Supporting Information

Sustainable, precious metal-free C-N cross coupling through photocatalysis

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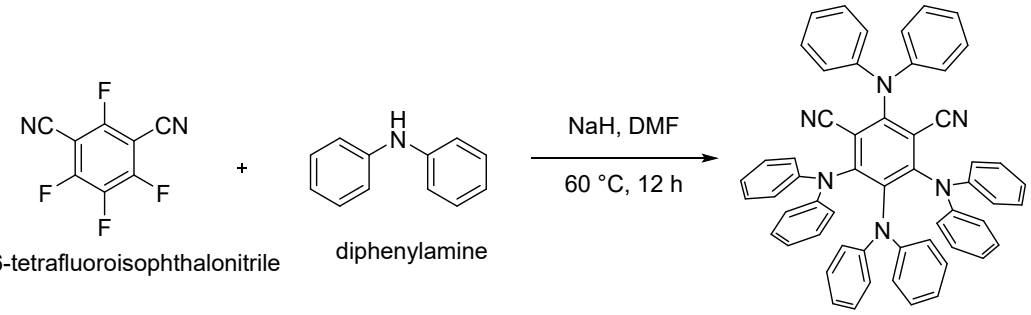
1. General information:

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H, ^{13}C and 19F-NMR spectra were recorded on a Bruker AV-III400 (400 MHZ) spectrometer. ^{1}H, ^{13}C and 19F-NMR spectra were recorded in $CDCl_3$ (δ 7.26, 77.0 ppm), DMSO-d_6 (δ 2.50, 39.98 ppm) with tetramethyl silane (TMS) as the internal standard. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). Liquid chromatography – mass spectroscopic studies (LC-MS) were recorded in waters Acquity H class plus with PDA eλ Detector and for mass waters SQ Detector 2Z spray ESI. All reactions with oxygen- or moisture-sensitive reagents were carried out in glassware, which was dried before use by heating under vacuum. Dry nitrogen was used as inert gas atmosphere. Melting points were determined on Polmon melting point apparatus and reported values are uncorrected. All light promoted reactions were carried out in Biotage microwave vials (10 - 30 mL) under irradiation with the Blue LED strips (30W, maximum emission at around 450 nm) were purchased from EvoluChem with batch no. 220713-2 (LED0002113). The distance between the Biotage microwave vial and the light strips is about 3-4 cm. All prepared compounds were purified through column chromatography using 100-200 mesh silica. The photocatalyst 4DPAIPN was synthesized according to reported protocol.[1]

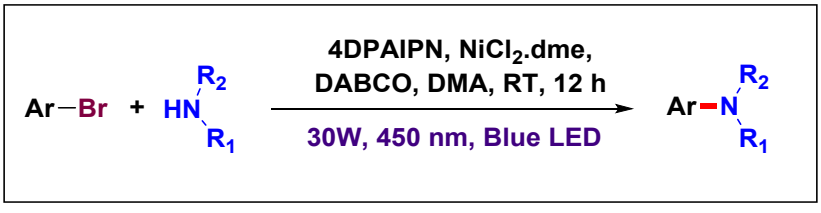
2. Experimental procedures:

2.1 Synthesis of 4DPAIPN:



NaH (60% in oil, 20.0 mmol) was added slowly to a stirred solution of diphenylamine (15.0 mmol) tetrafluoroisophthalonitrile (500 mg, 2.50 mmol) in dry DMF (30 mL) under a nitrogen atmosphere at room temperature. Then the reaction mixture was stirred at 60 °C for 12 h. Then, ice cooled was added to the reaction mixture which resulted in precipitation of solid. Solid was filtered and purified by column chromatography on silica gel with ethyl acetate / hexane, concentrated the desired fractions to afford 4DPAIN (1.3 g, 65%). The characterization data of 4DPAIPN was same as the reported.[1]

2.2 General experimental procedure:

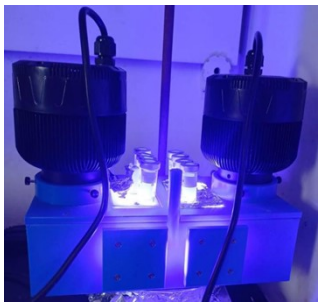


To a 10 mL Biotage microwave vial equipped with a magnetic stir bar was added the 4DPAIPN (0.005 equiv) and aryl bromide (1 equiv) under nitrogen condition. Then, DMA (10 vol), aromatic/aliphatic amine (1.5 equiv), $NiCl_2$.DME (0.05 equiv), DABCO (2 eq) were added. The reaction was stirred and irradiated with two 30 W blue (LED 450 nm) lamps for 12 h. The solvent was removed on a rotary evaporator under reduced

pressure and crude product was purified by silica gel flash column chromatography via gradient elution with hexane to hexane/ethyl acetate to give the desired products respectively.

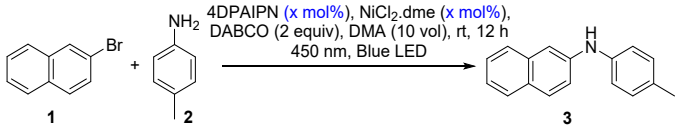
3. Light source and apparatus:

The reactions were performed using EvoluChem photoRedOx Box Duo, which manufactured by HepatoChem (US patent 10,906,022). This Photo reactor are equipped with eight 30 W blue light LEDs, and their power can be tuned by connecting a controller. The emission spectrum of blue LEDs is about 450 nm, the reaction was irradiated through a high-reflection channel from blue LED to the test tube, which length is 3-4 cm without any filters.


4. Optimization of the reaction condition:

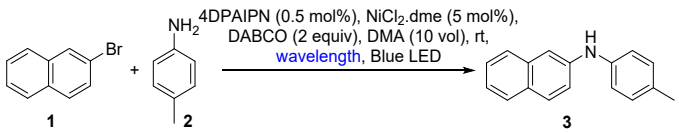
Table S1. Screening of different equivalent of 4DPAIPN & $NiCl_2$.dme on C-N coupling



S. NO	4DPAIPN (x mol%) & $NiCl_2$.dme (x mol%)	Yield (%)
1	4DPAIPN (0.5 mol%) & $NiCl_2$.dme (5 mol%)	82
2	4DPAIPN (0.2 mol%) & $NiCl_2$.dme (2 mol%)	67
3	4DPAIPN (0.1 mol%) & $NiCl_2$.dme (1 mol%)	54[a]

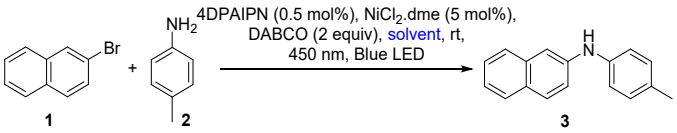
[a]After 24 h, there was not increased in product formation

Table S2. Screening of different wavelength on C-N coupling



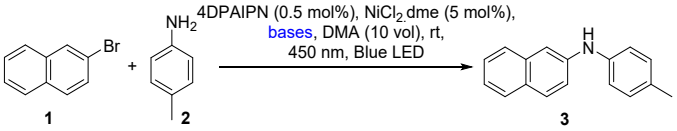
S. NO	Wavelength (nm)	Yield (%)
1	450	82
2	427	20
3	370	NR

Table S3. Screening of Solvents on C-N coupling



S. NO	Solvent	Yield (%)
1	EtOAc	NR
2	DMA	82
3	MeCN	70
4	DMF	10
5	DMSO	NR
6	MeOH	NR
7	DCM	NR

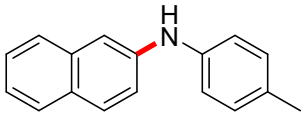
Table S4. Screening of bases on C-N coupling



S. NO	Bases	Yield (%)
1	DABCO	82
2	Et3N	70
3	DBU	NR
4	DIPEA	73
5	DMAP	38
6	Pyridine	NR
7	No base	NR

5. Characterization data:

N-(*p*-Tolyl) naphthalen-2-amine (3):



The title compound was prepared according to general procedure from 2-bromo naphthalene (100 mg, 0.48 mmol, 1 equiv) and *p*-toluidine (80 mg, 0.74 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (3% EtOAc/PE as an eluent) and product was isolated as an off-white solid (93 mg, 82% yield).

R_f: 0.5 (1:9 EtOAc/PE).

m.p. 97-99 ^oC

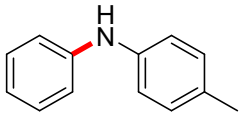
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.21 – 7.18 (m, 1H), 7.08 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.06 – 6.99 (m, 4H), 4.35 (bs, 1H), 2.27 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.7, 140.1, 134.7, 131.4, 130.0, 129.2, 128.9, 127.7, 126.4, 126.4, 123.2, 119.6, 119.4, 110.3, 20.8.

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{17}H_{16}N]$:234.13, found: 234.09.

Analytical data was in accordance with literature data.[2]

4-Methyl-N-phenylaniline (4):



The title compound was prepared according to general procedure from bromo benzene (100 mg, 0.64 mmol, 1 equiv) and *p*-toluidine (104 mg, 0.97 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (2% EtOAc/PE as an eluent) and product was isolated as an off-white solid (90 mg, 76% yield).

R_f: 0.5 (1:9 EtOAc/PE).

m.p. 83-85 °C.

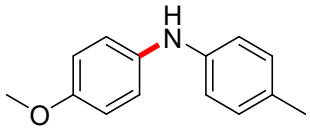
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.6, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.03 - 6.98 (m, 4H), 6.88 (t, *J* = 7.6 Hz, 1H), 2.30 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.0, 140.3, 131.0, 129.9, 129.4, 120.3, 118.9, 116.9, 20.8.

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{13}H_{14}N]$:184.11, found: 183.95.

Analytical data was in accordance with literature data.[3]

4-Methoxy-N-(*p*-tolyl) aniline (5):



The title compound was prepared according to general procedure from 1-bromo-4-methoxybenzene (100 mg, 0.54 mmol, 1 equiv) and *p*-toluidine (87 mg, 0.81 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (70 mg, 61% yield).

R_f: 0.4 (2:8 EtOAc/PE).

m.p. 82-84 °C

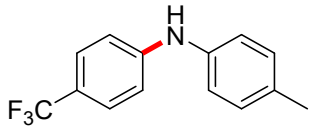
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.05 – 7.01 (m, 4H), 6.86 – 6.81 (m, 4H), 3.79 (s, 3H), 2.27 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.8, 142.4, 136.6, 129.8, 129.3, 127.8, 121.1, 116.6, 114.7, 55.6, 20.6.

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{14}H_{16}NO]$:214.12, found: 214.00.

Analytical data was in accordance with literature data.[4]

4-Methyl-*N*-(4-(trifluoromethyl)phenyl)aniline (6):



The title compound was prepared according to general procedure from 1-bromo-4-(trifluoromethyl)benzene (100 mg, 0.45 mmol, 1 equiv) and *p*-toluidine (74 mg, 0.69 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (79 mg, 70% yield).

R_f: 0.5 (1:9 EtOAc/PE).

m.p. 67-69 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 2.33 (s, 3H).

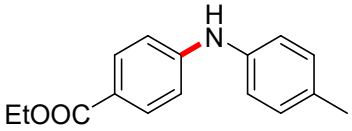
^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.5, 138.3, 133.0, 130.1, 126.7 126.7, 121.1, 121.0 (q, $J_{C\text{-}F}$ = 32 Hz), 114.6, 20.8.

^{19}F-NMR (376 MHz, $CDCl_3$) δ -61.3

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{14}H_{13}F_3N]$:252.10, found: 252.04.

Analytical data was in accordance with literature data.[5]

Ethyl 4-(p-tolylamino)benzoate (7):



The title compound was prepared according to general procedure from ethyl 4-bromobenzoate (100 mg, 0.44 mmol, 1 equiv) and *p*-toluidine (73 mg, 0.68 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (73 mg, 65% yield).

R_f: 0.5 (2:8 EtOAc/PE).

m.p. 83-85 °C

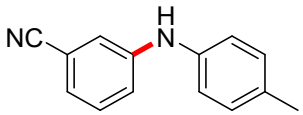
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91-7.87 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.92-6.89 (m, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.6, 148.7, 138.2, 133.0, 131.4, 130.0, 121.25, 120.9, 114.0, 60.4, 20.5, 14.4.

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{16}H_{18}NO_2]$:256.13, found: 256.04.

Analytical data was in accordance with literature data.[6]

3-(p-Tolylamino) benzonitrile (8):



The title compound was prepared according to general procedure from 3-bromobenzonitrile (100 mg, 0.55 mmol, 1 equiv) and *p*-toluidine (90 mg, 0.84 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (71 mg, 62% yield).

R_f: 0.5 (1:9 EtOAc/PE).

m.p. 73-75 °C

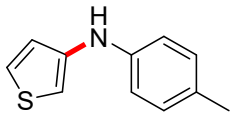
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.19 – 7.07 (m, 5H), 7.02 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.4, 138.2, 133.1, 130.2, 130.1, 122.9, 120.85, 119.9, 119.2, 118.0, 113.1, 20.8.

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{14}H_{13}N_2]$: 209.11, found: 208.99.

Analytical data was in accordance with literature data.[7]

***N*-(*p*-Tolyl)thiophen-3-amine (9):**



The title compound was prepared according to general procedure from 3-bromothiophene (100 mg, 0.62 mmol, 1 equiv) and *p*-toluidine (100 mg, 0.93 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (3% EtOAc/PE as an eluent) and product was isolated as an off-white solid (57 mg, 49% yield).

R_f: 0.4 (2:8 EtOAc/PE).

m.p. 50-52 °C

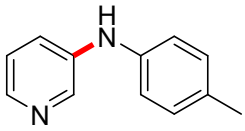
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.21 (m, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.91 – 6.85 (m, 3H), 6.65 – 6.63 (m, 1H), 5.61 (bs, 1H), 2.28 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.3, 142.0, 129.9, 129.6, 125.1, 122.5, 116.3, 104.9, 20.6.

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{11}H_{12}NS]$: 190.07, found: 190.08.

Analytical data was in accordance with literature data.[9]

N-(p-Tolyl)pyridin-3-amine (10):



The title compound was prepared according to general procedure from 3-bromopyridine (100 mg, 0.64 mmol, 1 equiv) and *p*-toluidine (106 mg, 0.99 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (65 mg, 55% yield).

