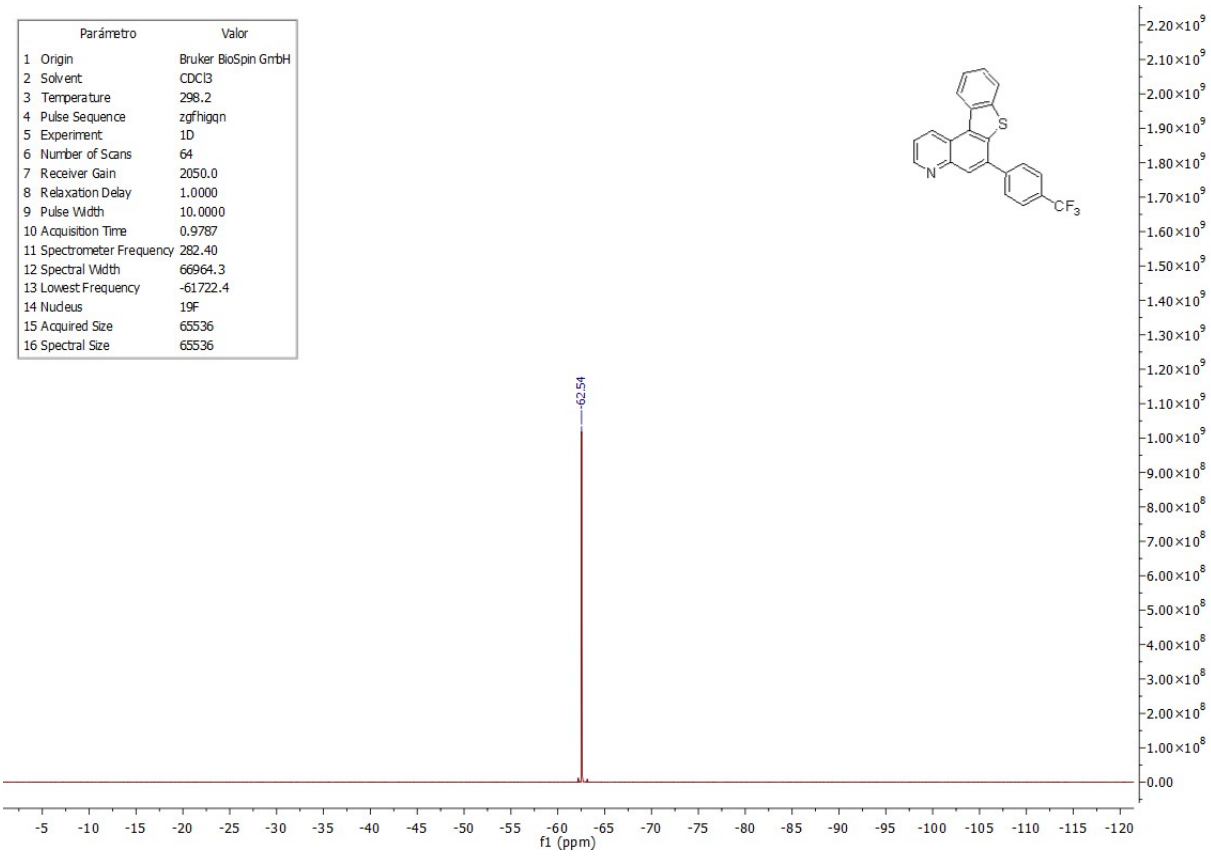
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	256.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1257.7
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768





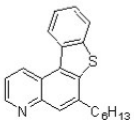
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.8
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1201.1
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768

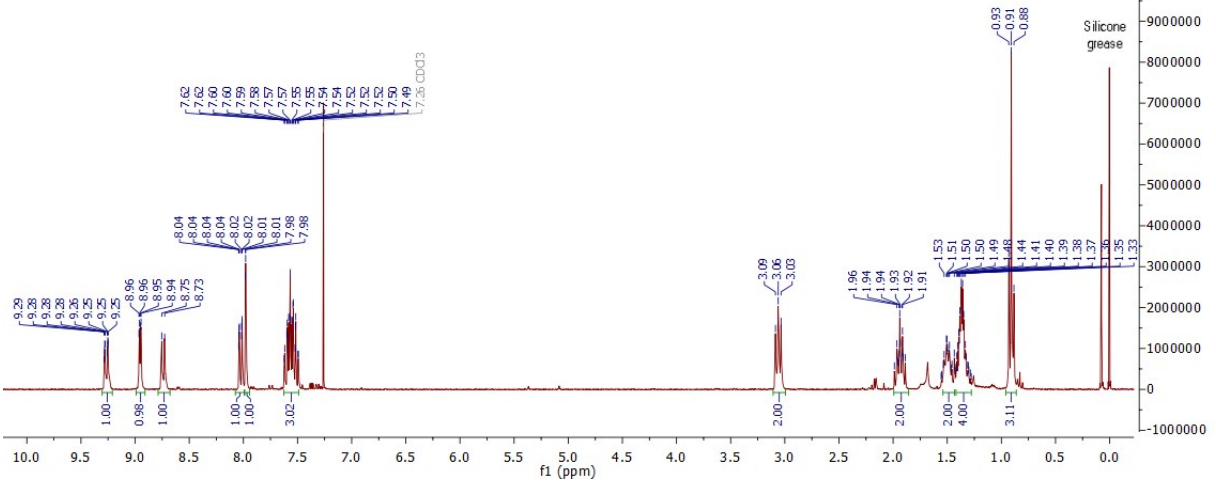




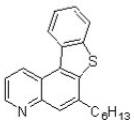
6-hexylbenzo[4,5]thieno[3,2-*f*]quinoline **7n**

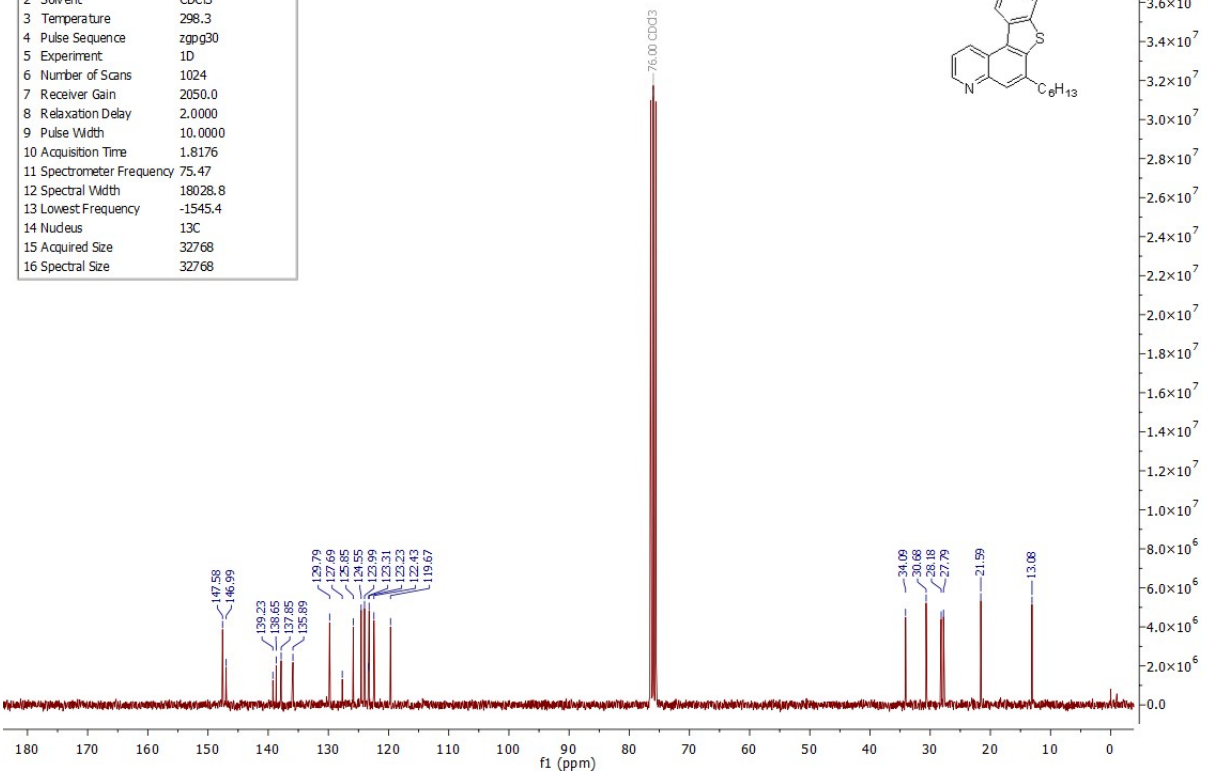
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	287.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	5.2954
11 Spectrometer Frequency	300.13
12 Spectral Width	6188.1
13 Lowest Frequency	-1246.6
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768



