Electronic Supplementary Information (ESI)

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General Equipment and general conditions

All reagents were purchased from commercial suppliers and were used without further purification except for DMF, which was stored under argon and activated molecular sieves. The reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel (60 F254) plates. Compounds were visualized by UV irradiation. Flash column chromatography was performed on silica gel 60 (230-400 mesh, 0.040-0.063 mm). Melting points (mp [°C]) were taken on samples in open capillary tubes and are uncorrected. 1H and 13C NMR spectra were recorded on a Bruker DPX 250 (13C, 62.9 MHz), Bruker avance II 250.13 (13C, 63 MHz), Bruker avance 400.13 (13C, 101MHz), or on a Bruker avance III HD nanobay 400.13 (13C, 101 MHz). Chemical shifts are given in parts per million from tetramethylsilane (TMS) as internal standard. The following abbreviations are used for the proton spectra multiplicities: b: broad, s: singlet, d: doublet, t: triplet, q: quartet, p: pentuplet, m: multiplet. Coupling constants (J) are reported in hertz (Hz). Multiplicities were determined by the DEPT 135 sequence. Attributions of protons and carbons were made with the help of HSQC and HMBC 2D NMRs. Eudesmane numbering of carbons was used instead of the IUPAC numbering. Microwaves-assisted reactions were carried out in a Biotage Initiator microwave synthesis instrument and temperatures were measured by IR-sensor. High-resolution mass spectra (HRMS) were performed on a Maxis UHR-q-TOF mass spectrometer Bruker 4G with an electrospray ionisation (ESI) mode.

1. General procedures, characterization and spectra

2A. Synthesis of Imidazo[1,2-*a*]pyridines

2A1. General procedure for the synthesis of 3a-e and characterization

General procedure: 2-amino pyridine (1.062 mmol), bromoacetophenone (1.062 mmol) and $NaHCO_3$ (2.124 mmol) were dissolved in eucalyptol (2mL) and the reaction was stirred at 105°C for 22 h. After completion the mixture was allowed to cool to room temperature. Then H_2O was added and the aqueous phase was extracted with AcOEt (3x15 mL). The organic phase was dried (Mg_2SO_4), filtered and concentrated under reduced pressure. The crude product was purified by recrystallization with pentane.

2-phenylimidazol[1,2a]pyridine (**3a**): White solid (171mg, 83%), m.p. 131-132°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ6.80 (t, *J* = 6.8 Hz, 1H), 7.20 – 7.22 (m, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 9.1 Hz, 1H), 7.86 (s, 1H), 7.95 (d, *J* = 7.3 Hz, 2H), 8.13 (d, *J* = 6.8 Hz, 1H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ108.2(CH), 112.7(CH), 117.4(CH), 125.1(CH), 125.7(CH), 126.1(2xCH), 128.2(CH), 128.8(2xCH), 133.2(C), 145.3(C), 145.4 (C) ppm.

2-(4-chlorophenyl)imidazo[1,2-a]pyridine (**3b**): White solid (192mg, 79%), m.p. 206-208°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ6.76 (t, *J* = 6.7 Hz, 1H), 7.13– 7.19 (m, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.80 (s, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 8.07 (d, *J* = 6.8 Hz, 1H) ppm.^{13}C NMR (100.6 MHz, $CDCl_3$) δ108.2(CH), 112.6(CH), 117.5(CH), 124.9(CH), 125.6(CH), 127.3(2xCH), 128.9(2xCH), 132.3(C), 133.7(C), 144.7(C), 145.7 (C) ppm.

2-(4-fluorophenyl)imidazo[1,2-a]pyridine (**3c**): White solid (205mg, 91%), m.p. 166-168°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ6.75 (t, *J* = 6.8 Hz, 1H),7.13 (d, *J* = 34.6 Hz, 3H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.77 (s, 1H), 7.86 – 7.95 (m, 2H), 8.07 (d, J = 6.7 Hz, 1H)ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ107.8(CH), 112.5(CH), 115.5(CH), 115.7(CH), 117.5(CH), 124.8(CH), 125.6(CH), 127.7(CH), 130.0 (C), 144.9(CH), 145.7(C), 161.5(C), 163.9 (C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.2 ppm.

2-(4-nitrophenyl)imidazo[1,2-a]pyridine (**3d**): Yellow solid (160mg, 63%), m.p. 262-264°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ6.85 (d, *J* = 13.5 Hz, 1H), 7.23 (d, *J* = 10.1 Hz, 1H), 7.66 (d, *J* = 9.2 Hz, 1H), 8.00 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 6.8 Hz, 1H), 8.30 (d, *J* = 8.9 Hz, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ109.9(CH), 113.2(CH), 118.0(CH), 124.2(2xCH), 125.6(CH), 125.8(CH), 126.4(2xCH), 140.2(C), 143.4(C), 146.1(C), 147.2 (C) ppm.

2-(4-methoxyphenyl)imidazo[1,2-a]pyridine (**3e**): White solid (183mg, 77%), m.p. 134-136°C . ^{1}H NMR (400 MHz, $CDCl_3$) δ3.85 (s, 3H), 6.77 (d, *J* = 13.5 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 16.9 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.77 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 6.8 Hz, 1H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ55.3(CH), 107.2(CH), 112.5(CH), 114.2(2xCH), 117.2(CH), 124.7(CH), 125.5(CH), 126.1(C), 127.4(2xCH), 132.4(C), 145.4 (C), 159.7 (C) ppm.

2A2. Procedure for the synthesis of 5 and characterization

2,3-diphenylimidazol[1,2-a]pyridine (**5**): 2-phenylimidazol[1,2a]pyridine **3a** (0.515mmol), Bromobenzene (0.772 mmol), KOAc (2.059 mmol) and $Pd(OAc)_2$ (5mol%) were added and the reaction was stirred at 150°C for 24h. After completion the mixture was allowed to cool to room temperature. Then H_2O was added and the aqueous phase was extracted with AcOEt (3x15mL). The organic phase was dried (Mg_2SO_4), filtered and concentrated under reduced pressure. The crude product was purified by recrystallization with pentane. White solid (84mg, 60%), m.p. 147-149°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ6.75 (t, *J* = 6.8 Hz, 1H), 7.20 – 7.24 (m, 1H), 7.28 – 7.32 (m, 3H), 7.47 – 7.57 (m, 5H), 7.68 – 7.70 (m, 3H), 7.98 (d, *J* = 6.9 Hz, 1H)ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ112.3 (CH), 117.5 (CH), 121.1 (C), 123.3 (CH), 124.7 (CH), 127.5 (CH), 128.1 (2xCH), 128.3 (2xCH), 144.8(C), 128.9 (CH), 129.5 (2xCH), 129.9 (C), 130.7 (2xCH), 134.1 (C), 142.4 (C) ppm.

2A3. General procedure for the synthesis of 6a-f and characterization

General procedure: 2-amino pyridine (1.062mmol), bromoacetophenone (1.062mmol) and $NaHCO_3$ (2.124mmol) were dissolved in eucalyptol (2mL) and the reaction was stirred at 105°C for 22h. Then, ArBr (1.594 mmol), KOAc (4.248 mmol) and $Pd(OAc)_2$ (5mol%) were added and the reaction was stirred at 150°C for 24h. After completion, the mixture was allowed to cool to room temperature. Then H_2O was added and the aqueous phase was extracted with AcOEt (3x15mL). The organic phase was dried (Mg_2SO_4), filtered and concentrated under reduced pressure. The crude product was purified by recrystallization with pentane.

2-(4-fluorophenyl)-3-(3,4,5-trimethoxyphenyl)imidazo[1,2-a]pyridine (**6a**)**:** Yellow solid (298mg, 74%), m.p. 193-195°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ3.80 (s, 6H),3.96 (s, 3H), 6.64 (s, 2H), 6.76 (d, *J* = 12.6 Hz, 1H), 7.00 (d, *J* = 17.6 Hz, 2H), 7.21 (d, *J* = 15.7 Hz, 1H), 7.68 (d, *J* = 27.1 Hz, 3H), 7.97 (d, *J* = 6.9 Hz, 1H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ56.3(2xCH), 61.0(CH), 107.6(2xCH), 112.4(CH), 115.1(CH), 115.3(CH), 117.5(CH), 120.7(C), 123.5(CH), 124.8(CH), 124.9(C), 129.5(CH), 129.6(CH), 130.2(C), 138.6(C), 141.2(C), 144.6(C), 154.3(C), 161.2(C), 163.6(C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5 ppm. HRMS: calcd for $C_{22}H_{20}FN_2O_3$ $[M+H]^+$ 379.1452, found 379.1450.

2-(4-fluorophenyl)-3-(p-tolyl)imidazo[1,2-a]pyridine (**6b**): Yellow solid (186mg , 58%), m.p. 123-125°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ2.45 (s, 3H), 6.71 (t, *J* = 6.8 Hz, 1H), 6.96 (t, *J* = 8.7 Hz, 2H), 7.15 – 7.20 (m, 1H), 7.31 (t, *J* = 5.4 Hz, 4H), 7.64 (t, *J* = 7.1 Hz, 3H), 7.92 (d, *J* = 6.9 Hz, 1H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ21.4(CH), 112.3(CH), 115.1(CH), 115.3(CH), 117.4(CH), 120.9(C), 123.4(CH), 124.7(CH), 126.5(C), 129.6(CH), 129.7(CH), 130.4(2xCH),

130.5(2xCH), 139.0(C), 141.3(C), 144.7(C), 161.1(C), 163.5 (C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.2 ppm. HRMS: calcd for $C_{20}H_{16}FN_2$ $[M+H]^+$ 303.1292, found 303.1291.

2-(4-fluorophenyl)-3-(4-nitrophenyl)imidazo[1,2-a]pyridine (**6c**): Yellow solid (354mg , 100%), m.p. 201-203°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ6.85 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.34 (m, 1H), 7.56 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 9.1 Hz, 1H), 8.07 (d, *J* = 6.9 Hz, 1H), 8.37 (d, *J* = 8.8 Hz, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ113.2(CH), 115.5(CH), 115.7(CH), 118.0(CH), 118.6(C), 122.8(CH), 124.8(2xCH), 125.8(CH), 129.6(C), 130.2(CH), 130.3(CH), 131.0(2xCH), 136.5(C), 143.6(C), 145.7(C), 147.5(C), 164.0 (C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.3 ppm. HRMS: calcd for $C_{19}H_{13}FN_3O_2$ $[M+H]^+$ 334.0986, found 334.0985.

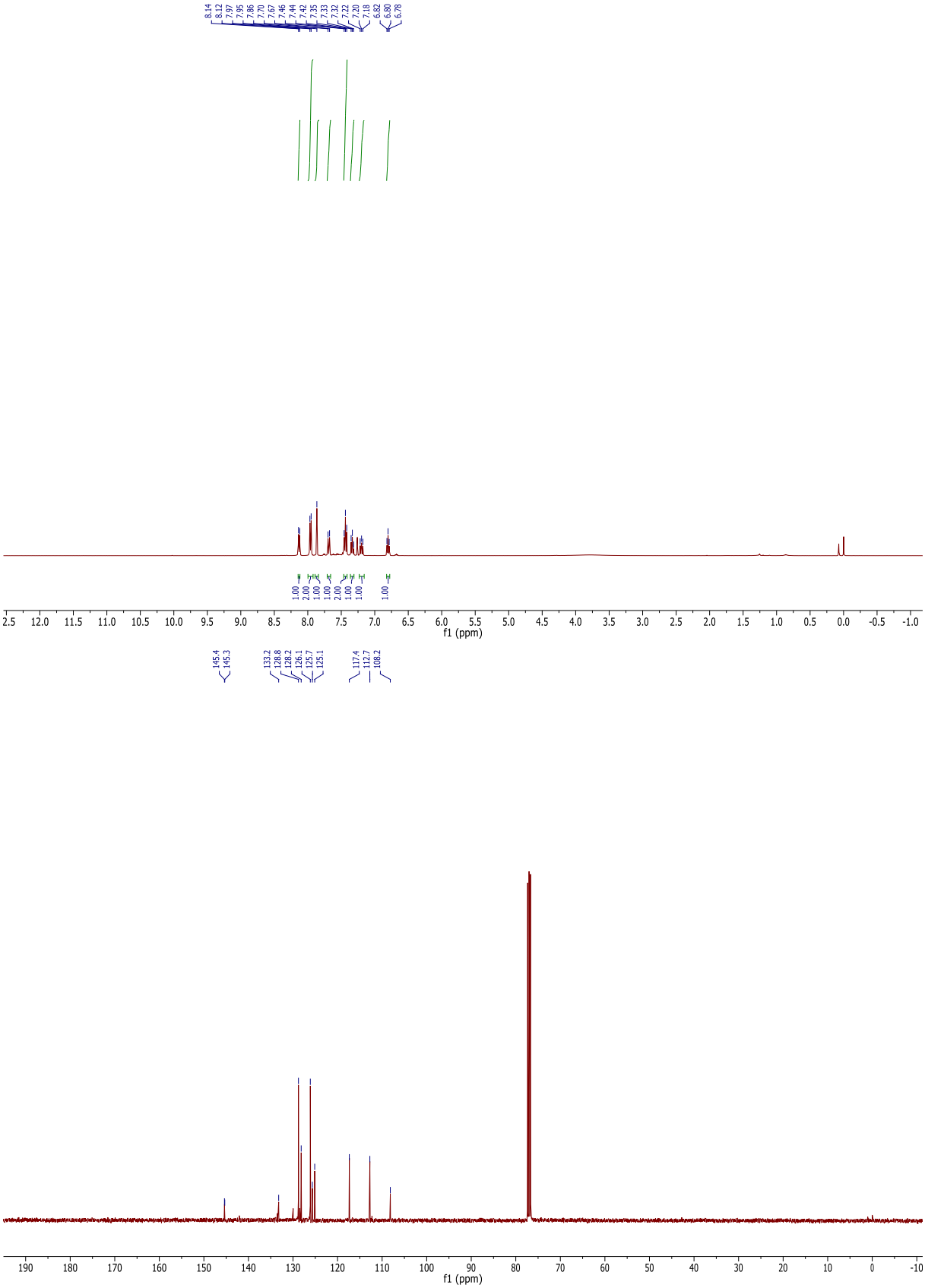
2-(4-fluorophenyl)-3-phenylimidazo[1,2-a]pyridine (**6d**): White solid (224mg, 73%), m.p. 106-108°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ6.72 (t, *J* = 6.8 Hz, 1H), 6.96 (t, *J* = 8.8 Hz, 2H), 7.16 – 7.22 (m, 1H), 7.41 – 7.55 (m, 5H), 7.60 – 7.69 (m, 3H), 7.94 (d, *J* = 6.9 Hz, 1H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ112.3(CH), 115.1(CH), 115.3(CH), 117.5(CH), 120.8(C), 123.3(CH), 124.8(CH), 129.0(CH), 129.6(2xCH), 129.7(CH), 129.8(CH), 130.3 (C), 130.7(2xCH), 141.5(C), 144.8(C), 161.1(C), 163.6 (C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6 ppm.

2-(4-fluorophenyl)-3-(thiophen-3-yl)imidazo[1,2-a]pyridine (**6e**): Yellow solid (206mg, 66%), m.p. 129-131°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ6.76 (t, *J* = 6.8 Hz, 1H), 6.99 (t, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 4.9 Hz, 1H), 7.18 – 7.22 (m, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.51 – 7.58 (m, 1H), 7.36 – 7.69 (m, 3H), 7.97 (d, *J* = 6.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ112.4 (CH), 115.1 (CH), 115.4 (CH), 115.9 (C), 117.5(CH), 123.6 (CH), 124.8 (CH), 126.3 (CH), 127.3 (CH), 128.7 (CH), 129.6 (CH), 129.7 (CH), 130.3 (C), 142.1 (C), 144.9 (C), 161.2 (C), 163.7 (C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5 ppm. HRMS: calcd for $C_{17}H_{12}FN_2S$ $[M+H]^+$ 295.0700, found 295.0697.

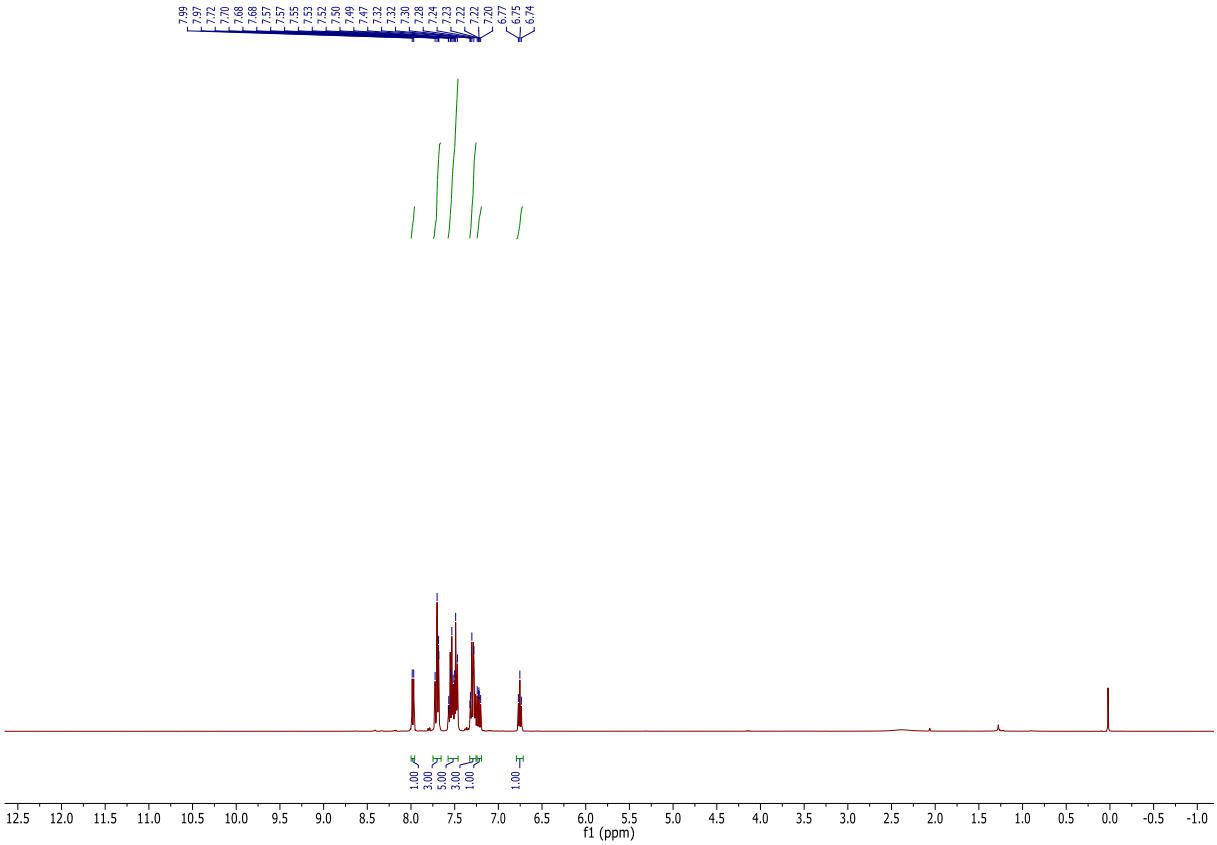
3-(2-(4-fluorophenyl)imidazo[1,2-a]pyridin-3-yl)quinolone (**6f**): Yellow solid (292mg , 81%), m.p. 170-172°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ6.77 (t, *J* = 6.8 Hz, 1H), 6.93 (t, *J* = 8.7 Hz, 2H), 7.21 – 7.26 (m, 1H), 7.60 (dt, *J* = 8.9, 4.7 Hz, 3H), 7.69 (d, *J* = 9.1 Hz, 1H), 7.77 – 7.84 (m, 3H), 7.99 (d, *J* = 6.9 Hz, 1H),8.17 (d, *J* = 8.5 Hz, 1H),8.26 (d, *J* = 1.9 Hz, 1H),8.88 (d, *J* = 2.1 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ112.9(CH), 115.4(CH), 115.7(CH), 117.4(C), 117.8(CH), 122.9(CH), 123.1(C), 125.5(CH), 127.5(CH), 127.9(CH), 129.6(CH), 129.8(CH), 129.9(CH), 129.9(C), 130.5(CH), 137.4(CH), 143.2(C), 145.4(C), 147.7(C), 151.7(CH), 161.3(C), 163.8 (C) ppm.^{19}F NMR (376 MHz, $CDCl_3$) δ -113.8 ppm. HRMS: calcd for $C_{22}H_{15}FN_3$ $[M+H]^+$ 340.1245, found 340.1244.

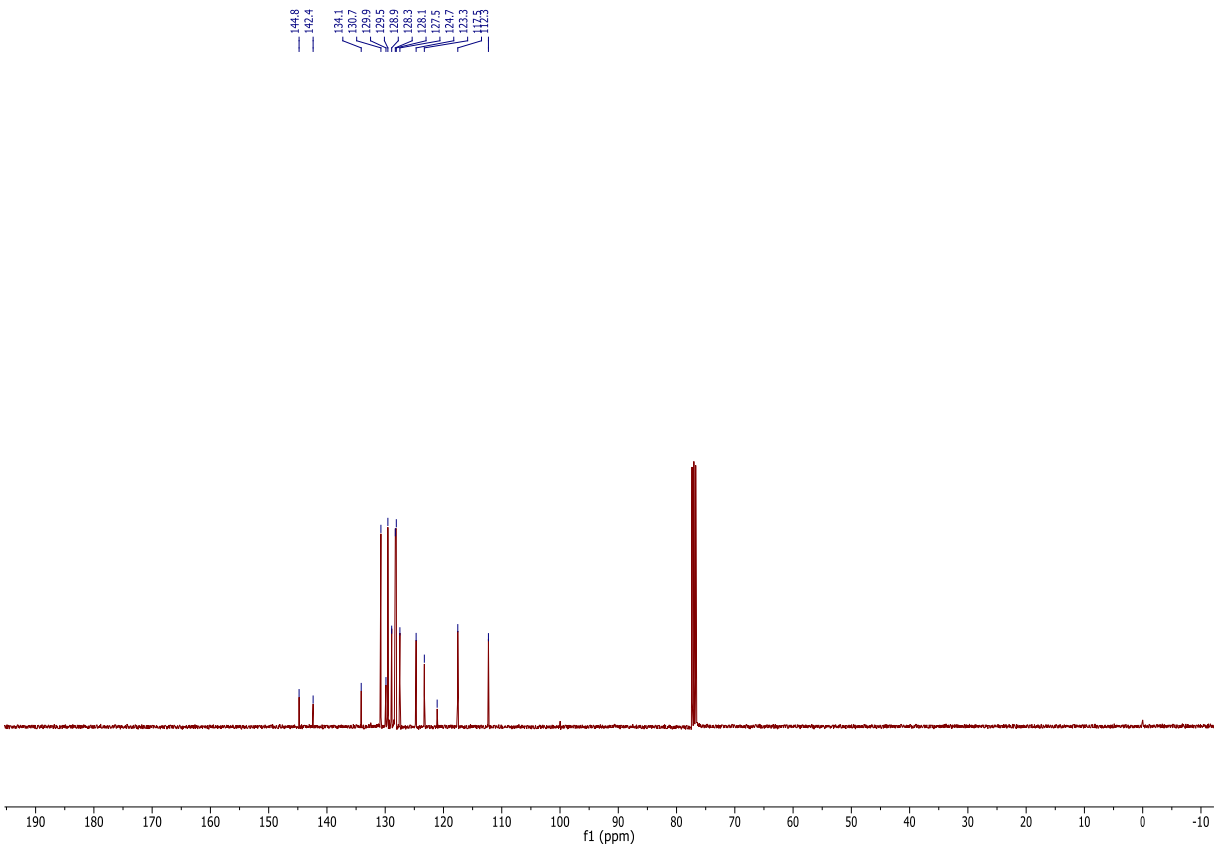
2A4. Spectra of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR

2-phenylimidazol[1,2a]pyridine (**3a**)

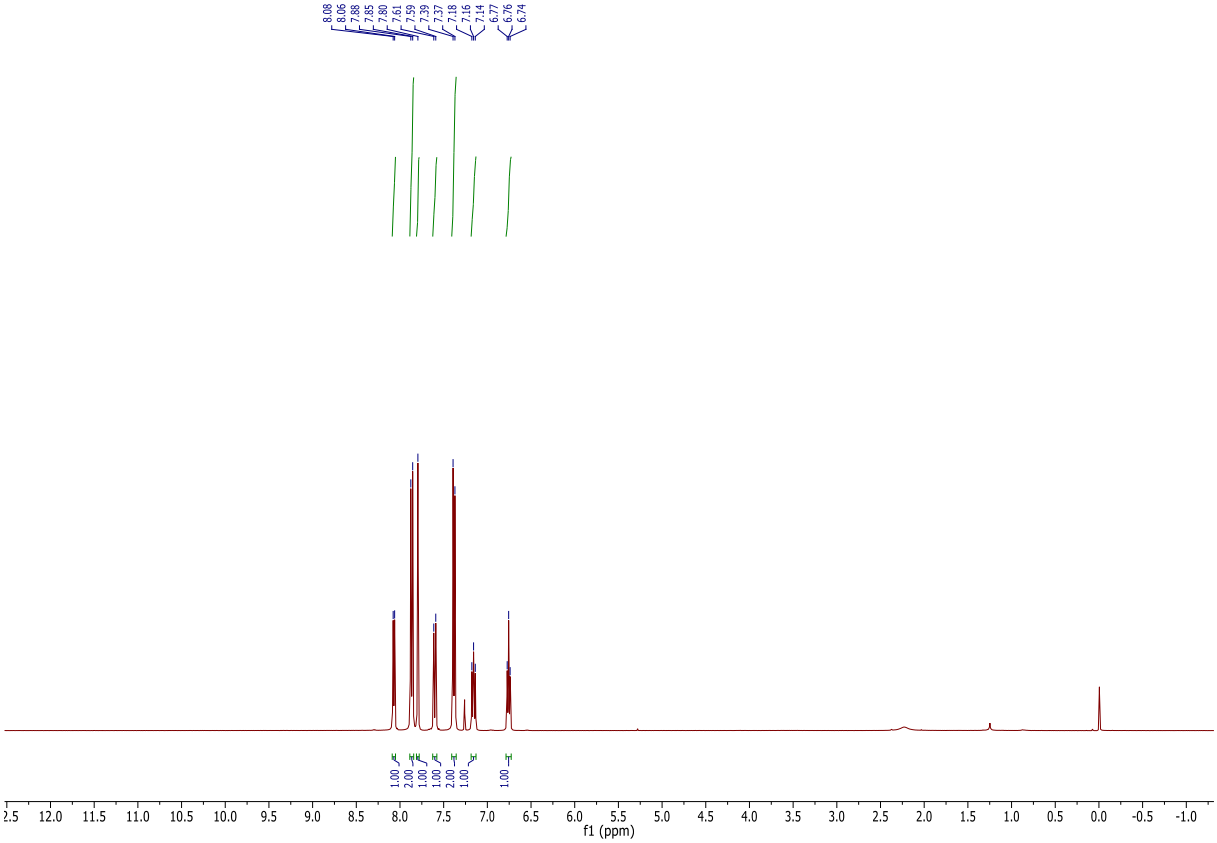


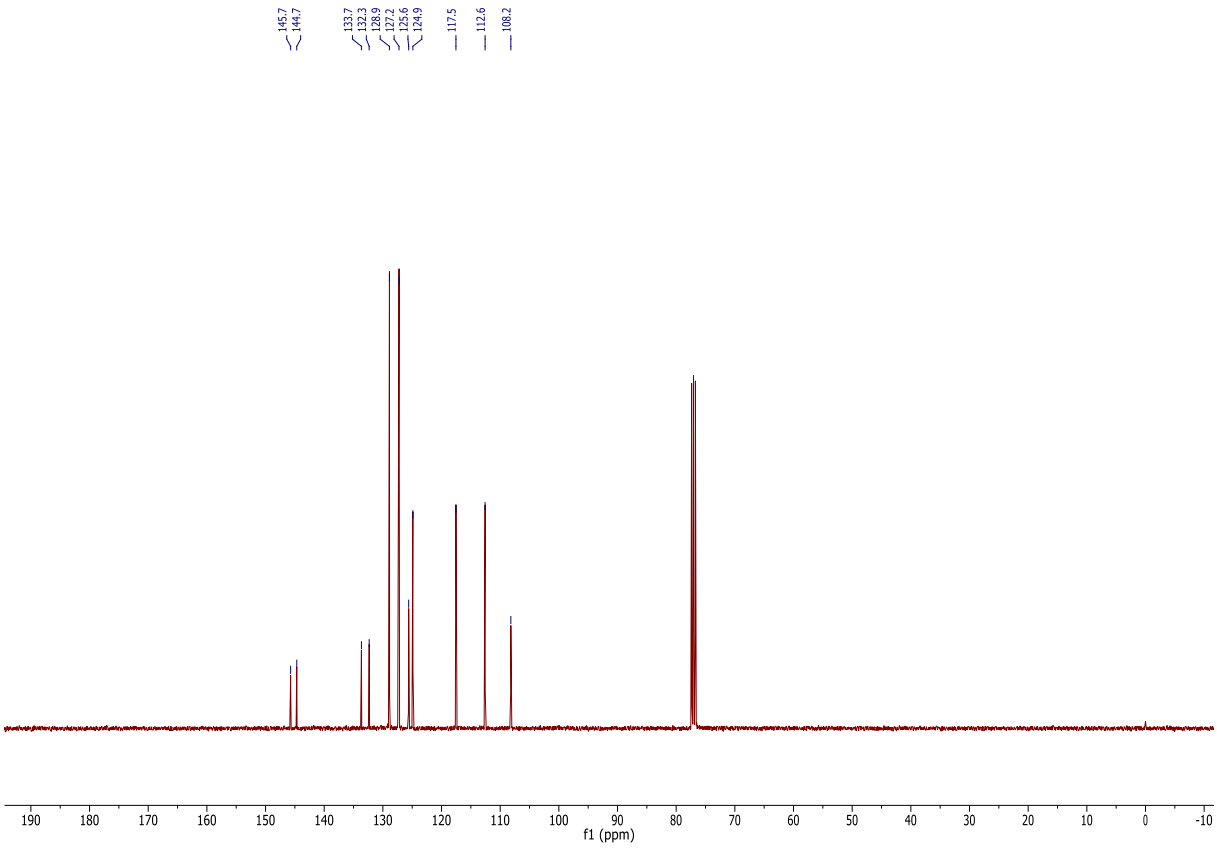
2,3-diphenylimidazol[1,2-a]pyridine (**5**)



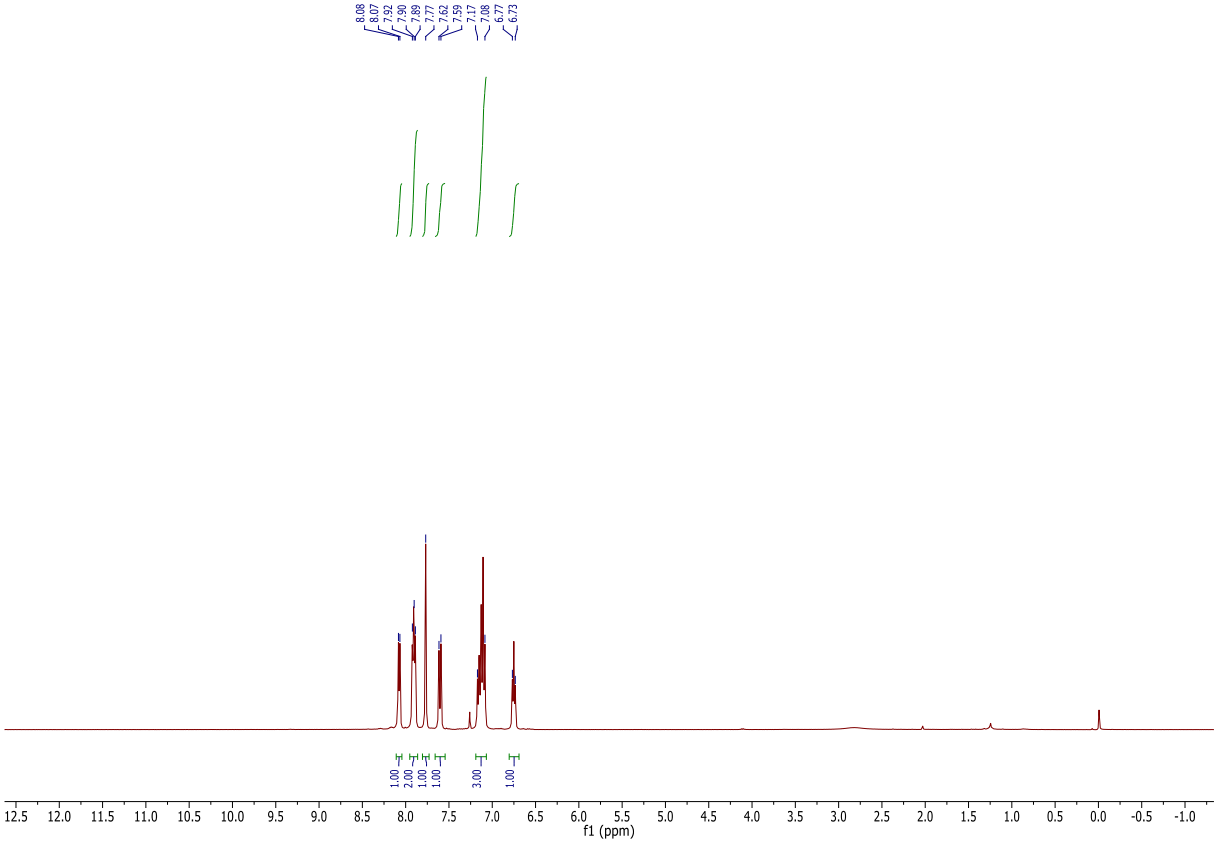


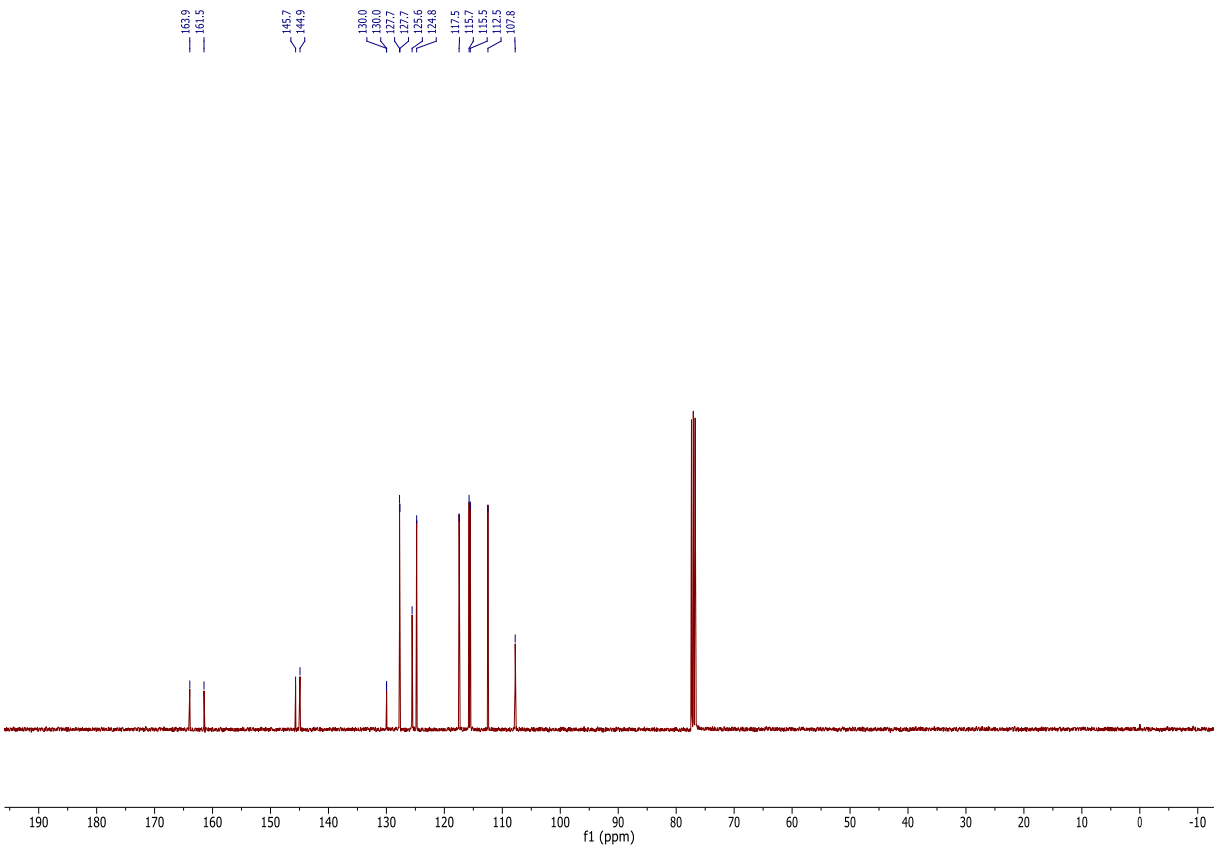
2-(4-chlorophenyl)imidazo[1,2-a]pyridine (**3b**)