R_f: 0.4 (2:8 EtOAc/PE).

m.p. 104-106 °C

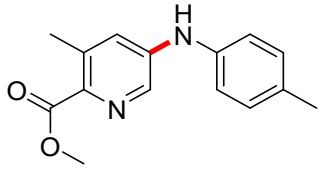
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 2.8 Hz, 1H), 8.11 (dd, *J* = 4.4, 0.8 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.15 – 7.01 (m, 3H), 7.01 (dd, *J* = 6.4, 2.0 Hz, 2H), 5.71 (s, 1H), 2.32 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.0, 140.8, 139.2, 139.1, 132.0, 130.0, 123.8, 122.4, 119.4, 20.8.

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{12}H_{13}N_2]$: 185.11, found: 184.94.

Analytical data was in accordance with literature data.[8, 9]

Methyl 3-methyl-5-(*p*-tolylamino) picolinate (11):



The title compound was prepared according to general procedure from methyl 5-bromo-3-methylpicolinate (100 mg, 0.44 mmol, 1 equiv) and *p*-toluidine (73 mg, 0.68 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (62 mg, 55% yield).

R_f: 0.5 (1:9 EtOAc/PE).

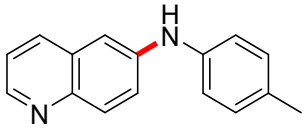
m.p. 94-96 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.10 - 7.06 (m, 3H), 6.04 (s, 1H), 3.92 (s, 3H), 2.56 (s, 3H), 2.35 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.2, 143.3, 138.4, 137.1, 136.4, 135.2, 133.8, 130.2, 122.4, 121.3, 52.1, 21.0, 20.9.

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{15}H_{17}N_2O_2]$: 257.13, found: 257.06.

***N*-(*p*-Tolyl)quinolin-6-amine (12):**



The title compound was prepared according to general procedure from 6-bromo quinoline (100 mg, 0.48 mmol, 1 equiv) and *p*-toluidine (80 mg, 0.74 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (12% EtOAc/PE as an eluent) and product was isolated as a light brown solid (64 mg, 56% yield).

R_f: 0.4 (3:7 EtOAc/PE).

m.p. 140–142 °C

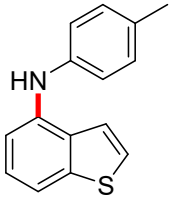
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.31 (d, *J* = 6.0 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 6.0 Hz, 1H), 7.20 – 7.13 (m, 6H), 6.32 (s, 1H), 2.36 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 151.3, 146.4, 143.2, 138.2, 137.9, 133.3, 130.1, 129.3, 123.9, 121.4, 119.8, 119.2, 105.3, 20.9.

LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{16}H_{15}N_2]$: 235.12, found: 235.12.

Analytical data was in accordance with literature data.[9]

_N_-(_p_-Tolyl)benzo[b]thiophen-4-amine (13):



The title compound was prepared according to general procedure from 4-bromobenzo[b]thiophene (100 mg, 0.47 mmol, 1 equiv) and *p*-toluidine (76 mg, 0.71 mmol, equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (59 mg, 52% yield).

R_f: 0.4 (2:8 EtOAc/PE).

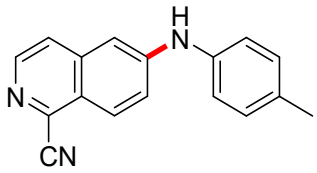
m.p. 99–101 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 5.6, 0.4 Hz, 1H), 7.31 (dd, *J* = 5.6, 0.8 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.11 – 7.07 (m, 3H), 7.11 – 6.96 (m, 2H), 2.30 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.3, 140.7, 139.0, 131.3, 131.1, 129.9, 125.3, 125.1, 120.1, 119.1, 115.4, 111.3, 20.8.

LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{15}H_{14}NS]$: 240.08, found: 240.03.

6-(p-Tolylamino)isoquinoline-1-carbonitrile (14):



The title compound was prepared according to general procedure from 6-bromoisoquinoline-1-carbonitrile (100 mg, 0.43 mmol, 1 equiv) and *p*-toluidine (70 mg, 0.65 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as a yellow semi solid (56 mg, 50% yield).

R_f: 0.4 (1:9 EtOAc/PE).

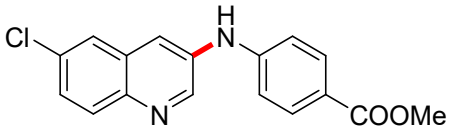
m.p. 153-155 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 6.0 Hz, 1H), 8.14 (d, *J* = 9.2 Hz, 1H),7.53 (dd, *J* = 5.6, 0.4 Hz, 1H), 7.32 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.16 (m, 3H), 6.17 (bs, 1H), 2.39 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.5, 143.6, 138.2, 137.0, 134.6, 133.7, 133.30, 126.9, 124.7, 122.5, 122.4, 122.2, 116.2, 104.5, 20.9.

LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{17}H_{14}N_3]$: 260.12, found: 260.42.

Methyl 4-((6-chloroquinolin-3-yl)amino)benzoate (15):



The title compound was prepared according to general procedure from 3-bromo-6-chloroquinoline (100 mg, 0.42 mmol, 1 equiv) and methyl 4-aminobenzoate (97 mg, 0.64 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (8% EtOAc/PE as an eluent) and product was isolated as a white solid (60 mg, 44% yield).

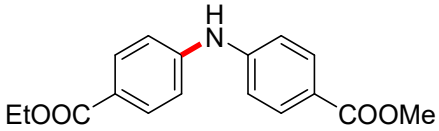
R_f: 0.4 (3:7 EtOAc/PE).

m.p. 168-170 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 2.8 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.68 (d, *J* = 2.4 Hz, 1H), 7.51 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.33 (bs, 1H), 3.91 (s, 3H).

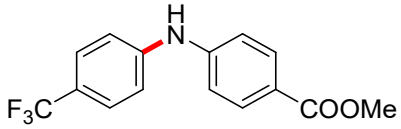
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.7, 146.2, 145.7, 142.6, 135.8, 133.3, 131.7, 130.7, 129.3, 128.3, 125.3, 123.1, 118.9, 115.9, 52.9.
LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{17}H_{14}ClN_2O_2]$: 313.07, found: 313.28.

Ethyl 4-((4-(methoxycarbonyl)phenyl)amino)benzoate (16):



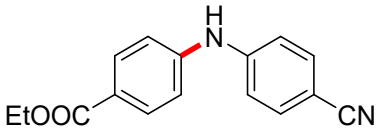
The title compound was prepared according to general procedure from ethyl 4-bromobenzoate (100 mg, 0.43 mmol, 1 equiv) and methyl 4-aminobenzoate (97 mg, 0.64 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (8% EtOAc/PE as an eluent) and product was isolated as a pale-yellow solid (55 mg, 42% yield).
R_f: 0.3 (2:8 EtOAc/PE).
m.p. 149-151 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.27 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 4H), 7.25 – 7.22 (m, 4H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 1.31 (t, *J* =7.2 Hz, 3H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 165.9, 165.4, 146.5, 146.4, 130.9, 130.9, 121.5, 121.1, 116.5, 116.3, 60.2, 51.7, 14.3.
LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{17}H_{18}NO_4]$: 300.12, found: 299.99.
Analytical data was in accordance with literature data.[15]

Methyl 4-((4-(trifluoromethyl)phenyl)amino)benzoate (17):



The title compound was prepared according to general procedure from 1-bromo-4-(trifluoromethyl)benzene (100 mg, 0.43 mmol, 1 equiv) and methyl 4-aminobenzoate (97 mg, 0.0.64 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (8% EtOAc/PE as an eluent) and product was isolated as a yellow solid (60 mg, 45% yield).
R_f: 0.3 (2:8 EtOAc/PE).
m.p. 147-149 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.23 (s, 1H), 7.88 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.22 (dd, *J* = 6.8, 2.0 Hz, 2H), 3.81 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 165.9, 146.7, 145.4, 131.0, 126.6, 126.6, 126.0, 123.3, 120.9, 120.77 (q, $J_{C\text{-}F}$ = 32 Hz), 117.2, 115.9, 51.6.
^{19}F-NMR (376 MHz, DMSO-d_6) δ -59.9
LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{15}H_{13}F_3NO_2]$: 296.09, found: 296.17.
Analytical data was in accordance with literature data.[16a]

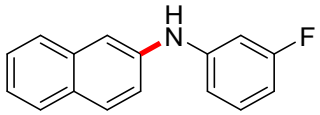
Ethyl 4-((4-cyanophenyl)amino)benzoate (18):



The title compound was prepared according to general procedure from ethyl 4-bromobenzoate (100 mg, 0.43 mmol, 1 equiv) and 4-aminobenzonitrile (76 mg, 0.0.64 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (8% EtOAc/PE as an eluent) and product was isolated as a yellow solid (66 mg, 56% yield).
R_f: 0.3 (2:8 EtOAc/PE).
m.p. 150-152 °C

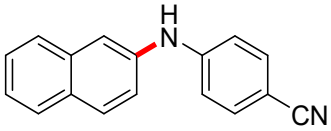
^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.37 (s, 1H), 7.92 – 7.88 (m, 2H), 7.71 – 7.67 (m, 2H), 7.26 – 7.23 (m, 4H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* =7.2 Hz, 3H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 165.3, 146.3, 145.8, 133.7, 130.9, 122.1, 119.6, 116.9, 116.7, 101.3, 60.2, 14.3.
LCMS (ESI)[M+H]$^+$calculated m/z for [$C_{16}H_{15}N_2O_2$]: 267.11, found: 267.02.
Analytical data was in accordance with literature data.[16b]

***N*-(3-Fluorophenyl)naphthalen-2-amine (19):**



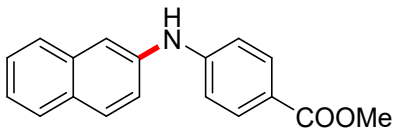
The title compound was prepared according to general procedure from 2-bromo naphthalene (100 mg, 0.48 mmol, 1 equiv) and 3-fluoro aniline (80 mg, 0.72 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (3% EtOAc/PE as an eluent) and product was isolated as an off-white solid (65 mg, 56% yield).
R_f: 0.4 (1:9 EtOAc/PE).
m.p. 52-54 °C
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.35 – 7.29 (m, 1H), 7.23 - 7.15 (m, 2H), 6.86 – 6.80 (m, 2H), 6.61 (td, *J* = 8.0, 1.6 Hz, 1H), 5.87 (s, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.9 (d, J_{C-F} = 243 Hz), 145.2 (d, J_{C-F} = 10 Hz), 139.7, 134.5, 130.6 (d, J_{C-F} = 10 Hz), 129.7, 129.4, 127.7, 126.7, 126.6, 124.1, 120.6, 113.4, 112.9, 107.5 (d, J_{C-F} = 21 Hz), 104.1 (d, J_{C-F} = 25 Hz).
^{19}F-NMR (376 MHz, $CDCl_3$) δ -112.06
LCMS (ESI)[M+H]$^+$calculated m/z for [$C_{16}H_{13}FN$]: 238.10, found: 238.07.
Analytical data was in accordance with literature data.[14]

4-(naphthalen-2-ylamino)benzonitrile (20):



The title compound was prepared according to general procedure from 2-bromo naphthalene (100 mg, 0.48 mmol, 1 equiv) and 4-aminobenzonitrile (85 mg, 0.72 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (8% EtOAc/PE as an eluent) and product was isolated as an off-white solid (61 mg, 51% yield).
R_f: 0.4 (3:7 EtOAc/PE).
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.47(dd, *J* = 8.4, 1.3 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.30 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.08 – 7.04 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.9, 137.6, 134.2, 133.8, 130.5, 129.6, 127.8, 126.9, 126.8, 124.9, 121.5, 119.9, 116.8, 115.2, 101.5.
LCMS (ESI)[M+H]$^+$calculated m/z for [$C_{17}H_{13}N_2$]: 245.11, found: 244.94.
Analytical data was in accordance with literature data.[14]

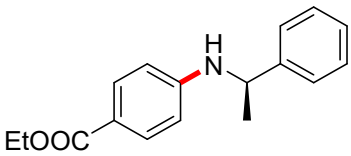
Methyl 4-(naphthalen-2-ylamino)benzoate (21):



The title compound was prepared according to general procedure from 2-bromo naphthalene (100 mg, 0.48 mmol, 1 equiv) and 4-aminobenzonitrile (110 mg, 0.72 mmol, 1.5 equiv). Purification was carried out by flash

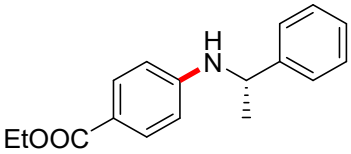
chromatography on silica (1% EtOAc/PE as an eluent) and product was isolated as an off-white solid (82 mg, 61% yield).
R_f: 0.4 (1:9 EtOAc/PE).
m.p. 171-173 °C
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.80 (t, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.46 (t, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.08, 147.93, 138.50, 134.31, 131.56, 130.12, 129.43, 127.74, 126.88, 126.69, 124.55, 121.41, 121.26, 115.54, 114.97, 51.97.
LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{18}H_{16}NO_2]$: 278.12, found: 278.23.
Analytical data was in accordance with literature data.[17]

Ethyl (R)-4-((1-phenylethyl)amino)benzoate (22):



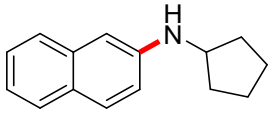
The title compound was prepared according to general procedure from ethyl 4-bromobenzoate (100 mg, 0.44 mmol, 1 equiv) and (R)-1-phenylethan-1-amine (80 mg, 0.0.66 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (8% EtOAc/PE as an eluent) and product was isolated as a yellow solid (62 mg, 52% yield).
R_f: 0.4 (3:7 EtOAc/PE).
m.p. 102-104 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.60 (d, *J* = 9.2 Hz, 2H), 7.35 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.30 (td, *J* = 7.6, 1.2 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.57 (quin, *J* = 6.8 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.23 (t, *J* =7.2 Hz, 3H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 165.8, 151.9, 145.2, 130.7, 128.4, 126.6, 125.8, 116.2, 111.7, 59.5, 51.7, 24.3, 14.3.
LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{17}H_{20}NO_2]$: 270.15, found: 270.02.