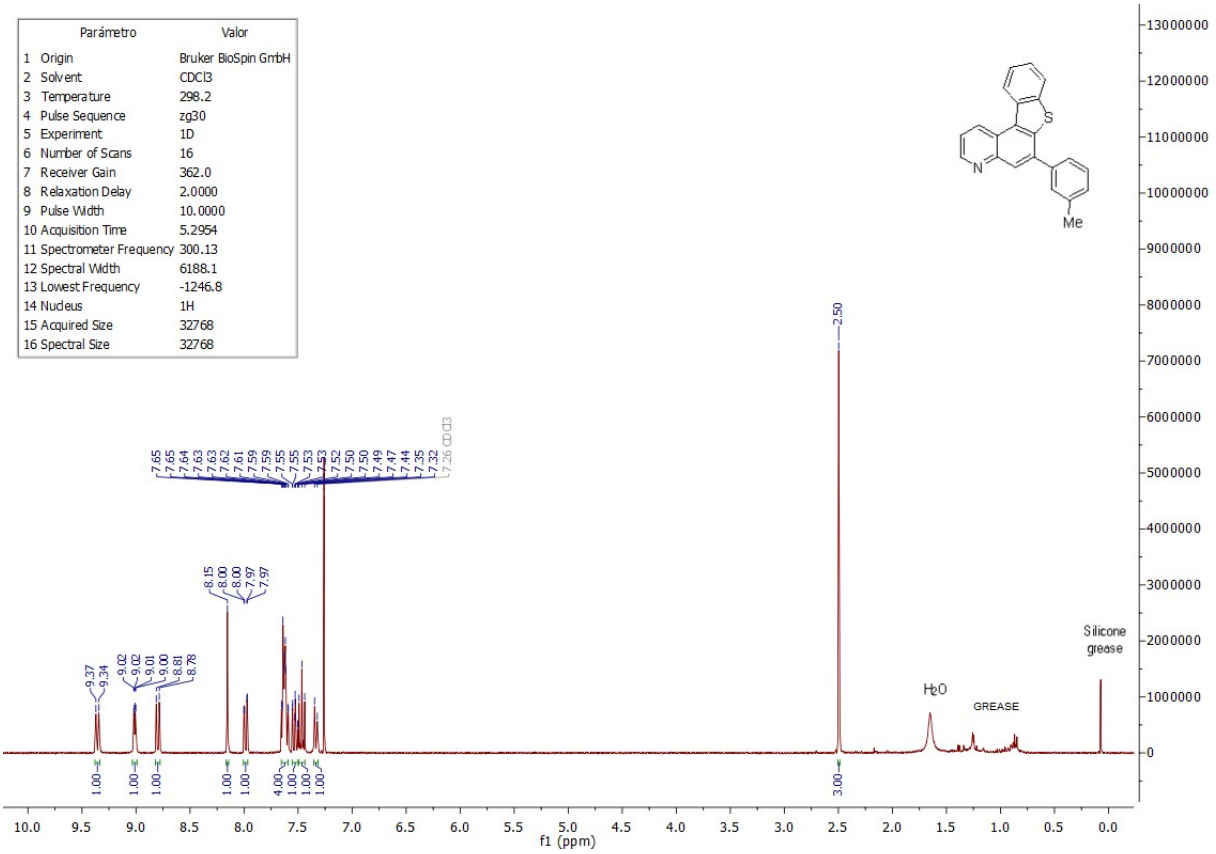


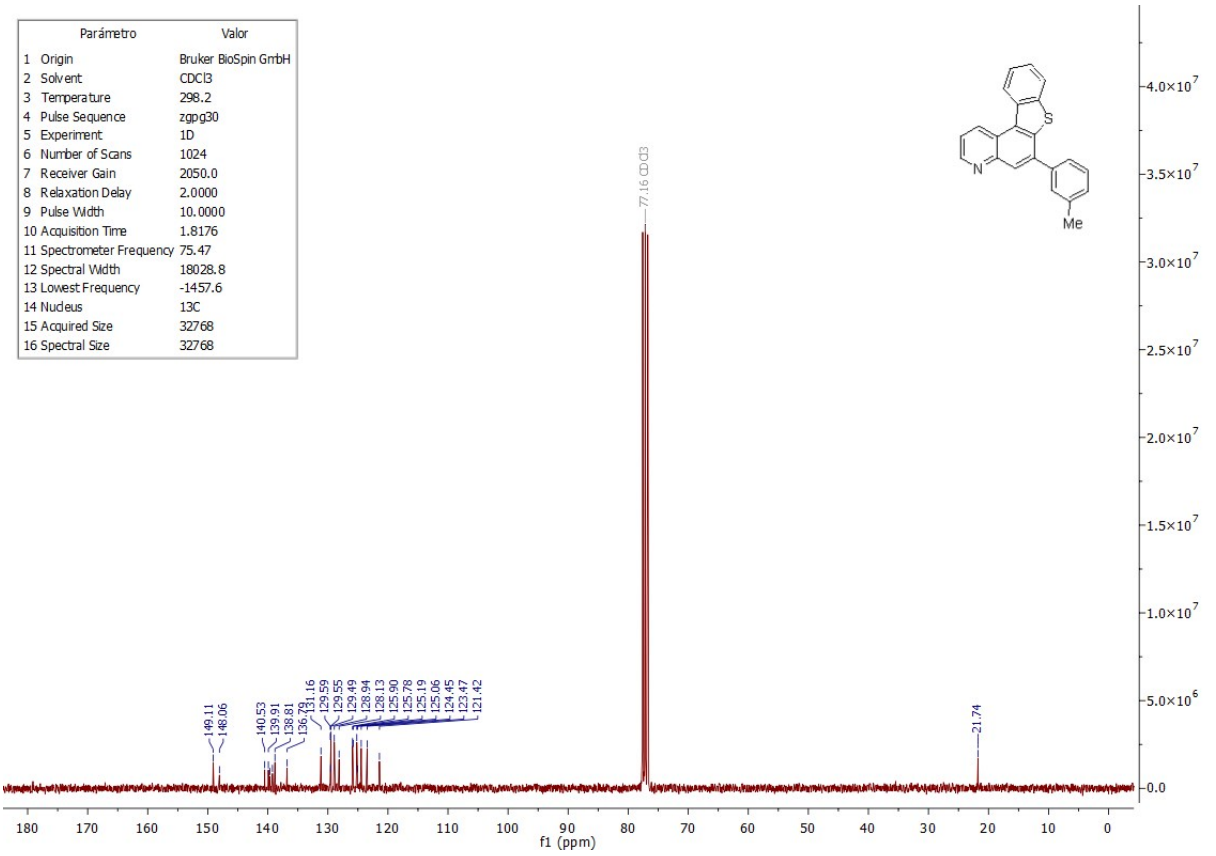
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.3
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.8176
11 Spectrometer Frequency	75.47
12 Spectral Width	18028.8
13 Lowest Frequency	-1545.4
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