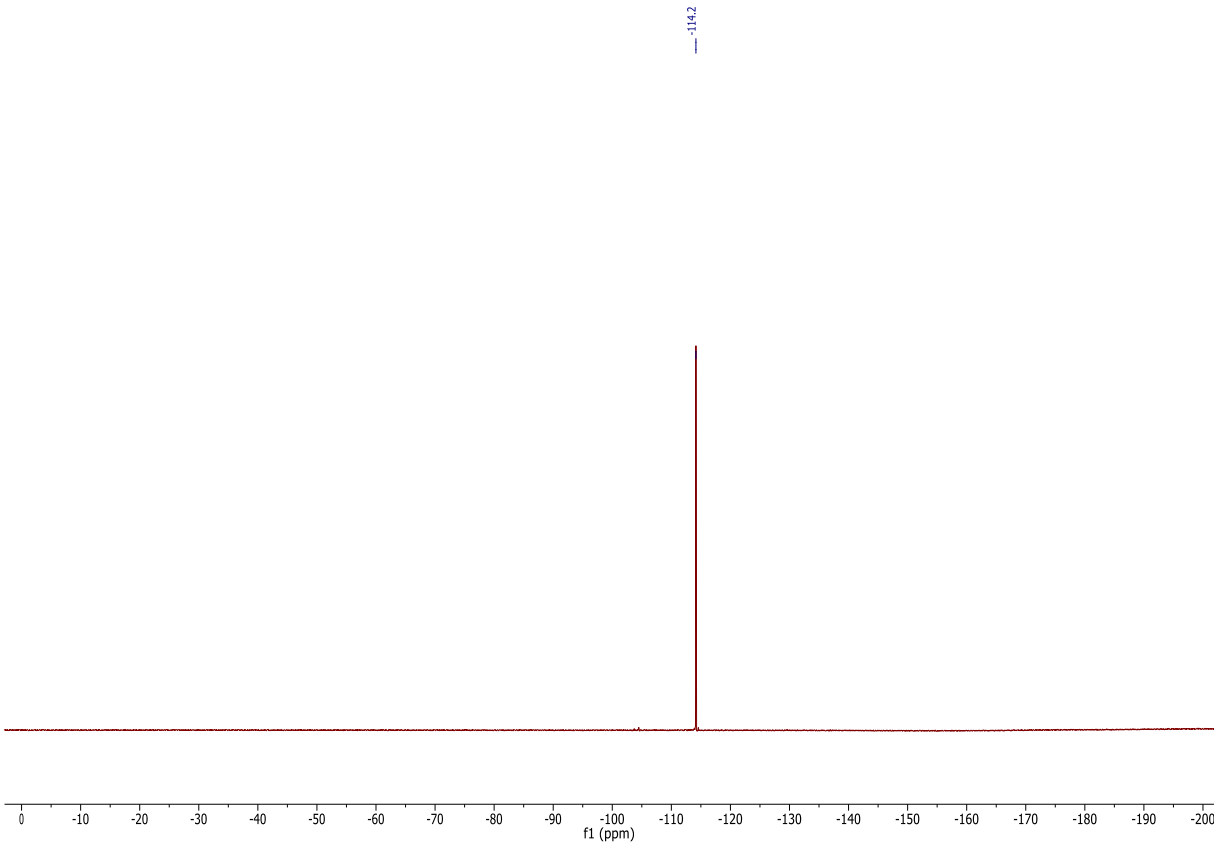




2-(4-fluorophenyl)imidazo[1,2-a]pyridine (**3c**)



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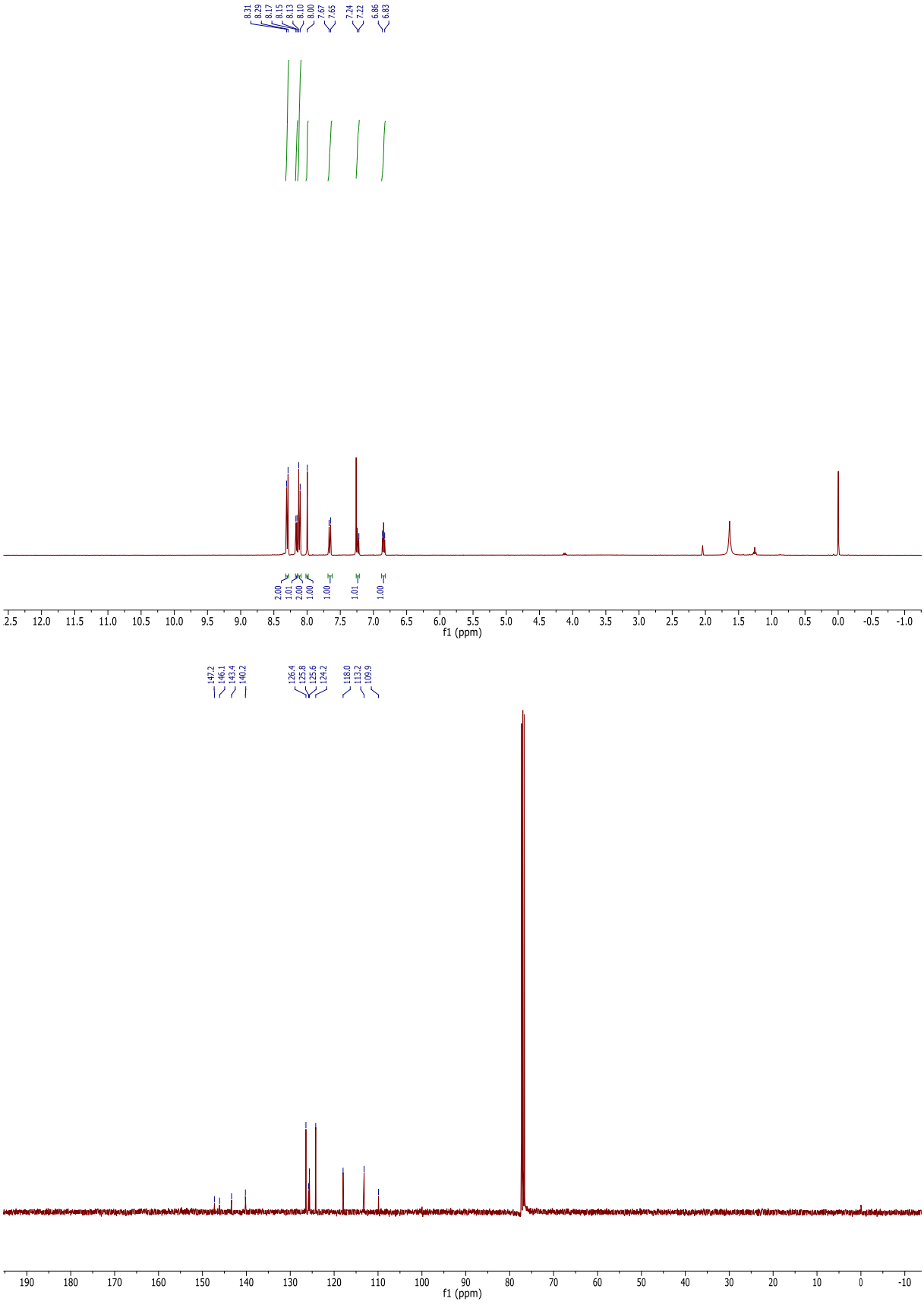
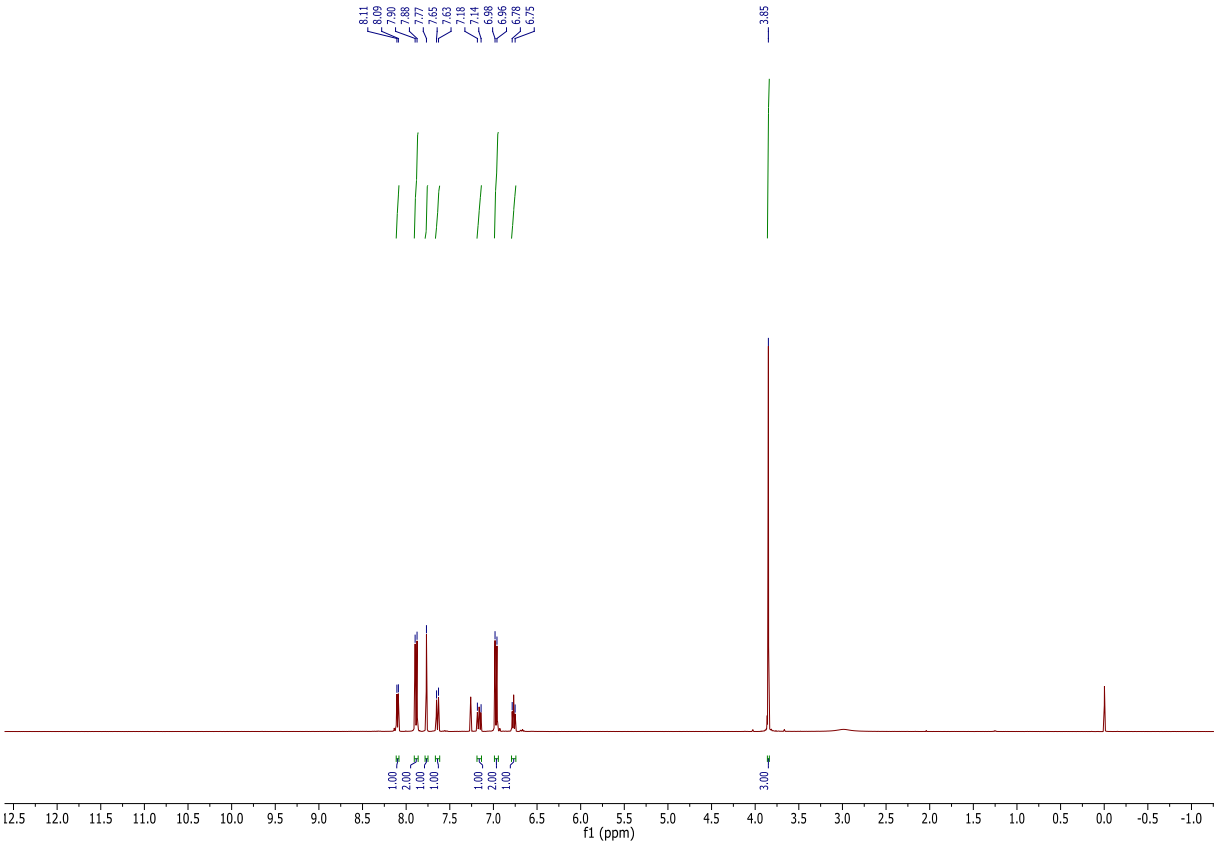
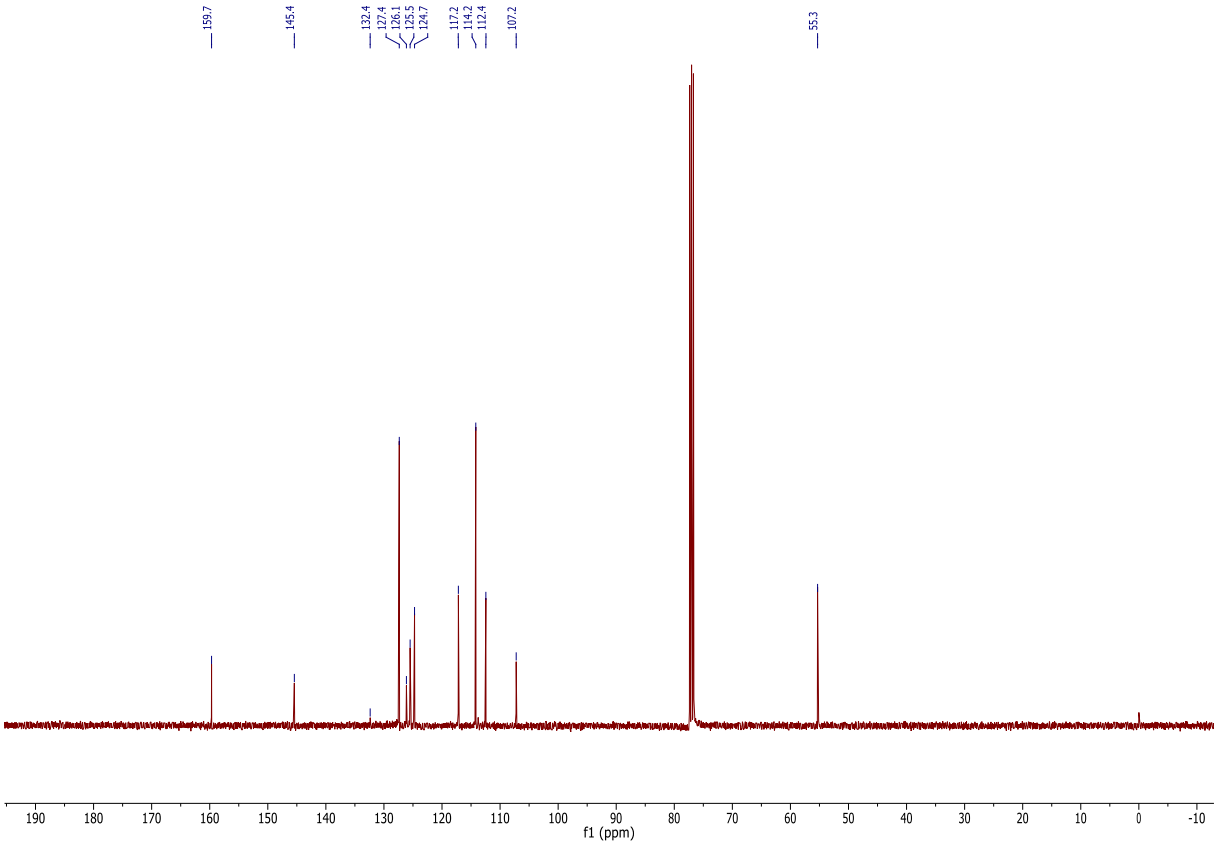
f1 (ppm)

2-(4-nitrophenyl)imidazo[1,2-a]pyridine (**3d**)

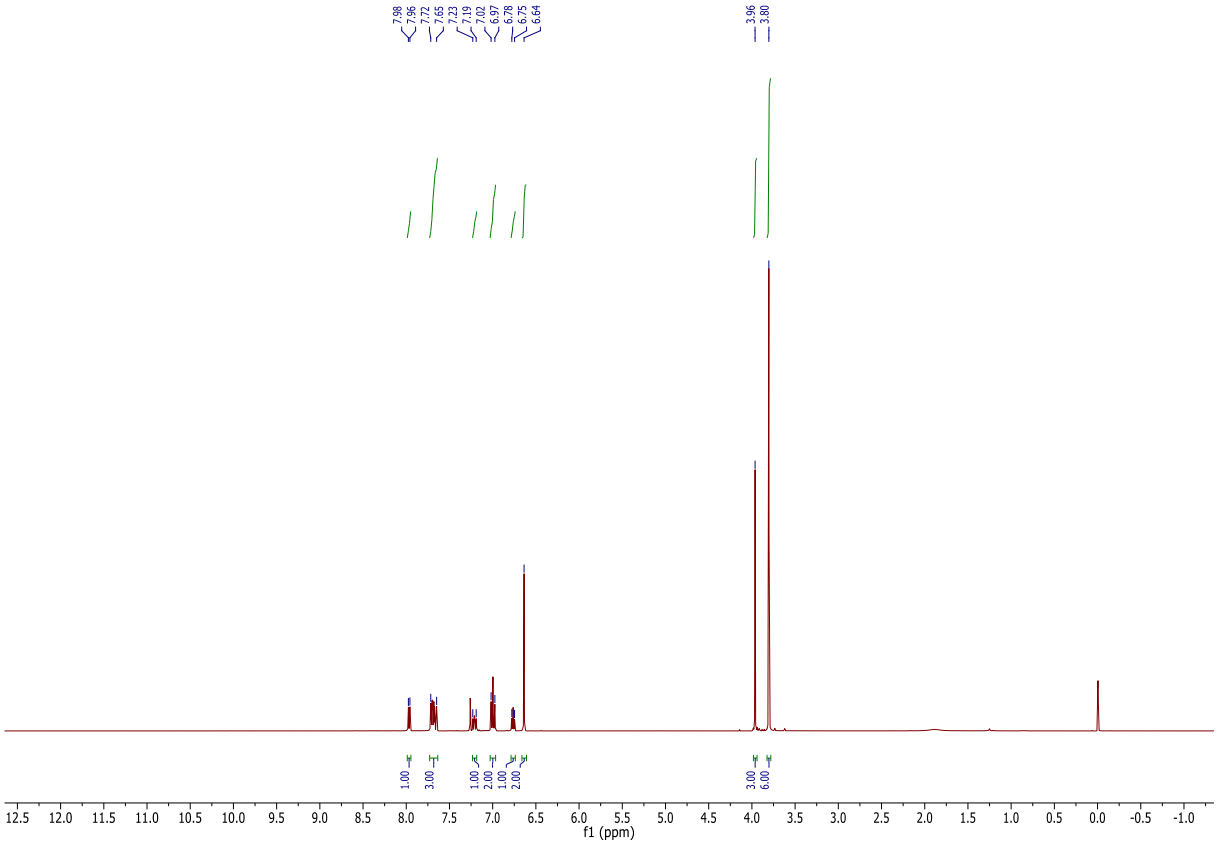


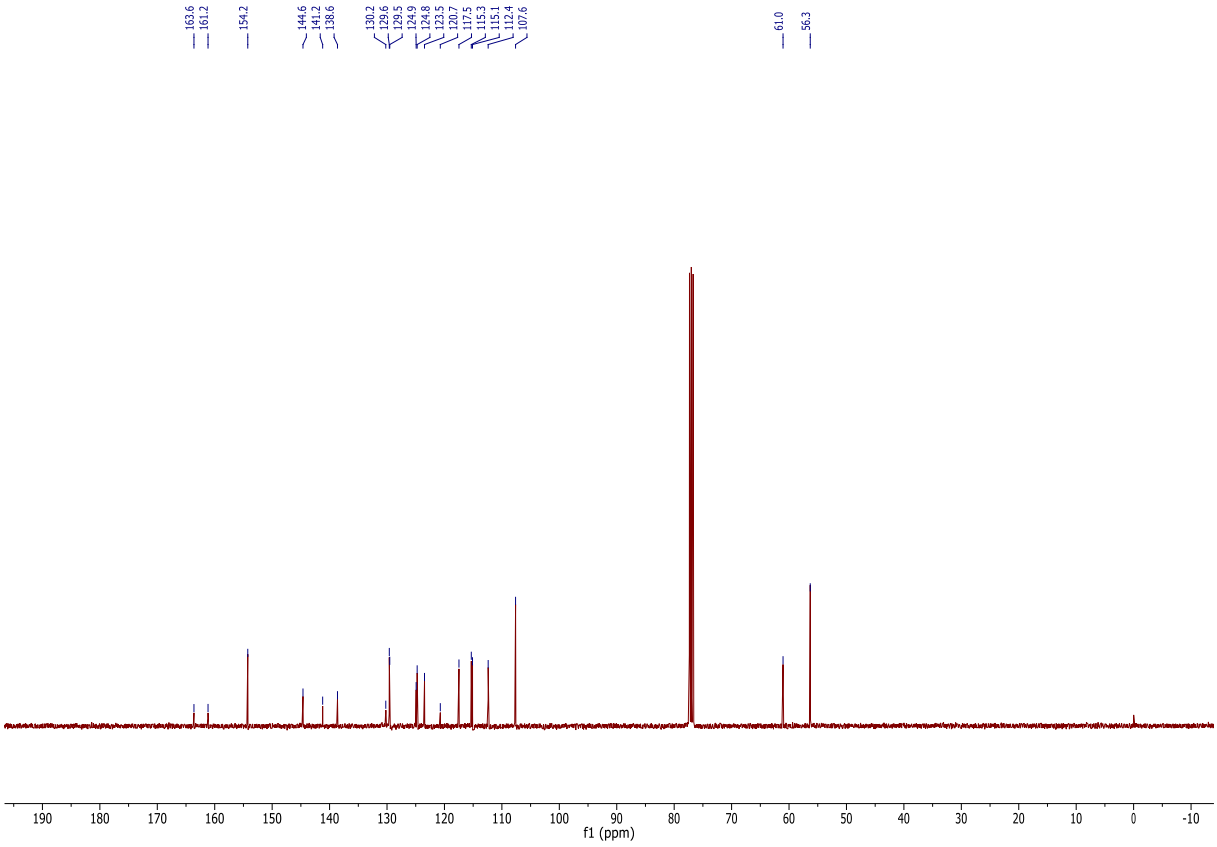
2-(4-methoxyphenyl)imidazo[1,2-a]pyridine (**3e**)

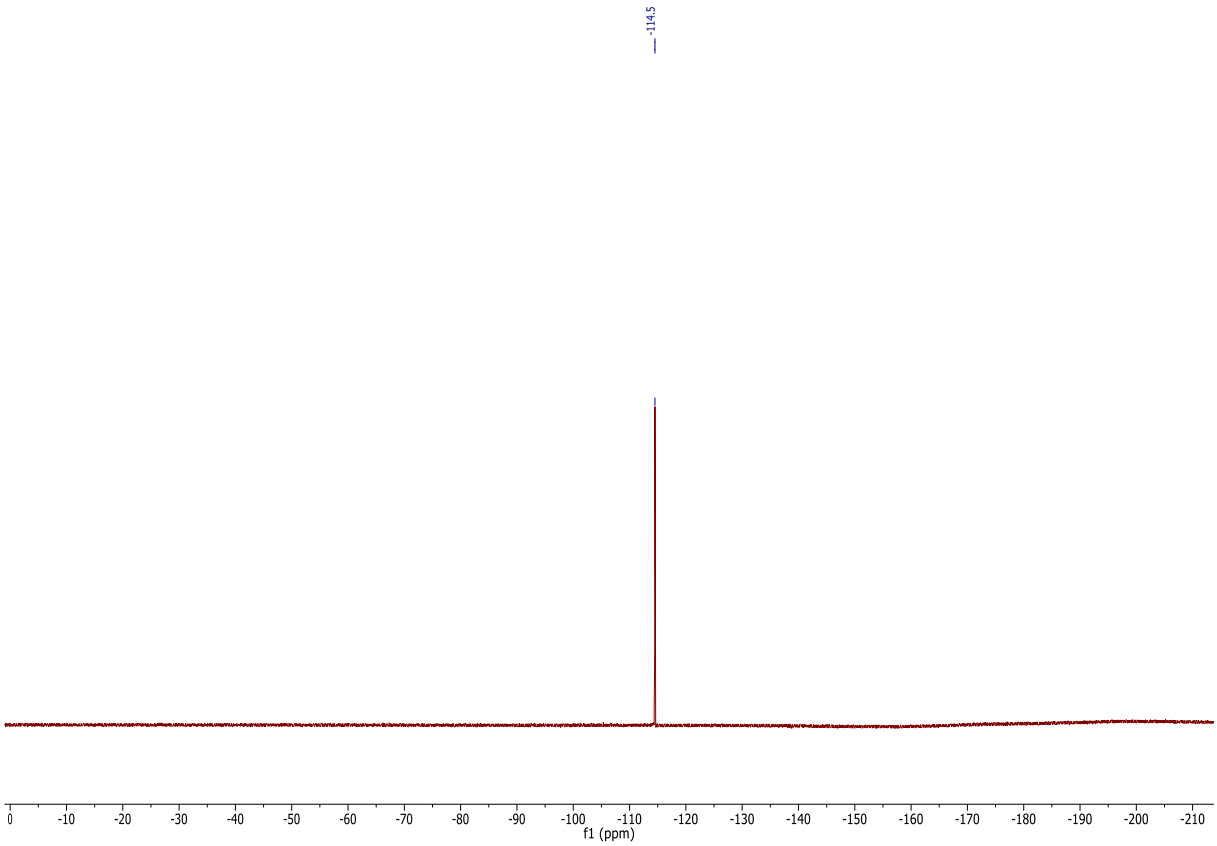




2-(4-fluorophenyl)-3-(3,4,5-trimethoxyphenyl)imidazo[1,2-a]pyridine (**6a**)



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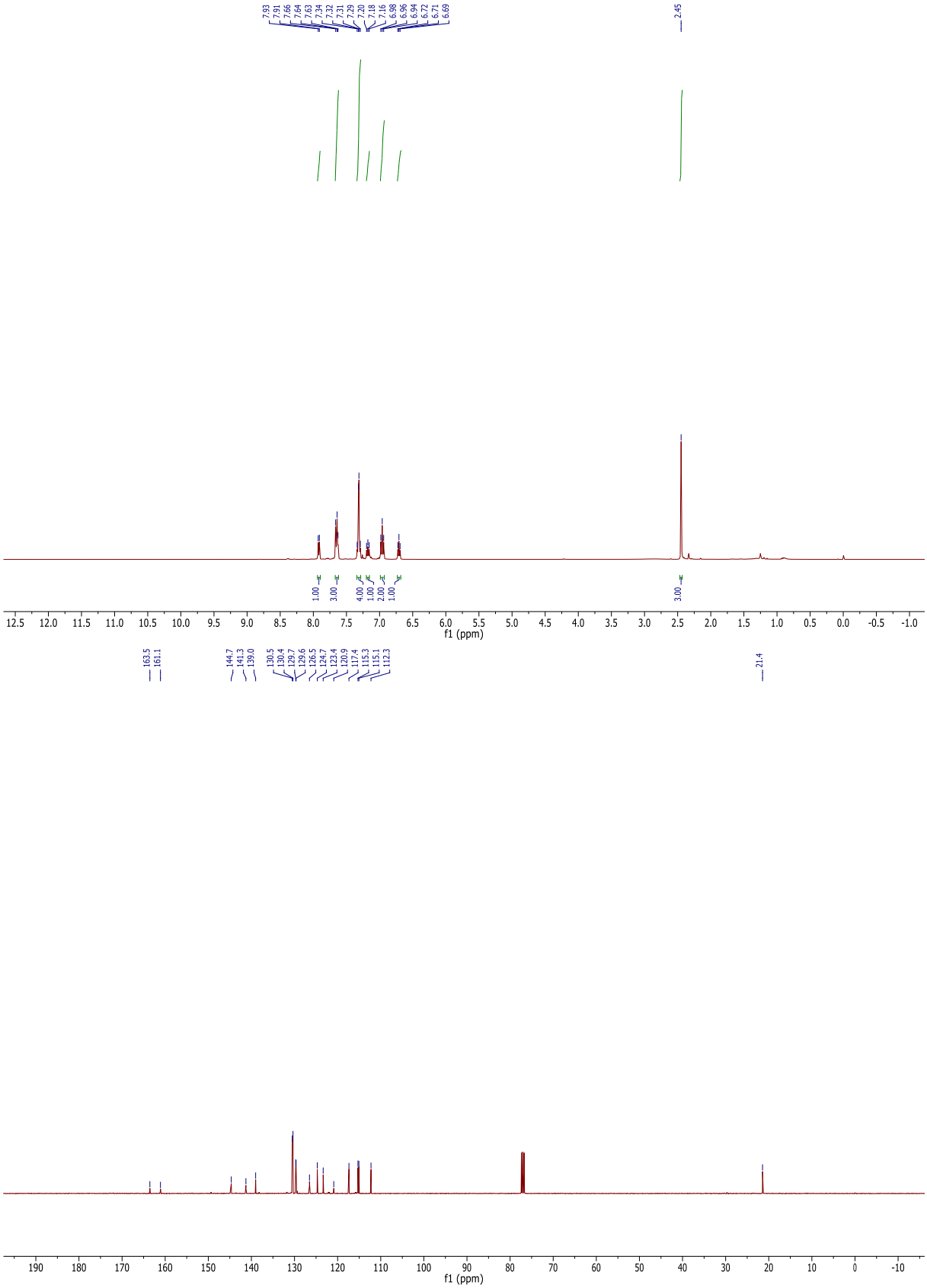
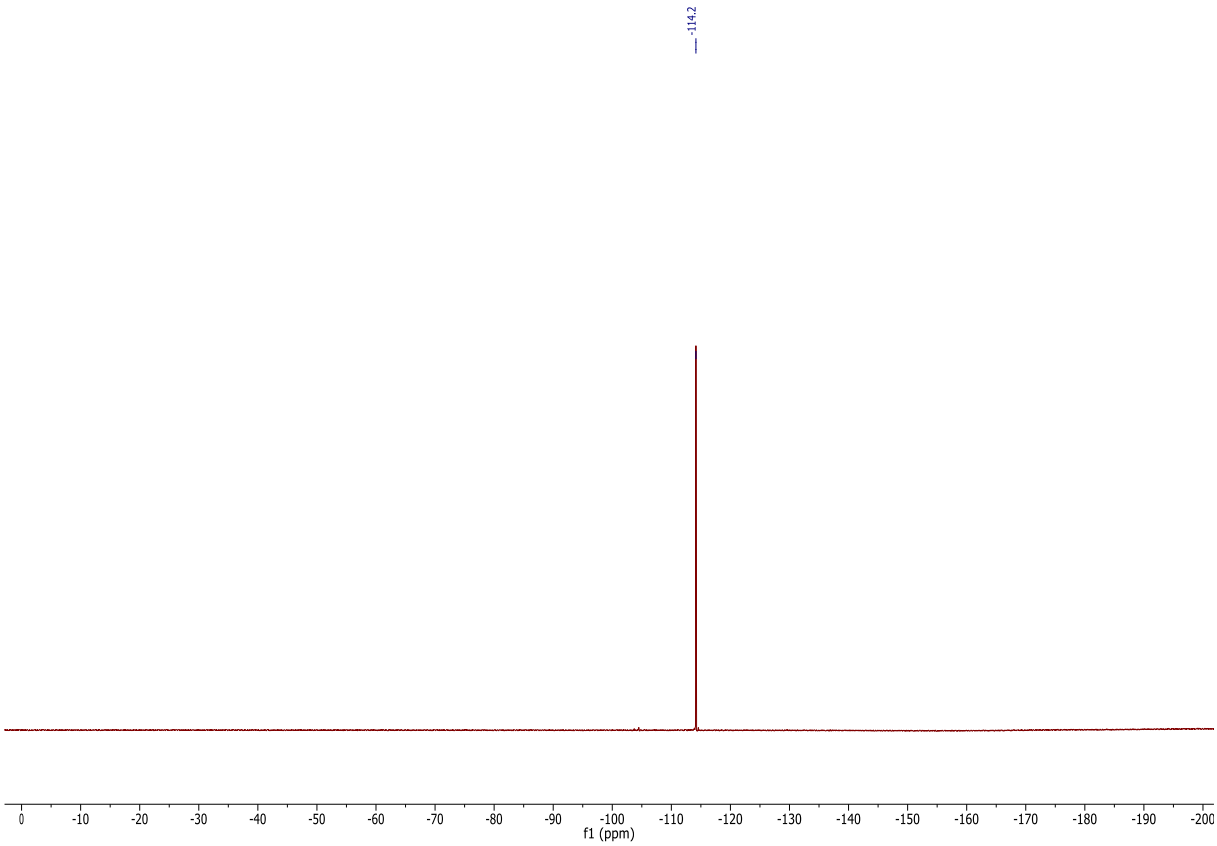
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

2-(4-fluorophenyl)-3-(p-tolyl)imidazo[1,2-a]pyridine (**6b**)