Ethyl (S)-4-((1-phenylethyl)amino)benzoate (23):



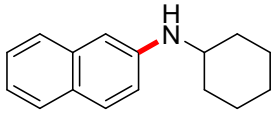
The title compound was prepared according to general procedure from ethyl 4-bromobenzoate (100 mg, 0.44 mmol, 1 equiv) and (S)-1-phenylethan-1-amine (80 mg, 0.0.66 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (8% EtOAc/PE as an eluent) and product was isolated as a yellow solid (56 mg, 47% yield).
R_f: 0.4 (3:7 EtOAc/PE).
m.p. 102-104 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.60 (d, *J* = 8.8 Hz, 2H), 7.35 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.30 (td, *J* = 7.6, 2.4 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.05 (d, *J* = 6.8 Hz, 1H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.57 (quin, *J* = 6.8 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.23 (t, *J* =7.2 Hz, 3H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 165.8, 151.9, 145.2, 130.7, 128.4, 126.6, 125.8, 116.2, 111.7, 59.5, 51.7, 24.3, 14.3.
LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{17}H_{20}NO_2]$: 270.15, found: 270.02.

N-Cyclopentylnaphthalen-2-amine (24):



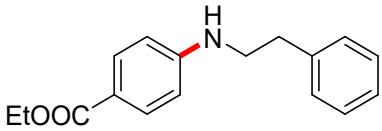
The title compound was prepared according to general procedure from 2-bromo naphthalene (100 mg, 0.48 mmol, 1 equiv) and cyclopentylamine (78 mg, 0.72 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (2% EtOAc/PE as an eluent) and product was isolated as an oil (66 mg, 64% yield).
R_f: 0.6 (1:9 EtOAc/PE).
^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.28 (td, *J* = 8.0, 0.8 Hz, 1H), 7.07 (td, *J* = 8.0, 0.8 Hz, 1H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 5.87 (d, *J* = 6.4 Hz, 1H), 3.83 – 3.75 (m, 1H), 2.01 – 1.93 (m, 2H), 1.74 – 1.62 (m, 2H), 1.61 – 1.45 (m, 4H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 146.9, 135.7, 128.6, 127.8, 126.7, 126.3, 125.8, 121.2, 119.1, 103.1, 54.0, 32.9, 24.3.
LCMS (ESI)[M+H]$^+$calculated m/z for [$C_{15}H_{18}N$]: 212.14, found: 212.02.

N-Cyclohexylnaphthalen-2-amine (25):



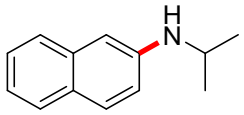
The title compound was prepared according to general procedure from 2-bromo naphthalene (100 mg, 0.48 mmol, 1 equiv) and cyclohexylamine (73 mg, 0.73 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (2% EtOAc/PE as an eluent) and product was isolated as an off-white semisolid (60 mg, 55% yield).
R_f: 0.5 (1:9 EtOAc/PE).
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 8.4, 3.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.78 (d, *J* = 2.0 Hz, 1H), 3.41 - 3.32 (m, 1H), 2.14 – 2.08 (m, 2H), 1.81 – 1.73 (m, 2H), 1.46 – 1.34 (m, 2H), 1.29 – 1.20 (m, 4H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.0, 135.4, 129.0, 127.7, 127.3, 126.3, 125.8, 121.7, 118.3, 104.8, 51.8, 33.4, 26.0, 25.1.
LCMS (ESI)[M+H]$^+$calculated m/z for [$C_{16}H_{20}N$]: 226.16, found: 226.16.
Analytical data was in accordance with literature data.[11]

Ethyl 4-(phenethylamino)benzoate (26):



The title compound was prepared according to general procedure from ethyl 4-bromobenzoate (100 0.44 mg, mmol, 1 equiv) and 2-phenylethan-1-amine (80 mg, 0.66 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (2% EtOAc/PE as an eluent) and product was isolated as a white semi-solid (49 mg, 41% yield).
R_f: 0.5 (1:9 EtOAc/PE).
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.22 (m, 1H), 7.22 (dd, *J* = 6.4, 2.0 Hz, 2H), 6.57 – 6.53 (m, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.45 (t, *J* = 6.8 Hz, 2H), 2.92 (t, *J* = 6.8 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, 151.6, 138.8, 131.6, 128.8, 128.7, 126.6, 118.8, 111.6, 60.2, 44.4, 35.3, 14.5.
LCMS (ESI)[M+H]$^+$ calculated m/z for [$C_{17}H_{20}NO_2$]: 270.15, found: 248.19.
Analytical data was in accordance with literature data.[5]

_N_-Isopropylnaphthalen-2-amine (27):



The title compound was prepared according to general procedure from 2-bromo naphthalene (100 mg, 0.48 mmol, 1.5 equiv) and isopropyl amine (45 mg, 0.76 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (2% EtOAc/PE as an eluent) and product was isolated as an off-white semi solid (40 mg, 45% yield).

R_f: 0.5 (1:9 EtOAc/PE).

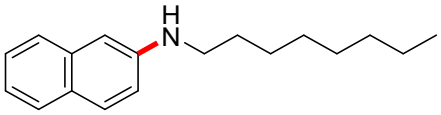
^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.63 – 7.52 (m, 3H), 7.27 (td, *J* = 8.0, 1.6 Hz, 1H), 7.07 (td, *J* = 8.0, 1.6 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.85 (d, *J* = 2.0 Hz, 1H), 5.70 (d, *J* = 7.6 Hz, 1H), 3.68 – 3.61 (m, 1H), 1.19 (d, *J* = 6.4 Hz, 6H).

^{13}C-NMR (100 MHz, DMSO-d_6) δ 146.4, 135.7, 128.8, 127.8, 126.6, 126.4, 125.8, 121.2, 119.1, 103.0, 43.5, 22.8.

LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{13}H_{16}N]$: 186.13, found: 186.07.

Analytical data was in accordance with literature data.[12]

N-Octylnaphthalen-2-amine (28):



The title compound was prepared according to general procedure from 2-bromo naphthalene (100 mg, 0.48 mmol, 1 equiv) and octylamine (95 mg, 0.74 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (1% EtOAc/PE as an eluent) and product was isolated as an off-white solid (57 mg, 46% yield).

R_f: 0.6 (1:9 EtOAc/PE).

m.p. 202–204 °C.

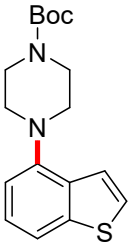
^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.62 – 7.53 (m, 3H), 7.30 – 7.24 (m, 1H), 7.09 – 7.03 (m, 1H), 6.96 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.58 (d, *J* = 2.0 Hz, 1H), 5.87 (t, *J* = 5.2 Hz, 1H), 3.07 (q, *J* = 6.8 Hz, 2H), 1.60 (q, *J* = 6.8 Hz, 2H), 1.41 – 1.25 (m, 10H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C-NMR (100 MHz, DMSO-d_6) δ 147.4, 135.7, 128.7, 127.8, 126.8, 126.4, 125.8, 121.2, 118.8, 102.4, 43.3, 31.8, 29.4, 29.2, 28.9, 27.3, 22.6, 14.4.

LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{18}H_{26}N]$: 256.21, found: 256.25.

Analytical data was in accordance with literature data.[13]

***tert*-Butyl 4-(benzo[b]thiophen-4-yl)piperazine-1-carboxylate (29):**



The title compound was prepared according to general procedure from 4-bromo thiophene (100 mg, 0.47 mmol, 1 equiv) and N-boc piperazine (135 mg, 0.75 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (99 mg, 66% yield).

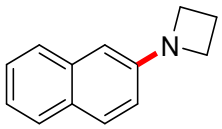
R_f: 0.6 (2:8 EtOAc/PE).

m.p. 45–47 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.41 (s, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.67 (t, *J* = 5.2 Hz, 4H), 3.10 (t, *J* = 5.2 Hz, 4H), 1.50 (s, 9H).

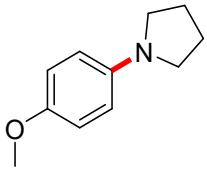
^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.8, 148.2, 141.2, 134.1, 125.3, 124.9, 121.6, 117.4, 112.4, 79.9, 52.1, 28.4.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{17}H_{14}N_3]$: 319.15, found: 319.21.
Analytical data was in accordance with literature data.[14, 18]

1-(Naphthalen-2-yl)azetidine (30):



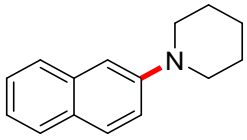
The title compound was prepared according to general procedure from 2-bromo naphthalene (100 mg, 0.48 mmol, 1 equiv) and azetidine (42 mg, 0.74 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (55 mg, 62% yield).
R_f: 0.4 (1:9 EtOAc/PE).
m.p. 60–62 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.73 – 7.60 (m, 2H), 7.63 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.19 – 7.14 (m, 1H), 6.81 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.65 (d, *J* = 2.4 Hz, 1H), 3.90 (t, *J* = 7.2 Hz, 4H), 2.34 (quin, *J* = 7.2 Hz, 2H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 149.8, 134.3, 128.6, 127.6, 126.6, 126.2, 125.6, 121.7, 114.6, 104.2, 52.0, 16.4.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{13}H_{14}N]$: 184.11, found: 183.99.
Analytical data was in accordance with literature data.[19]

1-(4-Methoxyphenyl)pyrrolidine (31):



The title compound was prepared according to general procedure from 1-bromo-4-methoxybenzene (100 mg, 0.54 mmol, 1 equiv) and pyrrolidine (60 mg, 0.84 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as a brown semisolid (61 mg, 64% yield).
R_f: 0.4 (3:7 EtOAc/PE).
^{1}H-NMR (400 MHz, DMSO-d_6) δ 6.78 (d, *J* = 9.2 Hz, 2H), 6.48 (d, *J* = 9.2 Hz, 2H), 3.65 (s, 3H), 3.14 (t, *J* = 6.8 Hz, 4H), 1.94 – 1.90 (m, 4H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 150.3, 142.8, 114.7, 112.5, 55.3, 47.8, 24.8.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{11}H_{16}NO]$: 178.12, found: 178.12.
Analytical data was in accordance with literature data.[20]

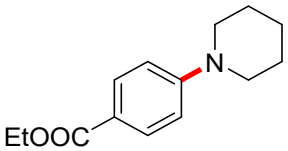
1-(Naphthalen-2-yl)piperidine (32):



The title compound was prepared according to general procedure from 2-naphthalene (100 mg, 0.48 mmol, 1.5 equiv) and piperidine (64 mg, 0.75 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white semisolid (46 mg, 45% yield).
R_f: 0.4 (1:9 EtOAc/PE).
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 3H), 7.40 – 7.34 (m, 1H), 7.30 – 7.23 (m, 2H), 7.12 (d, *J* = 1.6 Hz, 1H), 3.25 (t, *J* = 5.6 Hz, 4H), 1.80 – 1.72 (m, 4H), 1.67 – 1.57 (m, 2H).

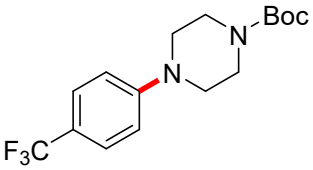
^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.2, 134.8, 128.3, 128.4, 127.5, 126.8, 126.2, 123.2, 120.3, 110.4, 51.1, 24.4, 22.8.
LCMS (ESI)$[M+H]^+$calculated m/z for $[C_{15}H_{18}N]$: 212.14, found: 212.11.
Analytical data was in accordance with literature data.[12]

Ethyl 4-(piperidin-1-yl)benzoate (33):



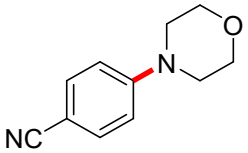
The title compound was prepared according to general procedure from ethyl-4-bromo-benzoate (100 mg, 0.44 mmol, 1 equiv) and piperidine (60 mg, 0.70 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (8% EtOAc/PE as an eluent) and product was isolated as an off-white solid (63 mg, 61% yield).
R_f: 0.4 (2:8 EtOAc/PE).
m.p. 80-82 °C
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 6.88 – 6.32 (m, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.34 – 3.29 (m, 4H), 1.71 – 1.59 (m, 6H), 1.36 (t, *J* = 7.2 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.7, 154.4, 131.1, 118.9, 113.5, 60.2, 48.8, 29.6, 25.3, 24.3, 14.4.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{14}H_{20}NO_2]$: 234.15, found: 234.27.
Analytical data was in accordance with literature data.[21]

***tert*-Butyl 4-(4-(trifluoromethyl)phenyl)piperazine-1-carboxylate (34):**



The title compound was prepared according to general procedure from 1-bromo-4-(trifluoromethyl)benzene (100 mg, 0.45 mmol, 1 equiv) and boc piperazine (130 mg, 0.69 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (3% EtOAc/PE as an eluent) and product was isolated as an off-white solid (72 mg, 49% yield).
R_f: 0.6 (1:9 EtOAc/PE).
m.p. 125-127 °C
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.59 (t, *J* = 6.8 Hz, 4H), 3.24 (t, *J* = 6.8 Hz, 4H), 1.49 (s, 9H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.6, 153.2, 126.4, 120.8 (q, $J_{C\text{-}F}$ = 33 Hz), 114.9, 80.1, 48.1, 28.4.
^{19}F-NMR (376 MHz, $CDCl_3$) δ -61.7
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{16}H_{22}F_3N_2O_2]$: 331.16, found: 331.47.
Analytical data was in accordance with literature data.[22]

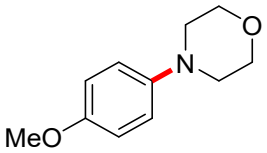
4-Morpholinobenzonitrile (35):



The title compound was prepared according to general procedure from 4-bromo benzonitrile (100 mg, 0.55 mmol, 1 equiv) and morpholine (72 mg, 0.82 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as a yellow solid (80 mg, 77% yield).
R_f: 0.4 (2:8 EtOAc/PE).