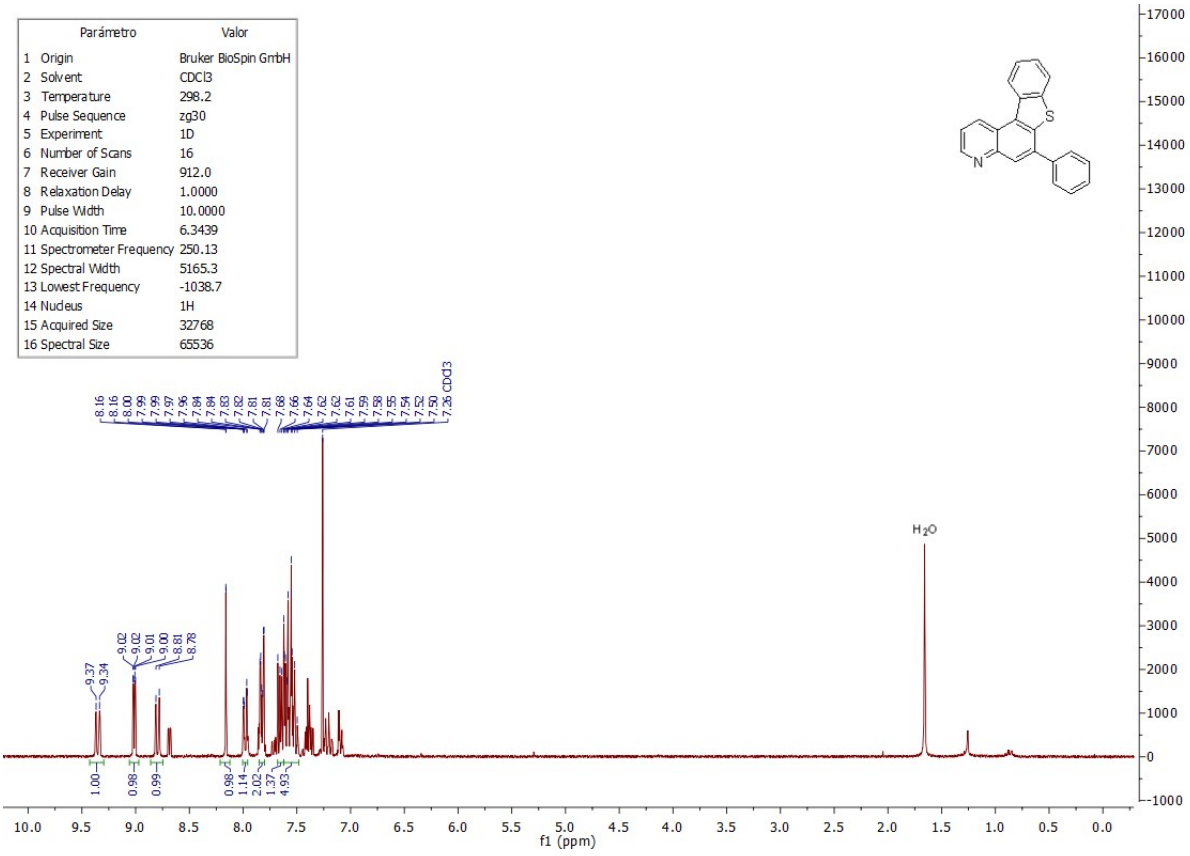


6-(*m*-tolyl)benzo[4,5]thieno[3,2-*f*]quinoline **7o**

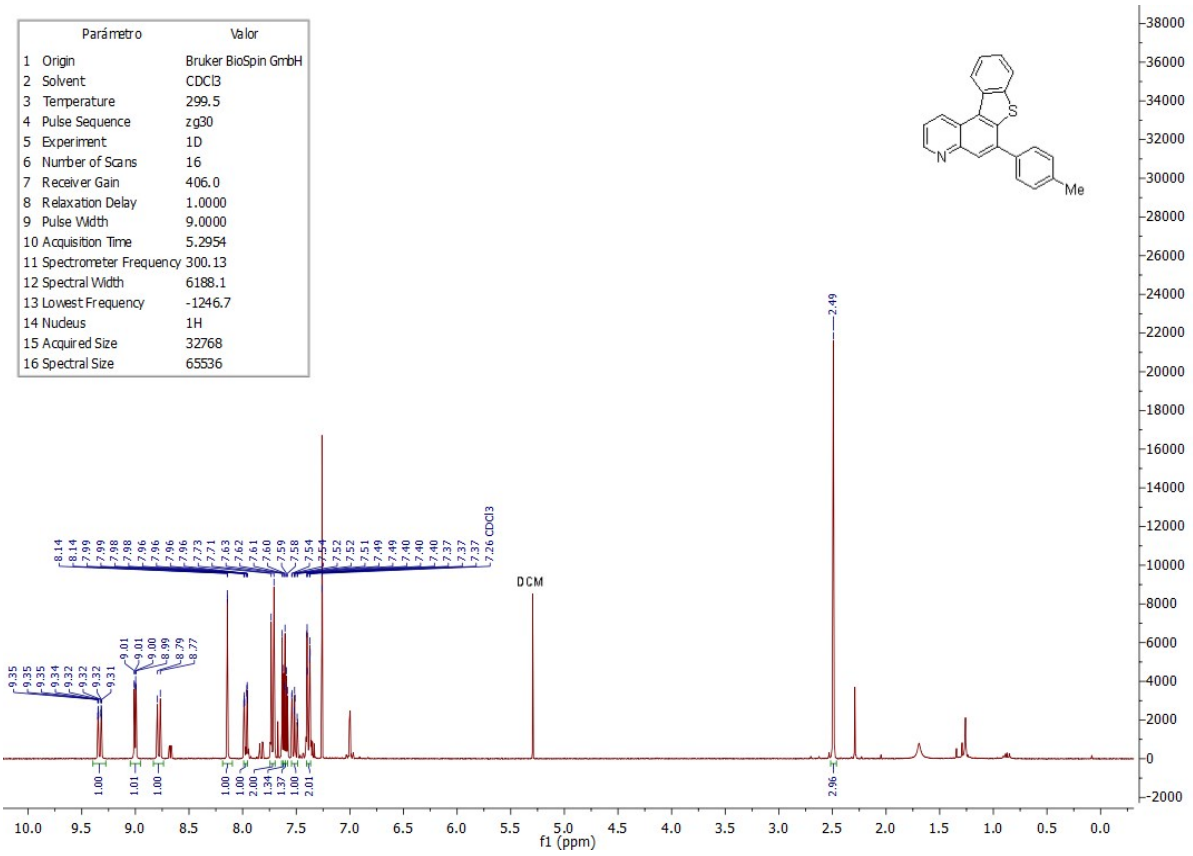


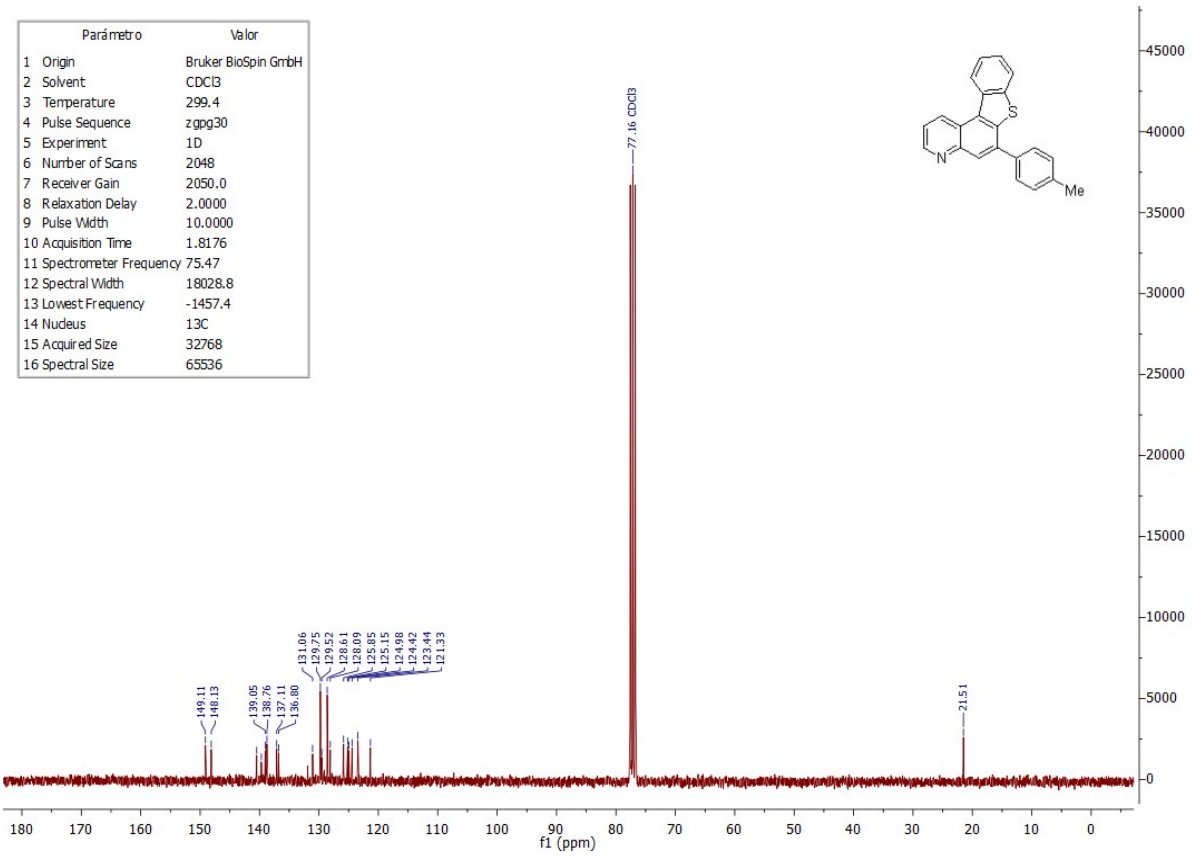


6-phenylbenzo[4,5]thieno[3,2-*f*]quinoline **7p**



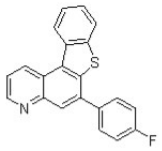
6-(*p*-tolyl)benzo[4,5]thieno[3,2-*f*]quinoline **7q**