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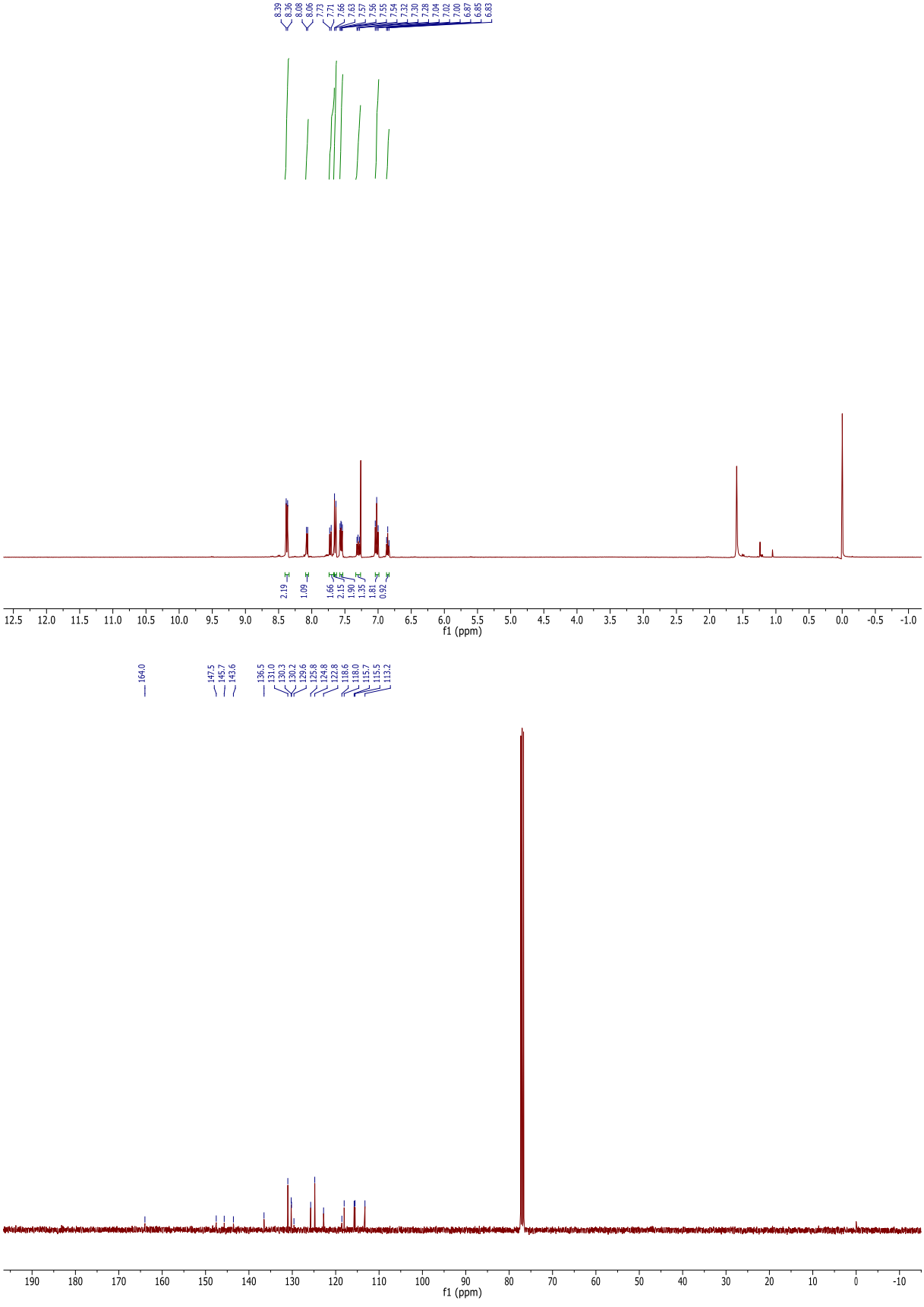
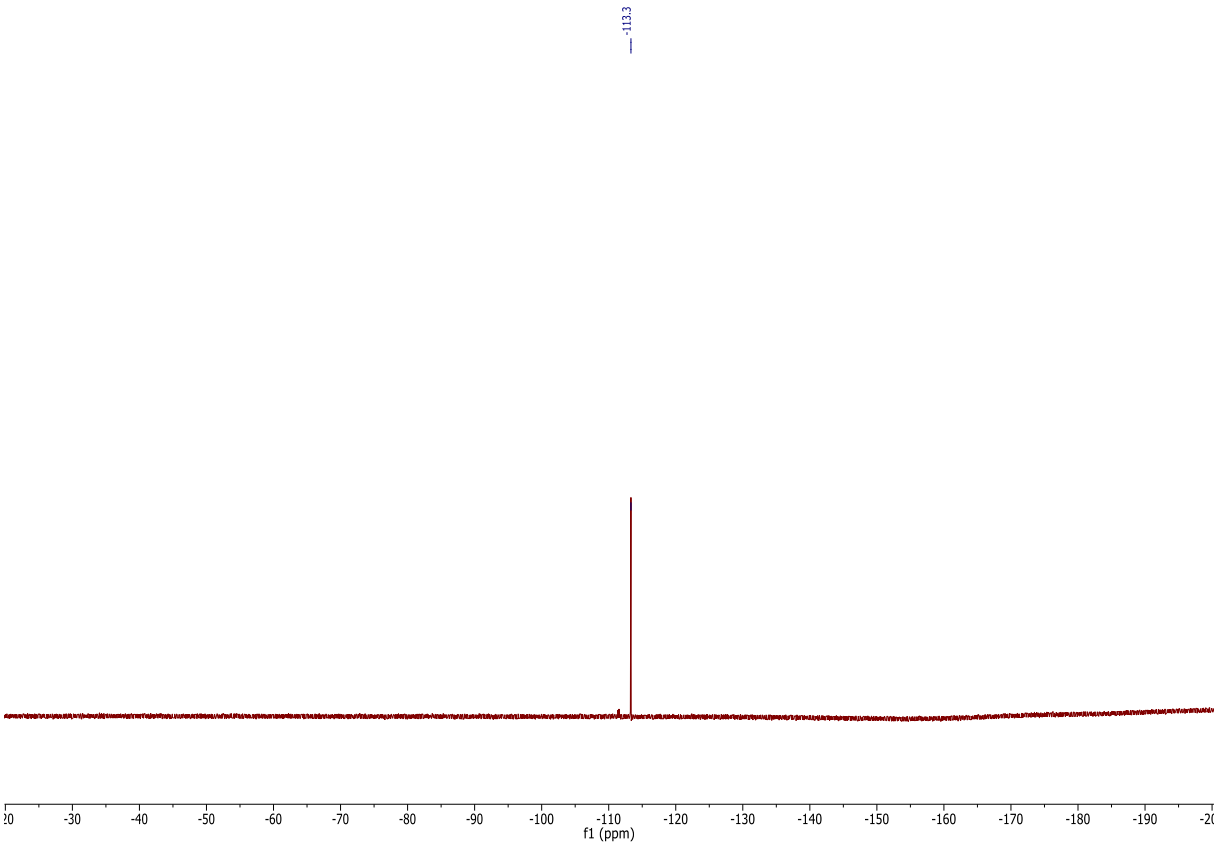
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

2-(4-fluorophenyl)-3-(4-nitrophenyl)imidazo[1,2-a]pyridine (**6c**)

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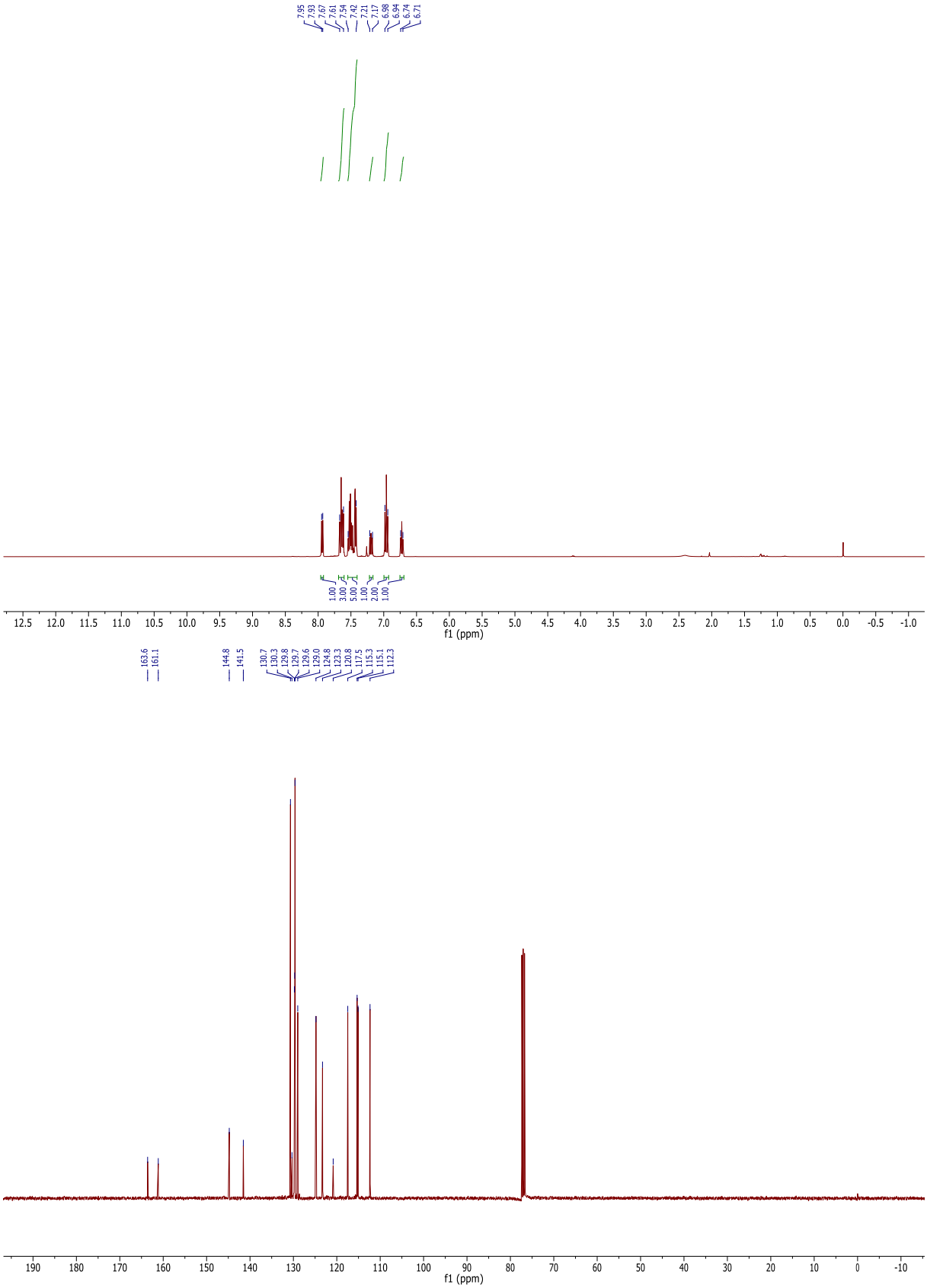
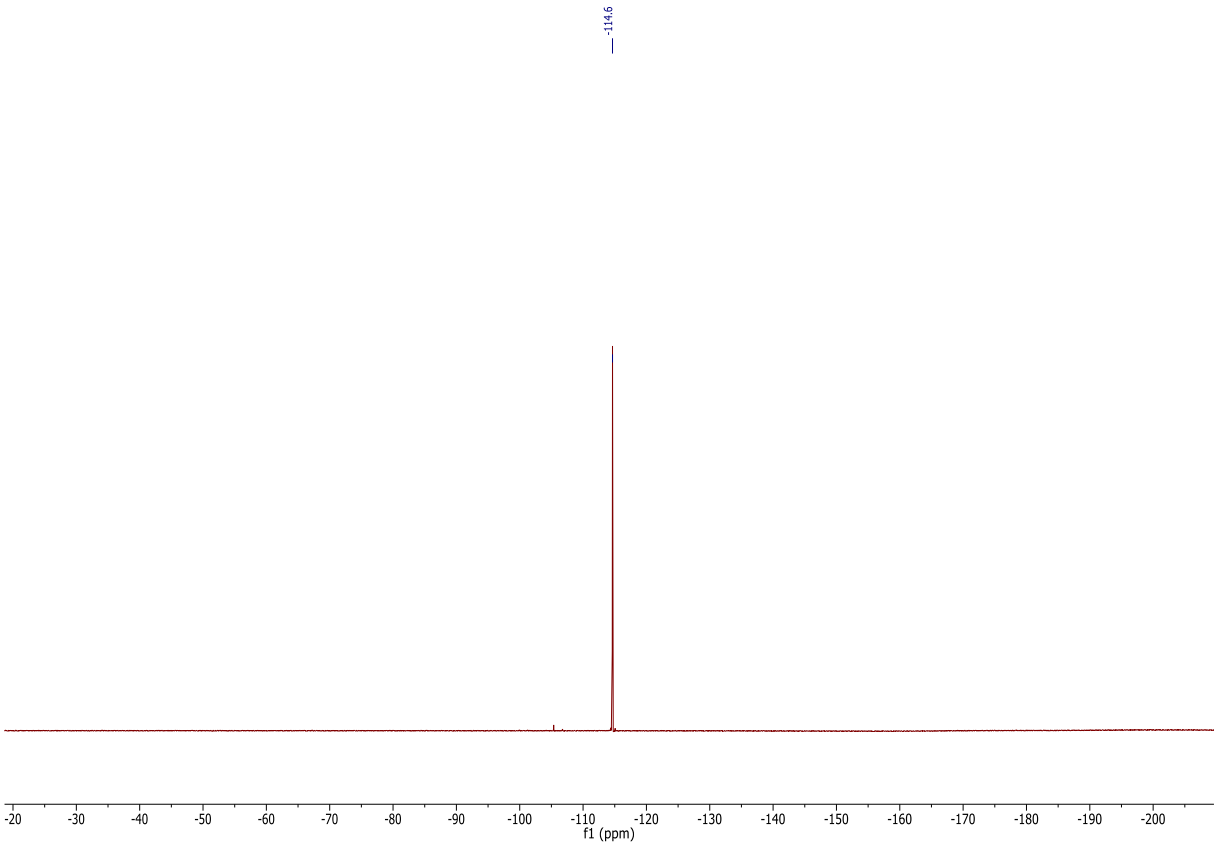
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

2-(4-fluorophenyl)-3-phenylimidazo[1,2-a]pyridine (**6d**)

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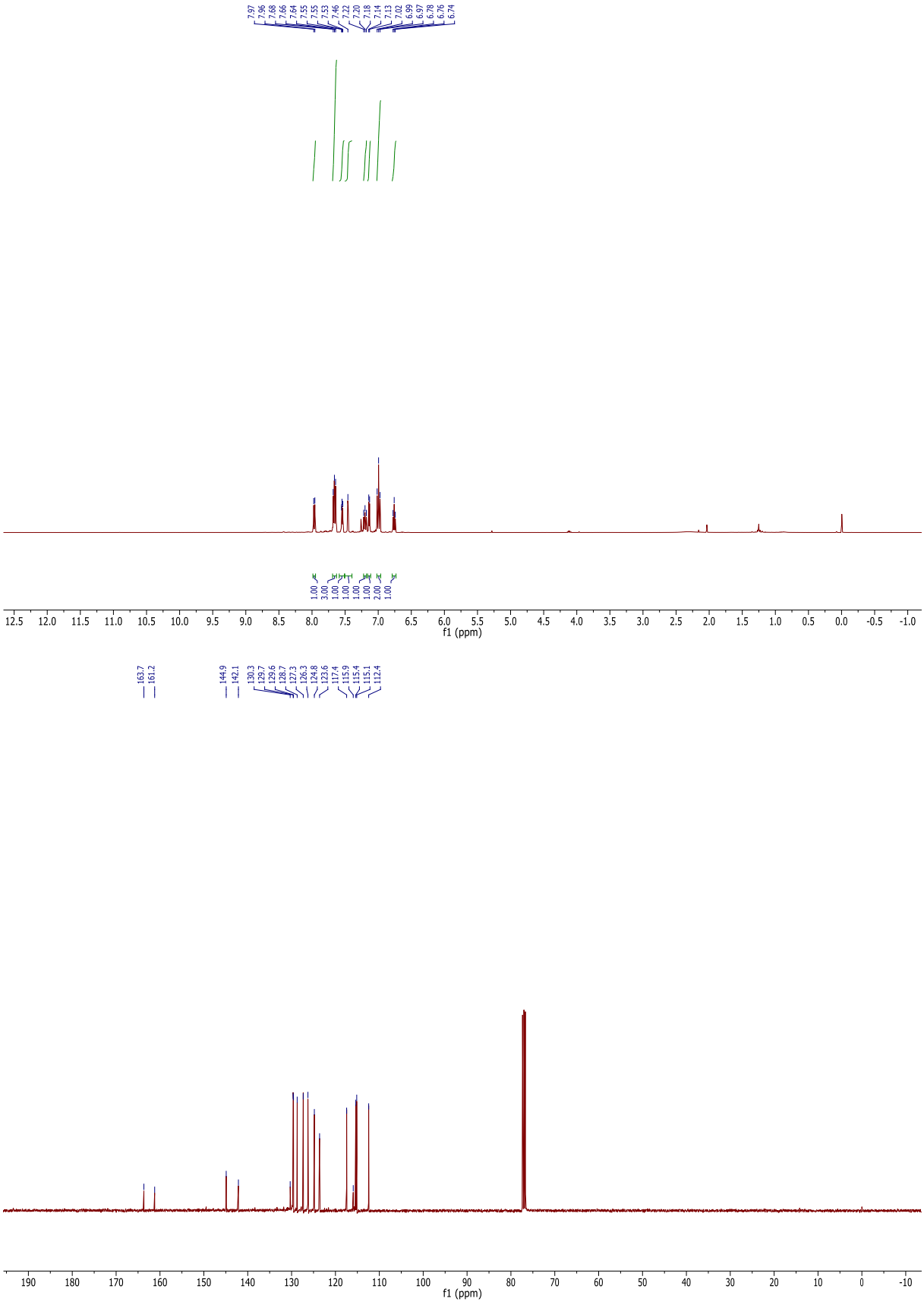
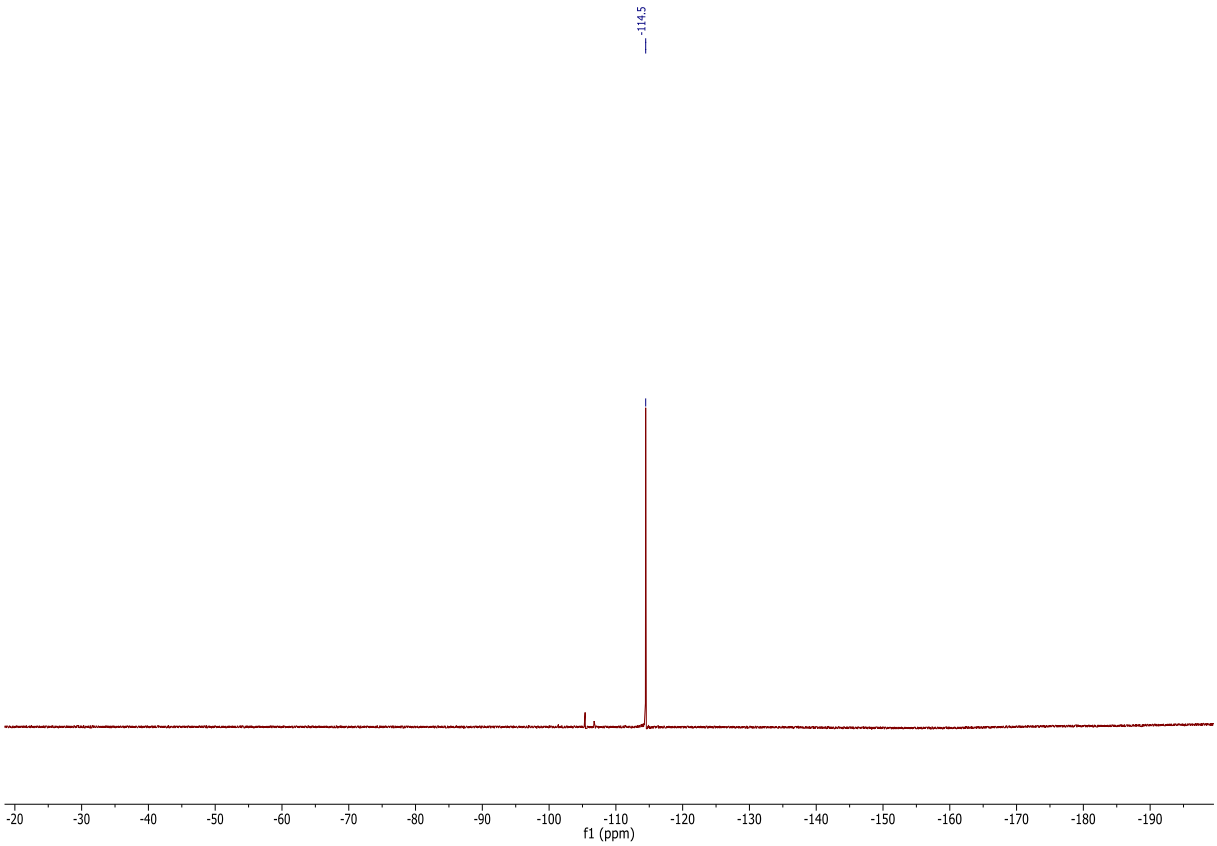
f1 (ppm)

2-(4-fluorophenyl)-3-(thiophen-3-yl)imidazo[1,2-a]pyridine (**6e**)

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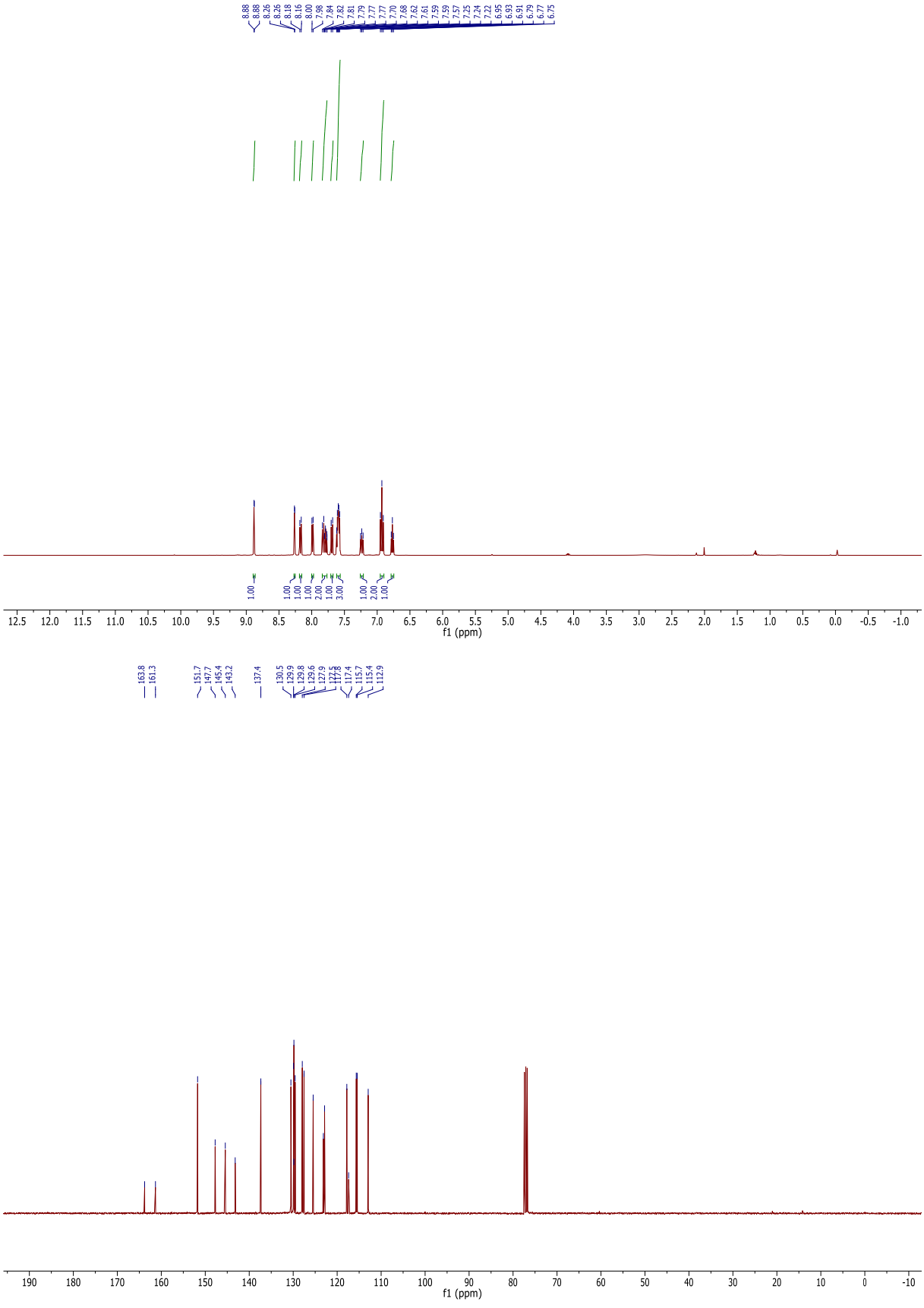
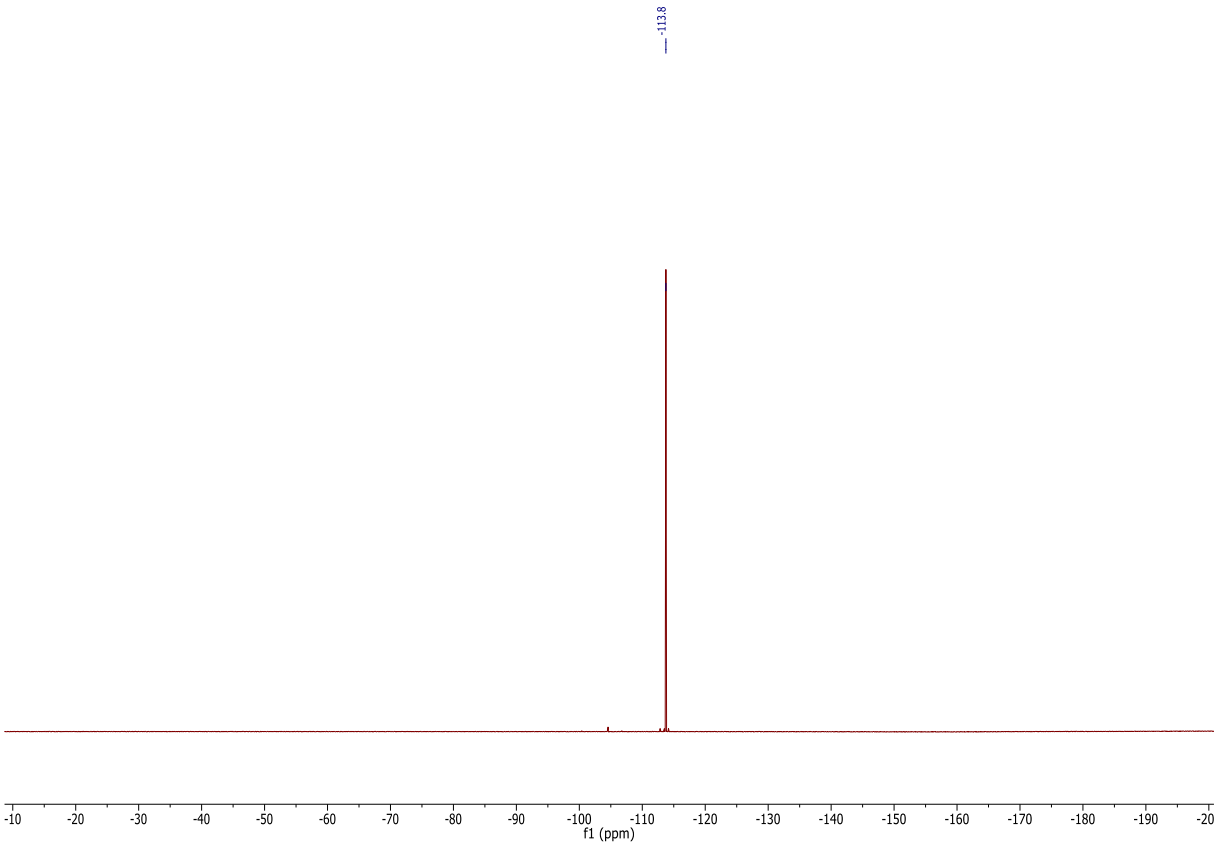
f1 (ppm)

3-(2-(4-fluorophenyl)imidazo[1,2-a]pyridin-3-yl)quinoline (**6f**)

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-190
-20
f1 (ppm)

2B. Suzuki-Miyaura coupling reaction

2B1. General procedure for the synthesis of 9a-e, 11a-e, 13, 15, 17a-e and characterization

General procedure: A mixture of chloro compound (50 mg), boronic acid (1.5 eq.), $Pd(PPh_3)_4$ (0.1 eq.) Na_2CO_3 or K_2CO_3 (2 eq.) in Eucalyptol (3 mL) was stirred at 100 °C for 14 - 24 h. The reaction was followed by TLC. After completion the reaction was then cooled to room temperature and the mixture was concentrated under vacuum. The solid obtained was purified by flash chromatography using a mixture of AcOEt/petroleum ether.

4-(p-tolyl)thieno[3,2-d]pyrimidine (**9a**): white solid (65 mg, 99%), m.p. 117-119 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 5.5 Hz, 1H), 8.01 (d, *J* = 5.5 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 2H), 9.27 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.5 (CH), 125.0 (CH), 127.9 (C), 128.5 (2xCH), 129.8 (2xCH), 134.5 (C), 136.0 (CH), 141.5 (C), 154.9 (CH), 160.0 (C), 162.0 (C) ppm. HRMS: calcd. for $C_{13}H_{11}N_2S$ $[M+H]^+$ 227.0637, found 227.0635.

4-(thieno[3,2-d]pyrimidin-4-yl)benzonitrile (**9b**): white solid (48 mg, 69%), m.p. 213-215 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 5.5 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 8.10 (d, *J* = 5.5 Hz, 1H), 8.33 (d, *J* = 8.3 Hz, 2H), 9.34 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 114.6 (C), 118.1 (C), 125.2 (CH), 129.2 (2xCH), 132.8 (2xCH), 136.5 (CH), 141.3 (C), 155.0 (CH), 157.8 (C), 162.6 (C) ppm. HRMS: calcd. for $C_{13}H_8N_3S$ $[M+H]^+$ 238.0433, found 238.0430.

4-(3-(trifluoromethyl)phenyl)thieno[3,2-d]pyrimidine (**9c**): white solid (58 mg, 71%), m.p. 111-113 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 5.5 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 5.5 Hz, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 9.30 (s, 1H), 8.48 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 121.1 (d, *J* = 282.8 Hz, CF_3), 125.1 (CH), 125.6 (CH), 127.6 (CH), 128.0 (C), 129.6 (CH), 131.6 (CH), 131.6 (d, *J* = 40.4 Hz, CF), 136.4 (CH), 138.0 (C), 154.9 (CH), 158.3 (C), 162.4 (C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.75 ppm. HRMS: calcd. for $C_{13}H_8F_3N_2S$ $[M+H]^+$ 281.0355, found 281.0353.

4-(benzo[b]thiophen-2-yl)thieno[3,2-d]pyrimidine (**9d**): white solid (62 mg, 79%), m.p. 173-175 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ7.39 – 7.46(m, 2H), 7.62 (d, *J* = 5.5 Hz, 1H), 7.90 – 7.94 (m, 2H), 8.04 (d, *J* = 5.5 Hz, 1H), 8.26 (s, 1H), 9.23 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ122.6 (CH), 124.9 (CH), 125.0 (2xCH), 125.8 (C), 126.5 (CH), 126.8 (CH), 135.6 (CH), 140.0 (C), 141.2 (C), 141.9 (C), 153.9 (C), 154.5 (CH), 162.3 (C) ppm. HRMS: calcd. for $C_{14}H_9N_2S_2$ $[M+H]^+$ 269.0202, found 269.0200.

4-(benzofuran-2-yl)thieno[3,2-d]pyrimidine (**9e**): white solid (42 mg, 64%), m.p. 145-147 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 5.5 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.83 (s, 1H), 8.06 (d, *J* = 5.5 Hz, 1H), 9.23 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 110.0 (CH), 112.0 (CH), 122.5 (CH), 123.9 (CH), 124.4 (CH), 125.6 (C), 126.8 (CH), 127.9 (C), 137.4 (CH), 150.2 (C), 152.6 (C), 154.5 (CH), 155.9 (C), 162.5 (C) ppm. HRMS: calcd. for $C_{14}H_9N_2OS$ $[M+H]^+$ 253.0430, found 253.0428.

5-methyl-7-(p-tolyl)-[1,2,4]triazolo[1,5-a]pyrimidine (**11a**): white solid (47 mg, 71%), m.p. 116-118 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 2.74 (s, 3H), 7.05 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 2H), 8.44 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.6 (CH), 25.2 (CH), 109.5 (CH), 126.9 (C), 129.2 (2xCH), 129.6 (2xCH), 142.40 (C), 147.3 (C), 155.6 (CH), 156.2 (C), 165.0 (C) ppm.

4-(5-methyl-[1,2,4]triazolo[1,5-a]pyrimidin-7-yl)benzonitrile(**11b**): white solid (31 mg, 44%), m.p. 262-264 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 3H), 7.12 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 2H), 8.49 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 25.3 (CH), 110.4 (CH), 115.3 (C), 117.8 (C), 129.9 (2xCH), 132.6 (2xCH), 133.9 (C), 145.0 (C), 156.0 (CH), 165.4 (C) ppm.

5-methyl-7-(3-(trifluoromethyl)phenyl)-[1,2,4]triazolo[1,5-a]pyrimidine(**11c**): white solid (43 mg, 52%), m.p. 148-150 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (s, 3H), 7.13 (s, 1H), 8.47 (s, 1H), 7.73 (t, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 8.30 – 8.33 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 25.2 (CH), 110.2 (CH), 123.6 (d, *J* = 272.7 Hz, CF_3), 126.2 (CH), 128.3 (CH), 129.5 (CH), 130.6 (C), 131.6 (d, *J* = 30.3 Hz, CF), 132.5 (CH), 145.5 (C), 155.9 (CH), 156.1 (C), 165.3 (C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.81 ppm. HRMS: calcd. for $C_{13}H_{10}F_3N_4$ $[M+H]^+$ 279.0852, found 279.0850.

5-methyl-7-(thiophen-3-yl)-[1,2,4]triazolo[1,5-a]pyrimidine(**11d**): yellow solid (31 mg, 48%), m.p. 135-137 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (s, 3H), 7.21 (s, 1H), 7.51 (dd, *J* = 3.0, 5.2 Hz, 1H), 7.78 (dd, *J* = 1.3, 5.2 Hz, 1H), 8.50 (s, 1H), 9.04 (dd, *J* = 1.3, 3.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 25.2 (CH), 107.8 (CH), 126.6 (CH), 126.8 (CH), 129.9 (C), 132.6 (CH), 141.3 (C), 155.6 (CH), 156.2 (C), 164.8 (C) ppm. HRMS: calcd. for $C_{10}H_9N_4S$ $[M+H]^+$ 217.0542, found 217.0539.

7-(benzofuran-2-yl)-5-methyl-[1,2,4]triazolo[1,5-a]pyrimidine(**11e**): white solid (42 mg, 56%), m.p. 207-209 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (s, 3H), 7.32 – 7.36 (m, 1H), 7.45 – 7.50 (m, 1H), 7.59 (d, *J* = 9.2 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 8.56 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 25.3 (CH), 106.4 (CH), 111.6 (CH), 116.5 (CH), 123.1 (CH), 124.1 (CH), 127.9 (CH), 128.2 (C), 136.5 (C), 144.1 (C), 155.5 (C), 155.8 (CH), 155.8 (C), 164.7 (C) ppm. HRMS: calcd. for $C_{14}H_{11}N_4O$ $[M+H]^+$ 251.0927, found 251.0926.