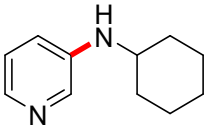
m.p. 76-78 °C
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 6.89 – 6.84 (m, 2H), 3.87 – 3.83 (m, 4H), 3.30 – 3.25 (m, 4H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.5, 133.485, 119.9, 114.1, 100.7, 66.4, 47.3.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{11}H_{13}N_2O]$: 189.10, found: 189.17.
Analytical data was in accordance with literature data.[10]

4-(4-methoxyphenyl)morpholine (36):



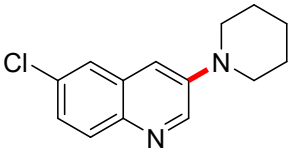
The title compound was prepared according to general procedure from 4-bromo benzonitrile (100 mg, 0.53 mmol, 1 equiv) and morpholine (72 mg, 0.82 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white solid (62 mg, 60% yield).
R_f: 0.4 (2:8 EtOAc/PE).
m.p. 65-67 °C
^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.91 – 6.84 (m, 4H), 3.86 (t, *J* = 4.8 Hz, 4H), 3.77 (s, 3H), 3.06 (t, *J* = 4.8 Hz, 4H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.0, 145.6, 117.9, 114.5, 67.0, 55.6, 50.9.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{11}H_{15}NO_2]$: 194.12, found: 194.32.
Analytical data was in accordance with literature data.[28]

N-Cyclohexylpyridin-3-amine (37):



The title compound was prepared according to general procedure from 3-bromo pyridine (100 mg, 0.55 mmol, 1 equiv) and cyclohexyl amine (72 mg, 0.82 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as a brown solid (71 mg, 59% yield).
R_f: 0.4 (2:8 EtOAc/PE).
m.p. 74-76 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.94 (d, *J* = 2.4 Hz, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.05 – 7.02 (m, 1H), 6.90 – 6.86 (m, 1H), 5.66 (d, *J* = 6.4 Hz, 1H), 3.40 – 3.38 (m, 1H), 1.92 – 1.88 m, 2H), 1.73 – 1.70 (m, 2H), 1.69 – 1.68 (m, 1H), 1.60 – 1.12 (m, 5H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 144.0, 136.1, 135.5, 123.7, 117.5, 50.0, 32.3, 25.5, 24.4.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{11}H_{17}N_2]$: 177.14, found: 177.53.
Analytical data was in accordance with literature data.[14]

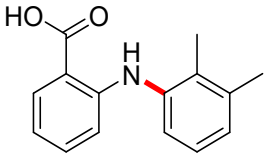
6-Chloro-3-(piperidin-1-yl)quinoline (38):



The title compound was prepared according to general procedure from 3-bromo-6-chloroquinoline (100 mg, 0.42 mmol, 1 equiv) and piperidine (55 mg, 0.64 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as a brown solid (50 mg, 49% yield).
R_f: 0.4 (2:8 EtOAc/PE).

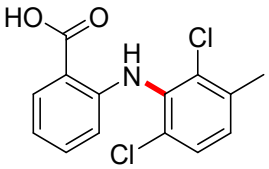
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 2.8 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.18 (d, *J* = 2.8 Hz, 1H), 3.28 (t, *J* = 5.2 Hz, 4H), 1.79 – 1.74 (m, 4H), 1.67 – 1.61 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.1, 145.4, 140.7, 132.5, 130.4, 129.9, 126.7, 125.0, 114.9, 50.2, 25.5, 24.0.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{14}H_{16}ClN_2]$: 247.10, found: 247.20.

Mefenamic acid:



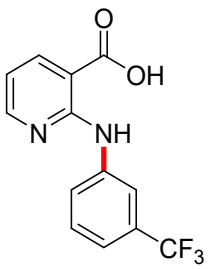
The title compound was prepared according to general procedure from 2-bromo benzoic acid (100 mg, 0.50 mmol, 1 equiv) and 2,3-dimethylaniline (91 mg, 0.75 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (2% EtOAc/PE as an eluent) and product was isolated as an off-white solid (52 mg, 43% yield).
R_f: 0.3 (3:7 EtOAc/PE).
m.p. 229-231 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.17 – 7.09 (m, 2H), 6.96 (dd, *J* = 7.2, 0.4 Hz, 1H), 6.84 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.72 (s, 1H), 6.64 – 6.59 (m,1H), 2.89 (s, 3H), 2.03 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 166.3, 152.6, 149.5, 138.6, 135.3, 131.4, 129.2, 127.6, 126.5, 120.5, 117.2, 115.5, 107.9, 20.1, 12.6.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{15}H_{16}NO_2]$: 242.12, found: 242.25.
Analytical data was in accordance with literature data.[3,6]

Meclofenac:



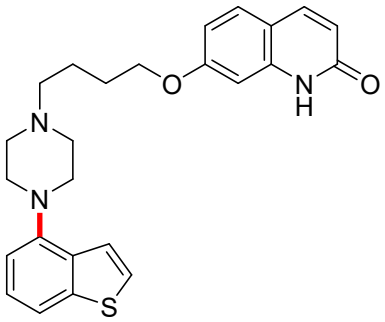
The title compound was prepared according to general procedure from 2-bromo benzoic acid (100 mg, 0.50 mmol, 1 equiv) and 2,3-dimethylaniline (131 mg, 0.75 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (2% EtOAc/PE as an eluent) and product was isolated as a white solid (70 mg, 58% yield).
R_f: 0.4 (1:9 EtOAc/PE).
m.p. 243-245 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 13.17 (bs, 1H), 9.55 (s, 1H), 7.91 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.37 – 7.30 (m, 2H), 6.78 (td, *J* = 7.6, 0.8 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 170.6, 147.6, 136.9, 135.1, 134.6, 134.0, 131.9, 130.9, 129.8, 128.5, 117.8, 113.4, 112.4, 20.6.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{14}H_{12}Cl_2NO_2]$: 296.02, found: 296.25.
Analytical data was in accordance with literature data.[23]

Niflumic acid:



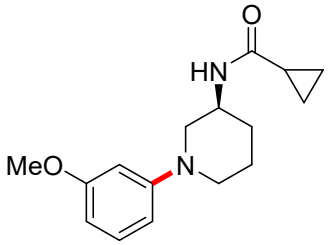
The title compound was prepared according to general procedure from 1-bromo-3-(trifluoromethyl)benzene (1.3 g, 5.8 mmol, 1 equiv) and 2-aminonicotinic acid (1.23 g, 8.9 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (2% EtOAc/PE as an eluent) and product was isolated as an off-white solid (1.31 g, 80% yield).
R_f: 0.4 (1:9 EtOAc/PE).
m.p. 201-203 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 13.72 (bs, 1H), 10.71 (s, 1H), 8.45 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.33 – 8.28 (m, 2H), 7.87 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 6.96 (dd, J = 7.6, 4.8 Hz, 1H), 2.39 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 169.4, 155.7, 152.9, 141.1, 141.0, 130.3, 129.8 (q, $J_{C\text{-}F}$ = 31 Hz), 126.1, 123.9, 118.6, 116.1, 116.0, 108.9.
^{19}F-NMR (376 MHz, DMSO-d_6) δ -61.1
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{13}H_{10}F_3N_2O_2]$: 283.07, found: 283.18.
Analytical data was in accordance with literature data.[24]

Brexpiprazole:



The title compound was prepared according to general procedure from 4-bromobenzo[b]thiophene (100 mg, 0.47 mmol, 1 equiv) and 7-(4-(piperazin-1-yl)butoxy)quinolin-2(1H)-one (210 mg, 0.69 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (20% EtOAc/PE as an eluent) and product was isolated as a white solid (84 mg, 41% yield).
R_f: 0.3 (3:7 EtOAc/PE).
m.p. 178-180 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 11.62 (s, 1H), 7.80 (d, *J* = 9.6 Hz, 1H), 7.69 (d, *J* = 5.2 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.40 (d, *J* = 5.6 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.82 – 6.78 (m, 2H), 6.29 (dd, *J* = 9.6, 1.6 Hz, 1H), 4.06 (t, *J* = 6.4 Hz, 2H), 3.08 3.05 (m, 4H), 2.68 – 2.65 (m, 4H), 2.47 – 2.43 (m, 2H), 1.83 – 1.77 (m, 2H), 1.68 – 1.60 (m, 2H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 160.9, 148.6, 140.8, 140.8, 133.8, 129.8, 126.3, 125.6, 122.4, 118.7, 117.1, 113.8, 112.5, 111.6, 99.0, 68.2, 57.8, 53.4, 52.0, 26.9, 23.0.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{25}H_{28}N_3O_2S]$: 434.19, found: 434.37.
Analytical data was in accordance with literature data.[25]

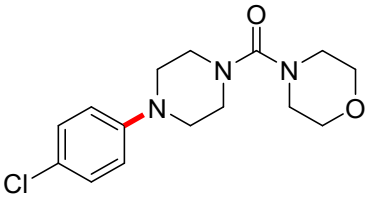
Melatonin receptor ligand:



The title compound was prepared according to general procedure from 1-bromo-3-methoxybenzene (100 mg, 0.54 mmol, 1 equiv) and (S)-N-(piperidin-3-yl)cyclopropanecarboxamide (136 mg, 0.81 mmol, equiv).

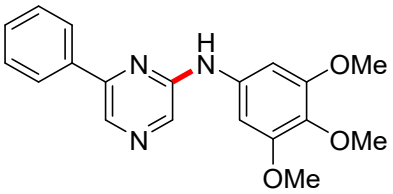
Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as an off-white semi-solid (85 mg, 56% yield).
R_f: 0.3 (3:7 EtOAc/PE).
^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.50 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.43 (t, *J* = 2.0 Hz, 1H), 6.32 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.75 – 3.72 (m, 1H), 3.70 (s, 3H), 3.59 – 3.49 (m, 2H), 2.81 – 2.72 (m, 1H), 2.56 (dd, *J* = 12.0, 9.6 Hz, 1H), 1.84 – 1.61 (m, 2H), 1.60 – 1.51 (m, 2H), 1.48 – 1.38 (m, 1H), 0.70 – 0.61 (m, 4H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 172.6, 160.7, 152.5, 130.1, 108.9, 104.2, 102.2, 55.3, 54.1, 49.2, 45.5, 30.4, 23.6, 13.9, 6.7.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{16}H_{23}N_2O_2]$: 275.18, found: 275.39.
Analytical data was in accordance with literature data.[26]

β-Hydroxysteroid dehydrogenase inhibitor:



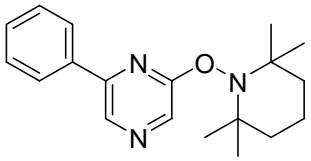
The title compound was prepared according to general procedure from 1-bromo-4-chlorobenzene (100 mg, 0.53 mmol, 1 equiv) and morpholino(piperazin-1-yl)methanone (158 mg, 0.79 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (5% EtOAc/PE as an eluent) and product was isolated as a white solid (106 mg, 65% yield).
R_f: 0.5 (1:9 EtOAc/PE).
m.p. 114-116 °C.
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 6.86 – 6.81 (m, 2H), 3.70 (t, *J* = 4.78 Hz, 4H), 3.42 (t, *J* = 4.8 Hz, 4H), 3.31(t, *J* = 5.2 Hz, 4H), 3.13 (t, *J* = 5.2 Hz, 4H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.7, 149.8, 129.0, 125.2, 117.7, 66.6, 49.2, 47.3, 46.6.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{15}H_{21}ClN_3O_2]$: 310.13 found: 310.26.
Analytical data was in accordance with literature data.[27]

BRAF inhibitor:



The title compound was prepared according to general procedure from 2-bromo-6-phenylpyrazine (100 mg, 0.43 mmol, 1 equiv) and 3,4,5-trimethoxyaniline (118 mg, 0.64 mmol, 1.5 equiv). Purification was carried out by flash chromatography on silica (20% EtOAc/PE as an eluent) and product was isolated as an off-white solid (79 mg, 55% yield).
R_f: 0.4 (5:5 EtOAc/PE).
m.p. 71-73 °C
^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.60 (s, 1H), 8.53 (s, 1H), 8.17 – 8.12 (m, 3H), 7.54 – 7.48 (m, 3H), 7.27 (s, 2H), 3.83 (s, 6H), 3.64 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-d_6) δ 152.8, 151.5, 147.7, 136.9, 136.6, 133.6, 132.0, 129.9, 129.6, 128.9, 126.4, 95.8, 60.2, 55.6.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{19}H_{20}N_3O_3]$: 338.15, found: 338.31.
Analytical data was in accordance with literature data.[18]

Tempo adduct



^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.59 (s, 1H), 8.02 – 7.97 (m, 2H), 7.53 – 7.40 (m, 3H), 1.75 – 1.60 (m, 5H), 1.50 – 1.44 (m, 1H), 1.33 (s, 6H), 1.08 (s, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.7, 149.8, 136.3, 134.2, 132.2, 129.6, 128.9, 127.2, 60.9, 39.8, 32.0, 20.6, 16.9.
LCMS (ESI)$[M+H]^+$ calculated m/z for $[C_{19}H_{26}N_3O_2]$: 312.21 found: 312.14