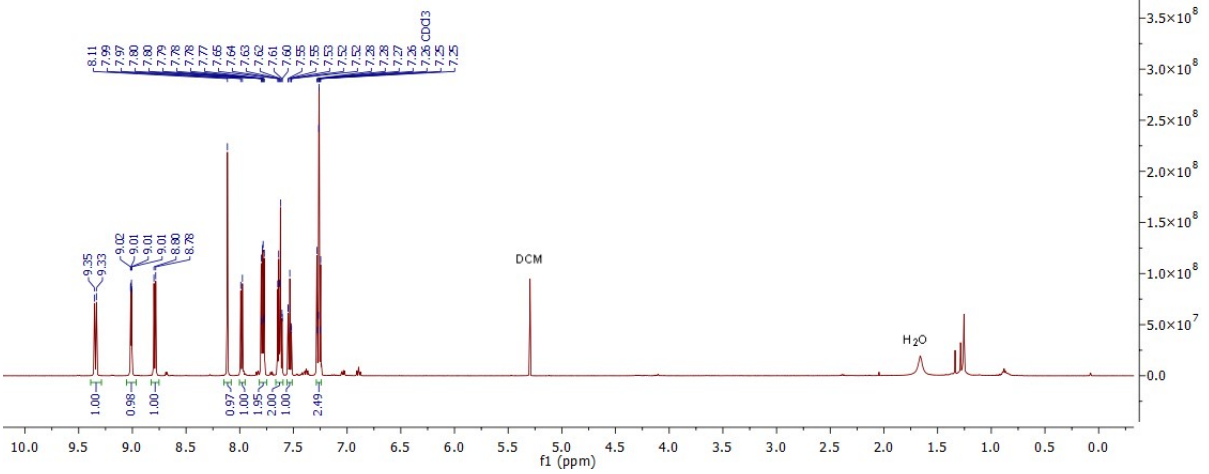




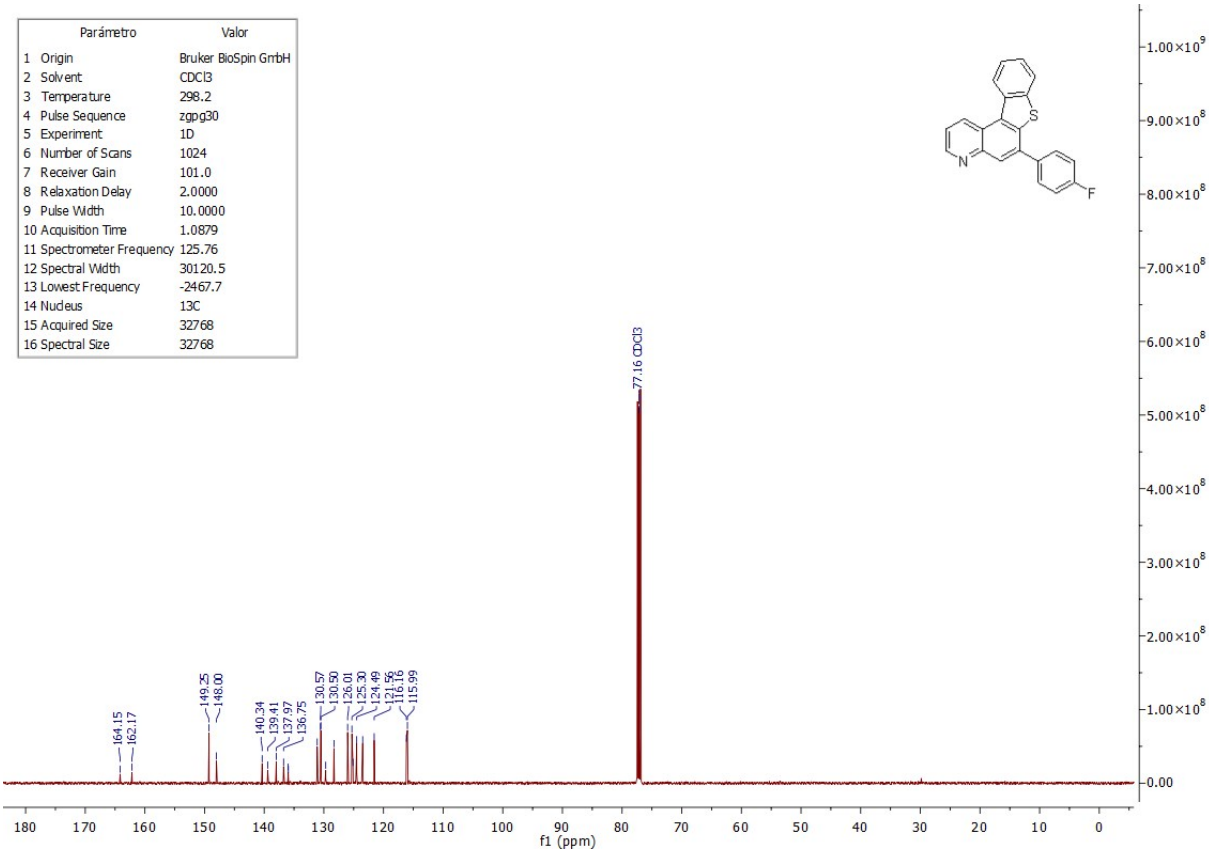
6-(4-fluorophenyl)benzo[4,5]thieno[3,2-*f*]quinoline **7r**

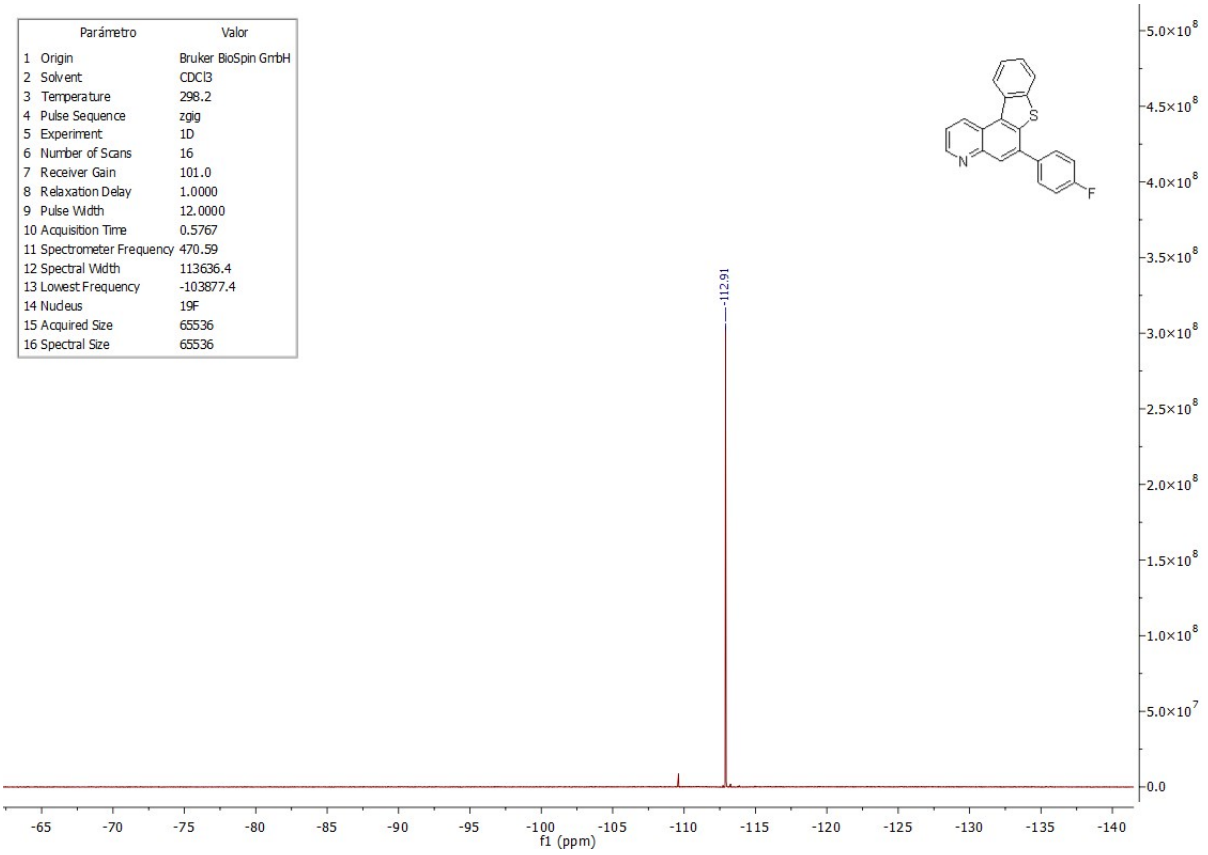
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	101.0
8 Relaxation Delay	1.0000
9 Pulse Width	8.0000
10 Acquisition Time	3.2768
11 Spectrometer Frequency	500.13
12 Spectral Width	10000.0
13 Lowest Frequency	-1923.9
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	65536