8-(p-tolyl)-[1,2,4]triazolo[4,3-a]pyrazine(**13**): white solid (50 mg, 74%), m.p. 208-210 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ2.46 (s, 3H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.99 (q, *J* = 4.6 Hz, 2H), 8.76 (d, *J* = 8.3 Hz, 2H), 8.96 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ21.6 (CH), 114.3 (CH), 128.9 (CH), 129.4 (2xCH), 129.7 (CH), 130.0 (CH), 131.9 (C), 136.1 (CH), 142.3 (C), 144.2 (C), 150.9 (C)ppm. HRMS: calcd. for $C_{12}H_{11}N_4$ $[M+H]^+$ 211.0978, found 211.0976.

6-(p-tolyl)-[1,2,4]triazolo[4,3-a]pyrazine(**15**): white solid (46 mg, 68 %), m.p. 242-244 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 8.38 (d, *J* = 1.6 Hz, 1H), 8.97 (s, 1H), 9.44 (d, *J* = 1.5 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 21.3 (CH), 111.0 (CH), 126.3 (2xCH), 129.9 (2xCH), 132.1 (C), 136.0 (CH), 139.8 (C), 140.8 (C), 143.3 (CH), 144.3 (C) ppm. HRMS: calcd. for $C_{12}H_{11}N_4$ $[M+H]^+$ 211.0978, found 211.0977.

4-(p-tolyl)furo[3,2-c]pyridine (**17a**): white solid (44 mg, 65%), m.p. 122-124 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ2.44 (s, 3H),7.06 – 7.08 (m, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 5.7 Hz, 1H), 7.68 (d, *J* = 2.2 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 8.57 (d, *J* = 5.7 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ21.4 (CH),105.7 (CH), 105.9 (CH), 122.0 (C), 128.3 (2xCH), 129.4 (2xCH), 136.5 (C), 139.0 (C), 144.3 (CH), 145.4 (CH), 153.4 (C), 160.3 (C) ppm. HRMS: calcd. for $C_{14}H_{12}NO$ $[M+H]^+$ 210.0913, found 210.0908.

4-(furo[3,2-c]pyridin-4-yl)benzonitrile (**17b**): white solid (38 mg, 53 %), m.p. 169-171 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ7.04 – 7.07 (m, 1H), 7.50 (d, *J* = 5.7 Hz, 1H), 7.77 (d, *J* = 2.3 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 8.62 (d, *J* = 5.7 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ105.2 (CH), 106.9 (CH), 112.5 (C), 118.7 (C), 122.6 (C), 129.0 (2xCH), 132.5 (2xCH), 143.5 (C), 144.6 (CH), 146.4 (CH), 150.9 (C), 160.4 (C) ppm. HRMS: calcd. for $C_{14}H_9N_2O$ $[M+H]^+$ 221.0709, found 221.0709.

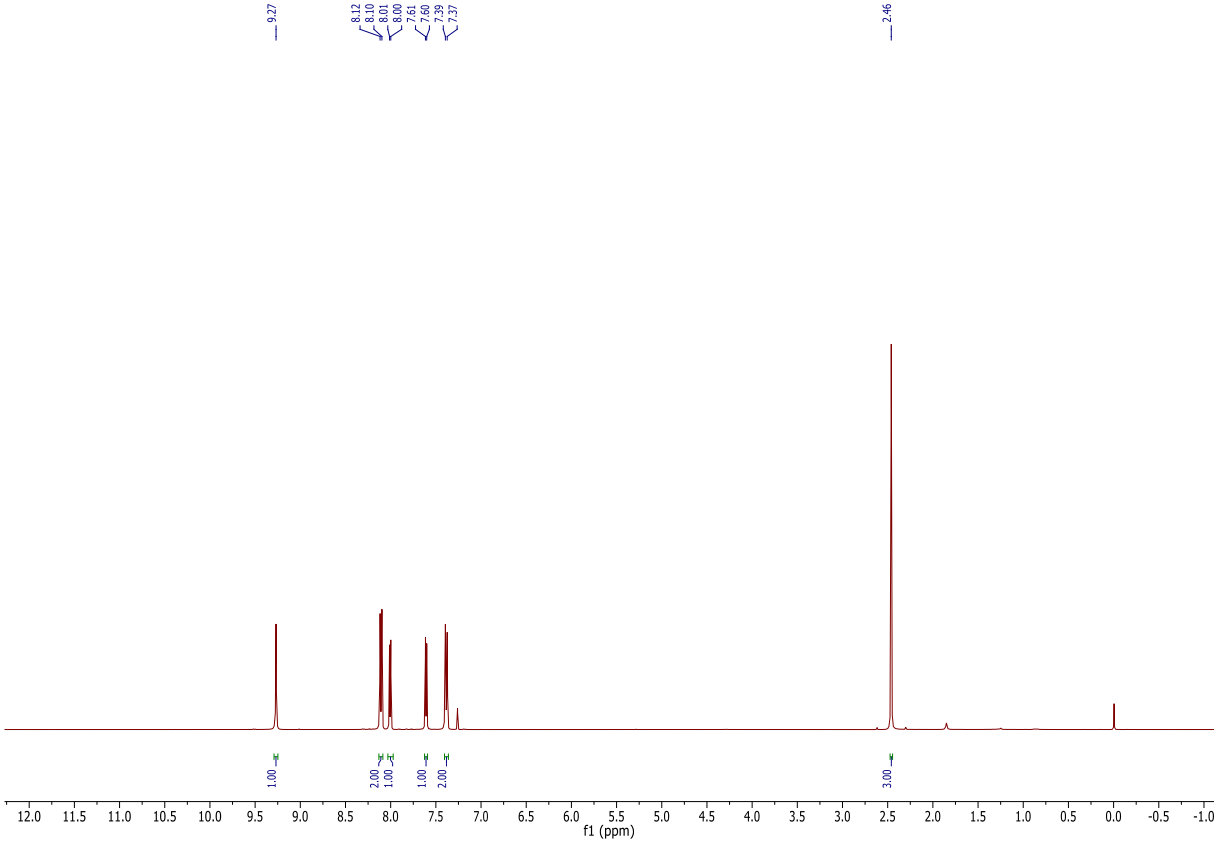
4-(3-(trifluoromethyl)phenyl)furo[3,2-c]pyridine (**17c**): white solid (84 mg, 98%), m.p. 89-91 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ7.04 – 7.07 (m, 1H), 7.48 (d, *J* = 5.7 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.70 – 7.76 (m, 2H), 8.15 (d, *J* = 7.7 Hz, 1H), 8.25 (s, 1H), 8.62 (d, *J* = 5.7 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (C), 151.6 (C), 146.1 (CH), 144.5 (CH), 139.9 (C), 131.6 (CH), 131.2 (q, *J* = 32.59 Hz, C), 129.9 (C), 129.2 (CH), 125.6 (CH), 125.3 (CH), 124.1 (q, *J* = 272.7 Hz, C), 106.6 (CH), 105.4 (CH) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ-62.61 ppm. HRMS: calcd. for $C_{14}H_9F_3NO$ $[M+H]^+$ 264.0631, found 264.0629.

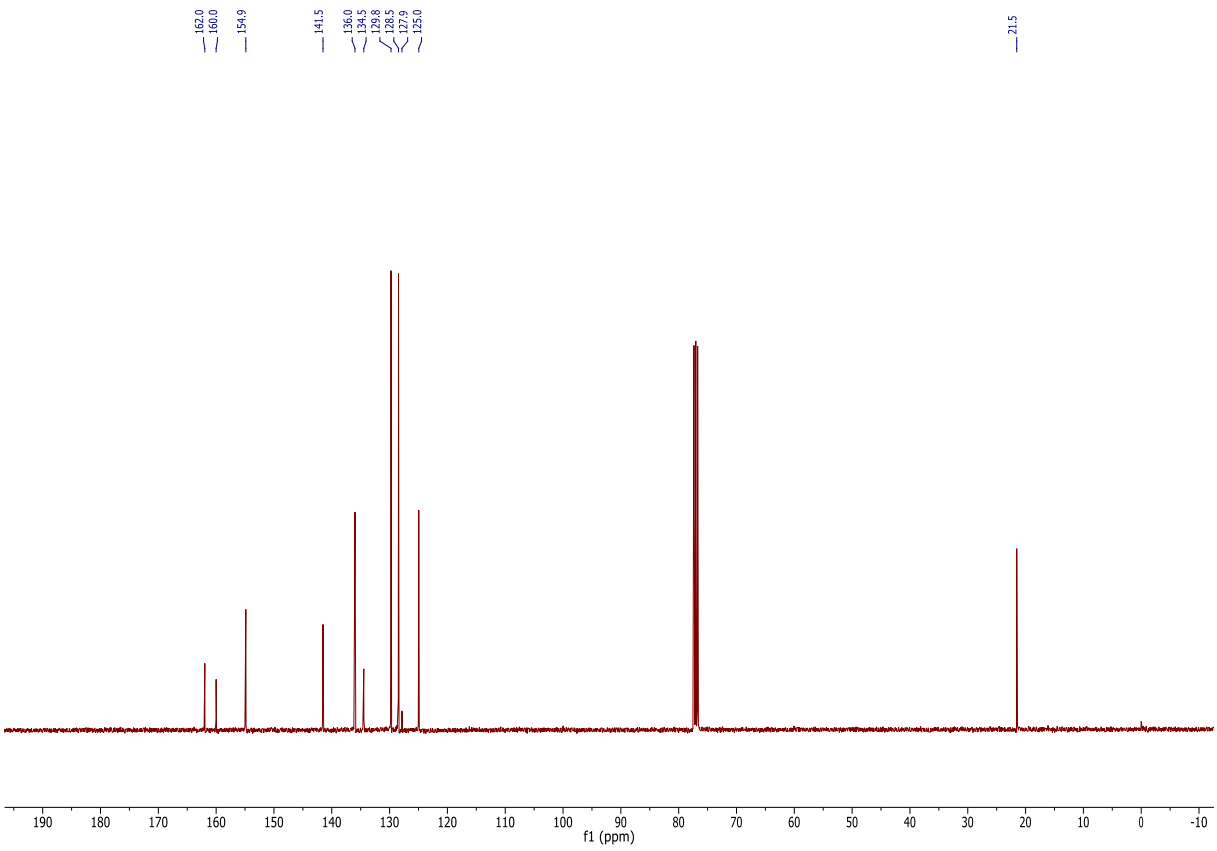
4-(thiophen-3-yl)furo[3,2-c]pyridine (**17d**): white solid (40 mg, 61%), m.p. 93-95 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ7.09 – 7.11 (m, 1H), 7.38 (d, *J* = 5.7 Hz, 1H), 7.46 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.70 (d, *J* = 2.2 Hz, 1H), 7.77 (d, *J* = 5.0 Hz, 1H), 7.91 – 7.94 (m, 1H), 8.52 (d, *J* = 5.7 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ105.6 (CH), 105.8 (CH), 121.6 (C), 125.0 (CH), 126.2 (CH), 127.5 (CH), 141.3 (C), 144.2 (CH), 145.6 (CH), 148.7 (C), 160.3 (C) ppm. HRMS: calcd. for $C_{11}H_8NOS$ $[M+H]^+$ 202.0321, found 202.0319.

4-(benzofuran-2-yl)furo[3,2-c]pyridine (**17e**): white solid (53 mg, 69 %), m.p. 105-107 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ7.23 – 7.28 (m, 1H),7.32 – 7.37 (m, 1H), 7.38 (d, *J* = 5.6 Hz, 1H), 7.49 (d, *J* = 2.1 Hz, 1H), 7.60 (s, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 2.2 Hz, 1H), 8.54 (d, *J* = 5.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ106.3 (CH), 106.5 (CH), 106.6 (CH), 111.5 (CH), 121.3 (C), 121.9 (CH), 123.3 (CH), 125.4 (CH), 128.5 (C), 143.5 (C), 144.5 (CH), 146.0 (CH), 155.3 (C), 155.4 (C), 160.5 (C) ppm. HRMS: calcd. for $C_{15}H_{10}NO_2$ $[M+H]^+$ 236.0706, found 236.0703.

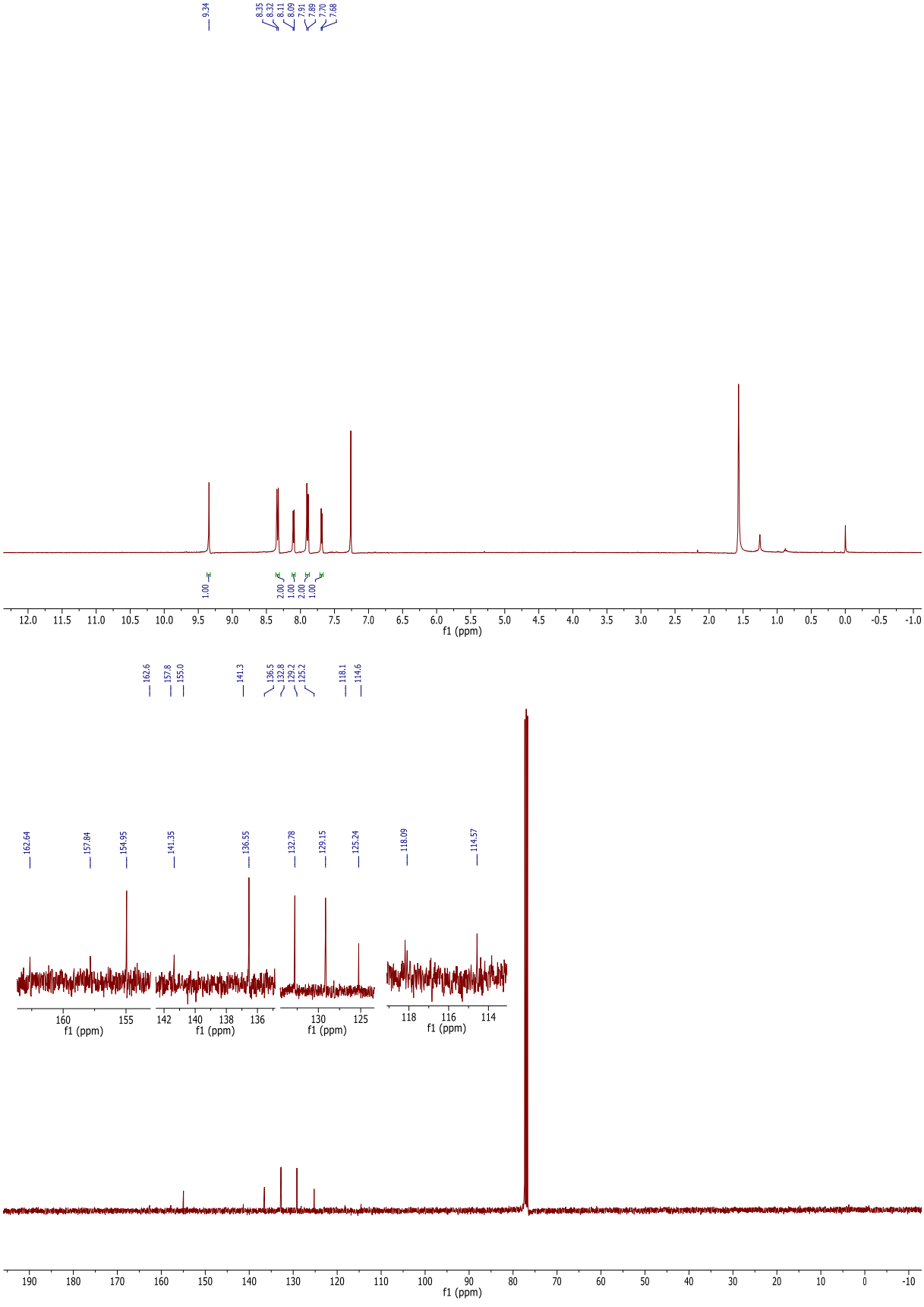
2B2. Spectra of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR

4-(p-tolyl)thieno[3,2-d]pyrimidine (**9a**)

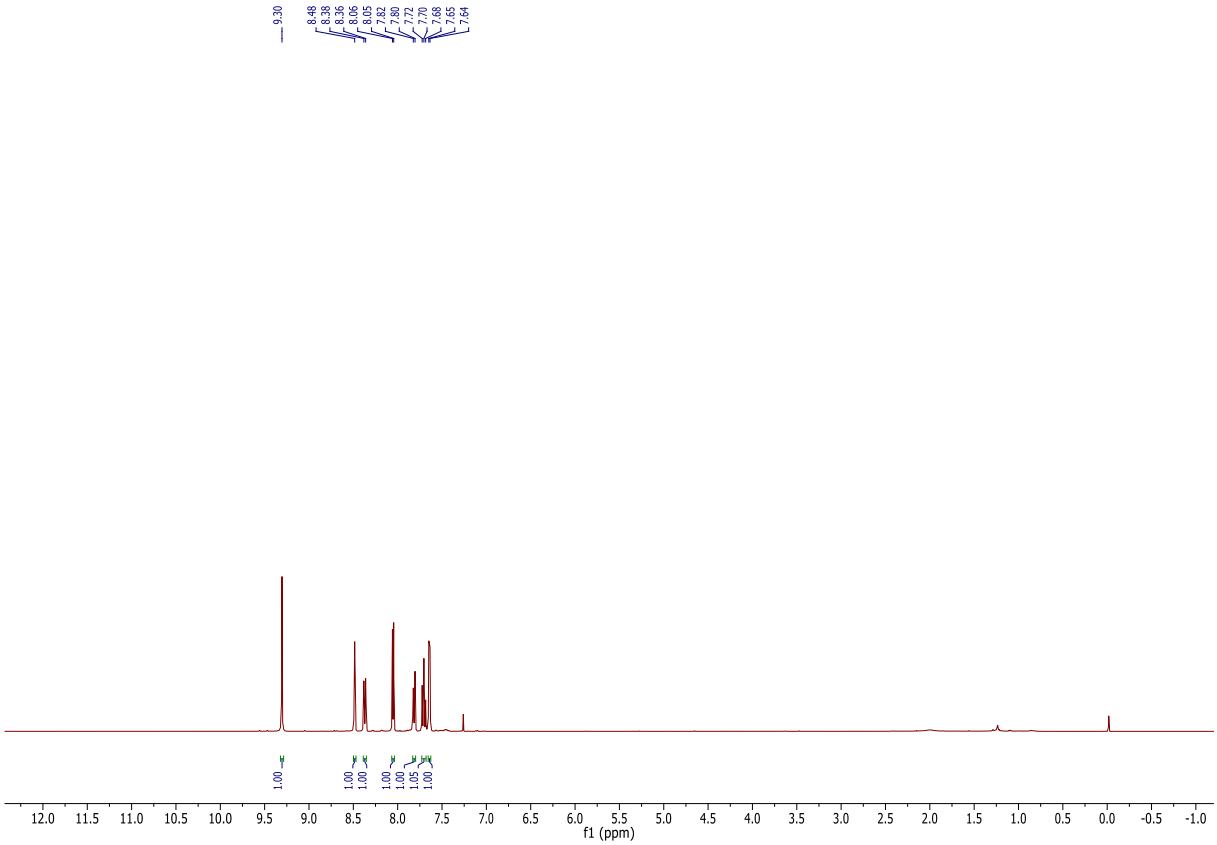


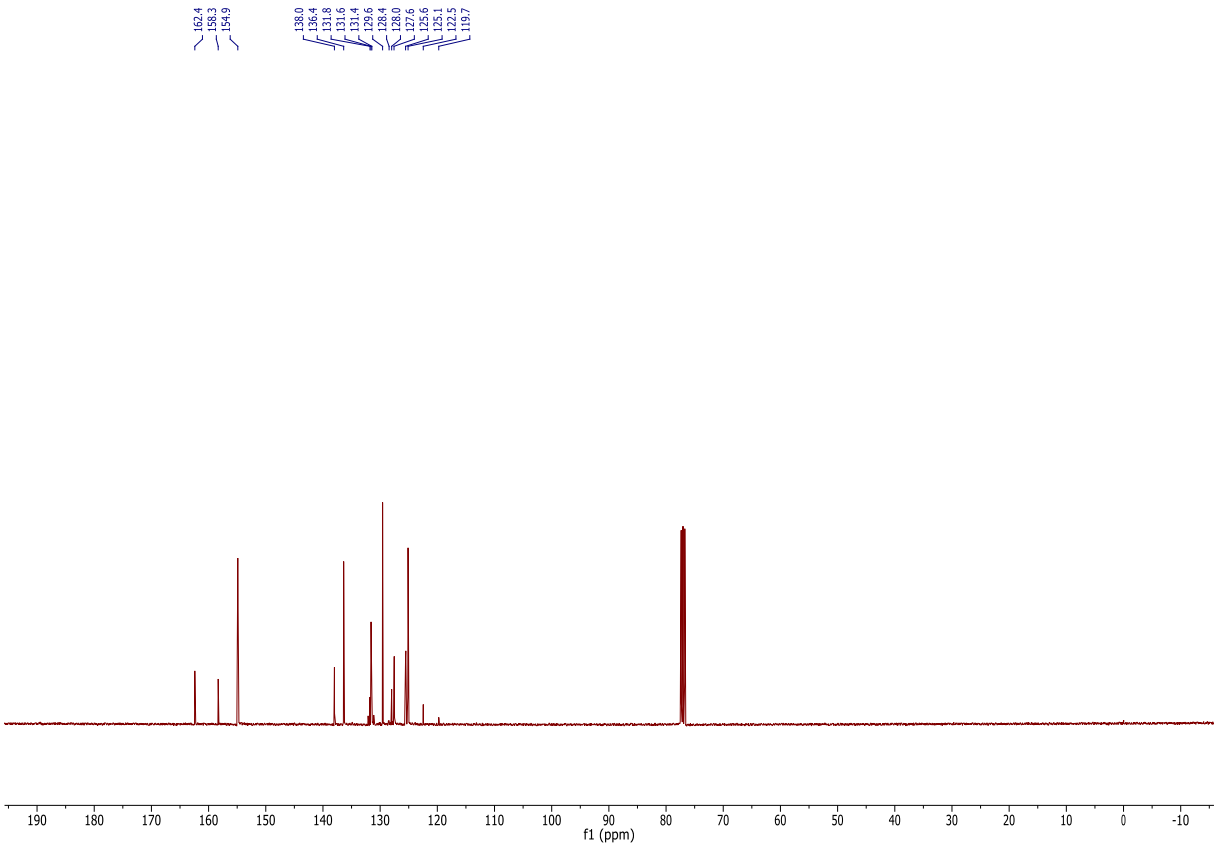


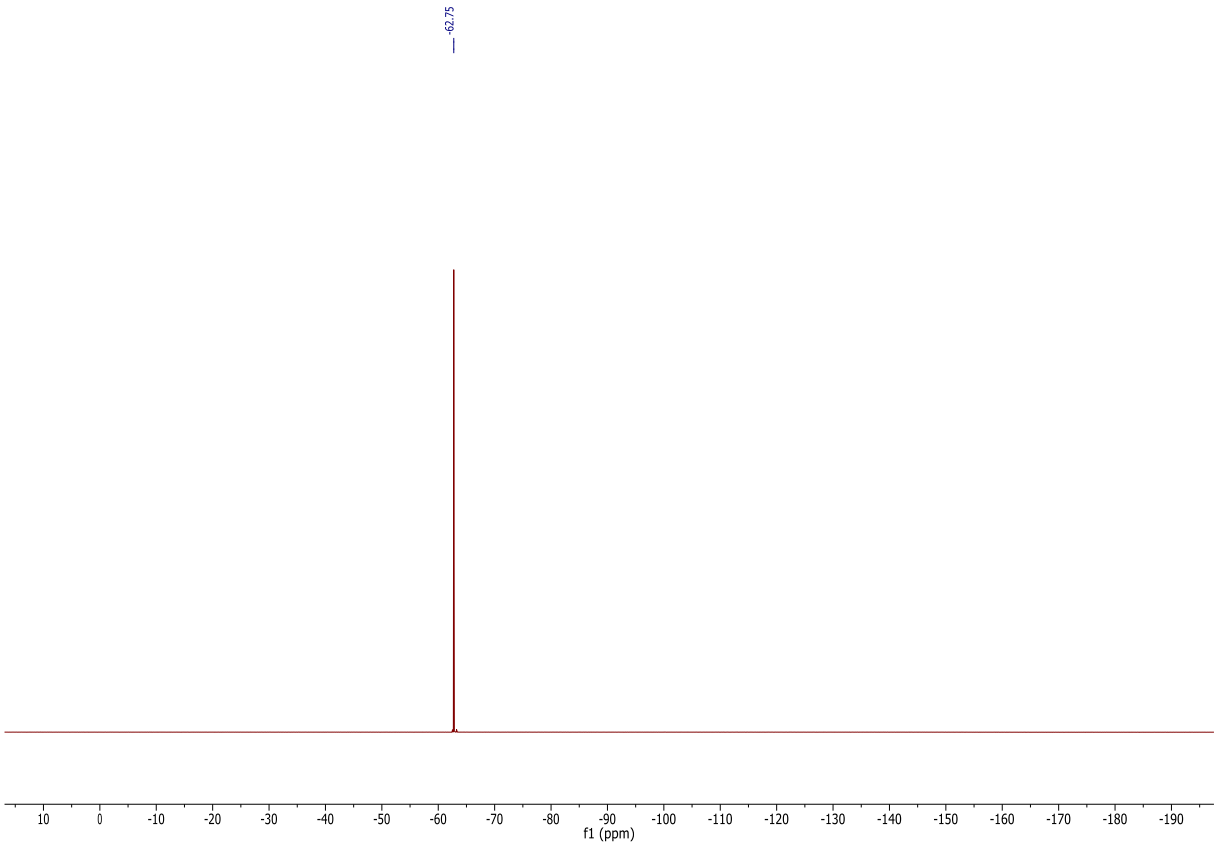
4-(thieno[3,2-d]pyrimidin-4-yl)benzonitrile (**9b**)



4-(3-(trifluoromethyl)phenyl)thieno[3,2-d]pyrimidine (**9c**)



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-160
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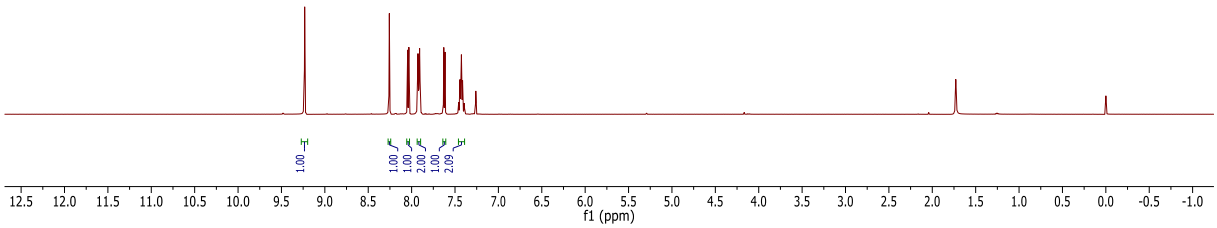
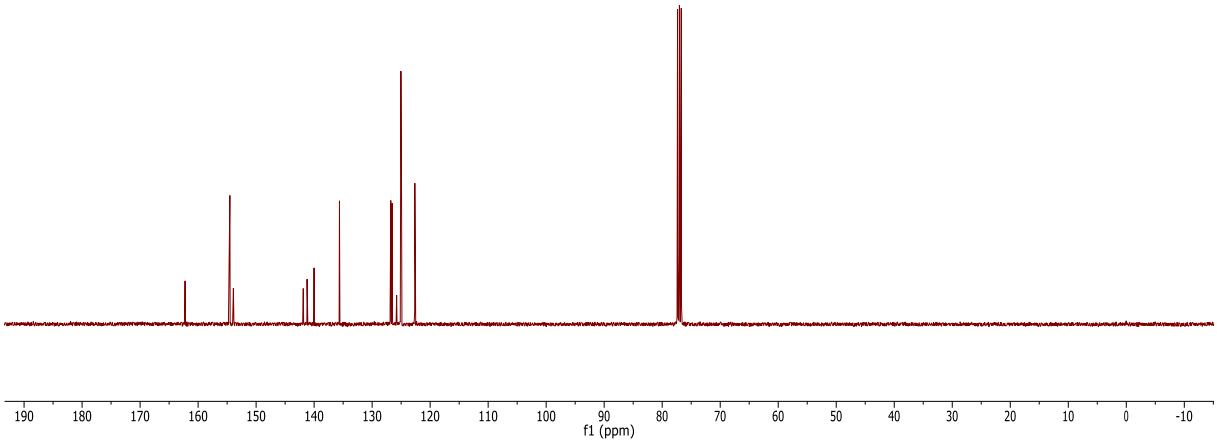
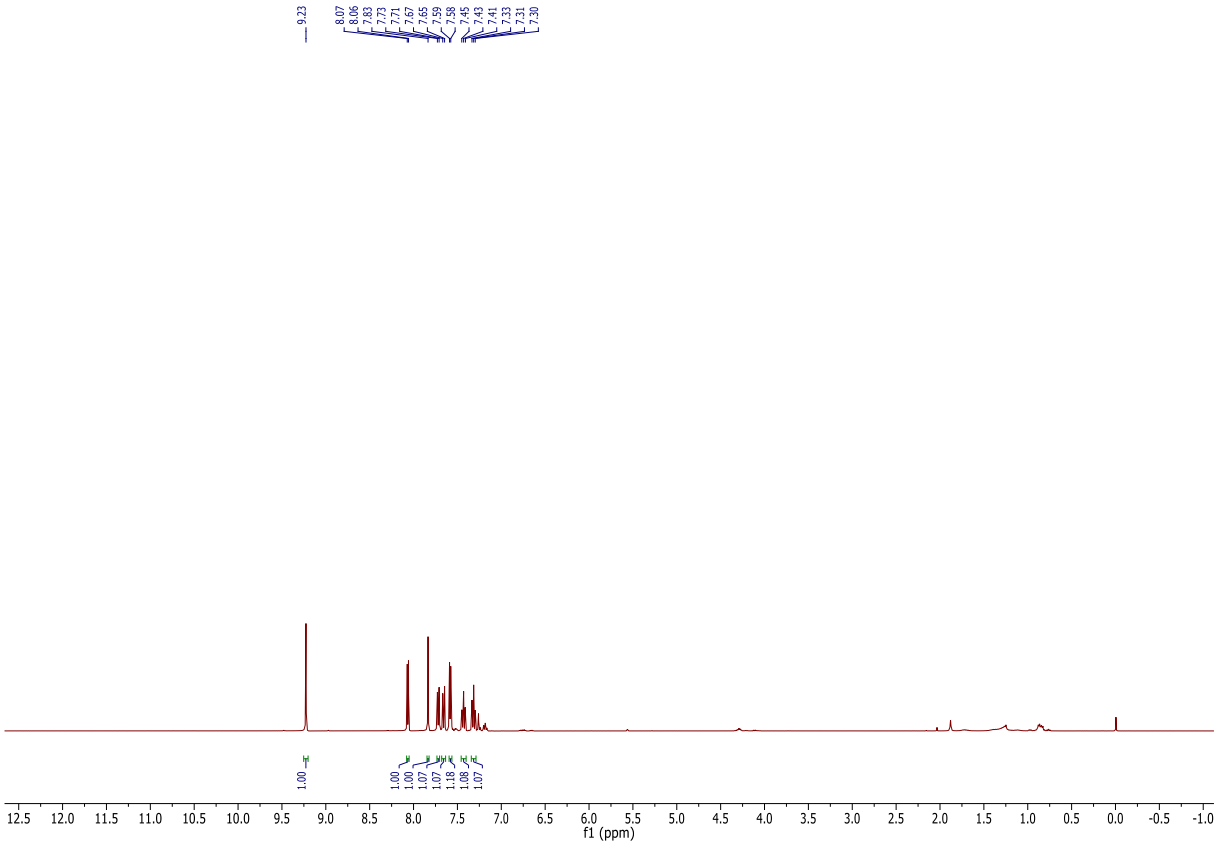
-180
-190
f1 (ppm)

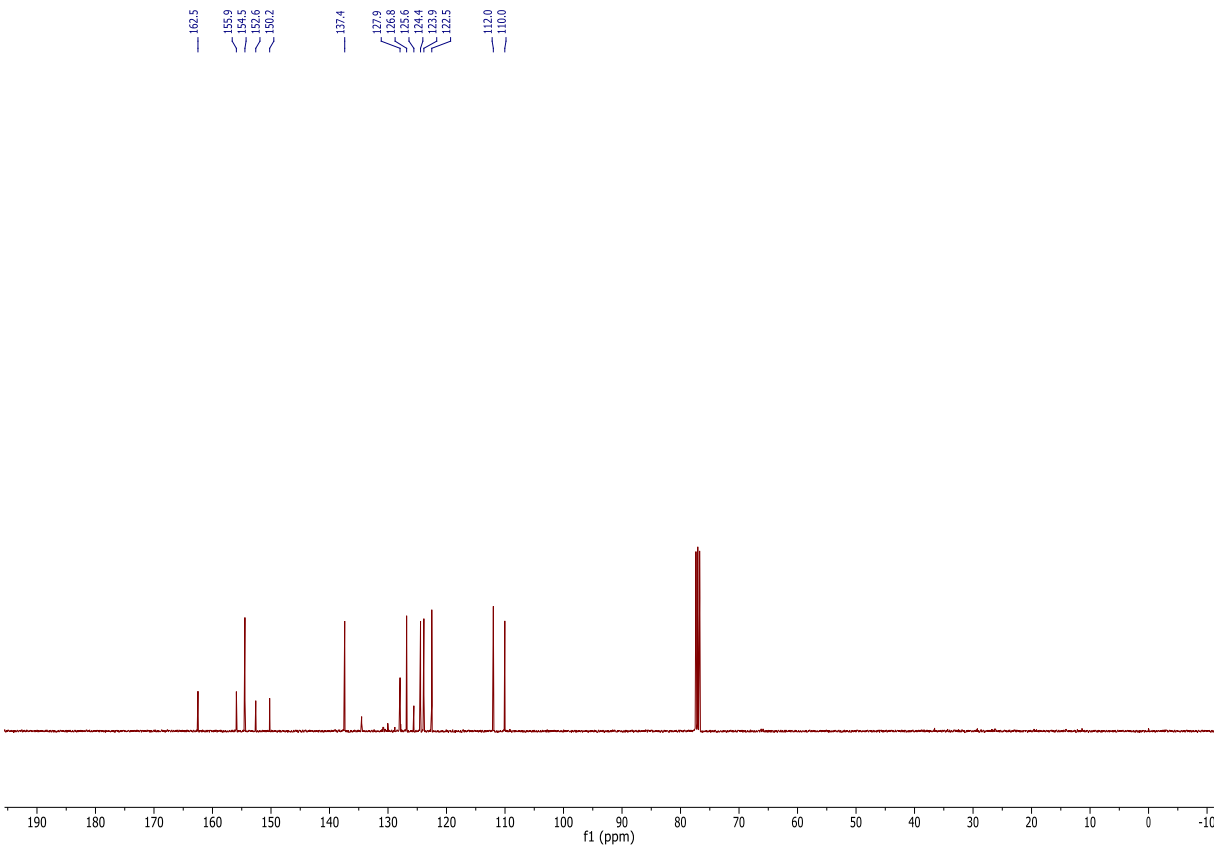
4-(benzo[b]thiophen-2-yl)thieno[3,2-d]pyrimidine(**9d**)