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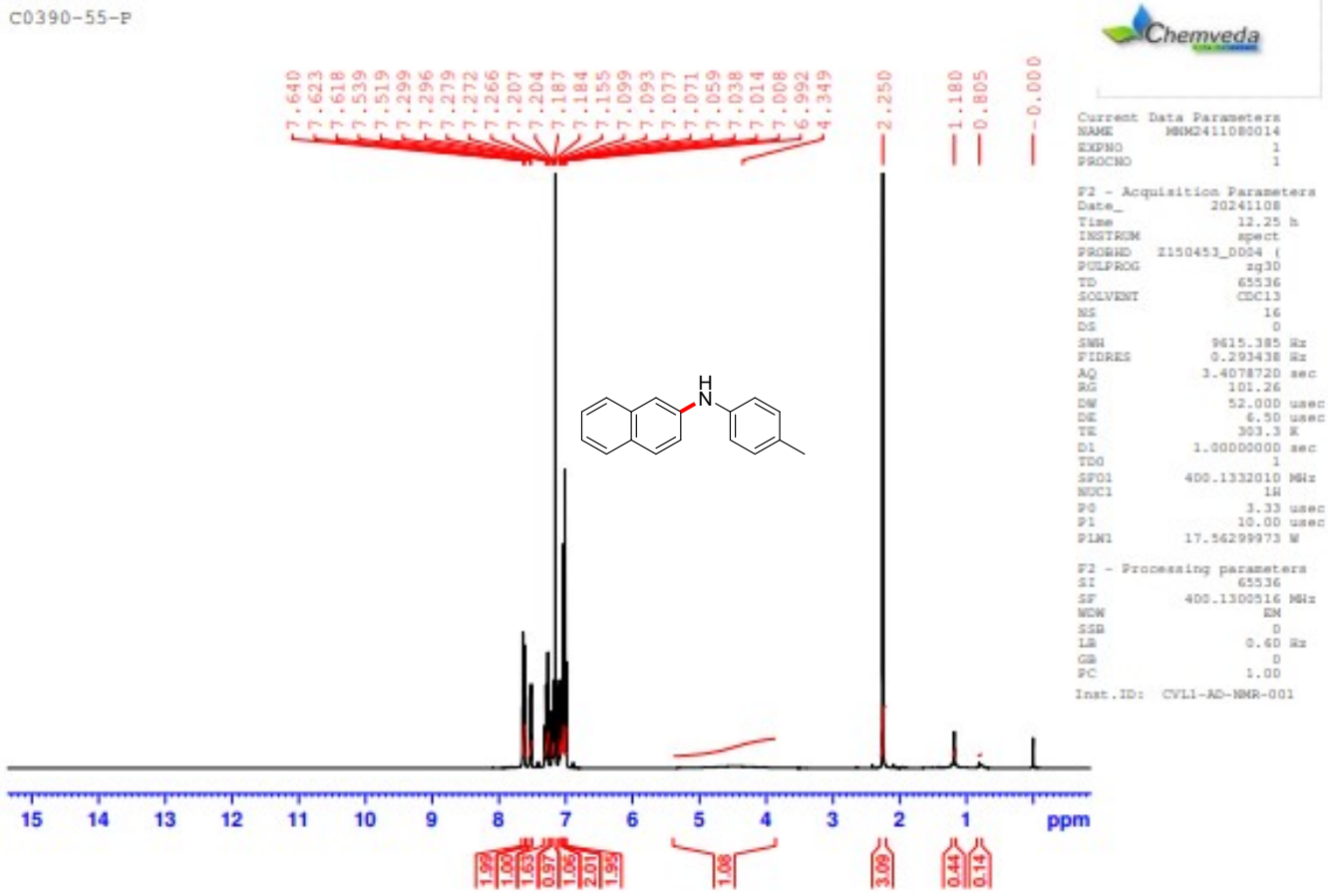
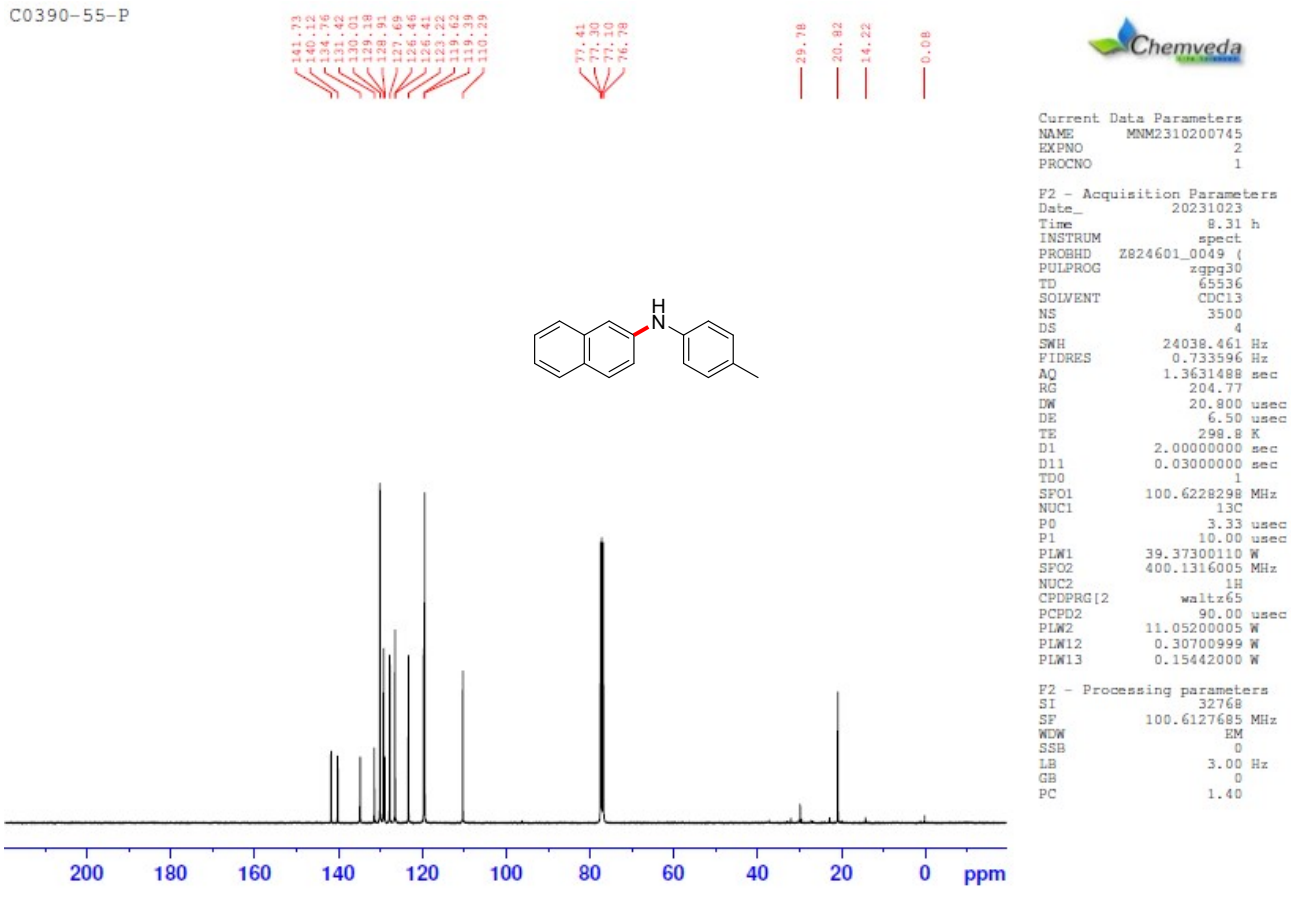
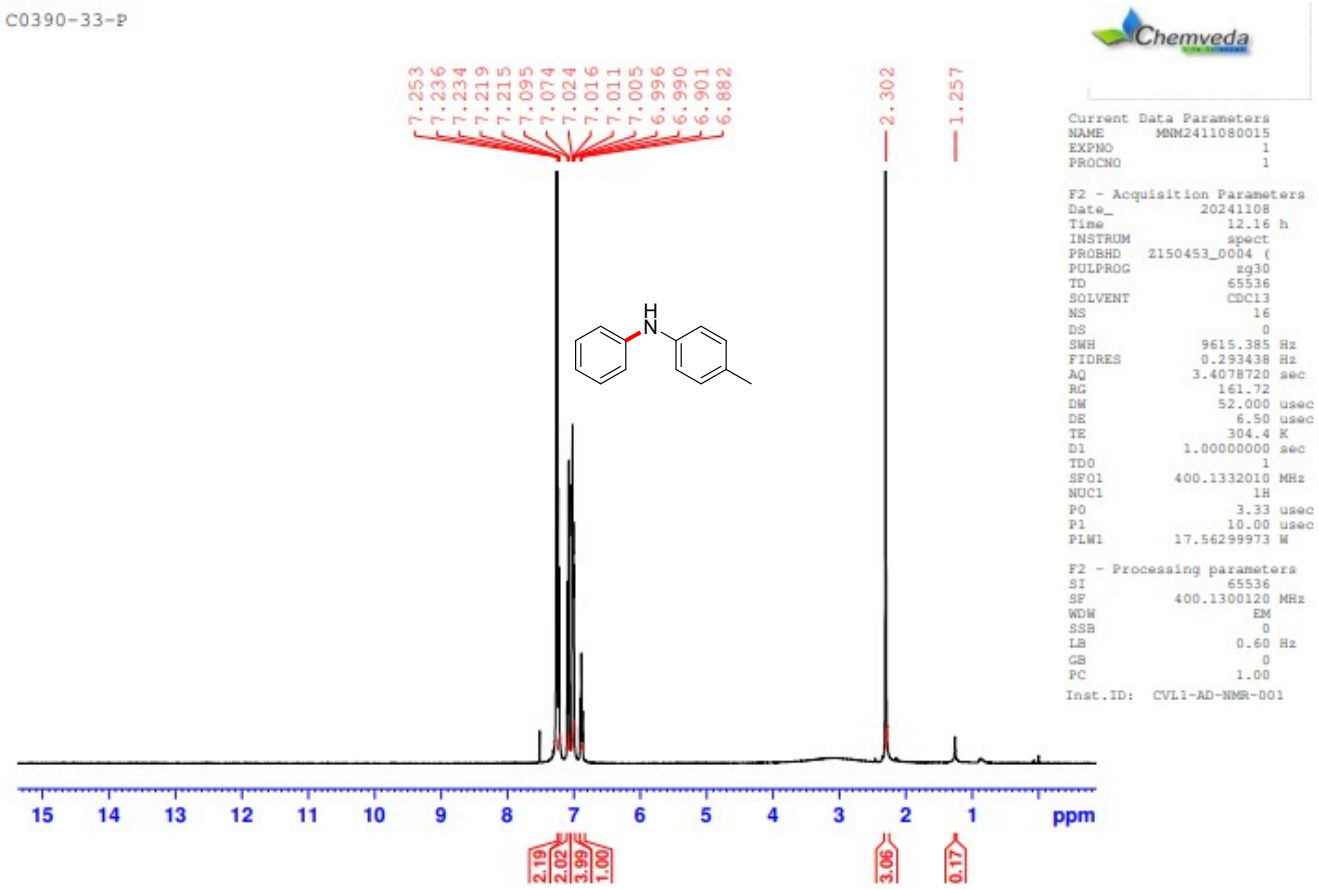
7. Copies of ^{1}H, ^{13}C and 19F NMR spectra of products:



N-(p-tolyl)naphthalen-2-amine (**3**) ^{1}H NMR (400 MHz, $CDCl_3$)



N-(p-tolyl)naphthalen-2-amine (**3**) ^{13}C NMR (100 MHz, $CDCl_3$)



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DE 6.50 usec
TE 304.4 K
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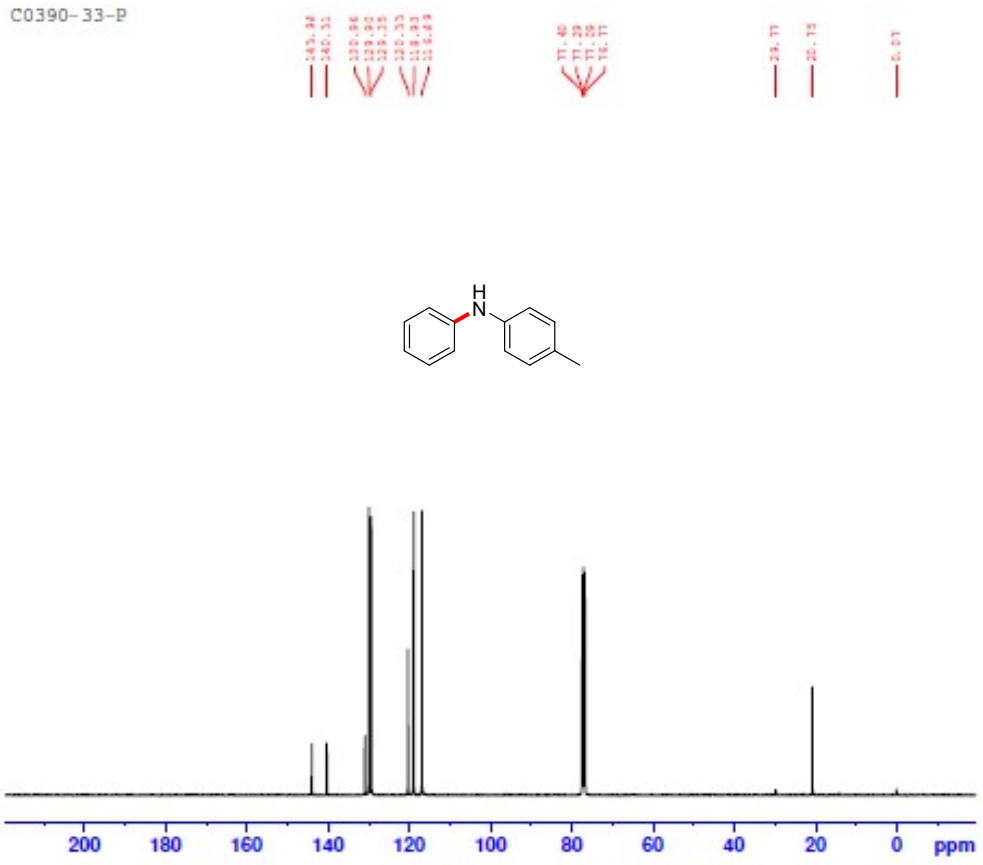
4-methyl-N-phenylaniline (**4**) ^{1}H NMR (400 MHz, CDCl3)