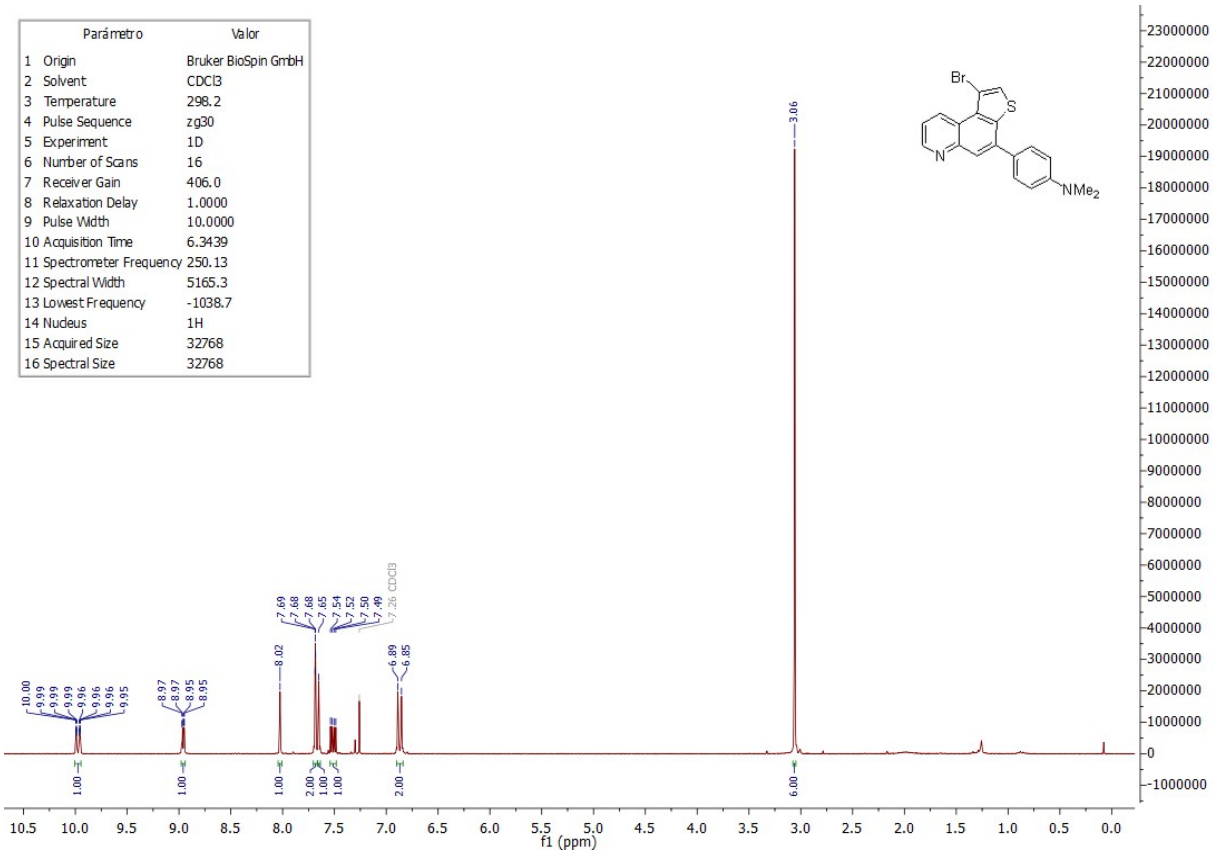
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	101.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.0879
11 Spectrometer Frequency	125.76
12 Spectral Width	30120.5
13 Lowest Frequency	-2467.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