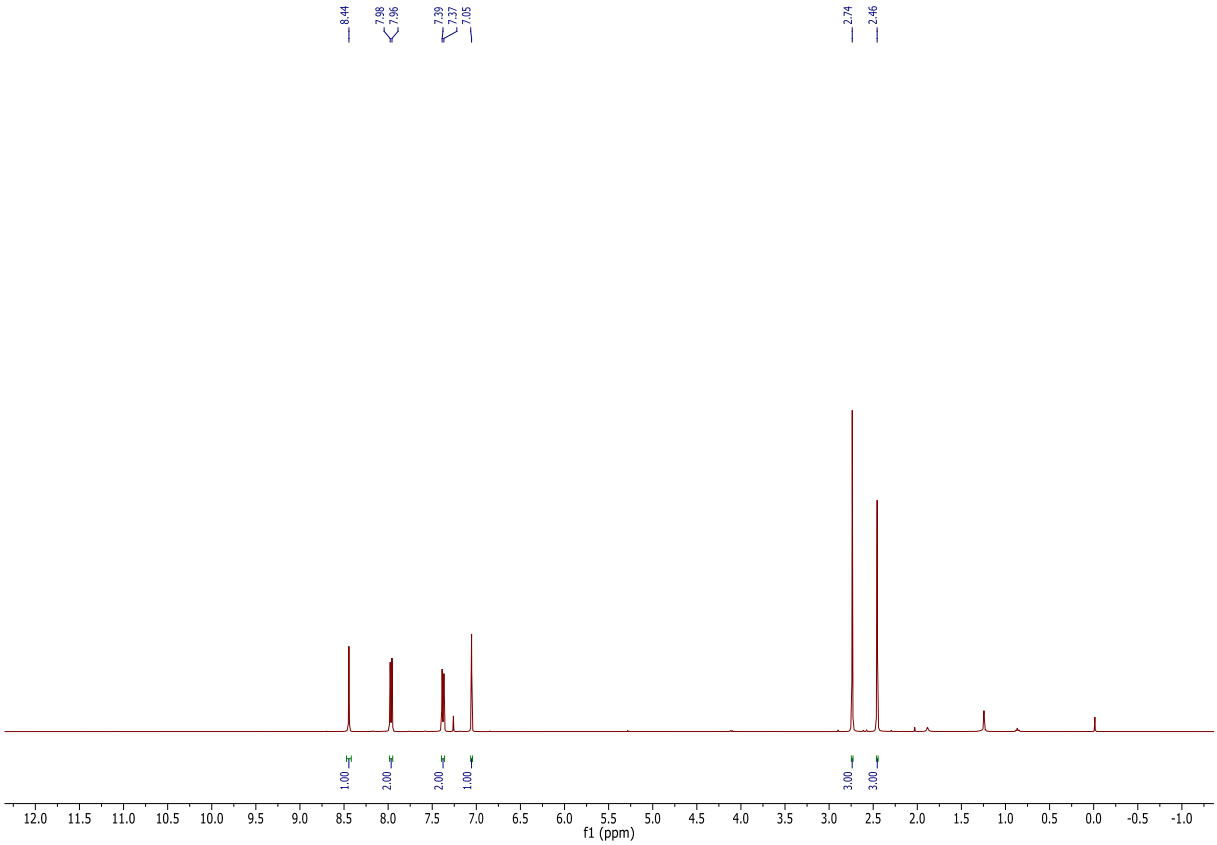


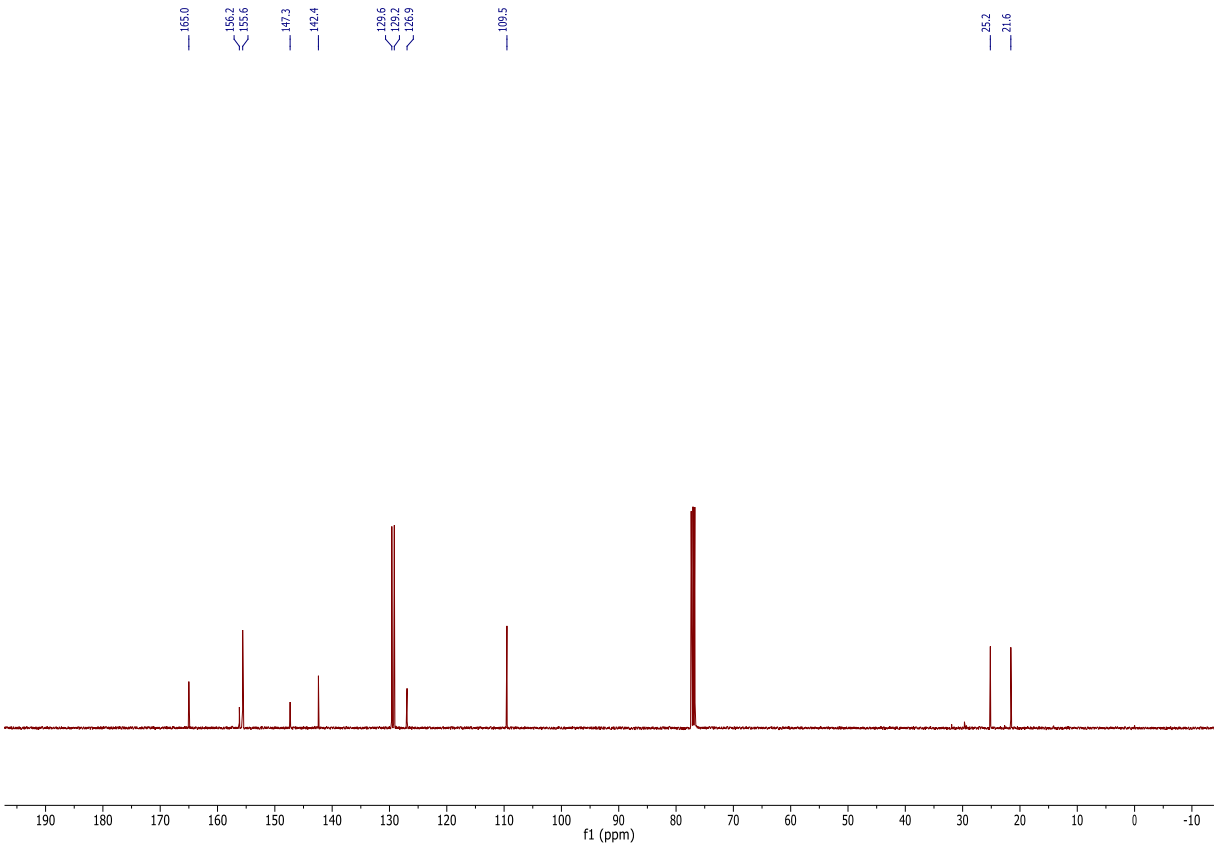
4-(benzofuran-2-yl)thieno[3,2-d]pyrimidine (**9e**)



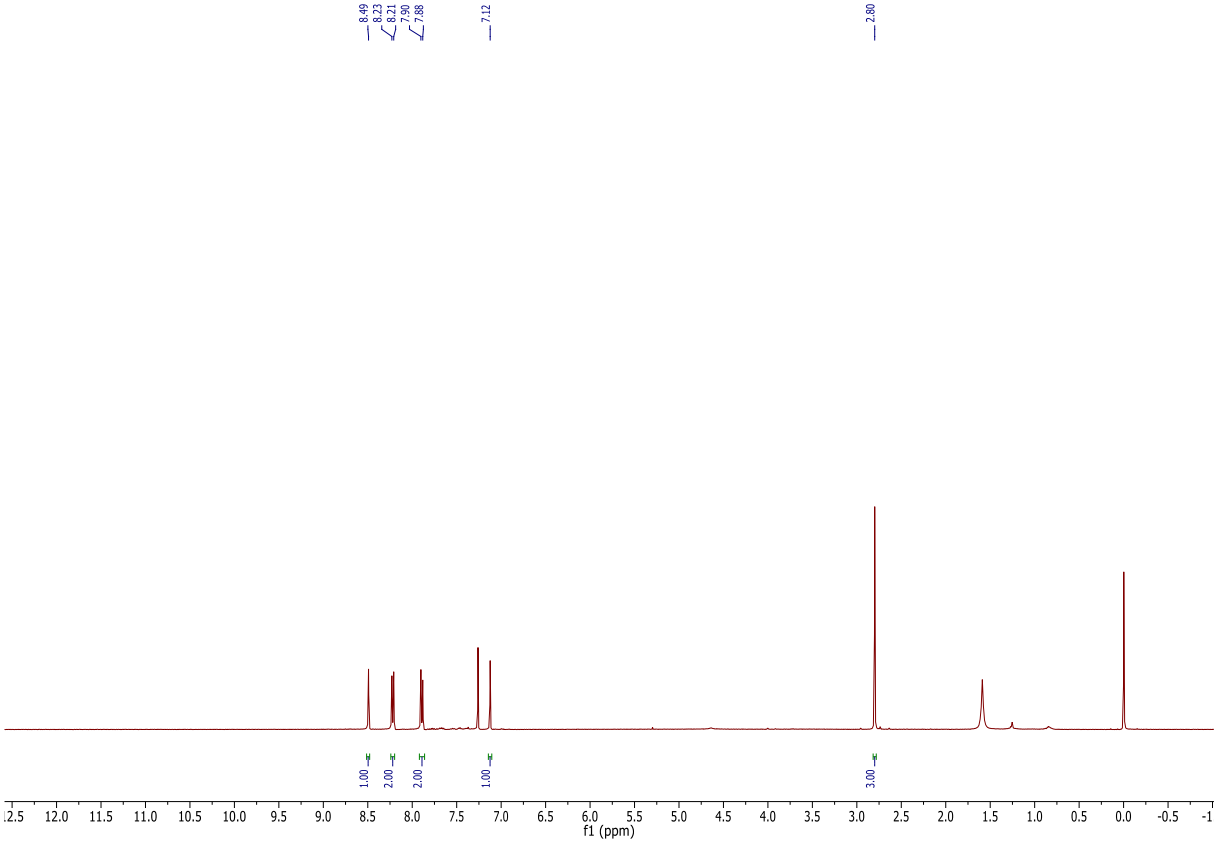


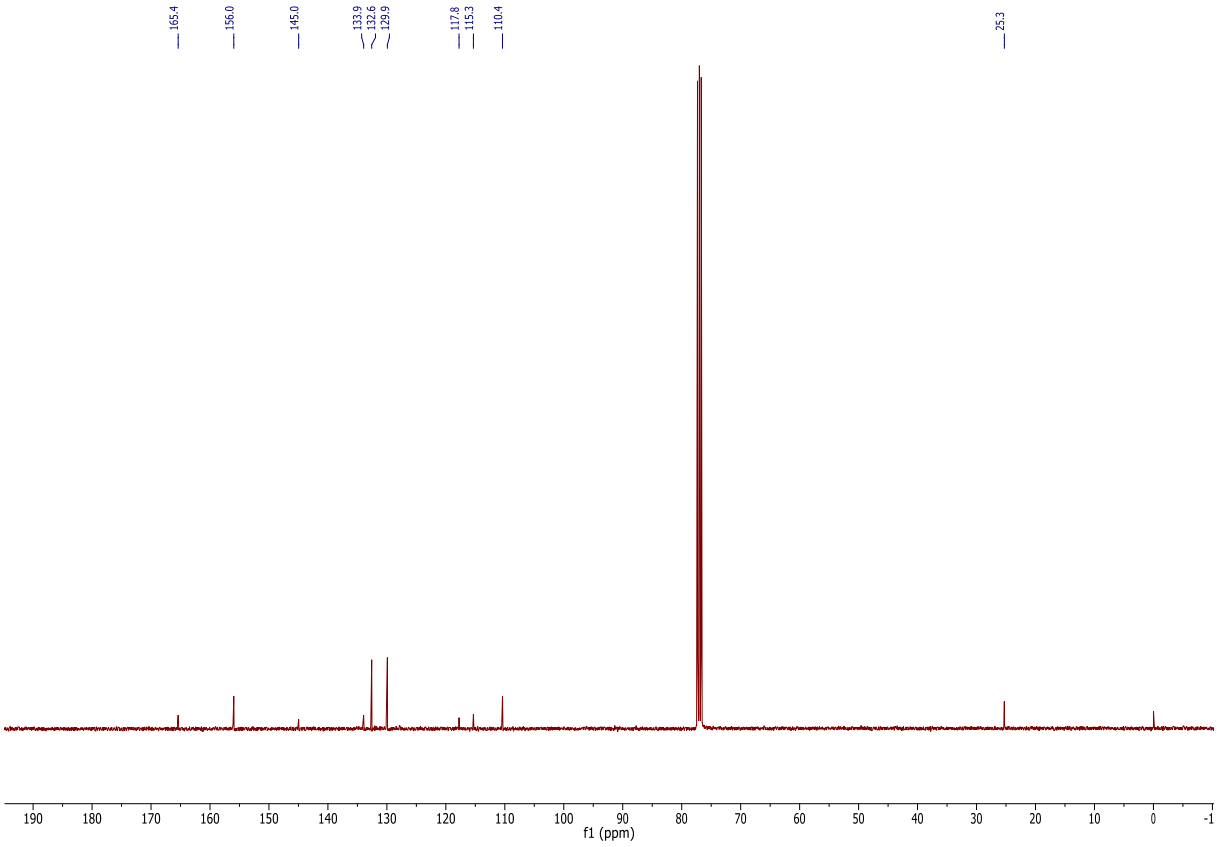
5-methyl-7-(p-tolyl)-[1,2,4]triazolo[1,5-a]pyrimidine (**11a**)



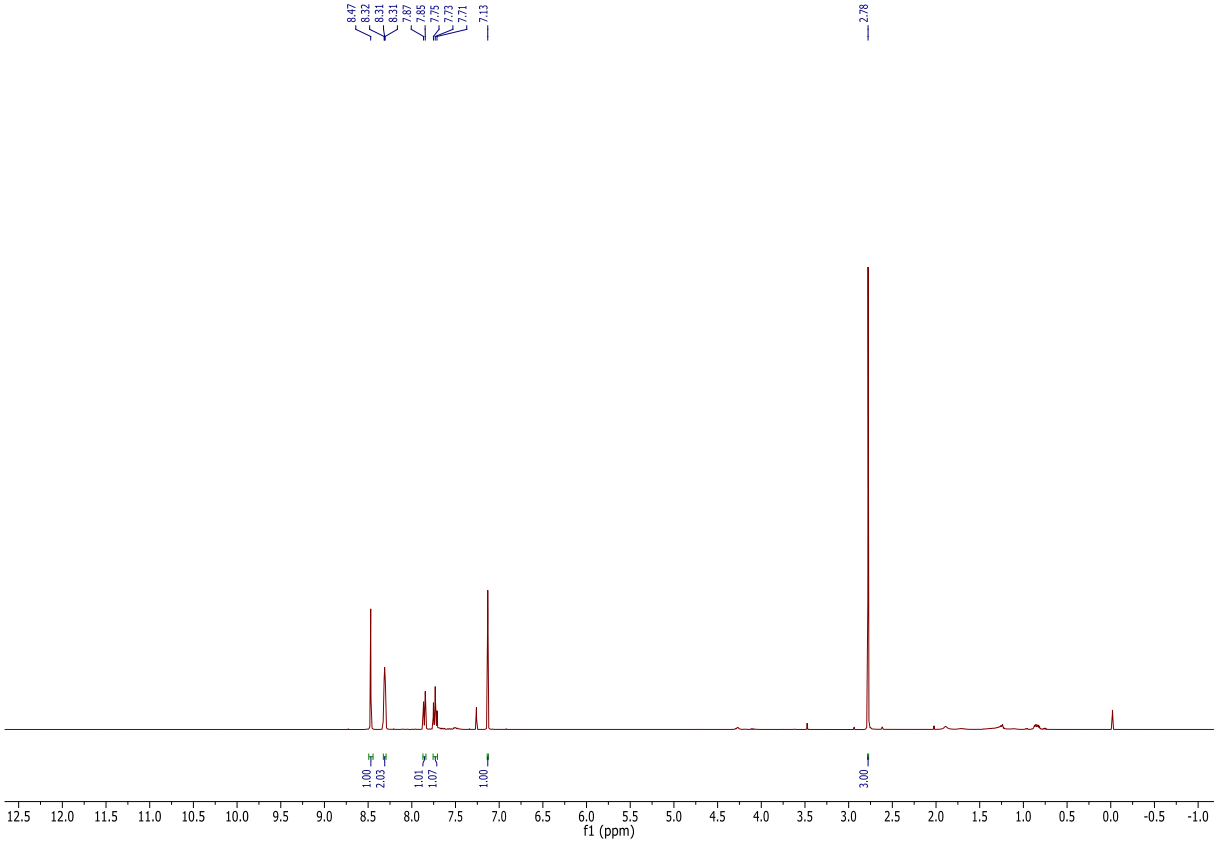


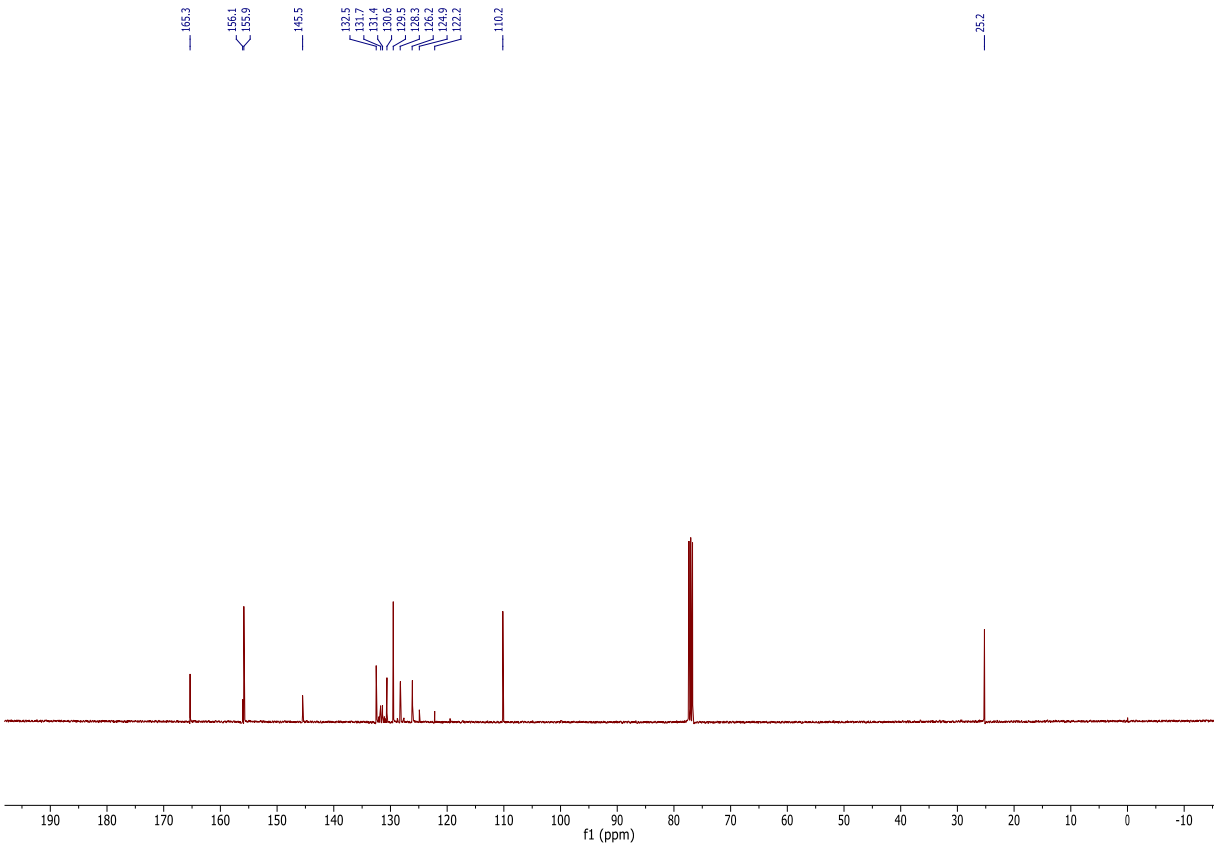
4-(5-methyl-[1,2,4]triazolo[1,5-a]pyrimidin-7-yl)benzonitrile(**11b**)

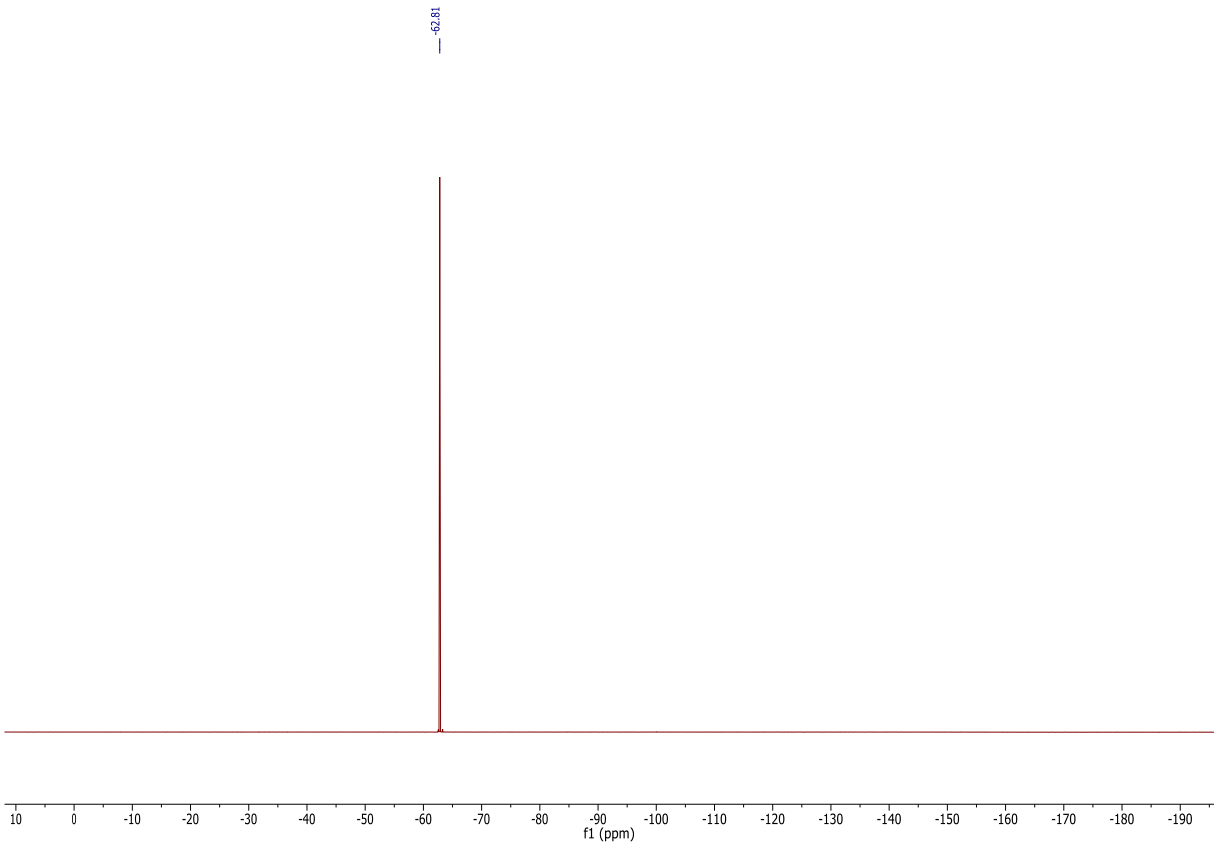




5-methyl-7-(3-(trifluoromethyl)phenyl)-[1,2,4]triazolo[1,5-a]pyrimidine(**11c**)



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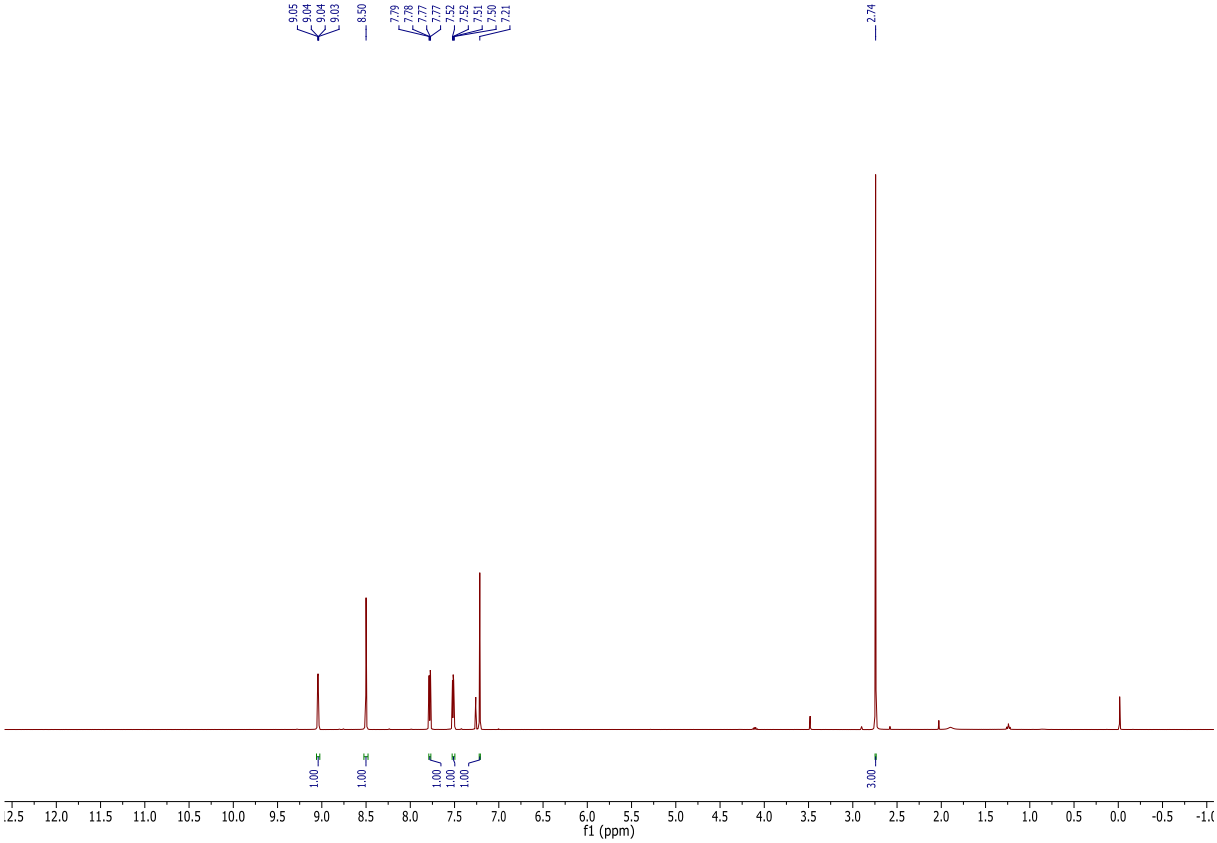
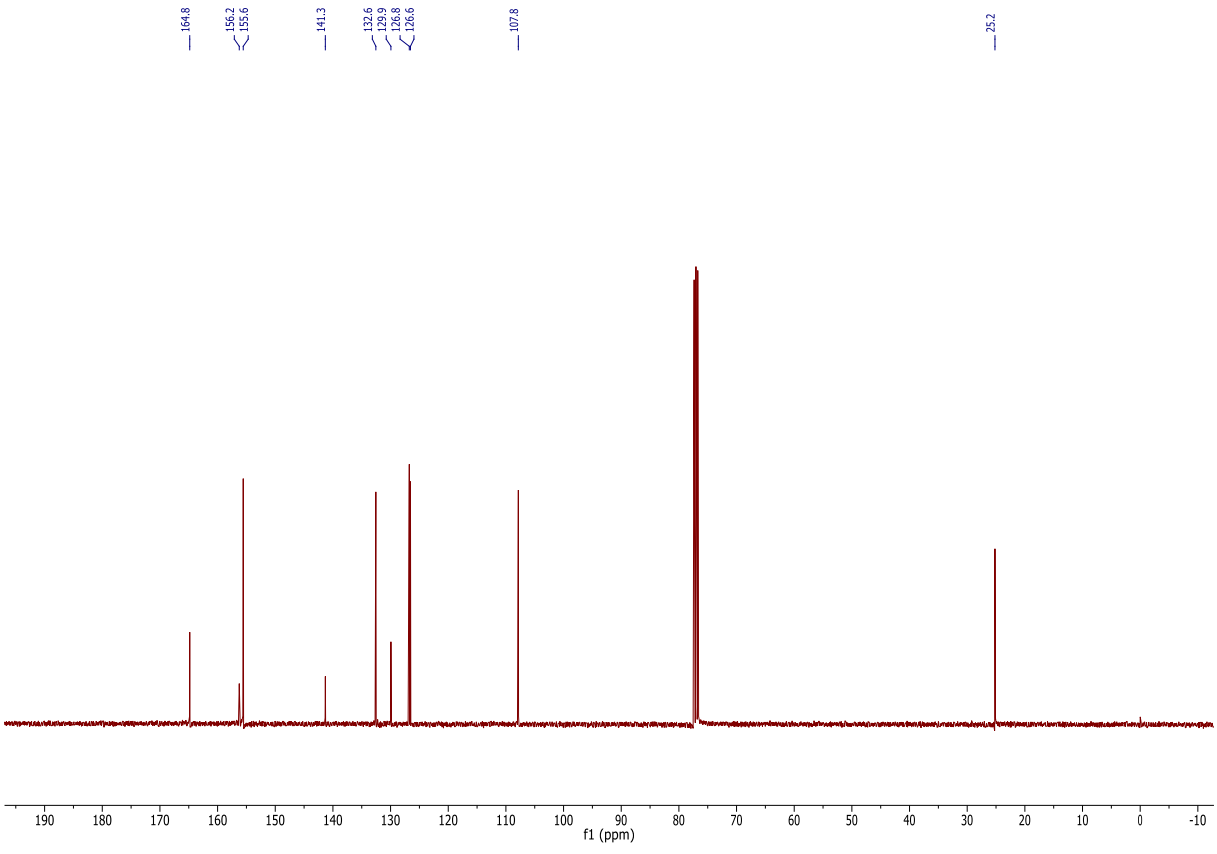
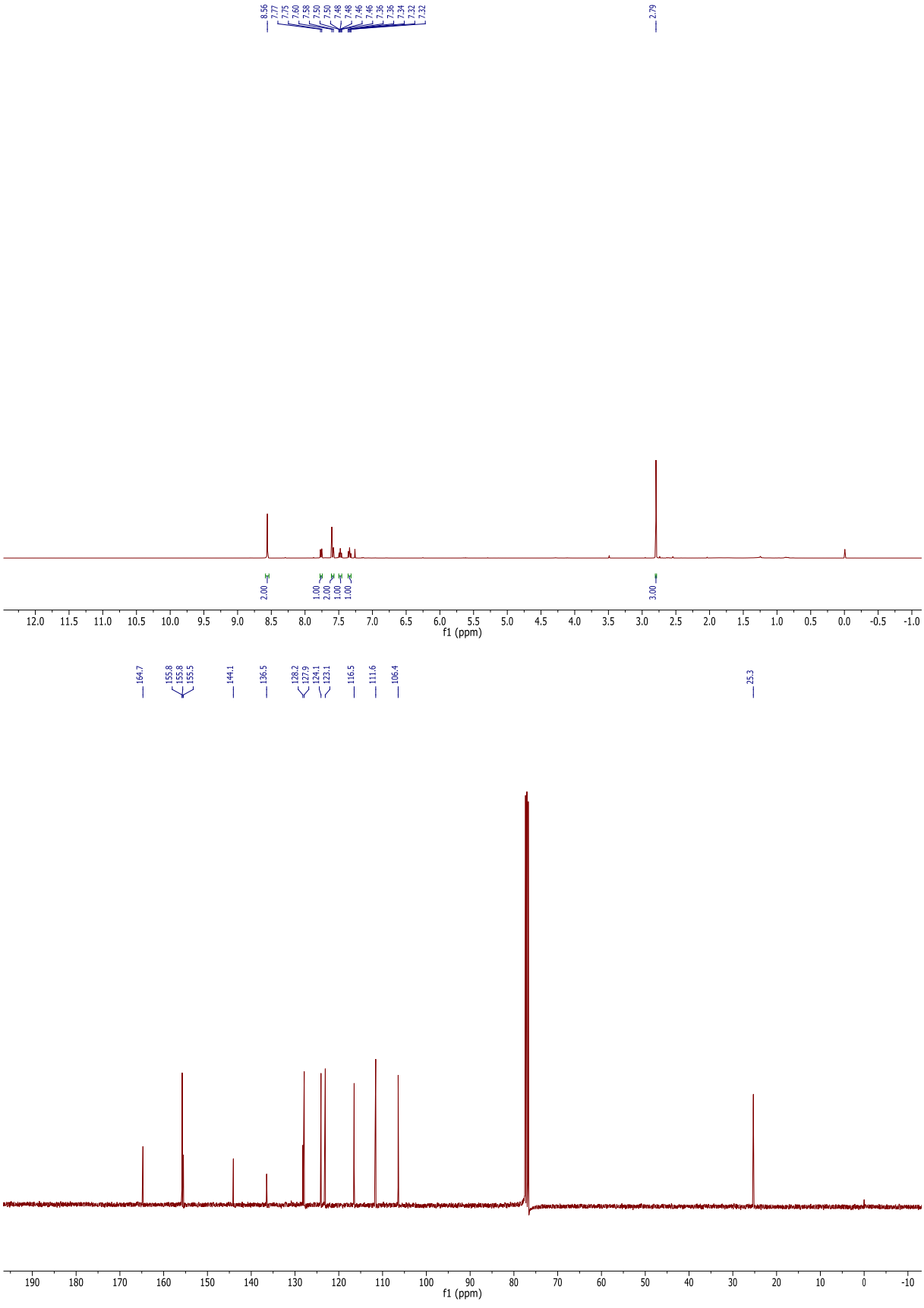
f1 (ppm)

5-methyl-7-(thiophen-3-yl)-[1,2,4]triazolo[1,5-a]pyrimidine (**11d**)