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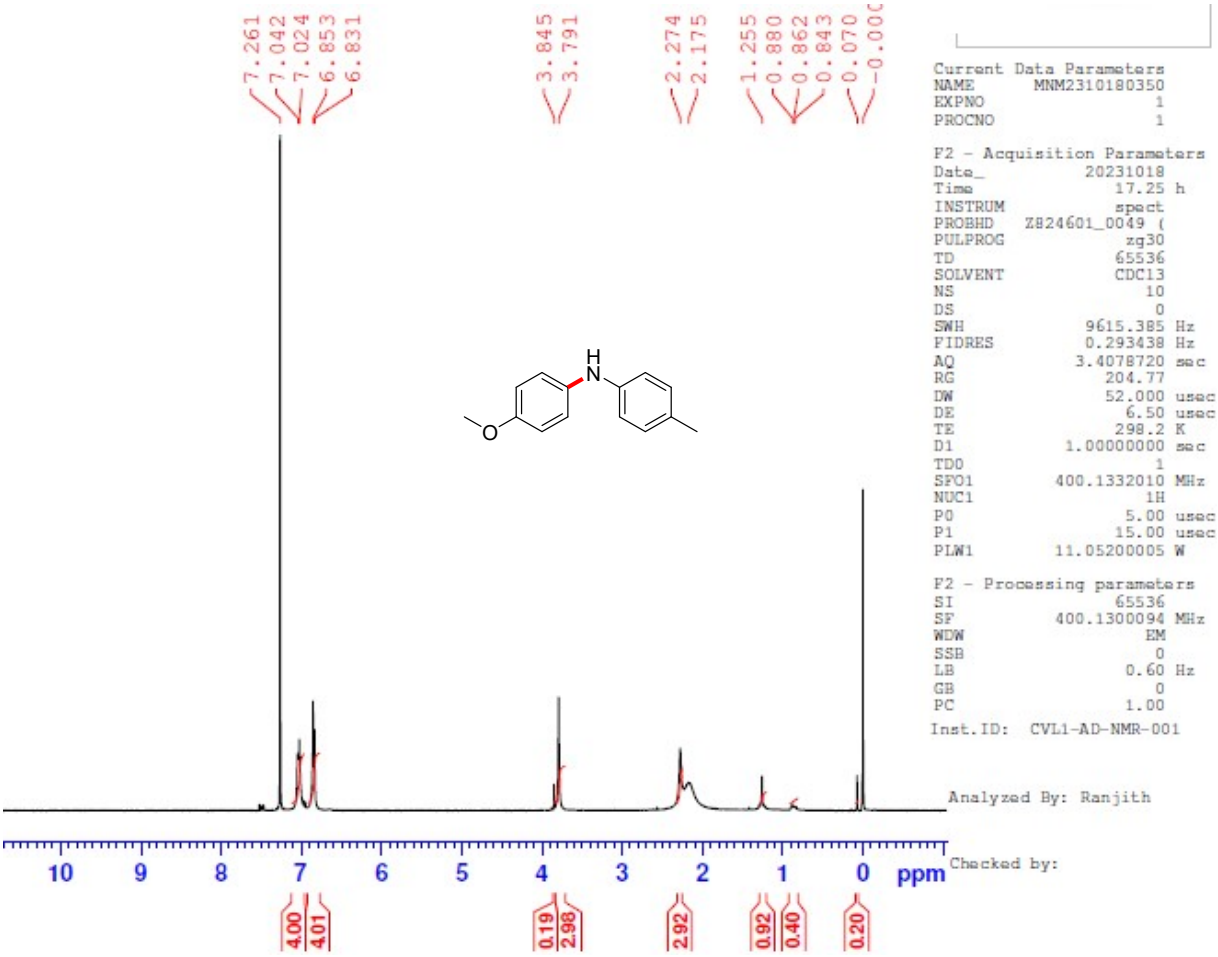
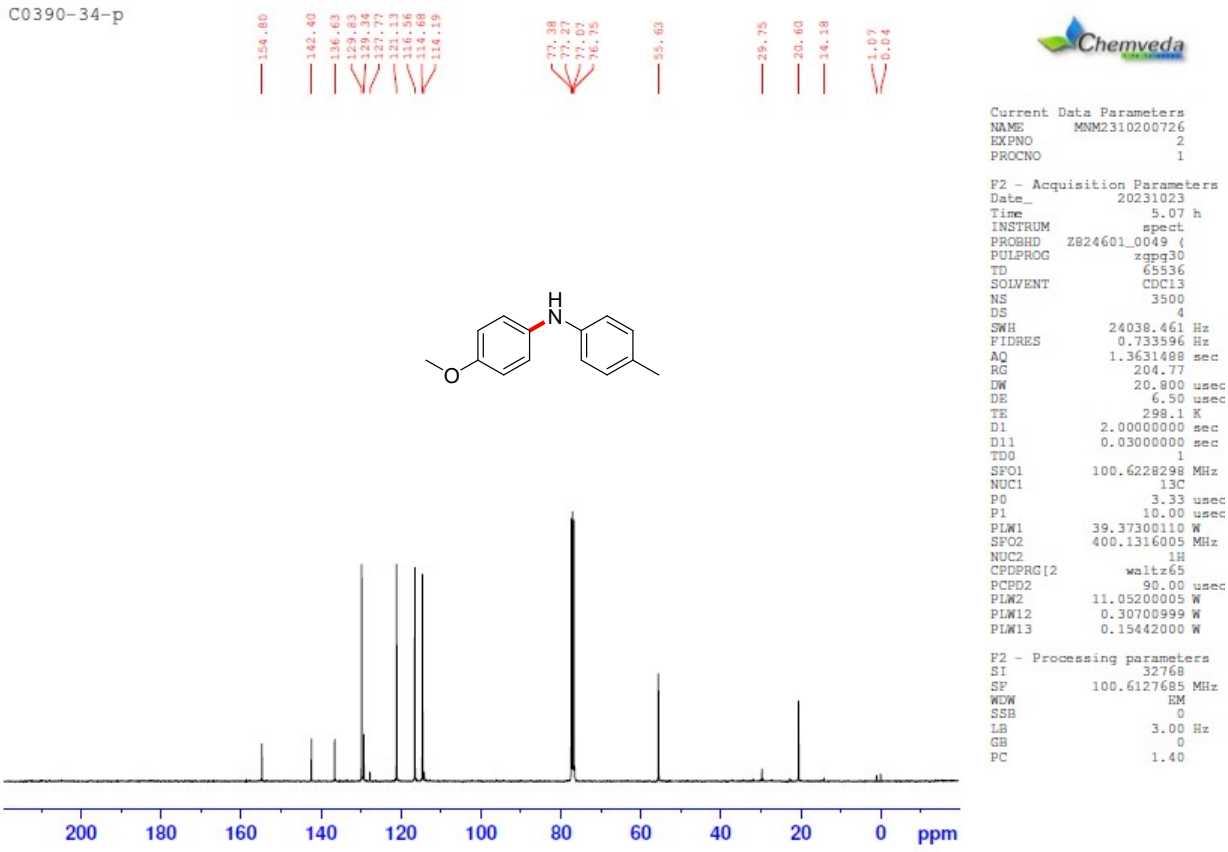
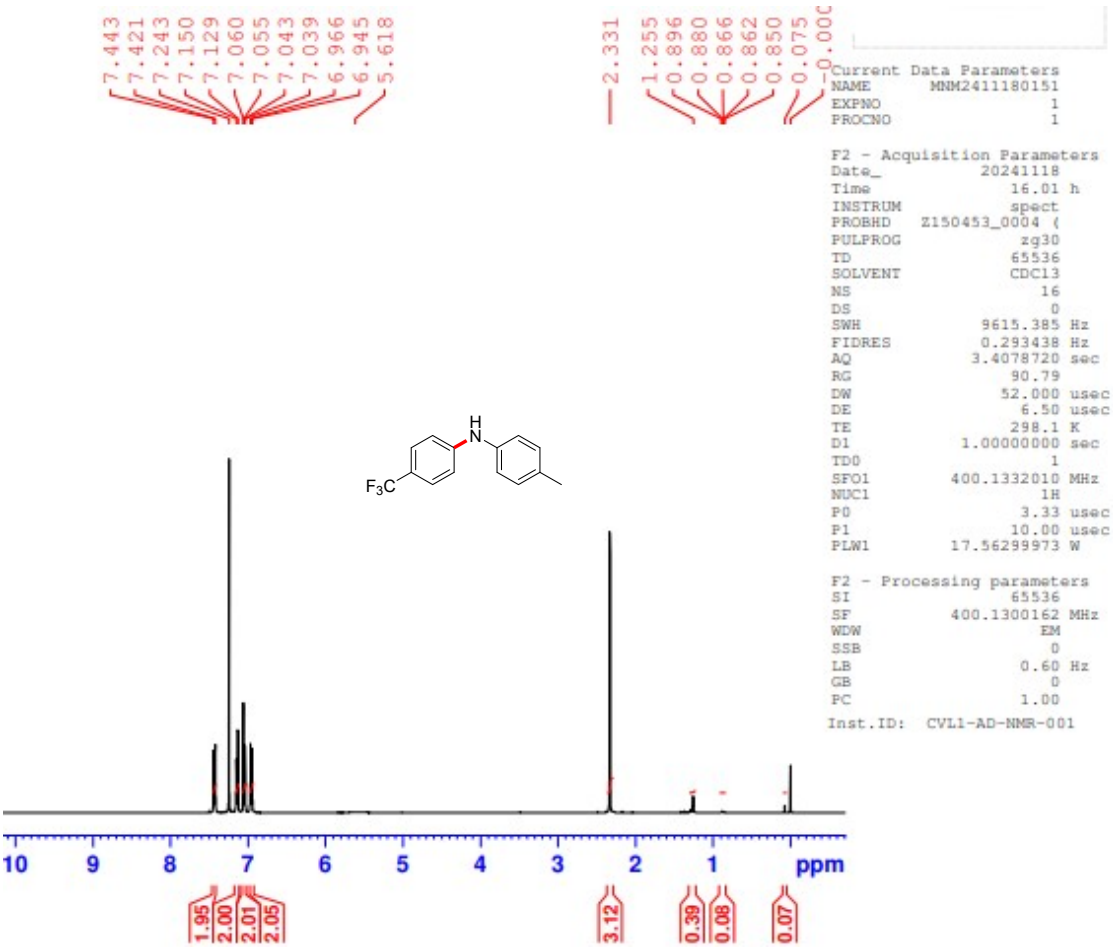
4-methyl-N-phenylaniline (**4**) ^{13}C NMR (100 MHz, CDCl3)



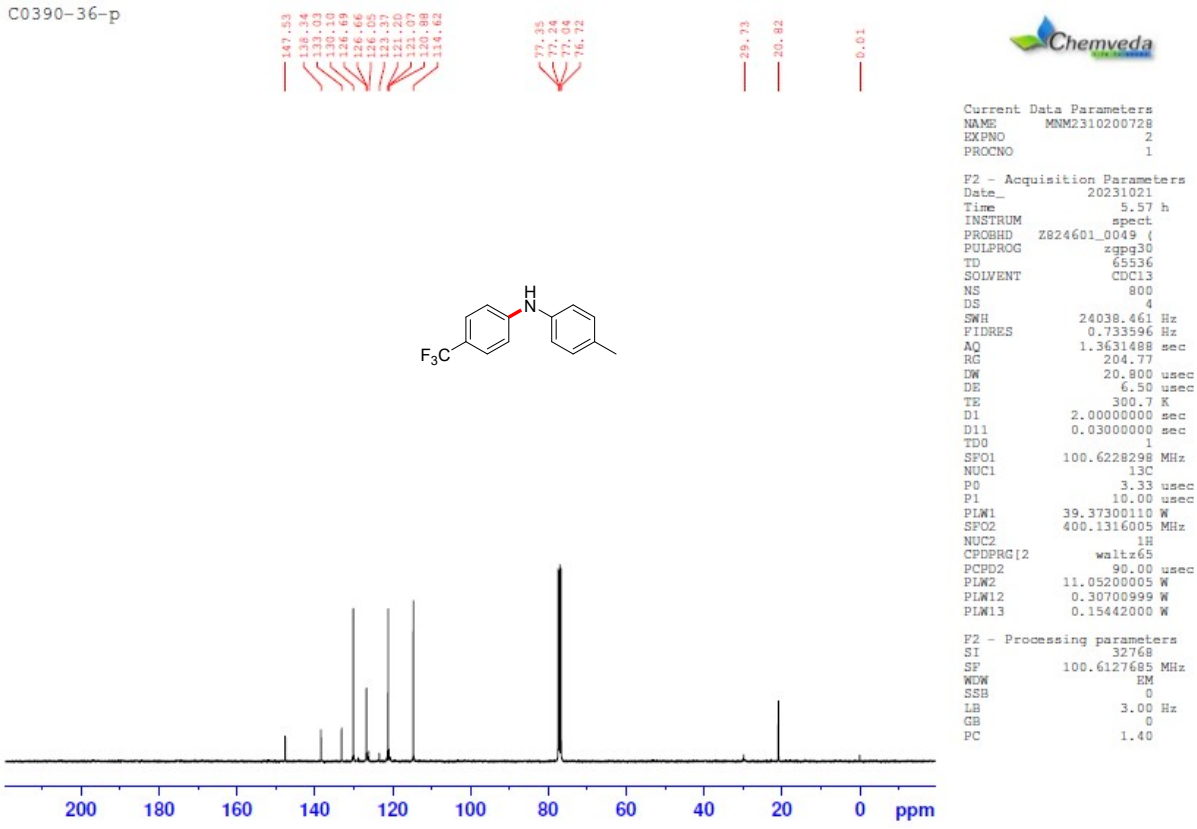
4-methoxy-N-(p-tolyl)aniline (**5**) ^{1}H NMR (400 MHz, $CDCl_3$)



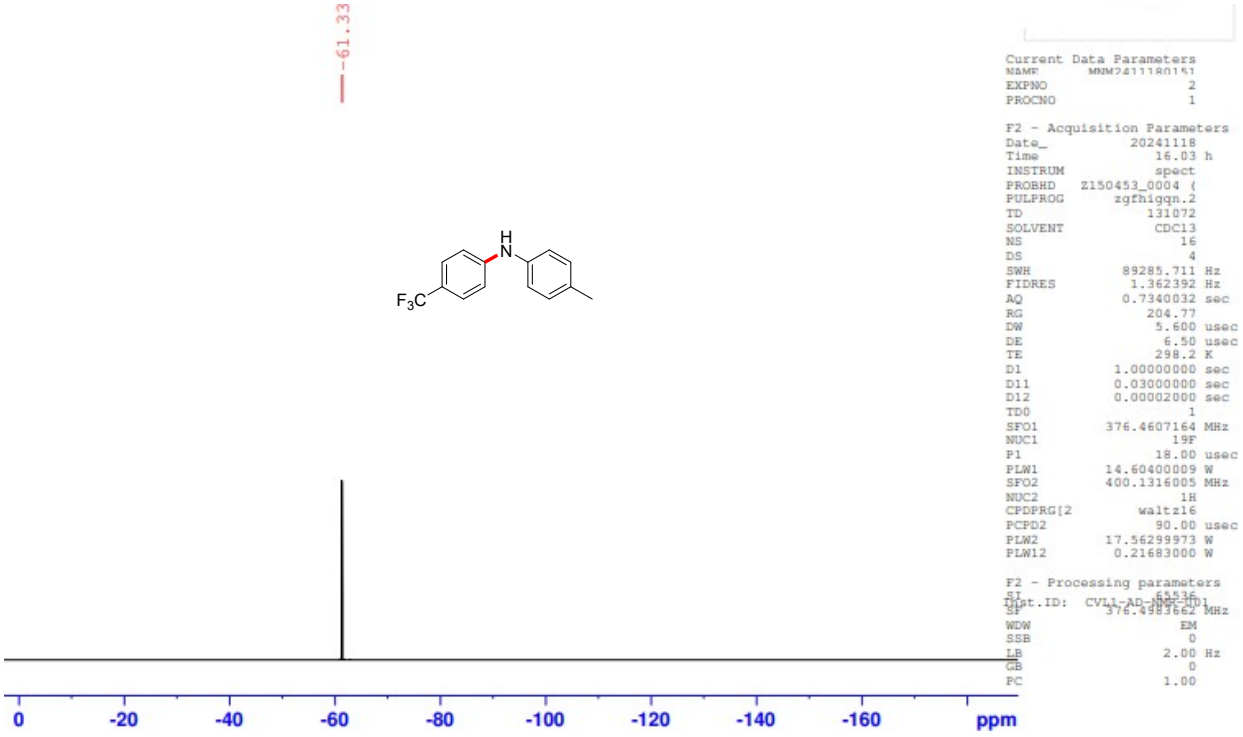
4-methoxy-N-(p-tolyl)aniline (**5**) ^{13}H NMR (100 MHz, $CDCl_3$)