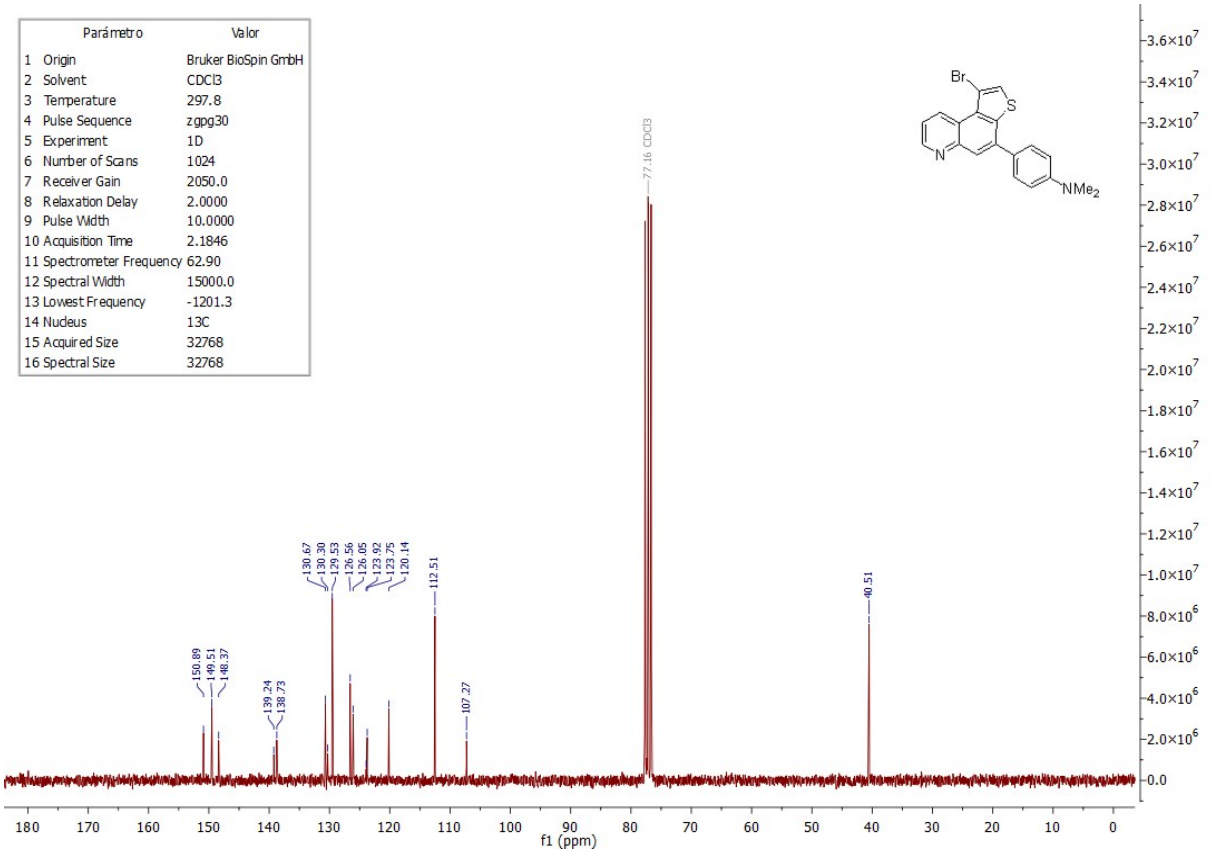


4-(1-bromothieno[3,2-*f*]quinolin-4-yl)-*N*,*N*-dimethylaniline **7t**

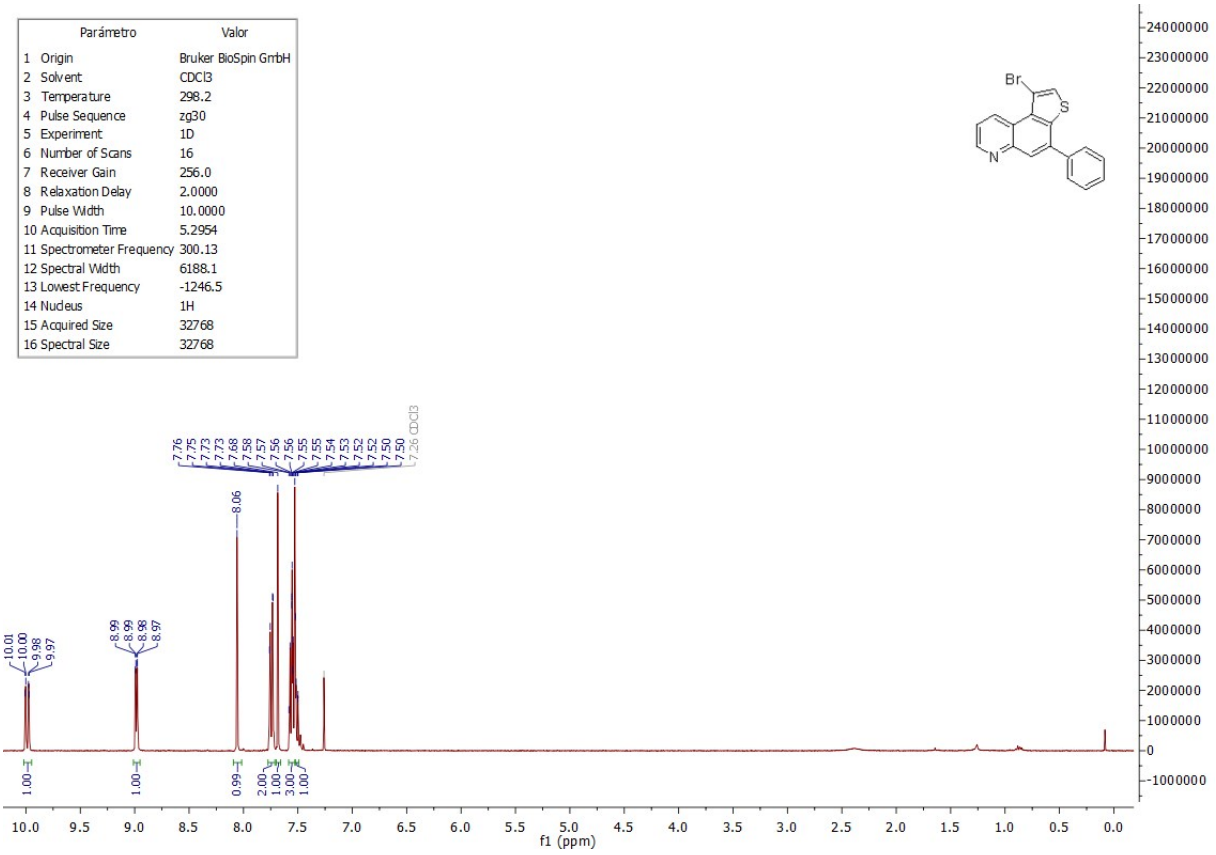
Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Pulse Sequence	zg30
5 Experiment	1D
6 Number of Scans	16
7 Receiver Gain	406.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
10 Acquisition Time	6.3439
11 Spectrometer Frequency	250.13
12 Spectral Width	5165.3
13 Lowest Frequency	-1038.7
14 Nucleus	1H
15 Acquired Size	32768
16 Spectral Size	32768

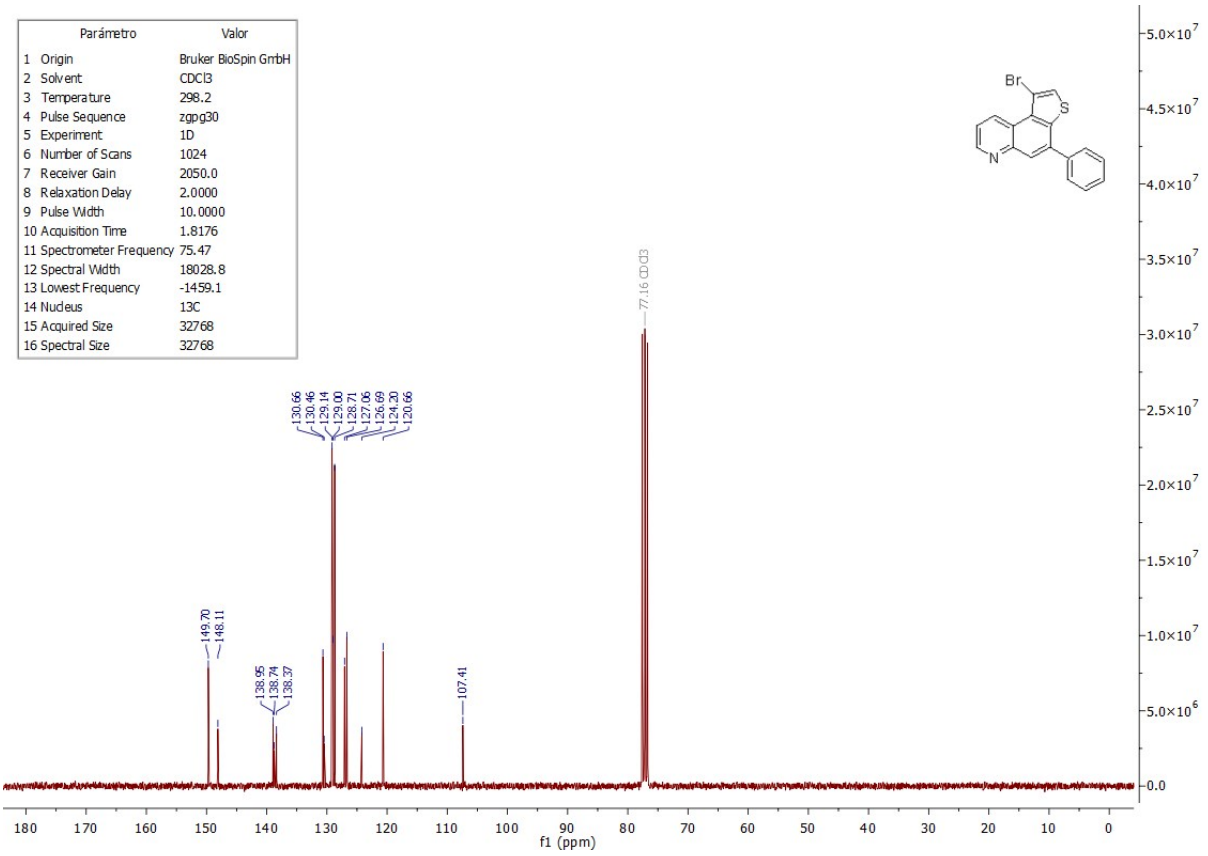


Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.8
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1201.3
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