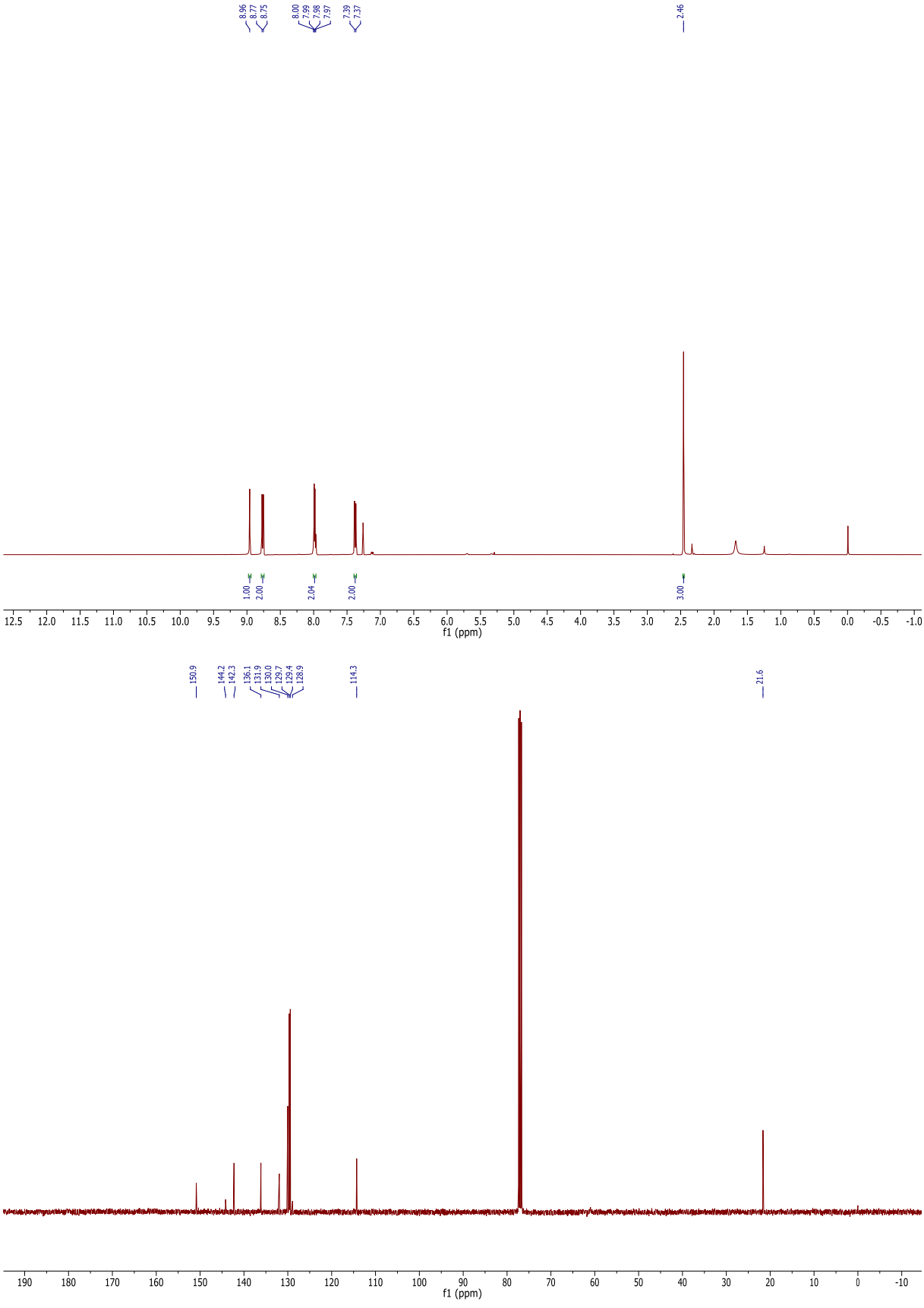




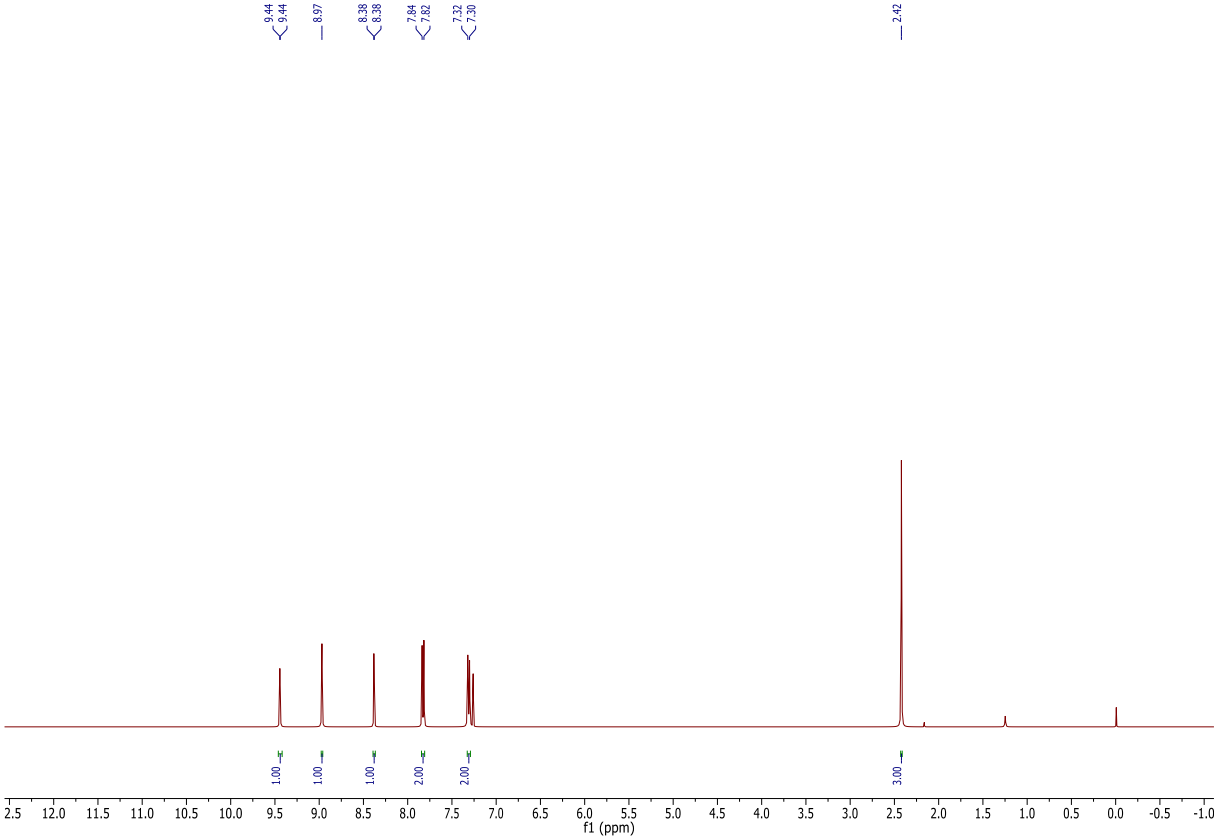
7-(benzofuran-2-yl)-5-methyl-[1,2,4]triazolo[1,5-a]pyrimidine (**11e**)

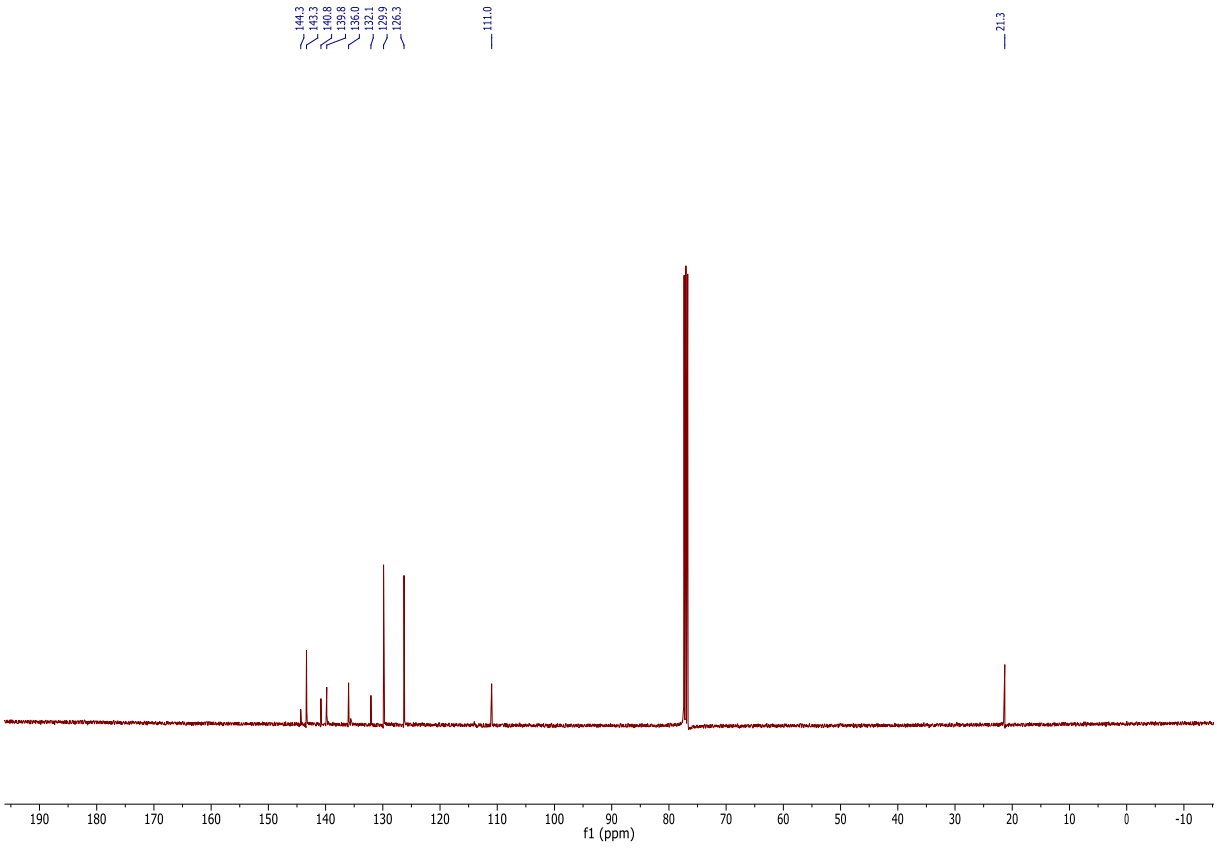


8-(p-tolyl)-[1,2,4]triazolo[4,3-a]pyrazine (**13**)

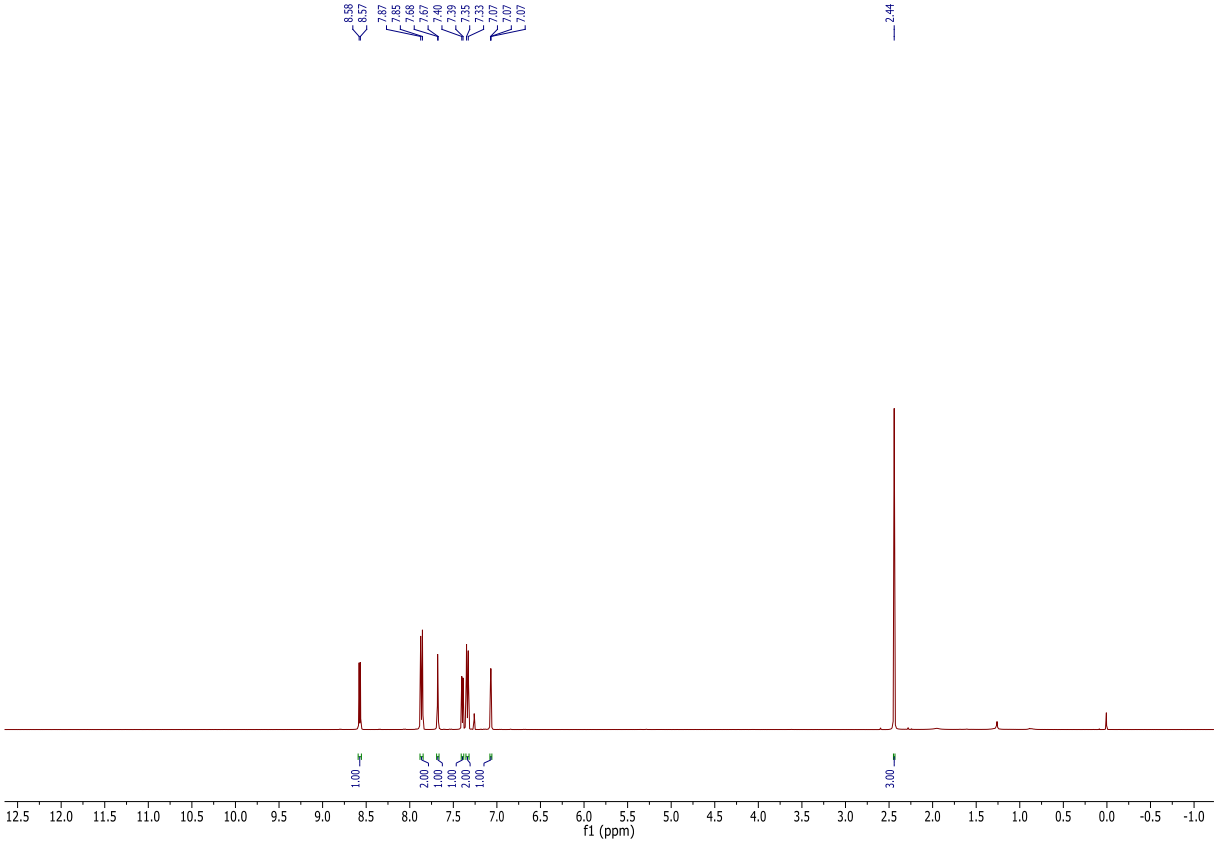


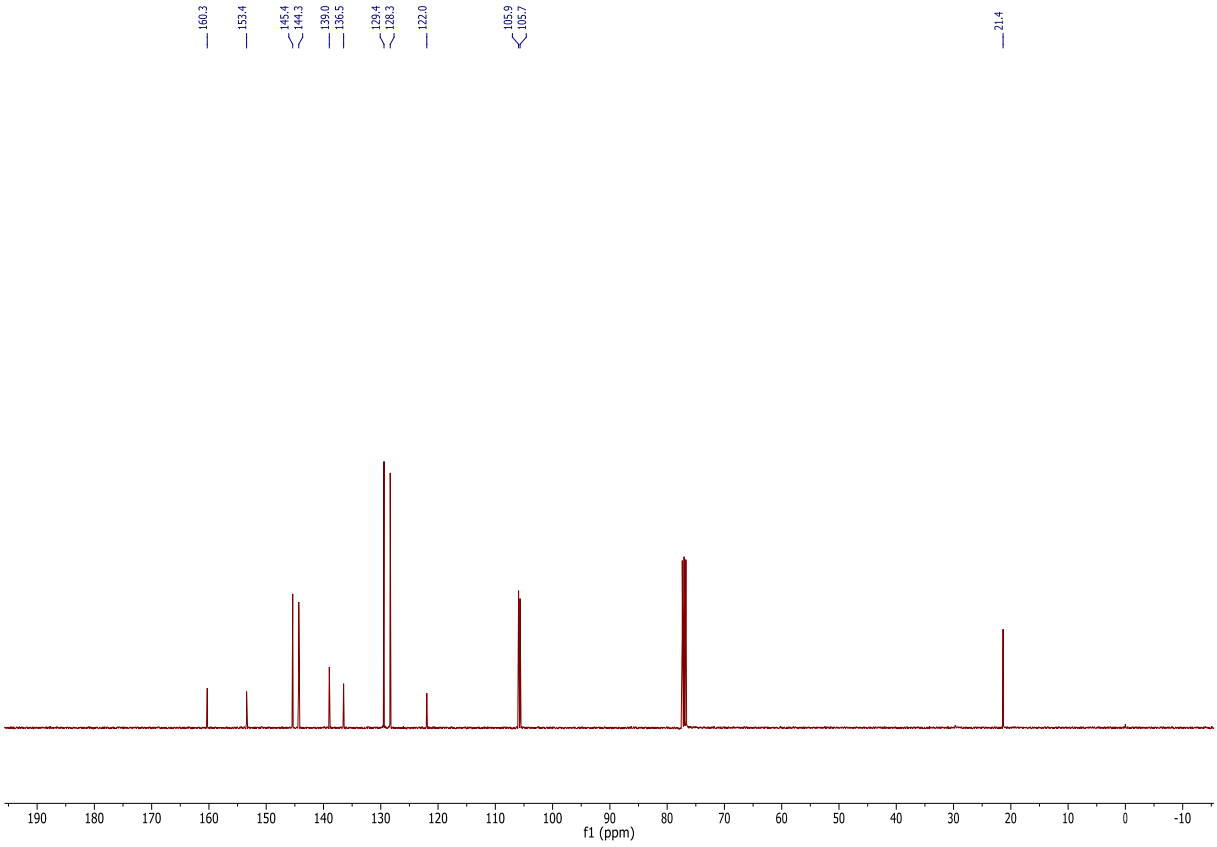
6-(p-tolyl)-[1,2,4]triazolo[4,3-a]pyrazine (**15**)



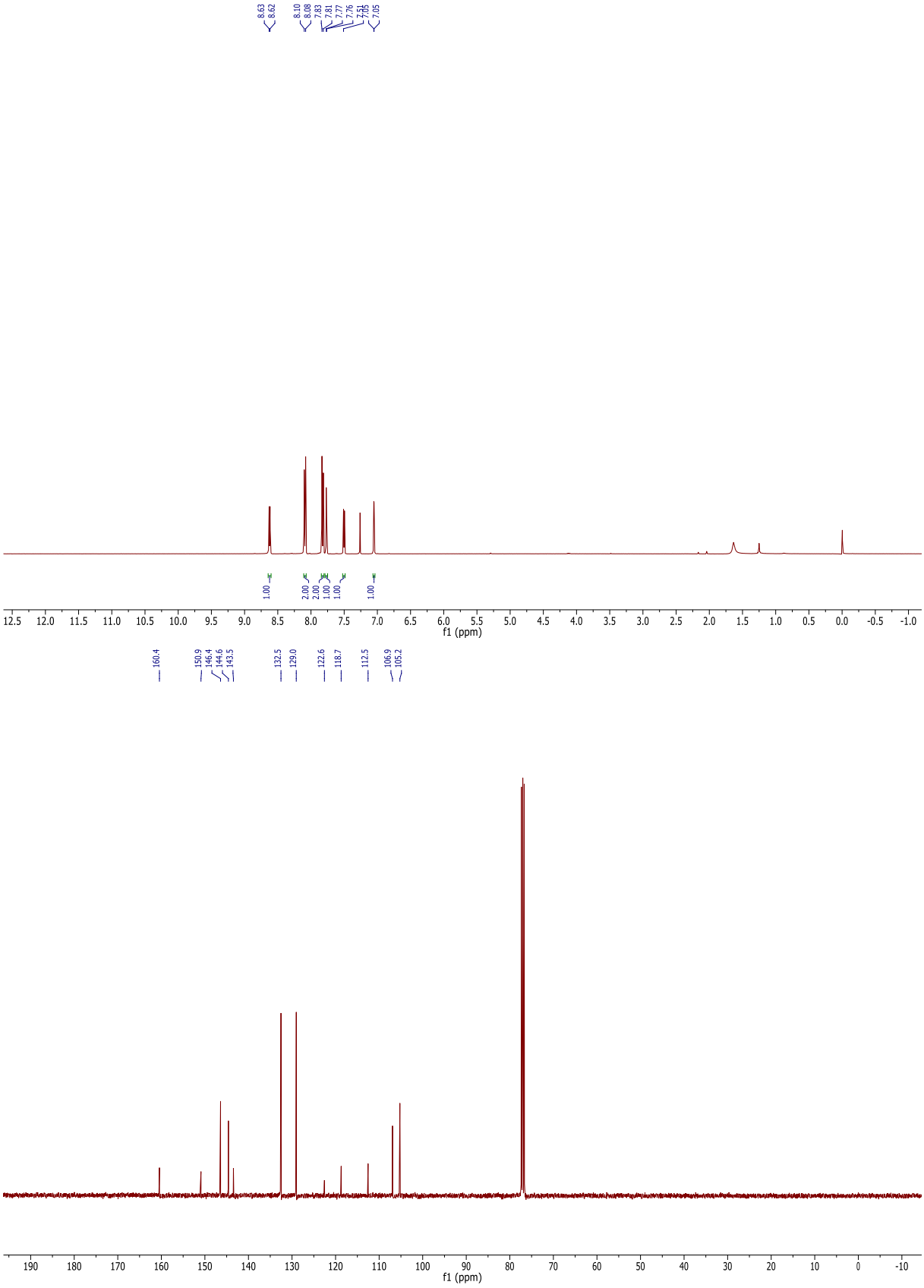


4-(p-tolyl)furo[3,2-c]pyridine (**17a**)

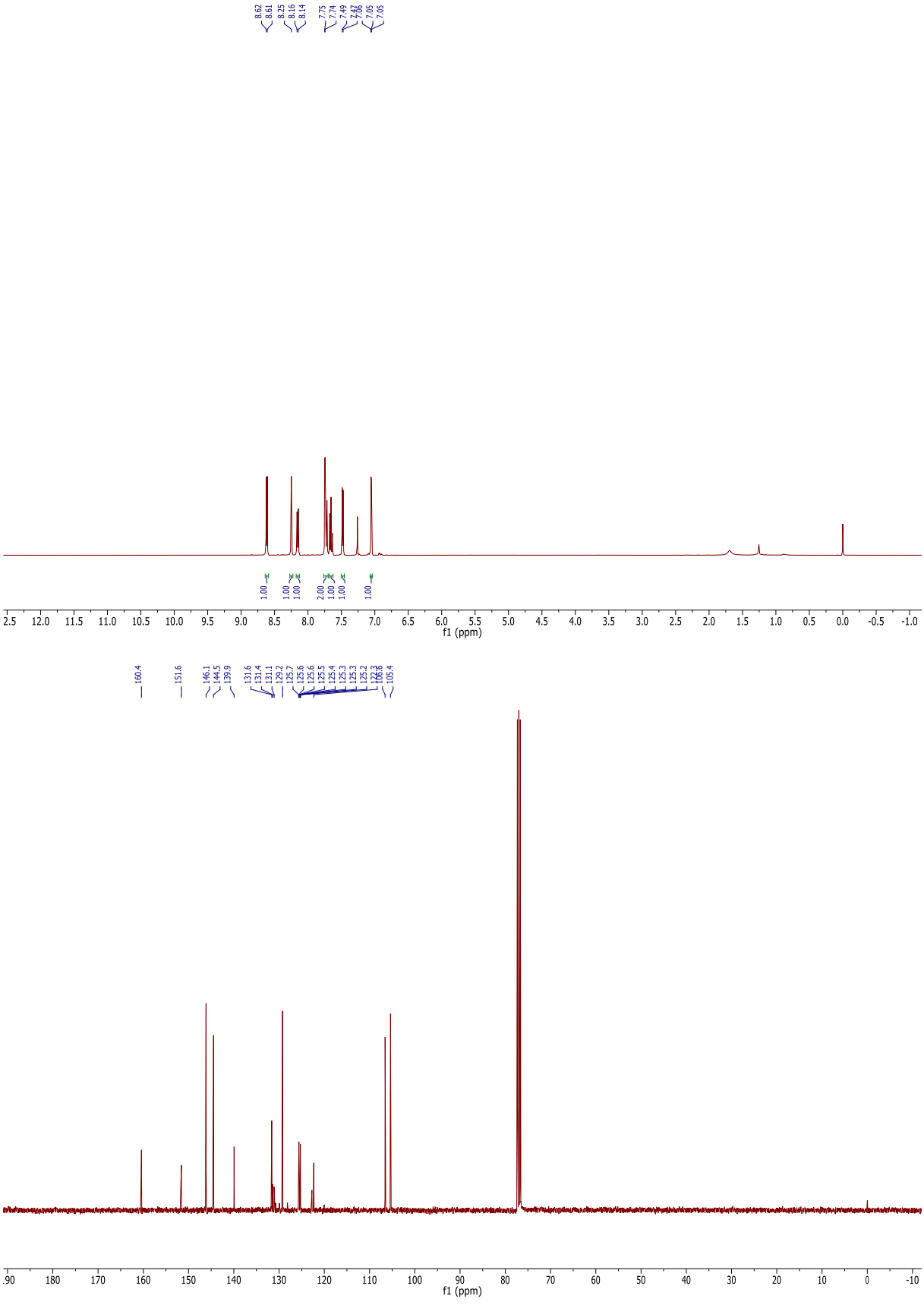


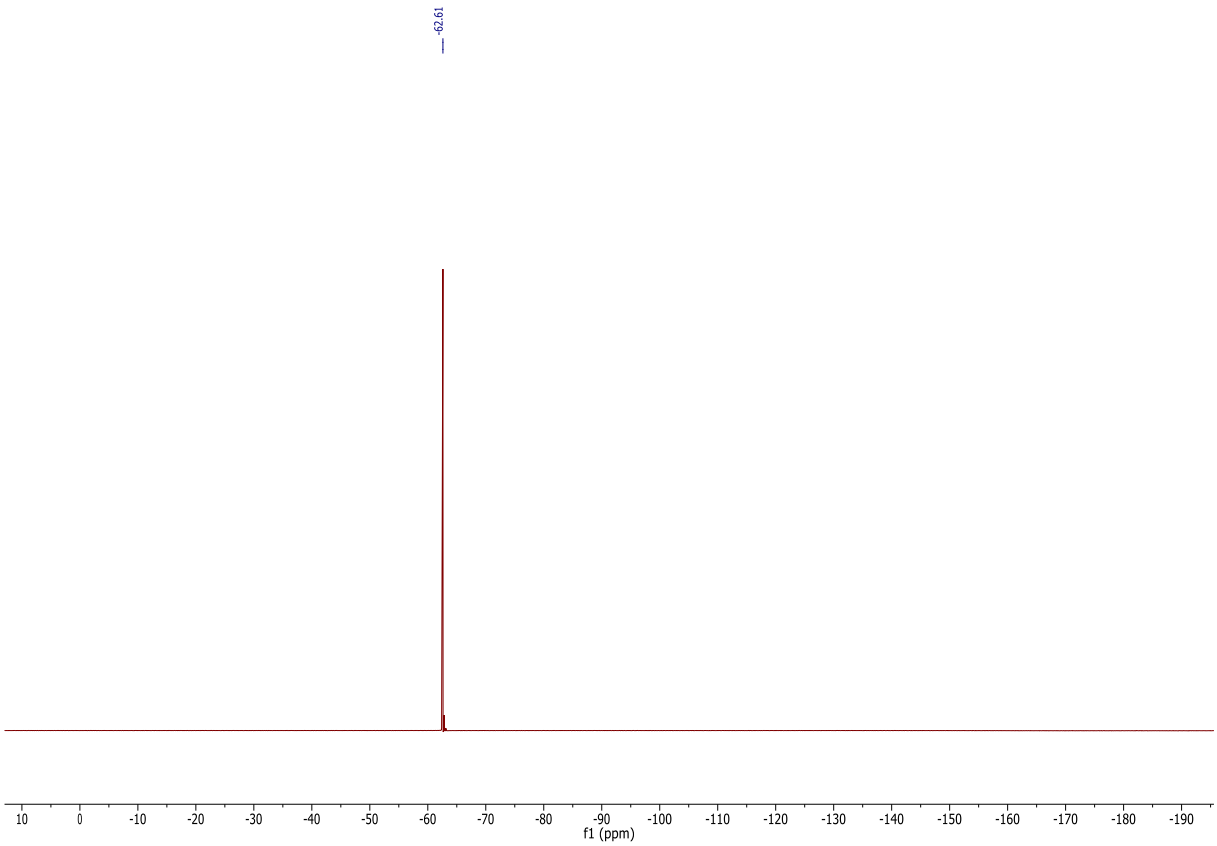


4-(furo[3,2-c]pyridin-4-yl)benzonitrile (**17b**)



4-(3-(trifluoromethyl)phenyl)furo[3,2-c]pyridine (**17c**)

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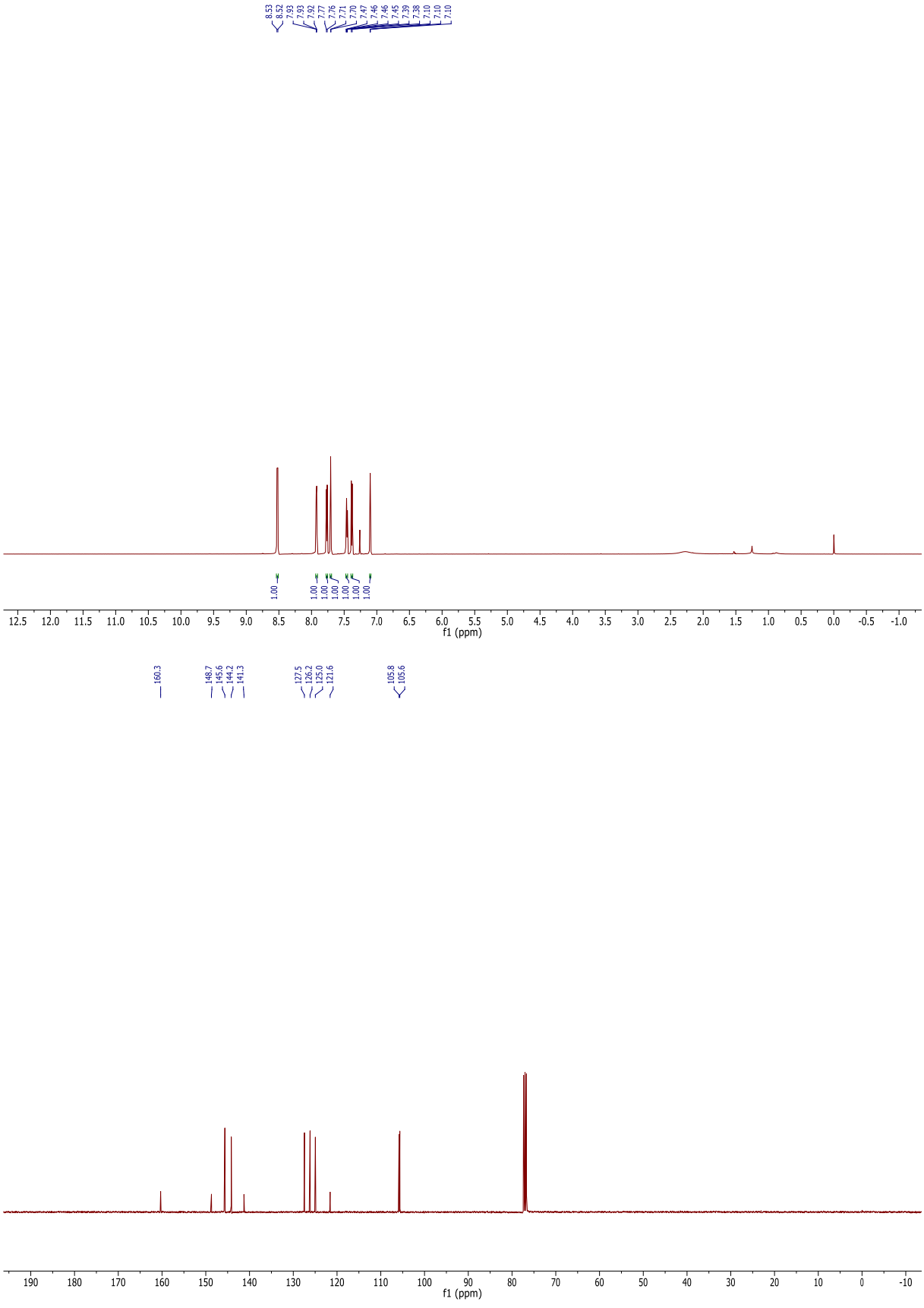
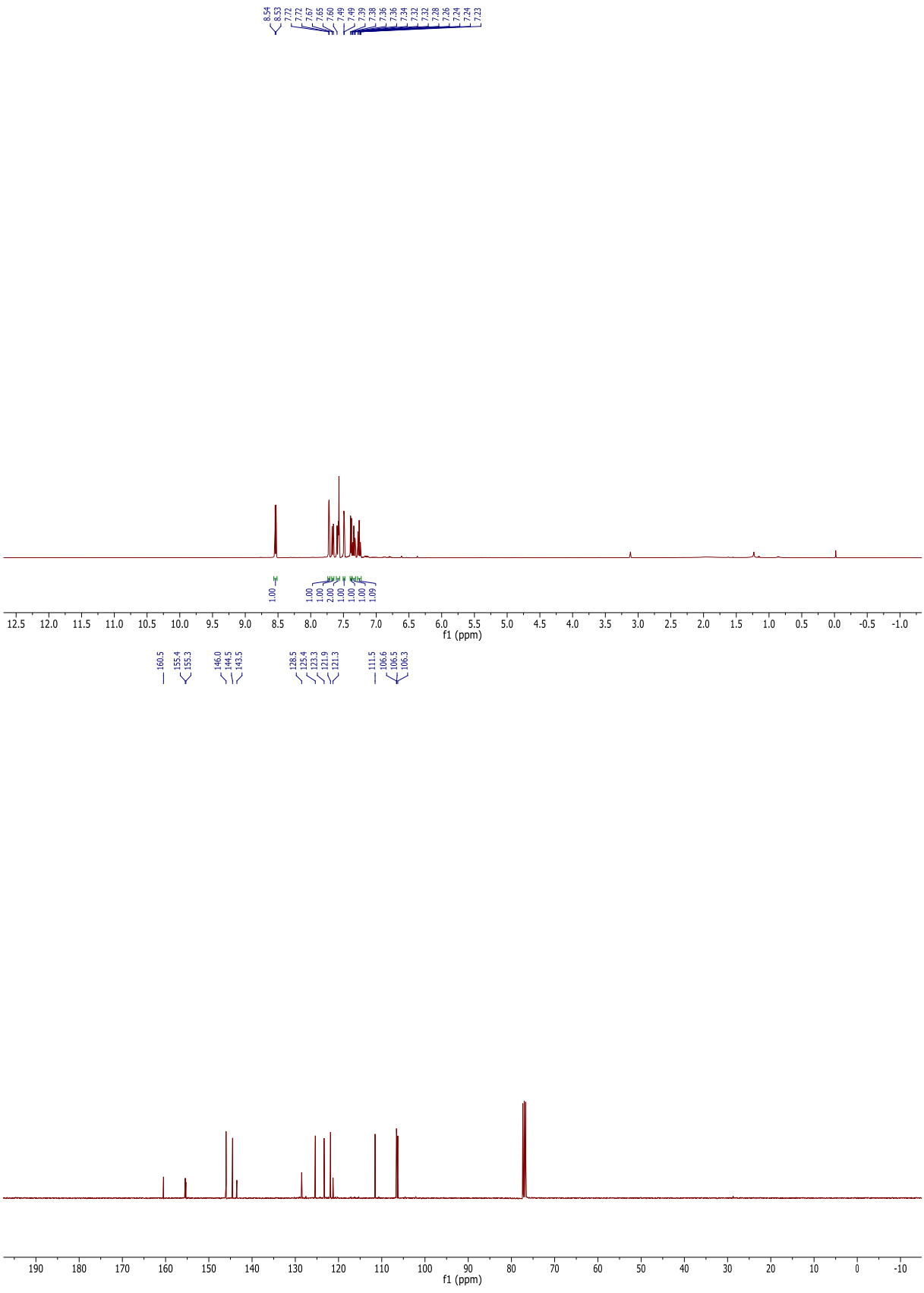
-170
-180
-190
f1 (ppm)

4-(thiophen-3-yl)furo[3,2-c]pyridine (**17d**)



4-(benzofuran-2-yl)furo[3,2-c]pyridine (**17e**)



2C. Sonogashira-Hagihara coupling reaction

2C1. General procedure for the synthesis of 19a-c, 20, 22, 24a,b,d,e and characterization

General procedure : A mixture of chloro compound (50 mg), acetylenes (1.5 eq.), $Pd(PhCN)_2Cl_2$ (0.1 eq.), $P(Cy_3)$ (0.2 eq.), Cs_2CO_3 (2 eq.) in Eucalyptol (3 mL) was stirred at 100 °C for 16 - 36 h. The reaction was followed by TLC. After completion the reaction was then cooled to room temperature and the mixture was concentrated under vacuum. The solid obtained was purified by flash chromatography using a mixture of AcOEt/petroleum ether.