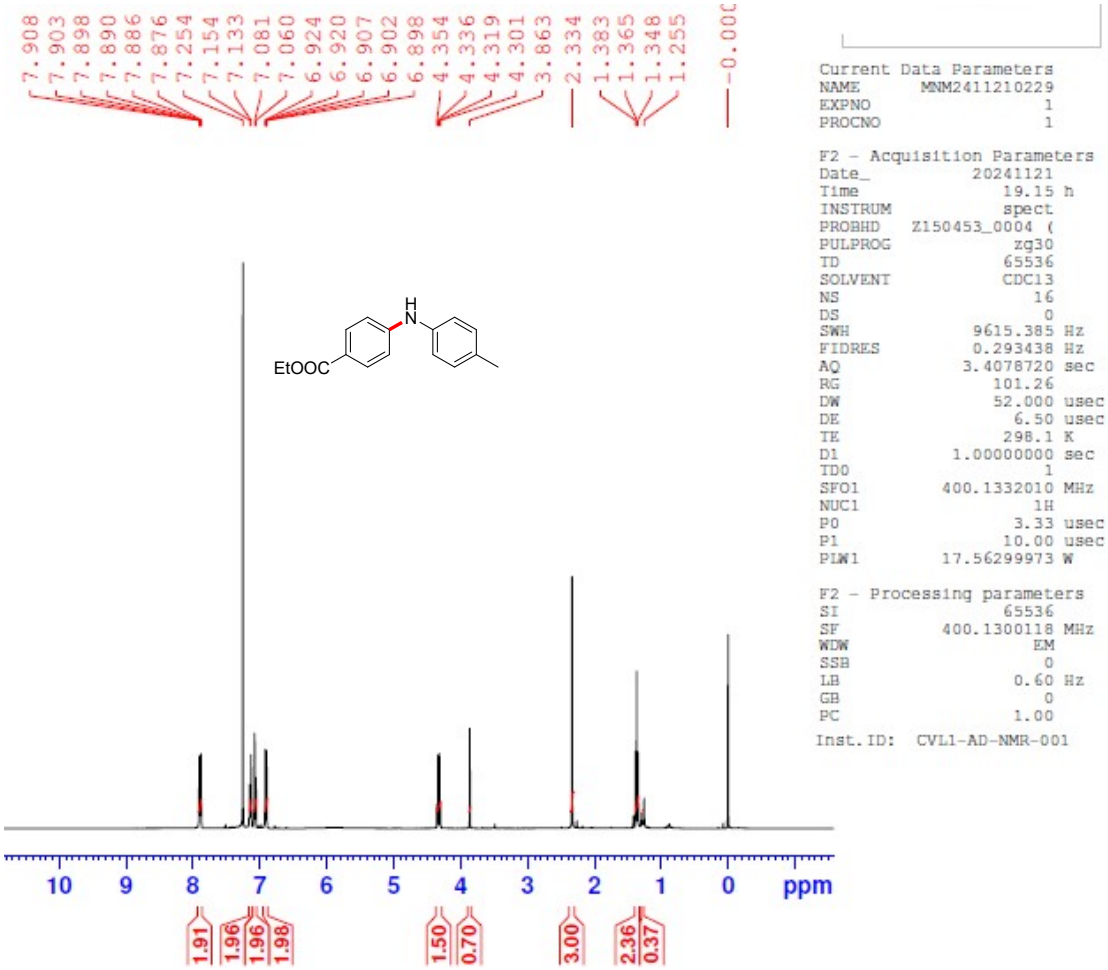
4-methyl-N-(4-(trifluoromethyl)phenyl)aniline (**6**) ^{1}H NMR (400 MHz, $CDCl_3$)



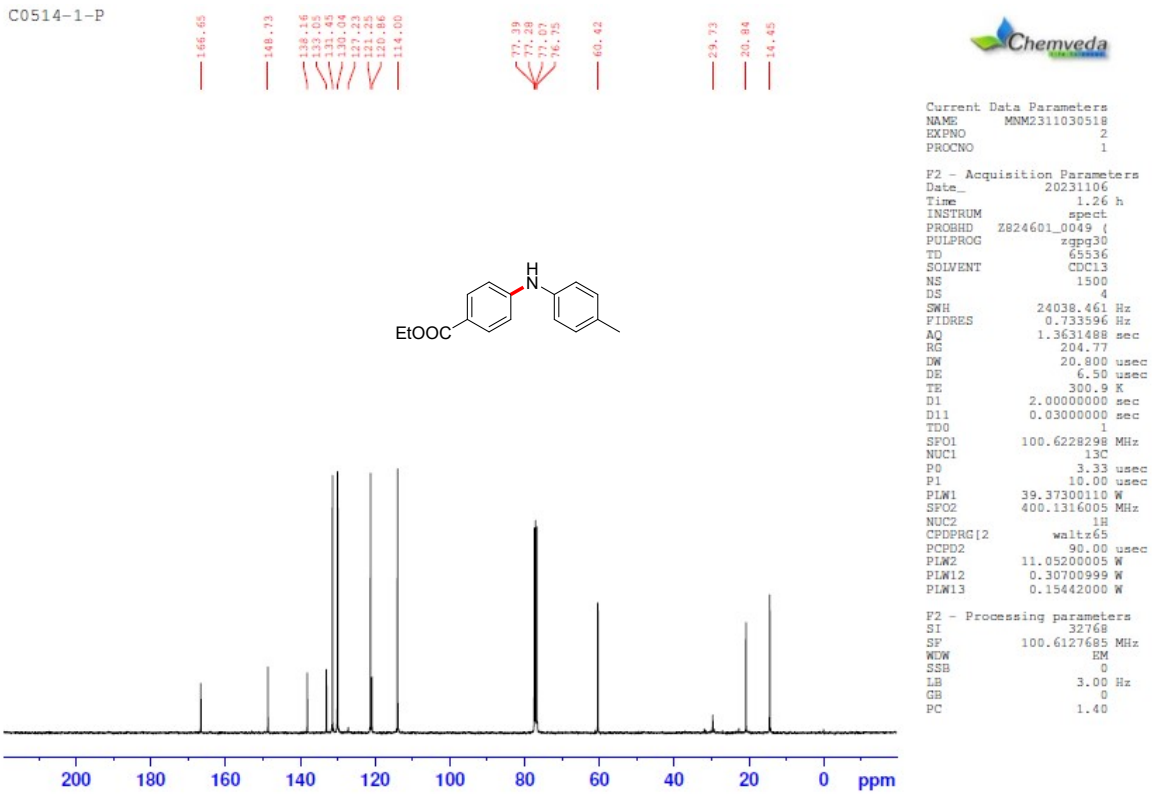
4-methyl-N-(4-(trifluoromethyl)phenyl)aniline (**6**) ^{13}C NMR (100 MHz, $CDCl_3$)



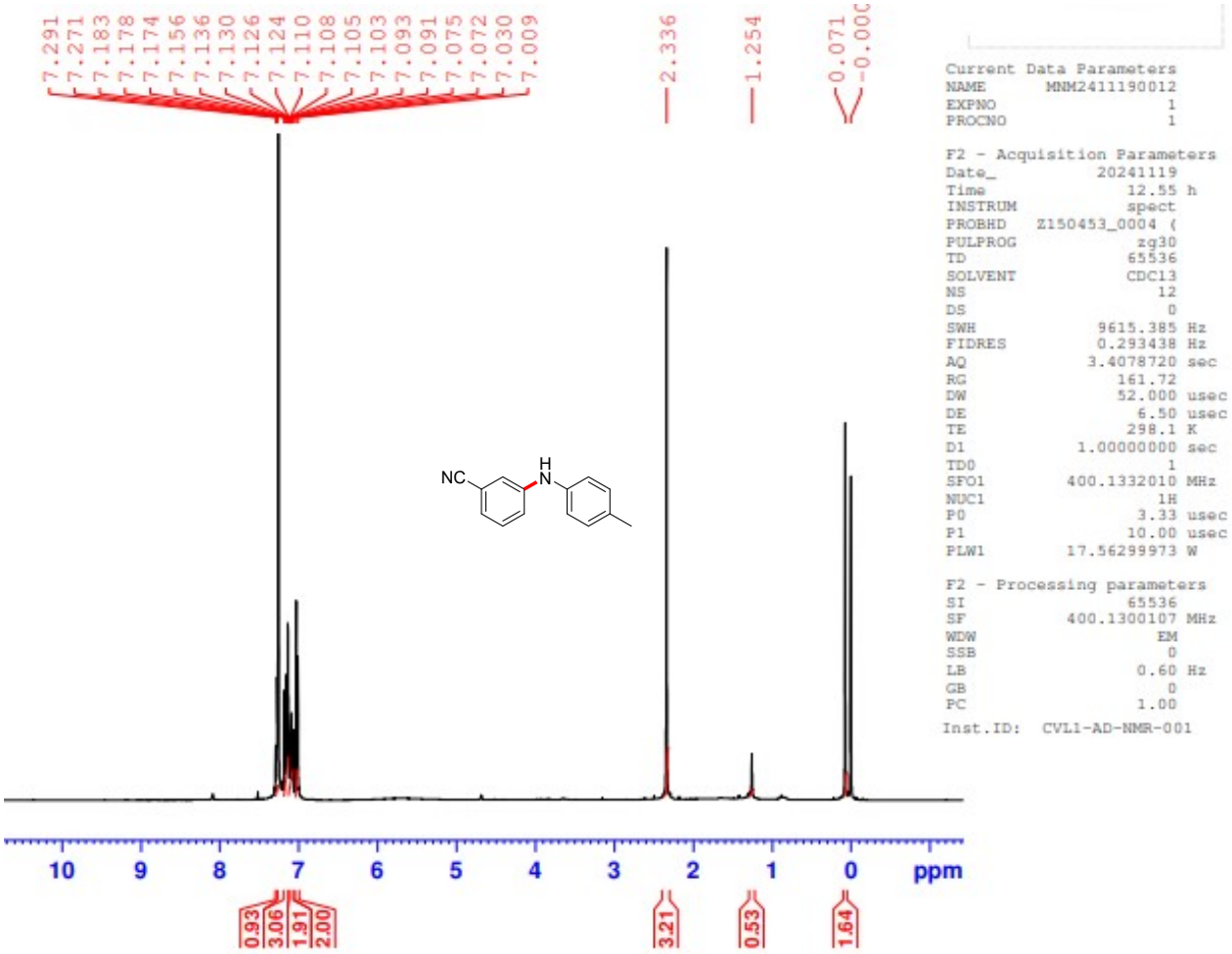
4-methyl-N-(4-(trifluoromethyl)phenyl)aniline (**6**) ^{19}F NMR (376 MHz, $CDCl_3$)



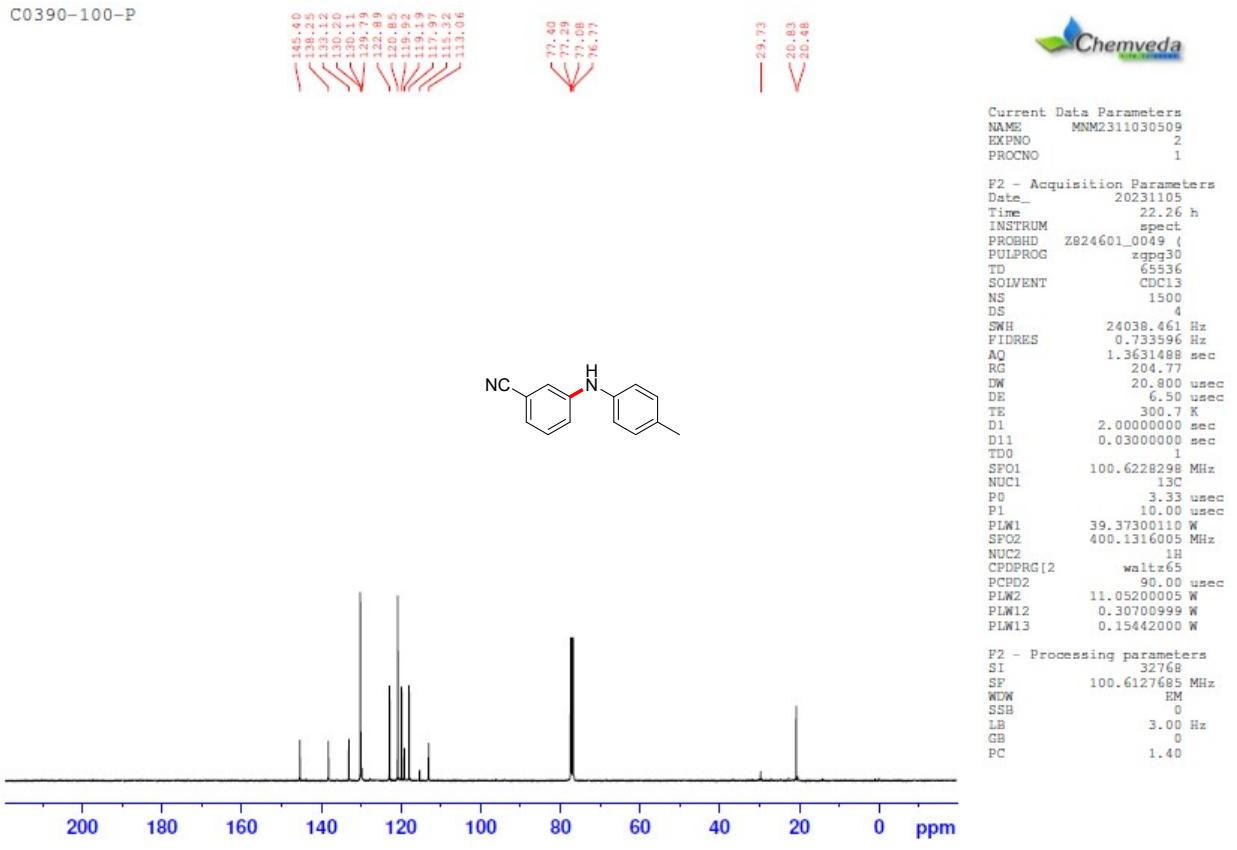
Ethyl 4-(p-tolylamino)benzoate (**7**) ^{1}H NMR (400 MHz, $CDCl_3$)