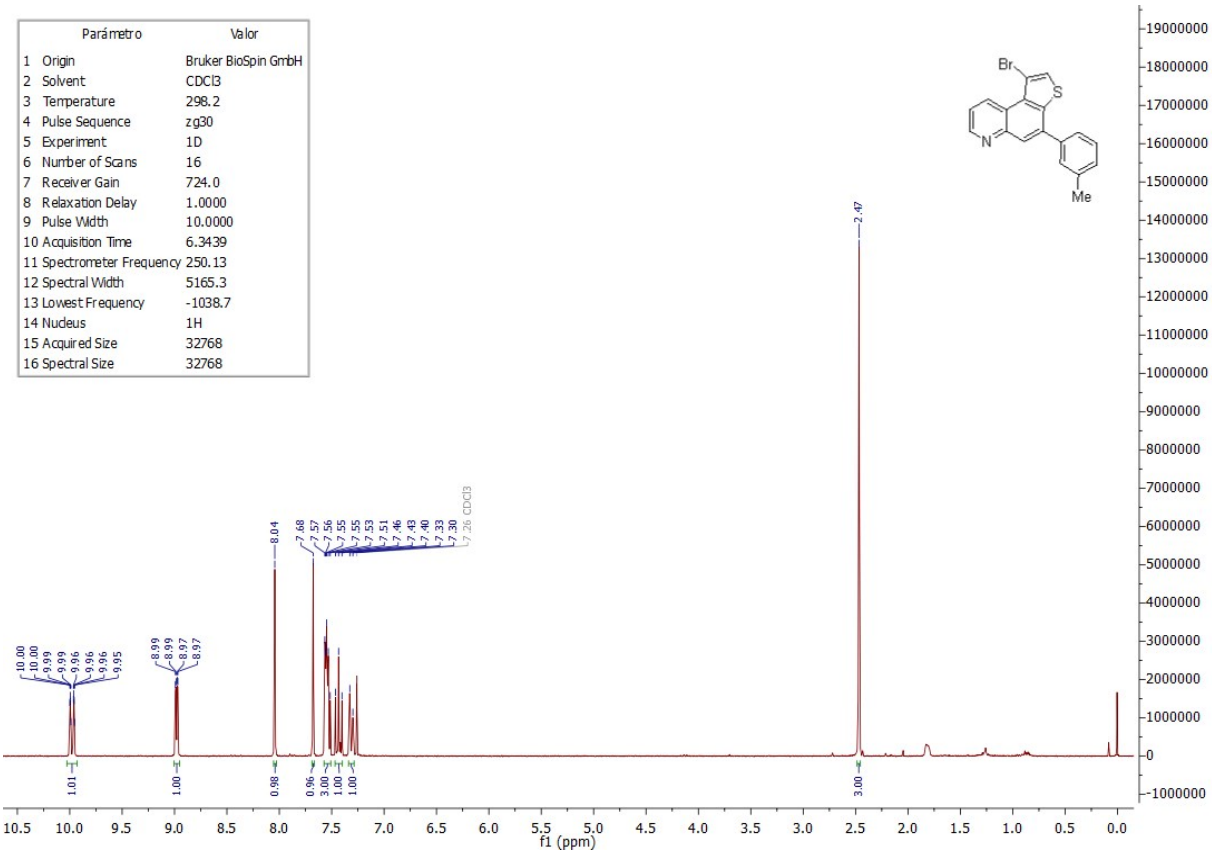
1-bromo-4-phenylthieno[3,2-*f*]quinoline **7u**



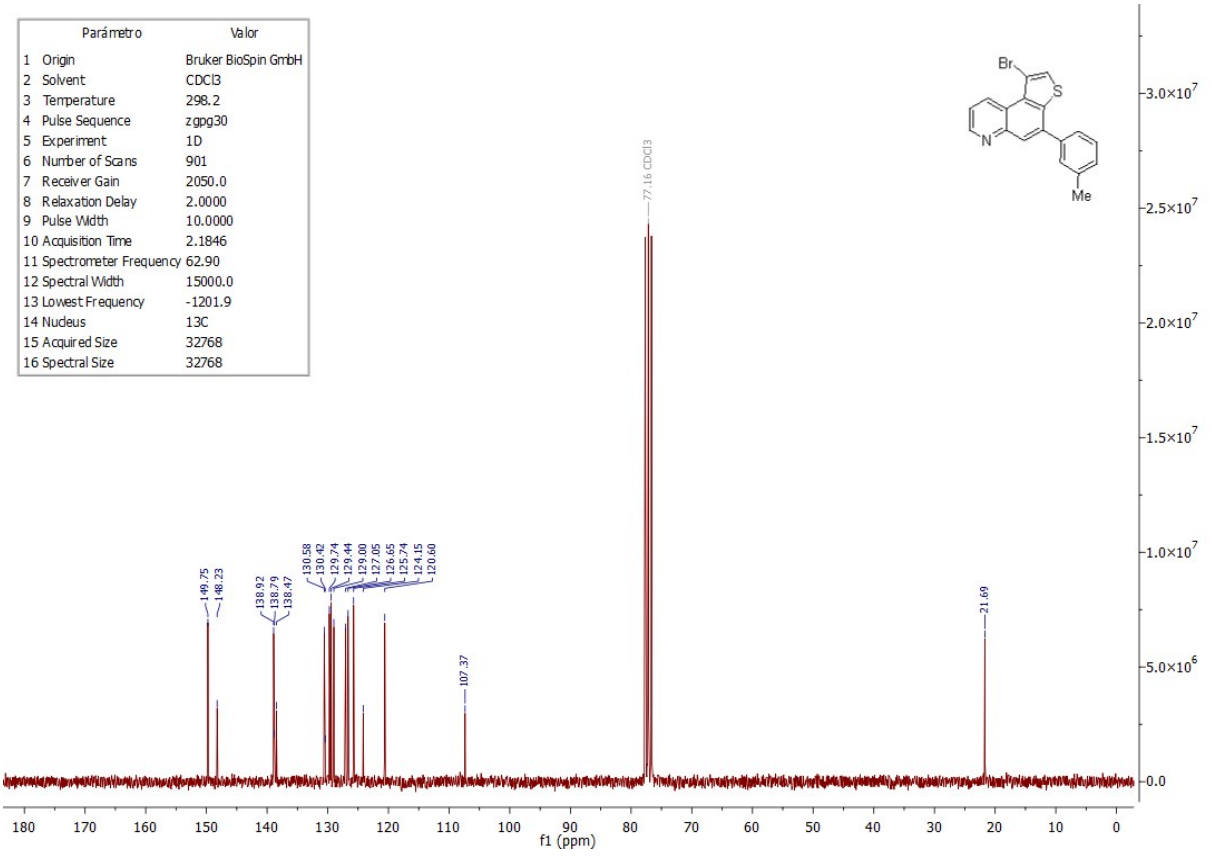


1-bromo-4-(*m*-tolyl)thieno[3,2-*f*]quinoline **7v**

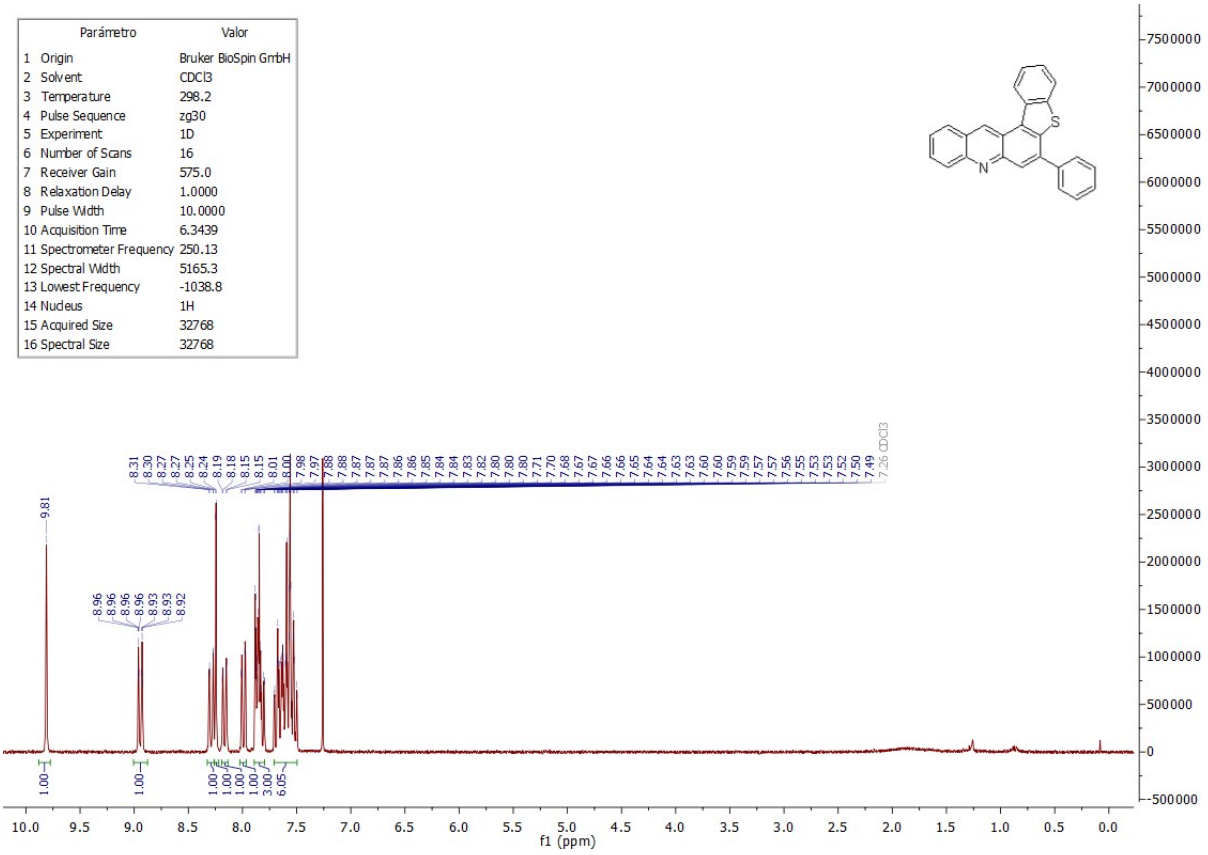
Parámetro		Valor
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	298.2
4	Pulse Sequence	zg30
5	Experiment	1D
6	Number of Scans	16
7	Receiver Gain	724.0
8	Relaxation Delay	1.0000
9	Pulse Width	10.0000
10	Acquisition Time	6.3439
11	Spectrometer Frequency	250.13
12	Spectral Width	5165.3
13	Lowest Frequency	-1038.7
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	32768