4-((4-methoxyphenyl)ethynyl)thieno[3,2-d]pyrimidine(**19a**): white solid (59 mg, 75%), m.p. 144-146 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 5.5 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 5.5 Hz, 1H),9.17 (s, 1H)ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 55.4 (CH), 84.5 (C), 98.8 (C), 112.8 (C), 114.3 (2xCH), 124.9 (CH), 132.8 (C), 134.3 (CH), 136.3 (CH), 145.8 (C), 154.7 (CH), 160.5 (C), 161.3 (C) ppm. HRMS: calcd. for $C_{15}H_{11}N_2OS$ $[M+H]^+$ 267.0587, found 267.0584.

3-(thieno[3,2-d]pyrimidin-4-ylethynyl)aniline(**19b**): yellow solid (60 mg, 81%), m.p. 149-151 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ3.81 (s, 2H), 6.76 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.98 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 5.5 Hz, 1H), 8.02 (d, *J* = 5.5 Hz, 1H), 9.19 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ84.5 (C), 98.5 (C), 117.2 (CH), 118.3 (CH), 121.5 (C), 122.9 (CH), 124.9 (CH), 129.6 (CH), 133.2 (C), 136.5 (CH), 145.6 (C), 146.5 (C), 154.7 (CH), 160.6 (C) ppm. HRMS: calcd. for $C_{14}H_{10}N_3S$ $[M+H]^+$ 252.0590, found 252.0587.

4-((4-fluoro-3-methylphenyl)ethynyl)thieno[3,2-d]pyrimidine(**19c**): white solid (45 mg, 57%), m.p. 158-160 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 7.06 (t, *J* = 8.9 Hz, 1H), 7.54 (t, *J* = 6.7 Hz, 2H), 7.58 (d, *J* = 5.5 Hz, 1H), 8.04 (d, *J* = 5.5 Hz, 1H), 9.20 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* =252.5 Hz, C), 160.7 (C), 154.8 (CH), 145.4 (C), 136.4 (CH), 135.9 (d, *J*= 5.9 Hz, CH), 133.0 (C), 132.1 (d, *J*= 8.8 Hz, CH), 125.9 (d,*J* = 18.4 Hz, C), 124.9 (CH), 116.6 (d, *J* = 3.8 Hz, C), 115.7 (d, *J* = 23.5 Hz, CH), 97.3 (C), 84.7 (C), 14.4 (CH) ppm.^{19}F NMR (376 MHz, $CDCl_3$) δ -111.55 ppm. HRMS: calcd. for $C_{15}H_{10}FN_2S$ $[M+H]^+$ 269.0543, found 269.0541.

4-(thiophen-3-ylethynyl)thieno[3,2-d]pyrimidine(**19d**): yellow solid (60 mg, 84%), m.p. 94-96 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ7.33 – 7.39 (m, 2H), 7.59 (d, *J* = 5.5 Hz, 1H),7.82 (dd, *J* = 2.8, 1.0 Hz, 1H), 8.04 (d, *J* = 5.5 Hz, 1H),9.20 (s, 1H), ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ85.0 (C), 93.2 (C), 120.1 (C), 124.9 (CH), 126.1 (CH), 130.1 (CH), 132.4 (CH), 132.9 (C), 136.5 (CH), 145.5 (C), 154.7 (CH), 160.7 (C) ppm. HRMS: calcd. for $C_{12}H_7N_2S_2$ $[M+H]^+$ 243.0045, found 243.0042.

4-(pyridin-3-ylethynyl)thieno[3,2-d]pyrimidine(**19e**): white solid (52 mg, 75%), m.p. 136-138 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 4.9, 7.8 Hz, 1H), 7.61 (d, *J* = 5.5 Hz, 1H), 7.98 (dt, *J* = 1.8, 7.9 Hz, 1H), 8.07 (d, *J* = 5.5 Hz, 1H), 8.66 – 8.69 (m, 1H), 8.94 – 8.92 (m, 1H),9.24 (s, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 87.9 (C), 93.8 (C), 118.2 (C), 123.3 (CH), 125.0 (CH), 133.1 (C), 136.7 (CH), 139.3 (CH), 144.7 (C), 150.4 (CH), 153.0 (CH), 154.8 (CH), 161.0 (C) ppm. HRMS: calcd. for $C_{13}H_8N_3S$ $[M+H]^+$ 238.0433, found 238.0430.

7-((4-methoxyphenyl)ethynyl)-5-methyl-[1,2,4]triazolo[1,5-a]pyrimidine (**20**): white solid (21 mg, 27%), m.p. 182-184 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (s, 3H), 3.86 (s, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.11 (s, 1H), 7.64 (d, *J* = 8.8 Hz, 2H), 8.51 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 25.0 (CH), 55.5 (CH), 104.5 (C), 112.0 (2xC), 113.6 (CH), 114.4 (3xCH), 131.0 (C), 134.5 (2xCH), 161.7 (2xC), 164.5 (C) ppm.

4-((4-methoxyphenyl)ethynyl)-7H-pyrrolo[2,3-d]pyrimidine(**22**): yellow solid (7 mg, 9%), m.p. 185-187 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ3.86 (s, 3H),6.75 – 6.79 (m, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 7.42 (s, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 8.89 (s, 1H), 10.50 (s, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ55.4 (CH), 85.1 (C), 96.4 (C), 100.9 (CH), 113.7 (C), 114.2 (2xCH), 119.7 (C), 126.0 (CH), 134.1 (2xCH), 143.0 (C), 151.3 (CH), 151.7 (C), 160.8 (C)ppm. HRMS: calcd. for $C_{15}H_{12}N_3O$ $[M+H]^+$ 250.0975, found 250.0974.

4-((4-methoxyphenyl)ethynyl)furo[3,2-c]pyridine (**24a**): yellow solid (38 mg, 47%), m.p. 91-93 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ3.84 (s, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 5.7 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 2.2 Hz, 1H), 8.49 (d, *J* = 5.7 Hz, 1H) ppm.^{13}C NMR (63 MHz, $CDCl_3$) δ55.4 (CH), 85.4 (C), 93.1 (C), 101.5 (C), 105.6 (CH), 106.6 (CH),114.2 (2xCH), 126.7 (C), 133.8 (2xCH), 137.9 (C), 144.8 (CH), 145.8 (CH), 159.2 (C), 160.4 (C) ppm. HRMS: calcd. for $C_{16}H_{12}NO_2$ $[M+H]^+$ 250.0863, found 250.0861.

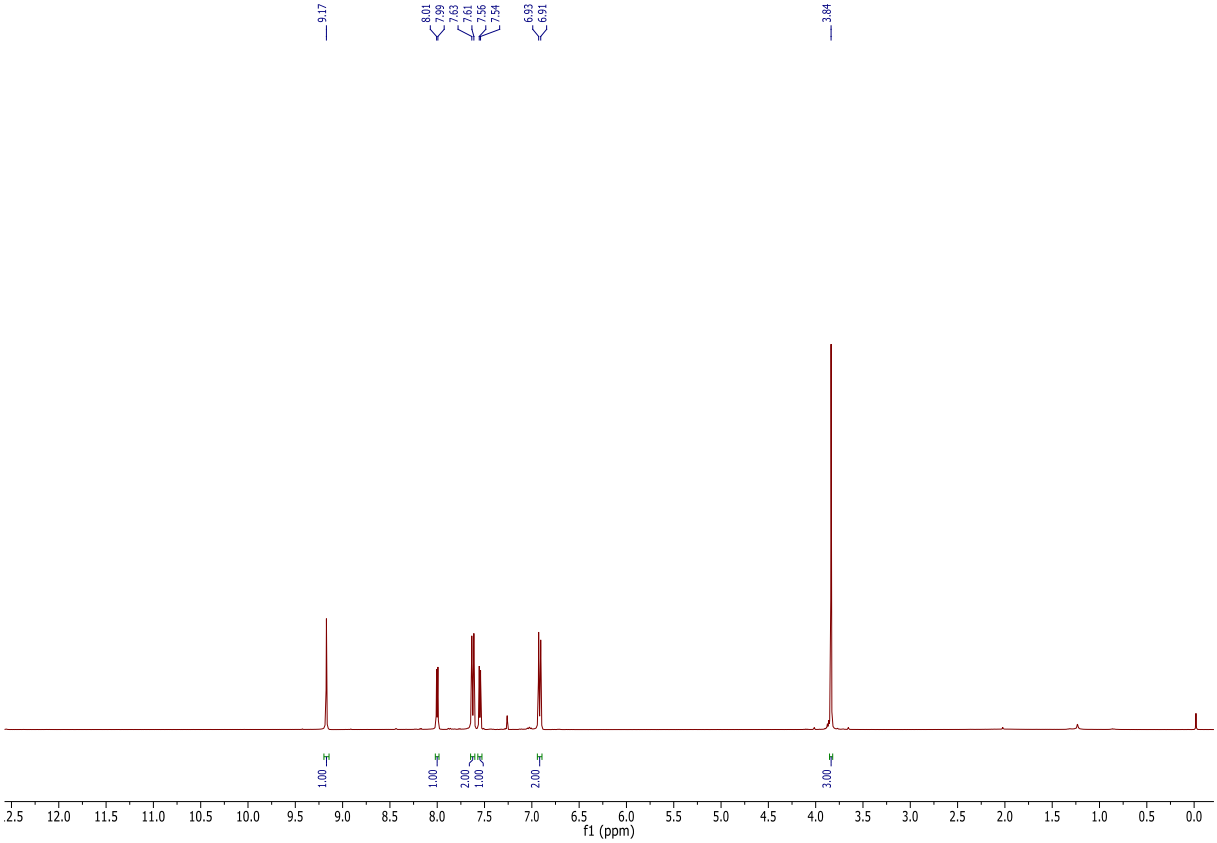
3-(furo[3,2-c]pyridin-4-ylethynyl)aniline (**24b**): white solid (39 mg, 51%), m.p. 119-121 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 2H), 6.71 (dd, *J* = 1.9, 7.6Hz, 1H), 6.94 – 6.96 (m, 1H),6.99– 7.01 (m, 1H), 7.05 (d, *J* = 7.6 Hz, 1H),7.15 (t, *J* = 7.8 Hz, 1H),7.40 (d, *J* = 6.4 Hz, 1H), 7.68 (d, *J* = 2.2 Hz, 1H), 8.49 (d, *J* = 5.7 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 85.8 (C), 93.1 (C), 105.5 (CH), 106.8 (CH), 116.2 (CH), 118.2 (CH), 122.5 (CH), 122.8 (C), 127.0 (C), 129.4 (CH), 137.6 (C), 144.8 (CH), 146.0 (CH), 146.4 (C), 159.2 (C) ppm. HRMS: calcd. for $C_{15}H_{11}N_2O$ $[M+H]^+$ 235.0866, found 235.0864.

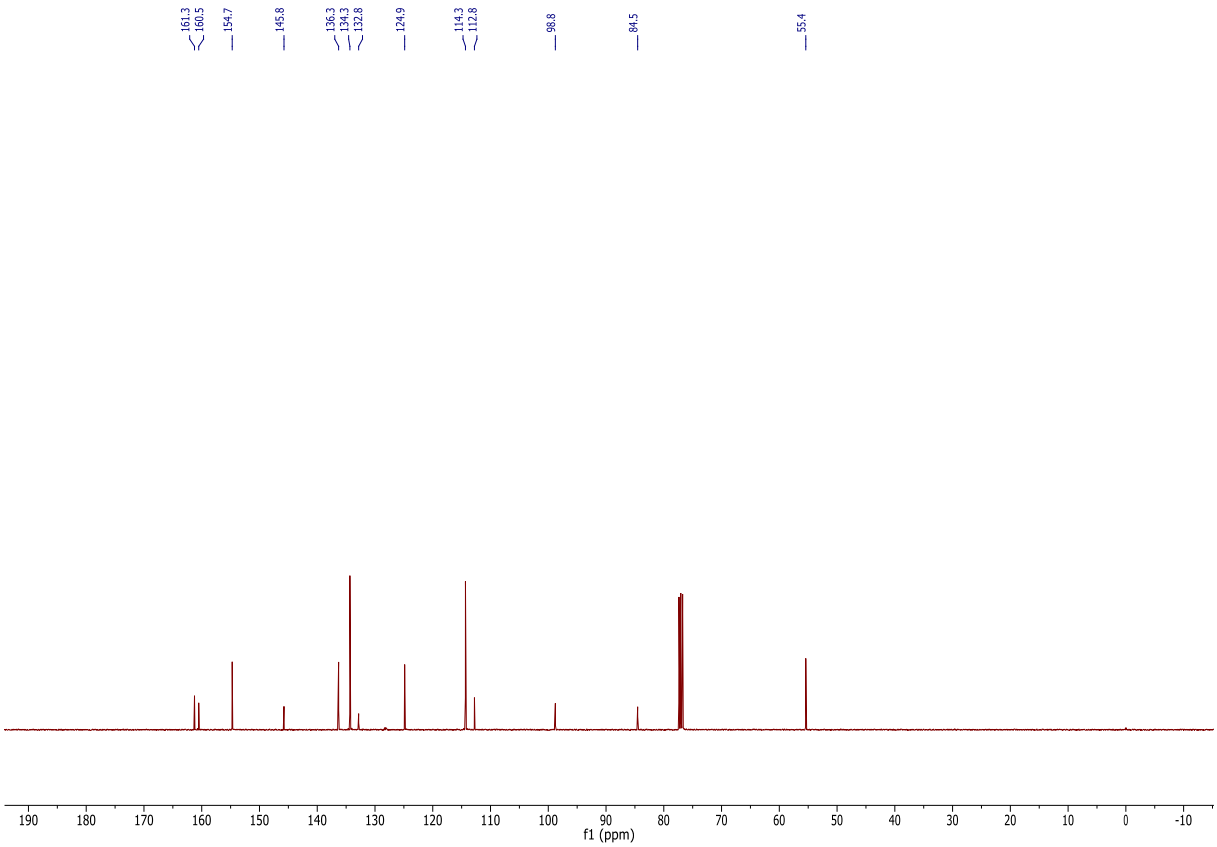
4-(thiophen-3-ylethynyl)furo[3,2-c]pyridine (**24d**): yellow solid (39 mg, 53%), m.p. 97-99 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ6.99 – 7.02 (m, 1H),7.28 – 7.31 (m, 1H), 7.32 – 7.34 (m, 1H), 7.41 (d, *J* = 5.7 Hz, 1H), 7.68 – 7.69 (m, 2H), 8.49 (d, *J* = 5.7 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ86.2 (C), 87.8 (C), 105.5 (CH), 106.8 (CH), 121.3 (C), 125.6 (CH), 126.8 (C), 130.0 (CH), 130.4 (CH), 137.5 (C), 144.9 (CH), 146.0 (CH), 159.2 (C) ppm. HRMS: calcd. for $C_{13}H_8NOS$ $[M+H]^+$ 226.0321, found 226.0320.

4-(pyridin-3-ylethynyl)furo[3,2-c]pyridine (**24e**): yellow solid (27 mg, 38%), m.p. 111-113 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ7.01 (dd, *J* = 2.3, 1.0 Hz, 1H), 7.33 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.46 (d, *J* = 5.6 Hz, 1H), 7.73 (d, *J* = 2.3 Hz, 1H),7.92 (dt, *J* = 7.9, 2.0 Hz, 1H), 8.52 (d, *J* = 5.6 Hz, 1H), 8.60 (dd, *J* = 5.0, 1.8 Hz, 1H), 8.87 (d, *J* = 2.4 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 88.9 (C), 89.5 (C), 105.3 (CH), 107.3 (CH), 119.4 (C), 123.1 (CH), 127.2 (C), 136.7 (C), 138.9 (CH), 145.0 (CH), 146.3 (CH), 149.4 (CH), 152.6 (CH), 159.2 (C) ppm. HRMS: calcd. for $C_{14}H_8N_2O$ $[M+H]^+$ 221.0709, found 221.0707.

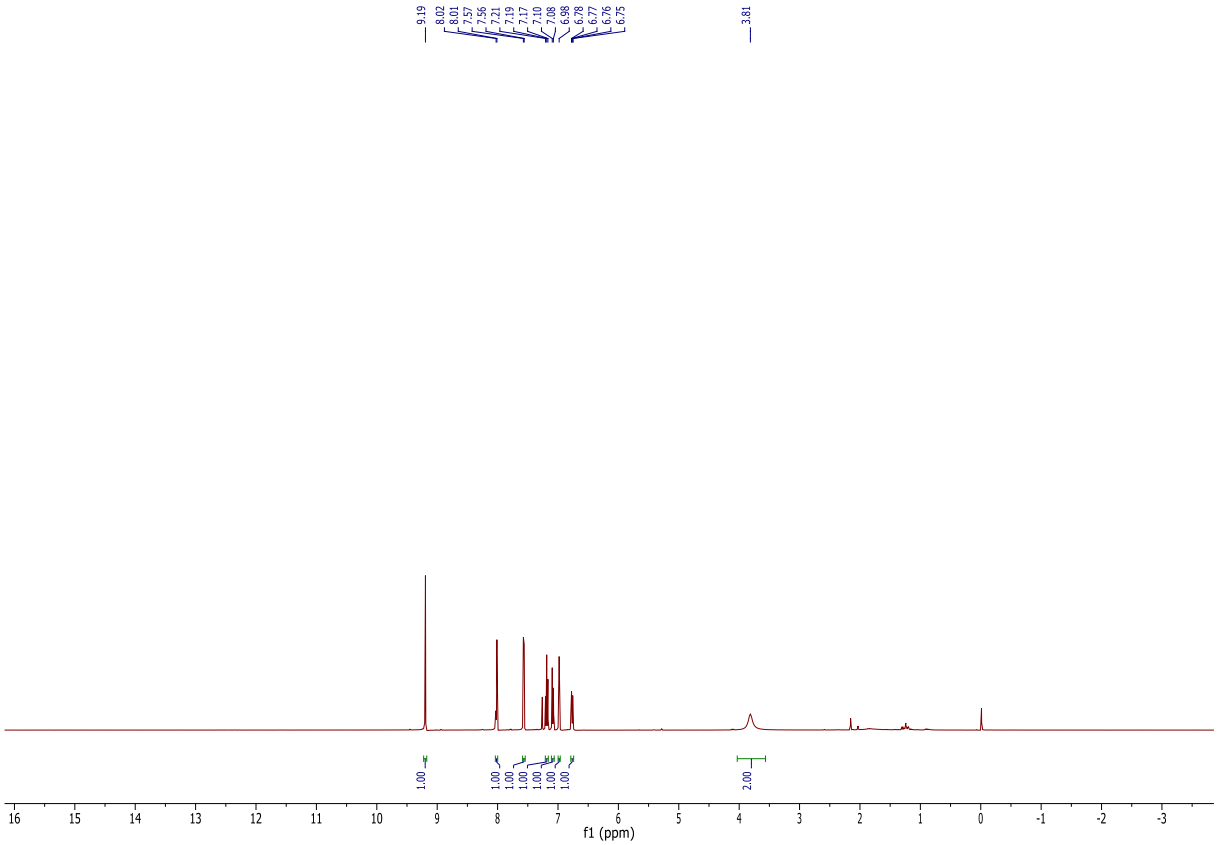
2C2. Spectra of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR

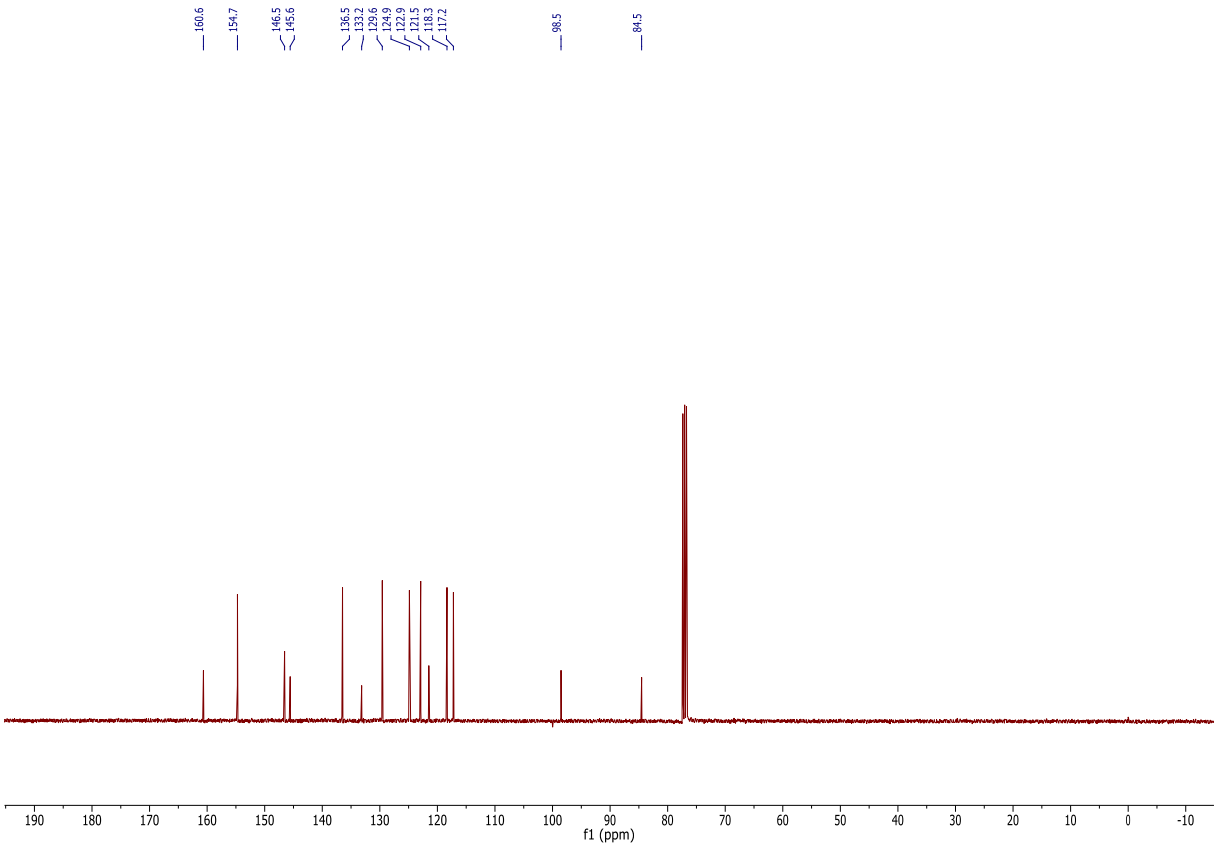
4-((4-methoxyphenyl)ethynyl)thieno[3,2-d]pyrimidine(**19a**)



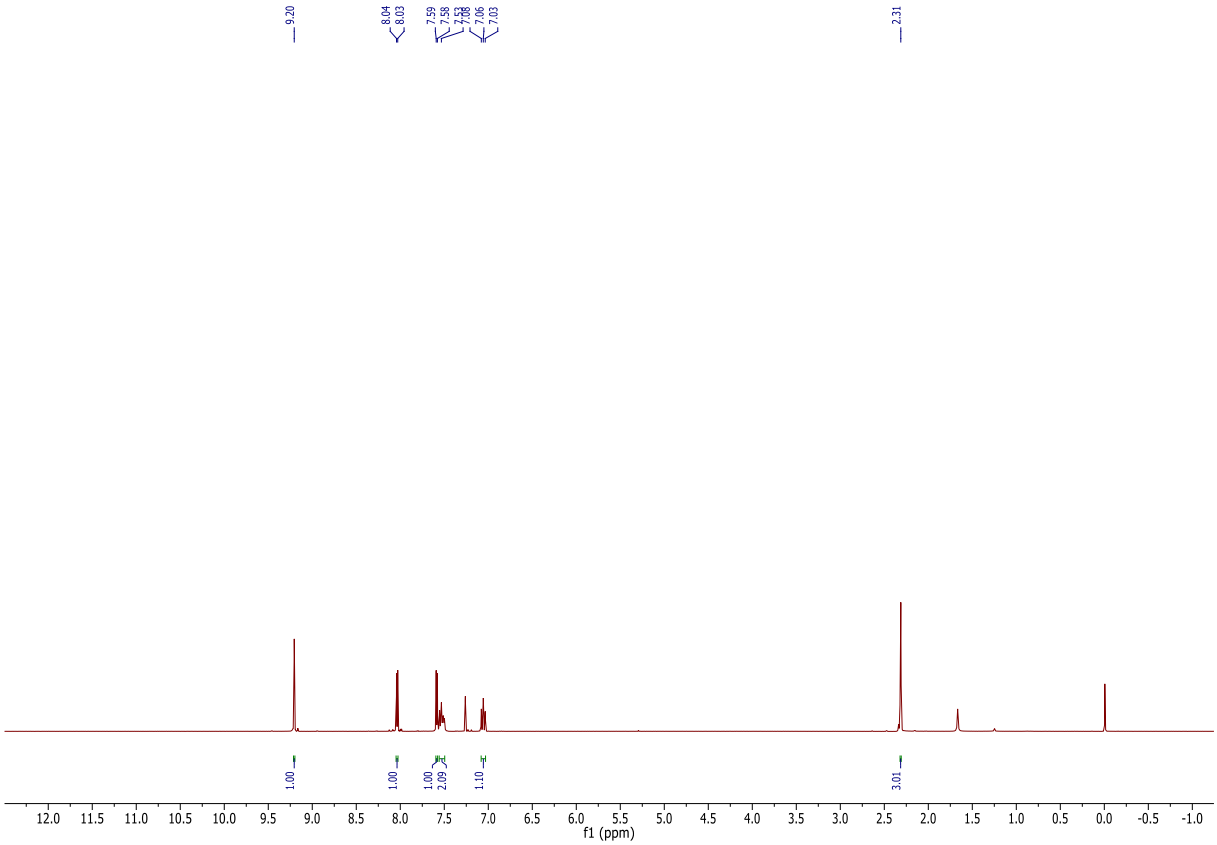


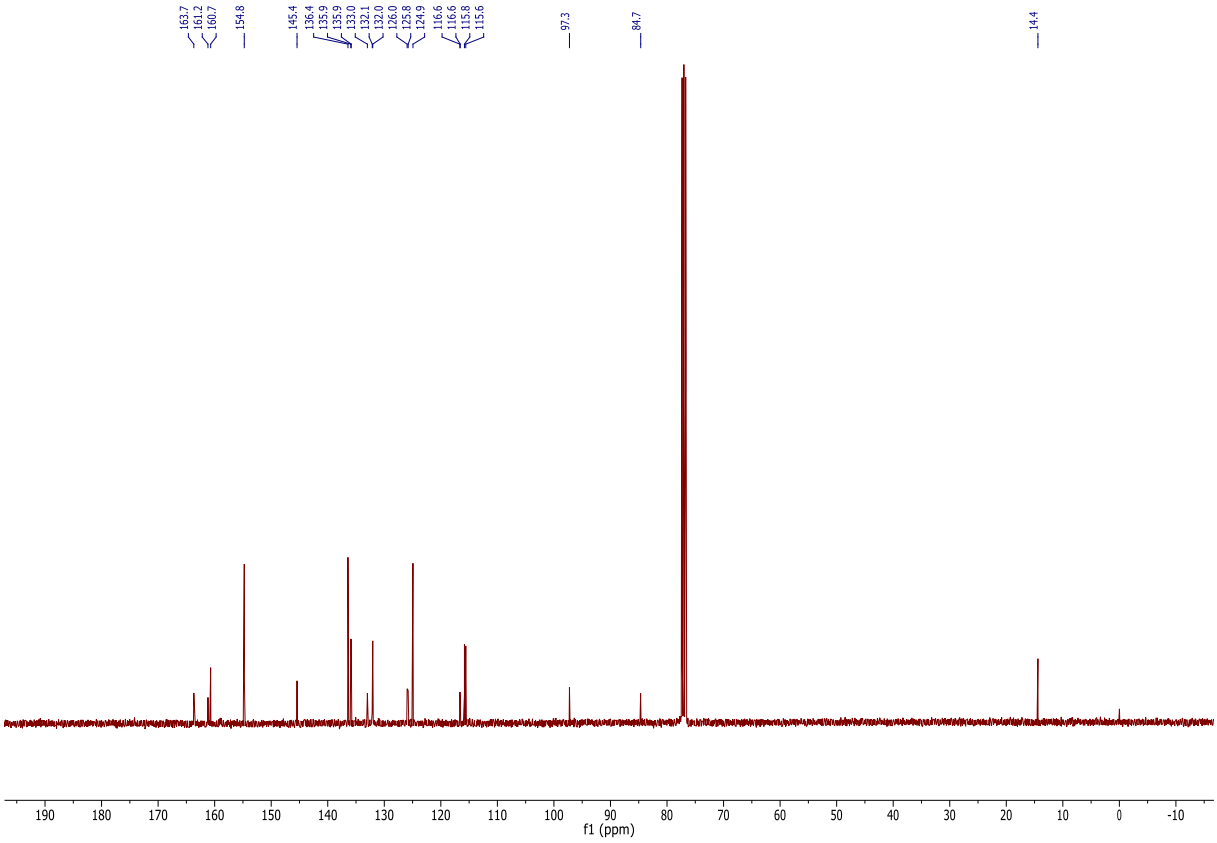
3-(thieno[3,2-d]pyrimidin-4-ylethynyl)aniline(**19b**)

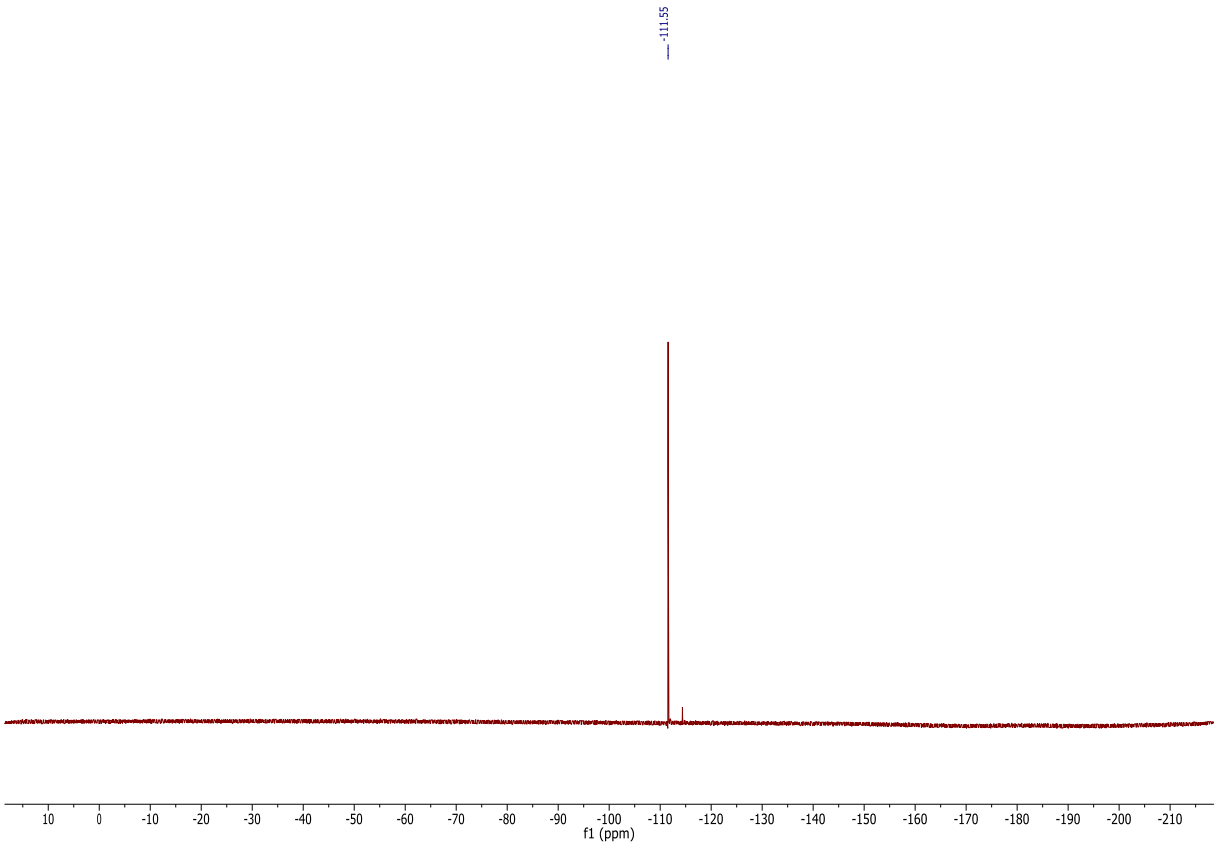




4-((4-fluoro-3-methylphenyl)ethynyl)thieno[3,2-d]pyrimidine(**19c**)



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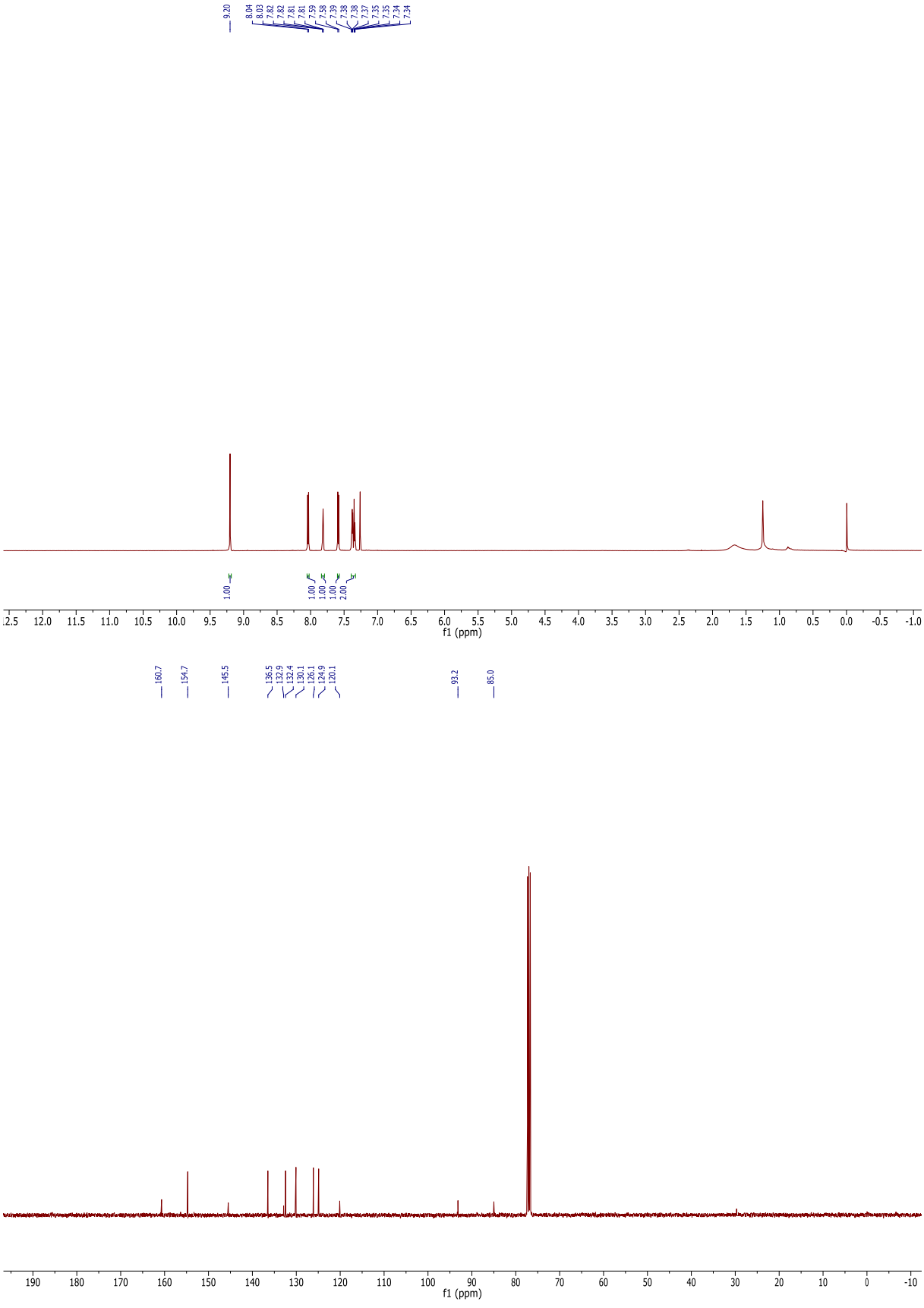
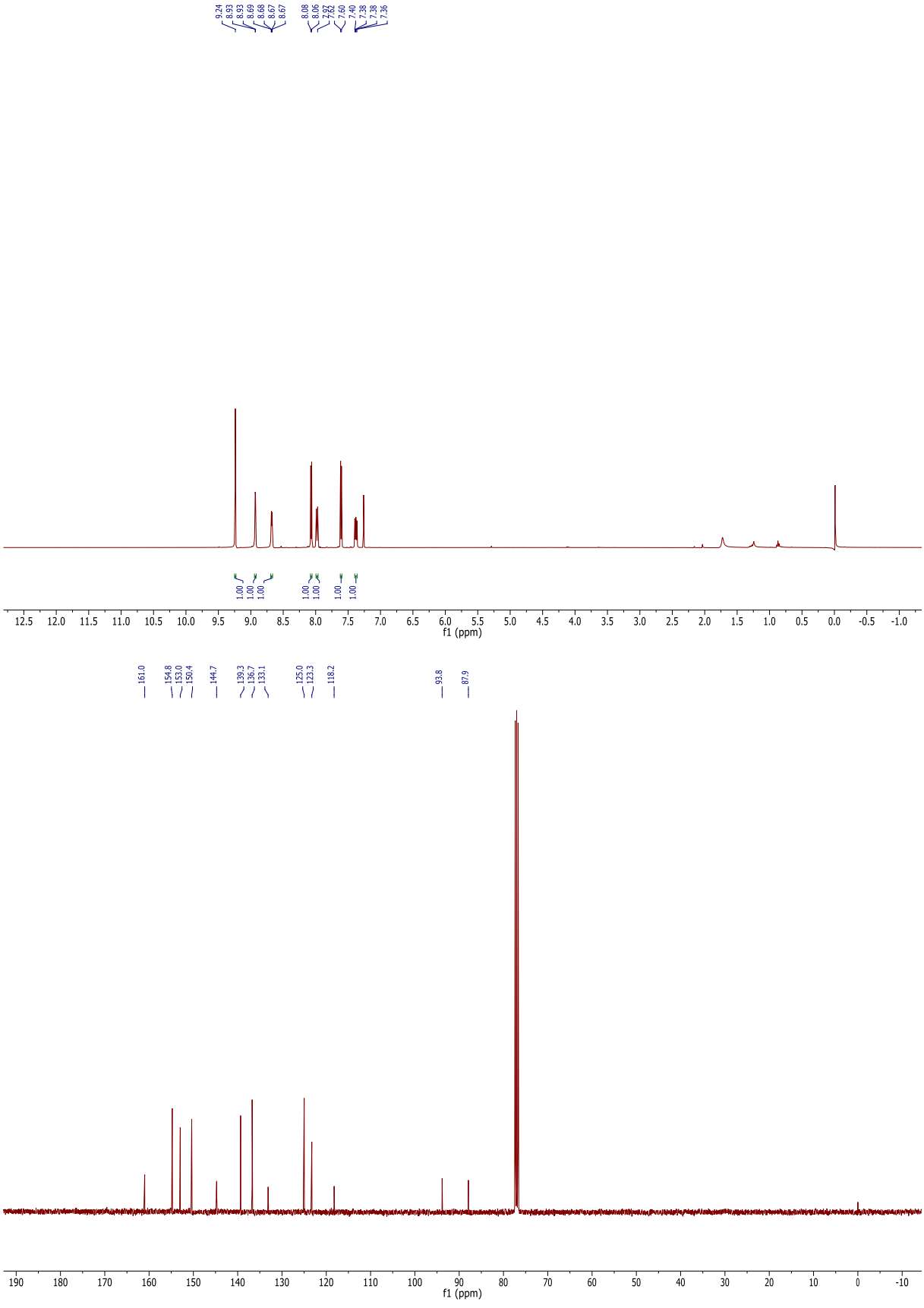
f1 (ppm)

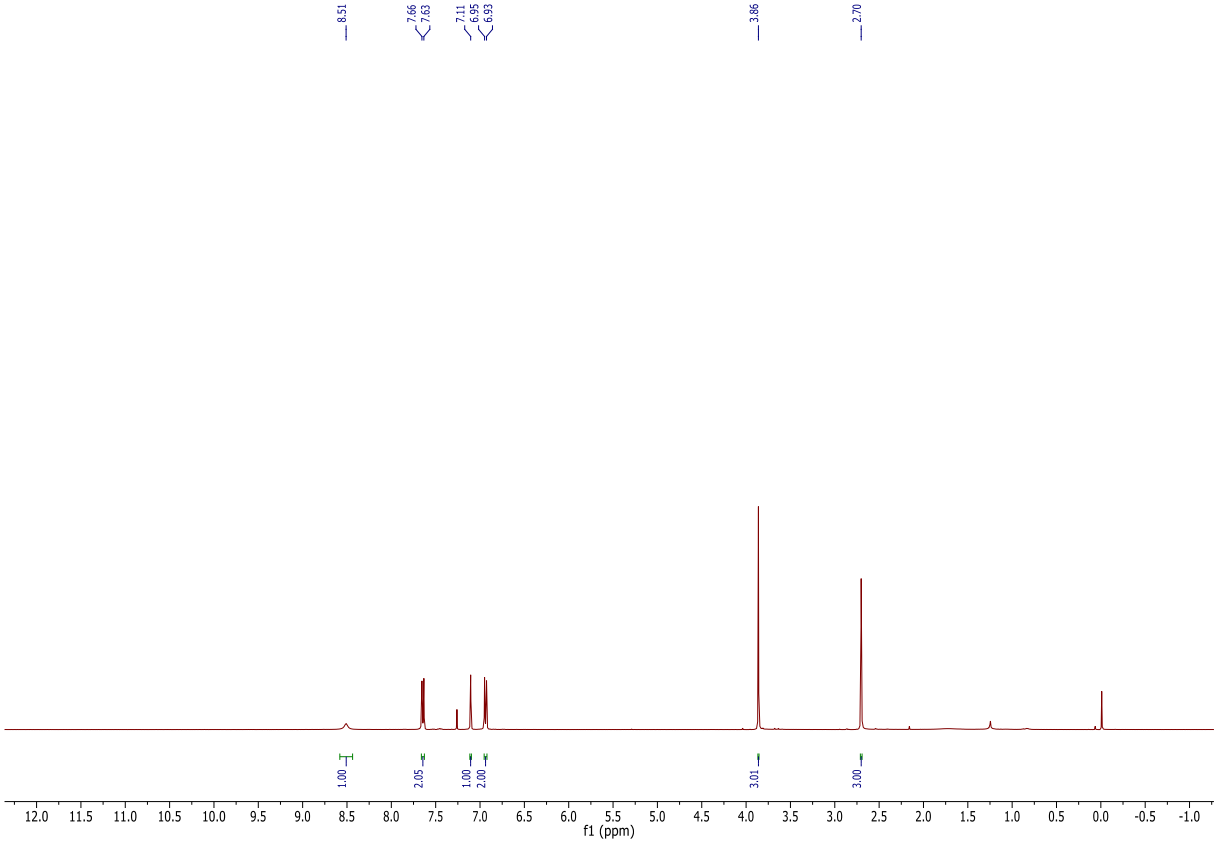
4-(thiophen-3-ylethynyl)thieno[3,2-d]pyrimidine(**19d**)

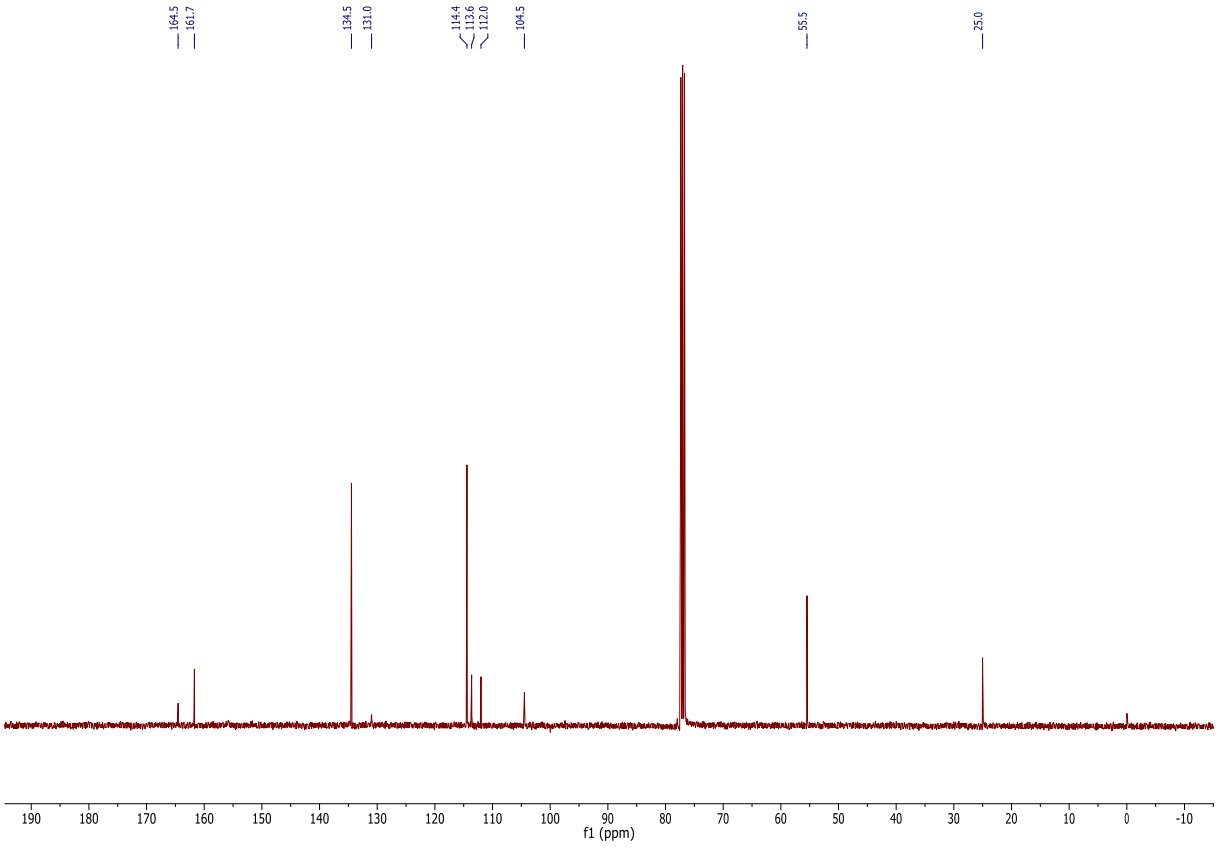


4-(pyridin-3-ylethynyl)thieno[3,2-d]pyrimidine(**19e**)

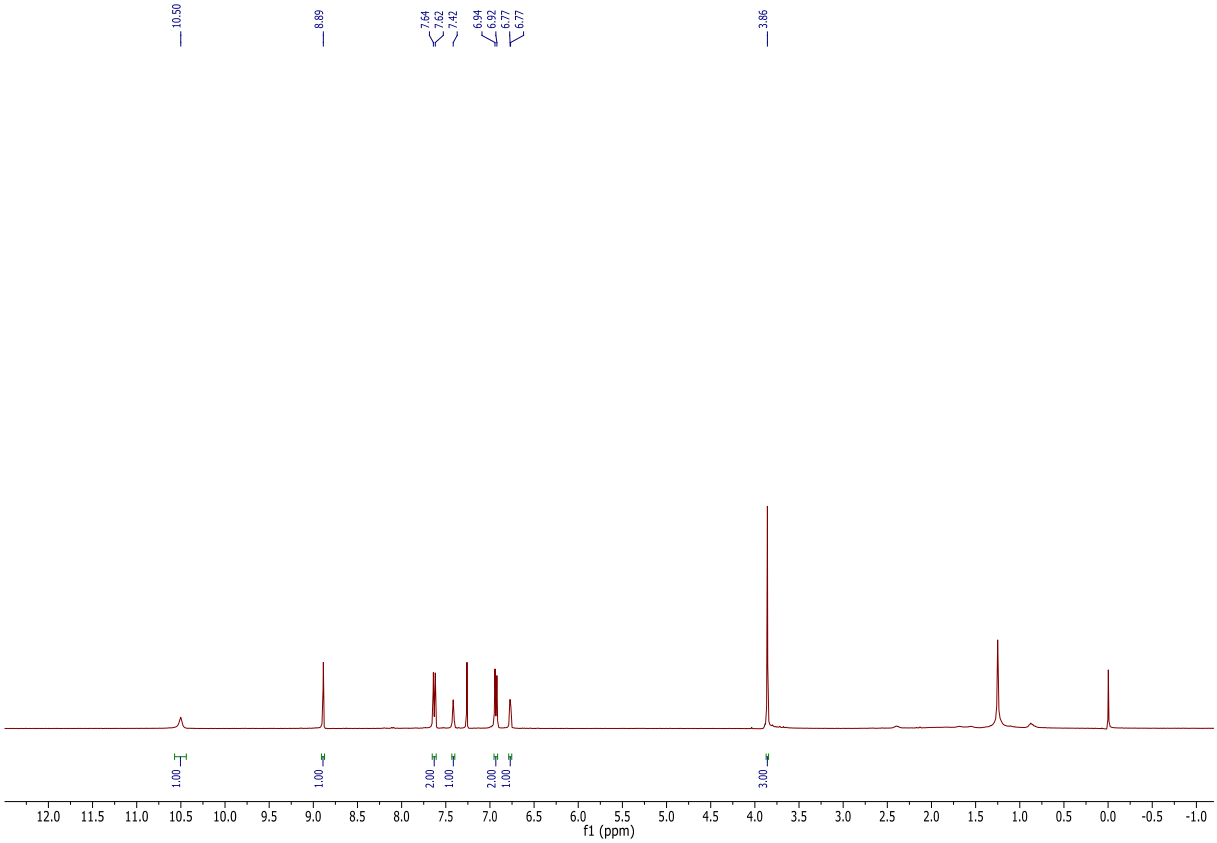


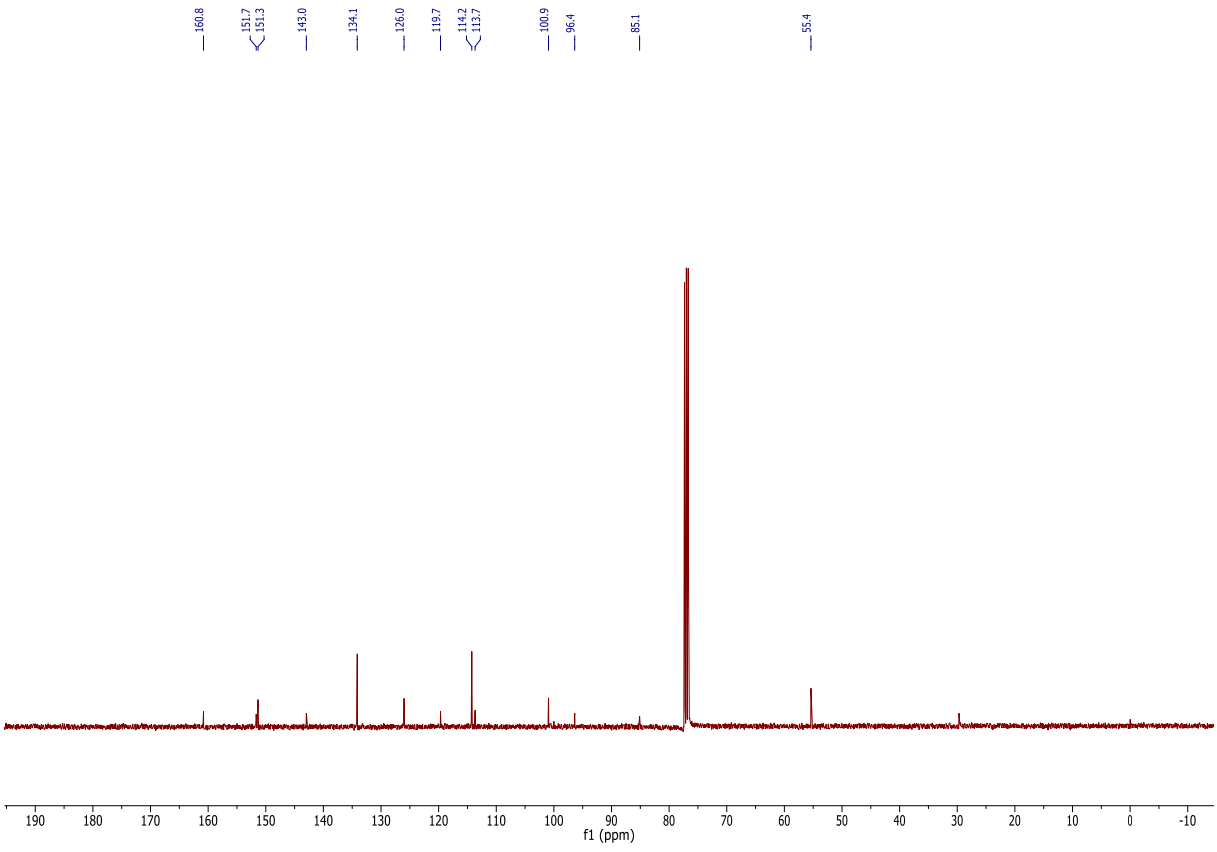
7-((4-methoxyphenyl)ethynyl)-5-methyl-[1,2,4]triazolo[1,5-a]pyrimidine(**20**)



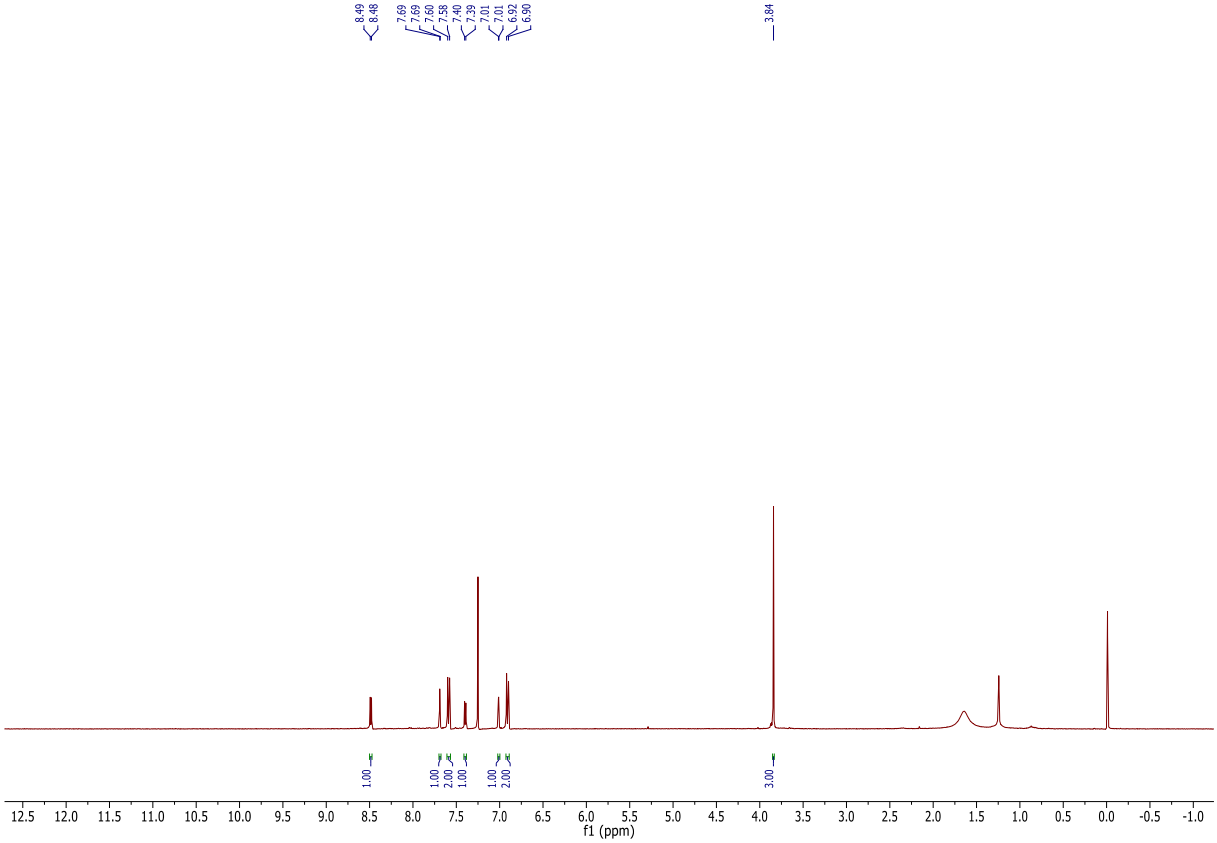


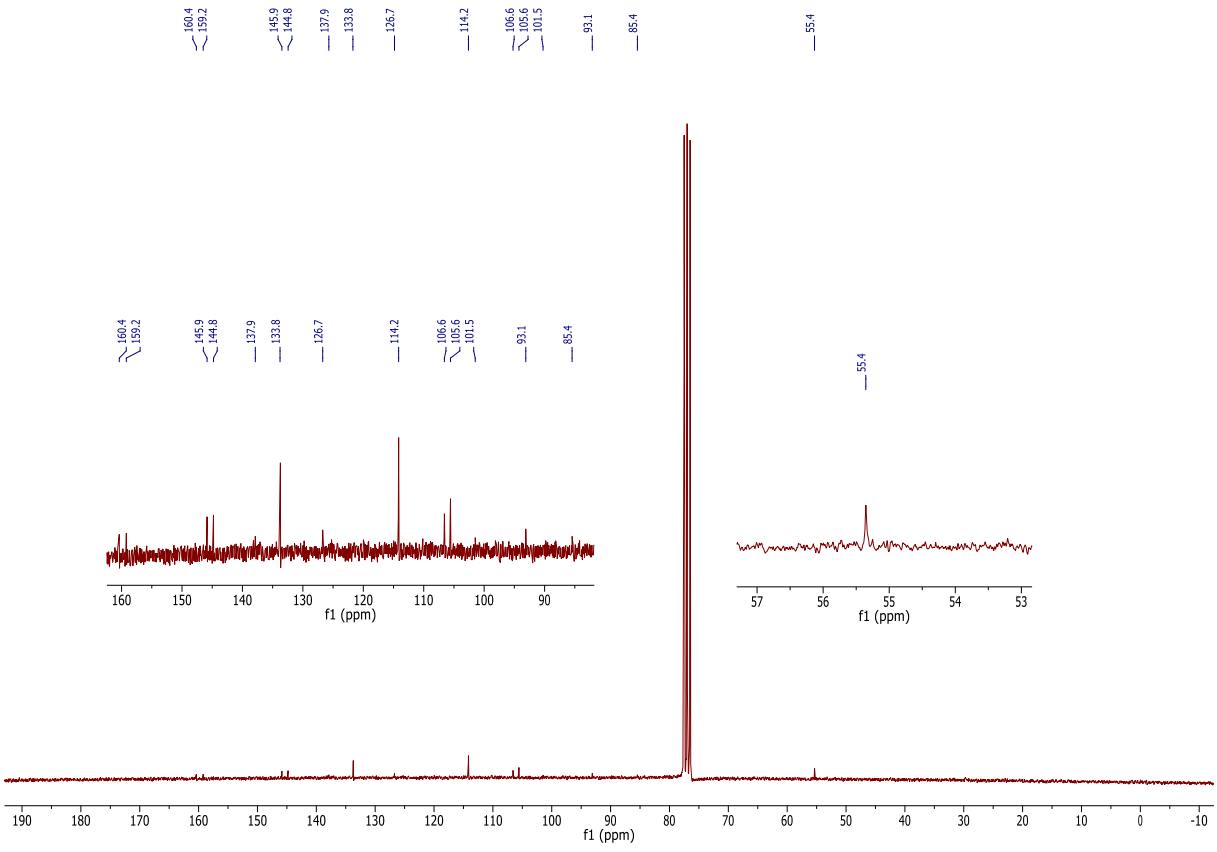
4-((4-methoxyphenyl)ethynyl)-7H-pyrrolo[2,3-d]pyrimidine(**22**)



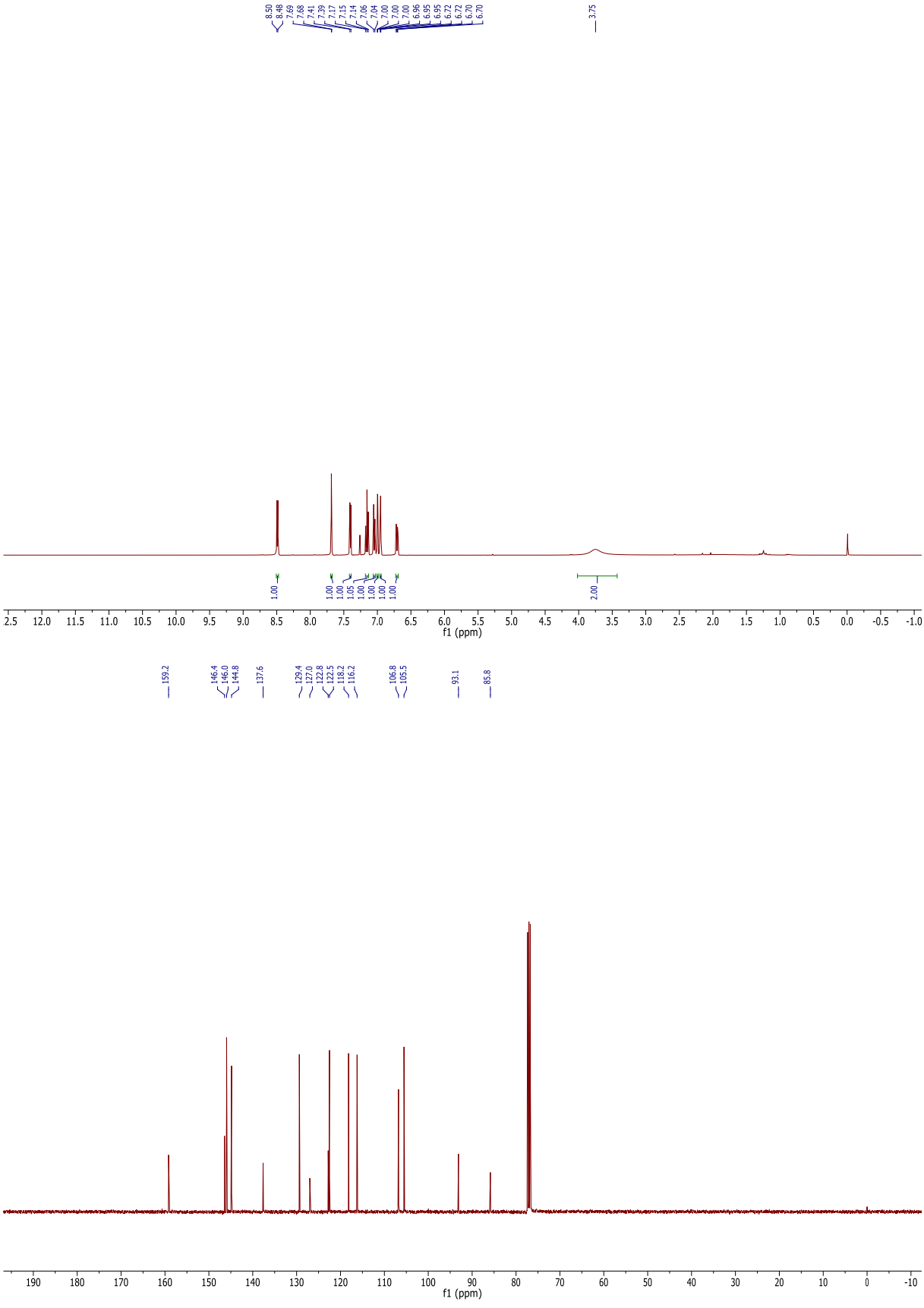


4-((4-methoxyphenyl)ethynyl)furo[3,2-c]pyridine (**24a**)

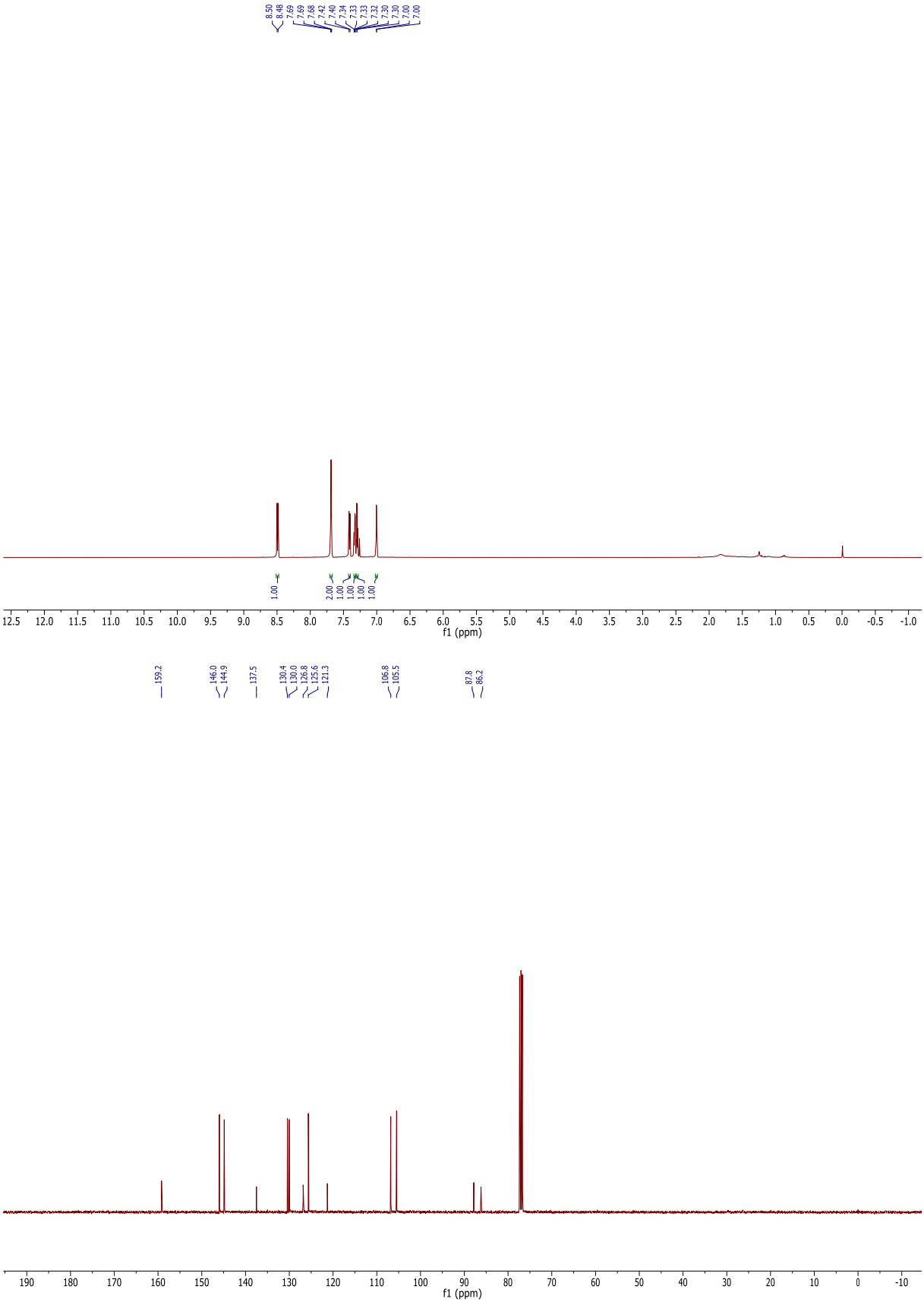




3-(furo[3,2-c]pyridin-4-ylethynyl)aniline (**24b**)



4-(thiophen-3-ylethynyl)furo[3,2-c]pyridine (**24d**)



4-(pyridin-3-ylethynyl)furo[3,2-c]pyridine (**24e**)