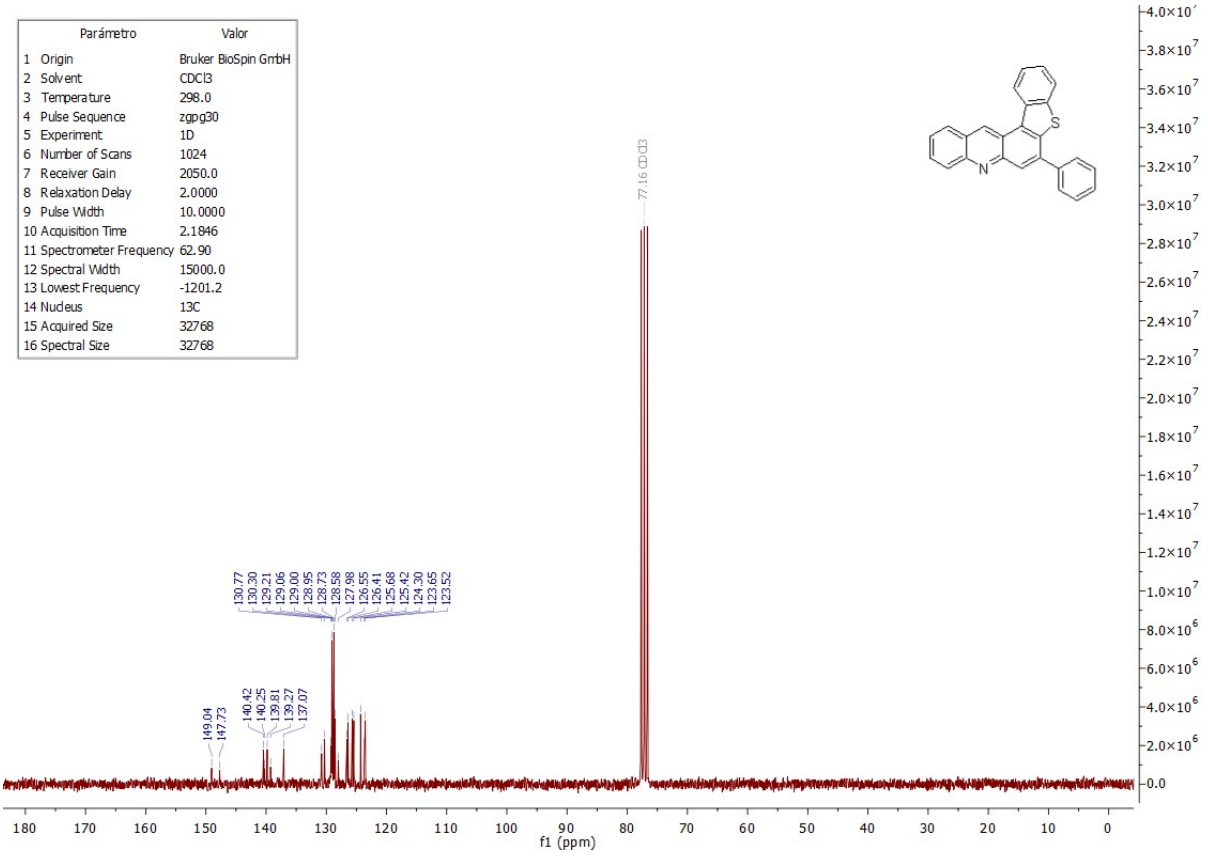


Parámetro		Valor
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	298.2
4	Pulse Sequence	zgpg30
5	Experiment	1D
6	Number of Scans	901
7	Receiver Gain	2050.0
8	Relaxation Delay	2.0000
9	Pulse Width	10.0000
10	Acquisition Time	2.1846
11	Spectrometer Frequency	62.90
12	Spectral Width	15000.0
13	Lowest Frequency	-1201.9
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	32768



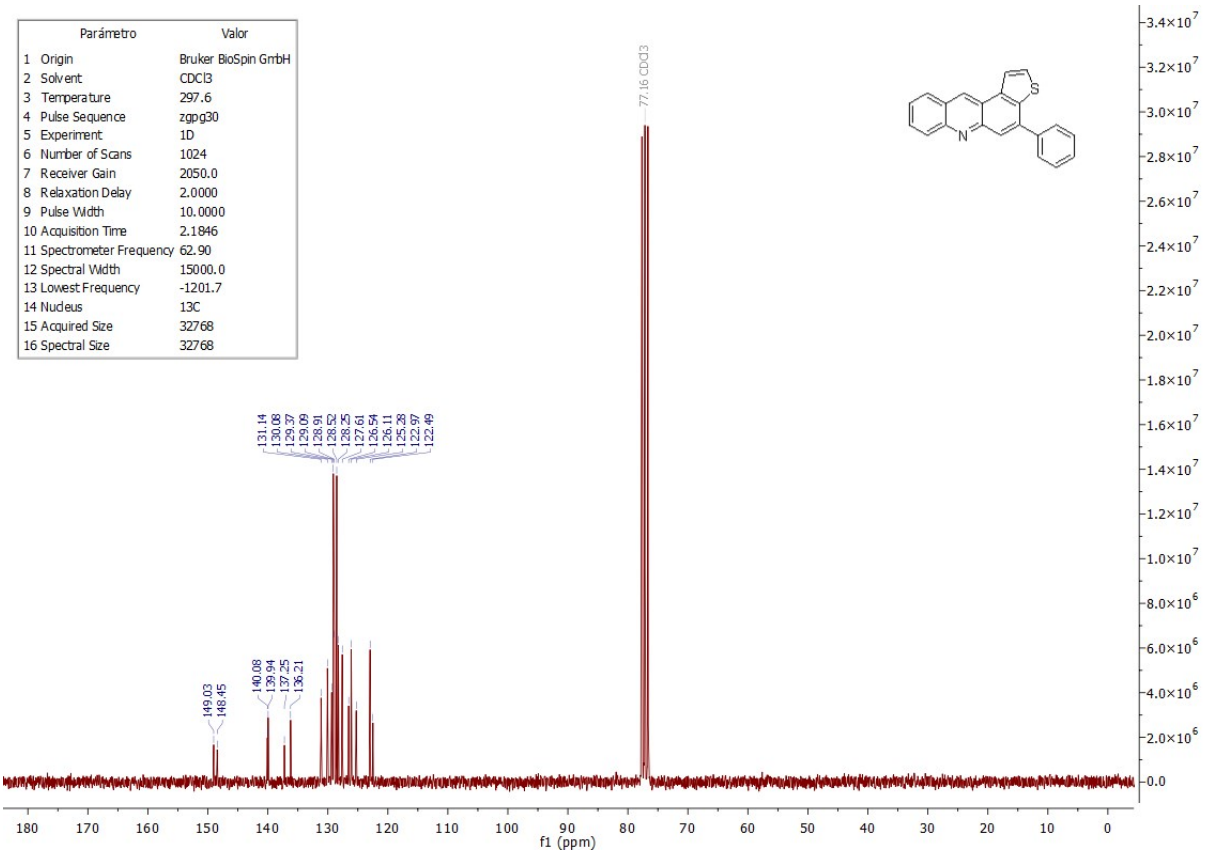
6-phenylbenzo[4,5]thieno[3,2-*a*]acridine **7w**





4-phenylthieno[3,2-*a*]acridine **7x**

Parámetro	Valor
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.6
4 Pulse Sequence	zgpg30
5 Experiment	1D
6 Number of Scans	1024
7 Receiver Gain	2050.0
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	2.1846
11 Spectrometer Frequency	62.90
12 Spectral Width	15000.0
13 Lowest Frequency	-1201.7
14 Nucleus	13C
15 Acquired Size	32768
16 Spectral Size	32768



Parámetro	Valor
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	362.0
8 Relaxation Delay	1.0000
9 Pulse Width	10.0000
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	32768