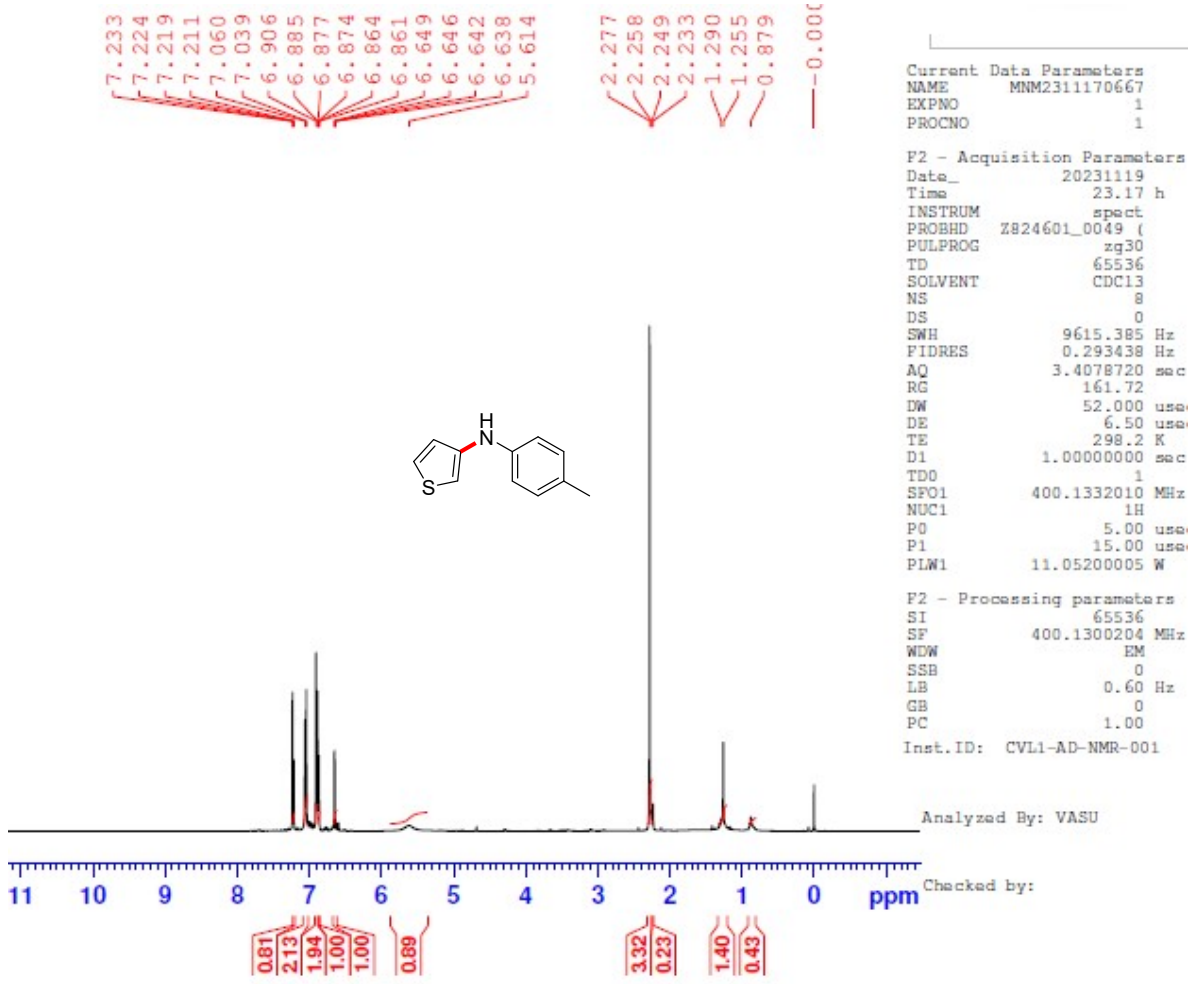
Ethyl 4-(p-tolylamino)benzoate (**7**) ^{13}C NMR (100 MHz, $CDCl_3$)



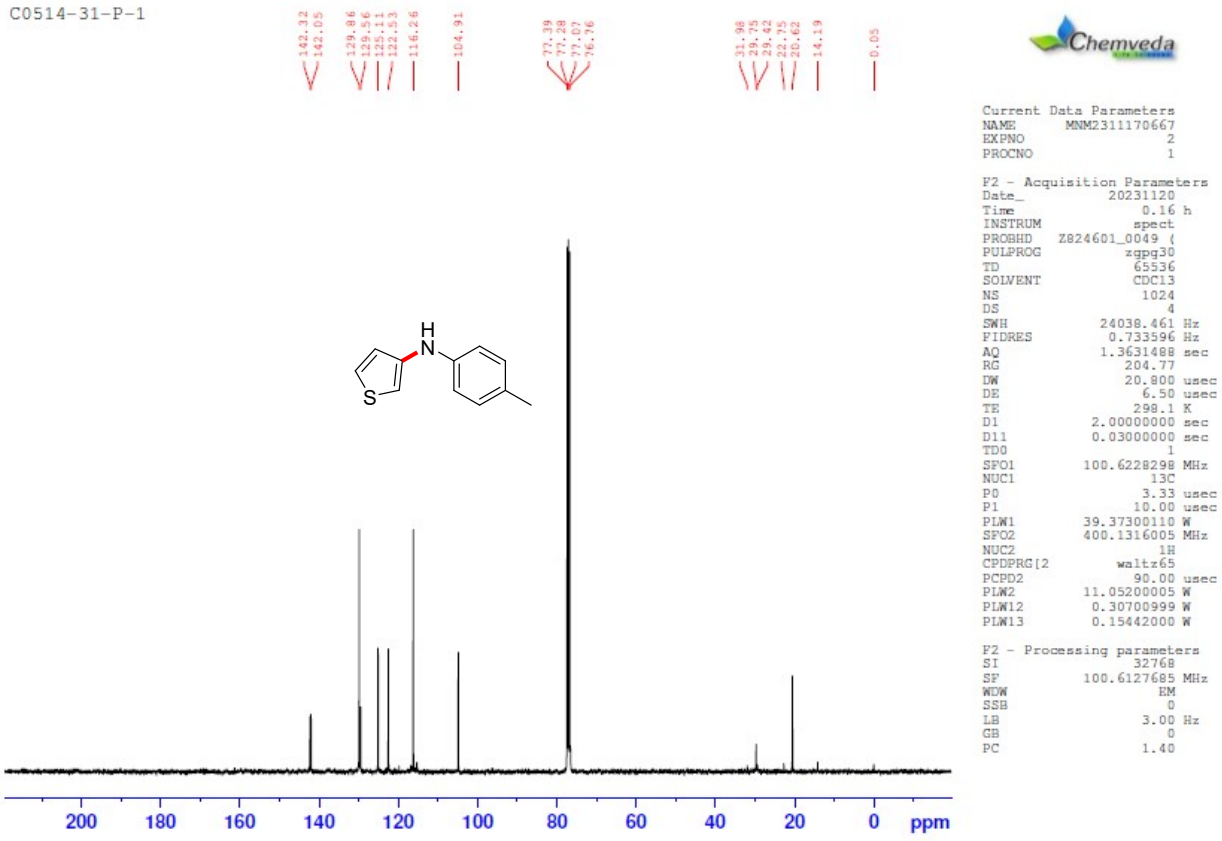
3-(p-tolylamino)benzonitrile (**8**) ^{1}H NMR (400 MHz, $CDCl_3$)



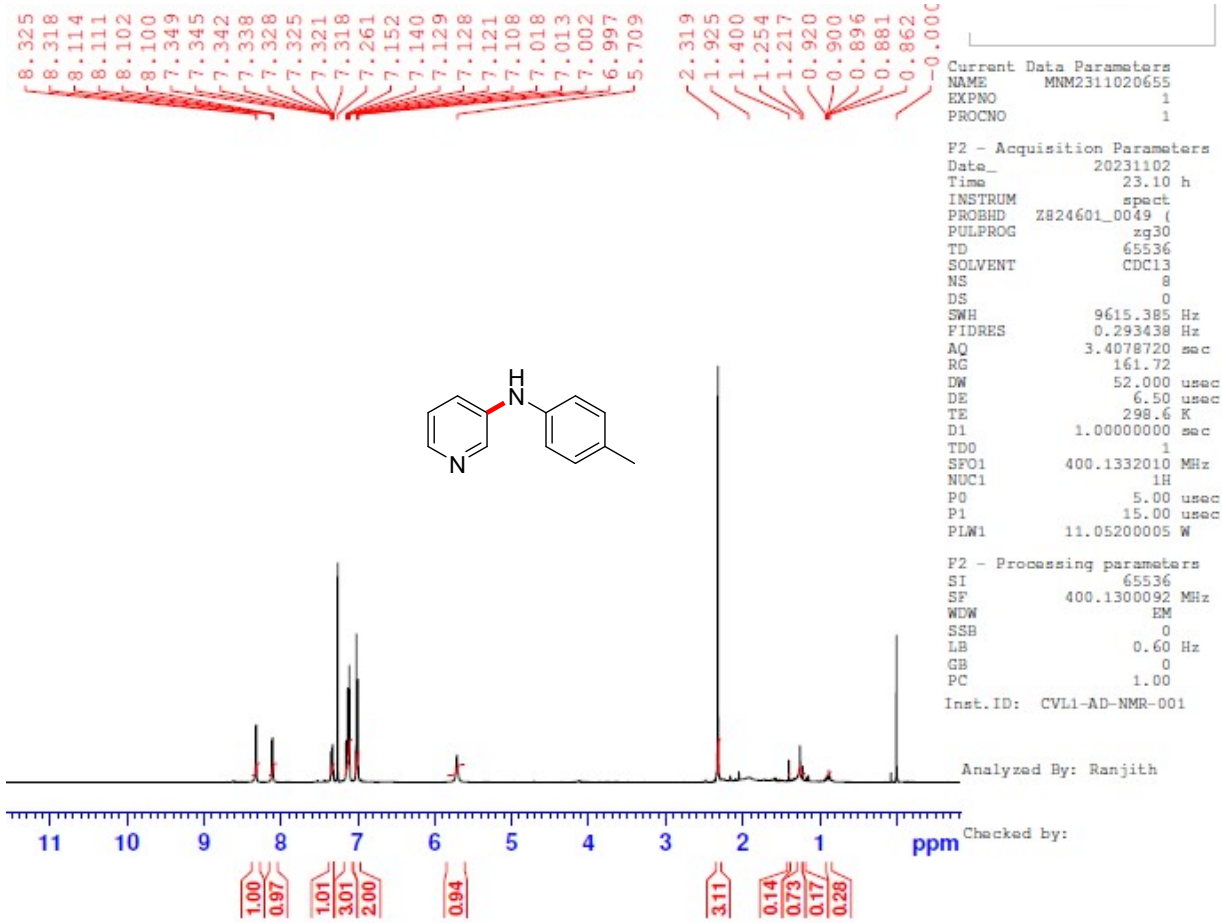
3-(p-tolylamino)benzonitrile (**8**) ^{13}C NMR (100 MHz, $CDCl_3$)



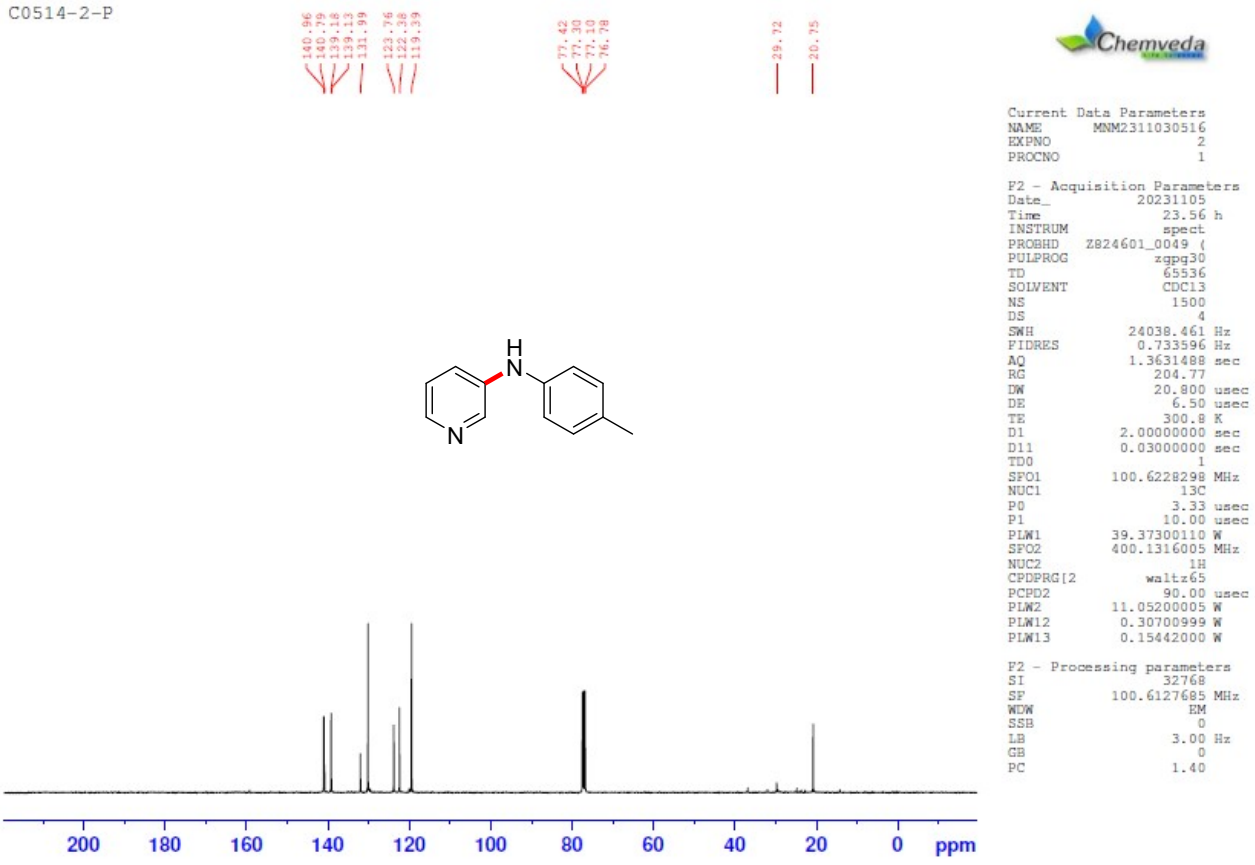
N-(p-tolyl)thiophen-3-amine (**9**) ^{1}H NMR (400 MHz, $CDCl_3$)



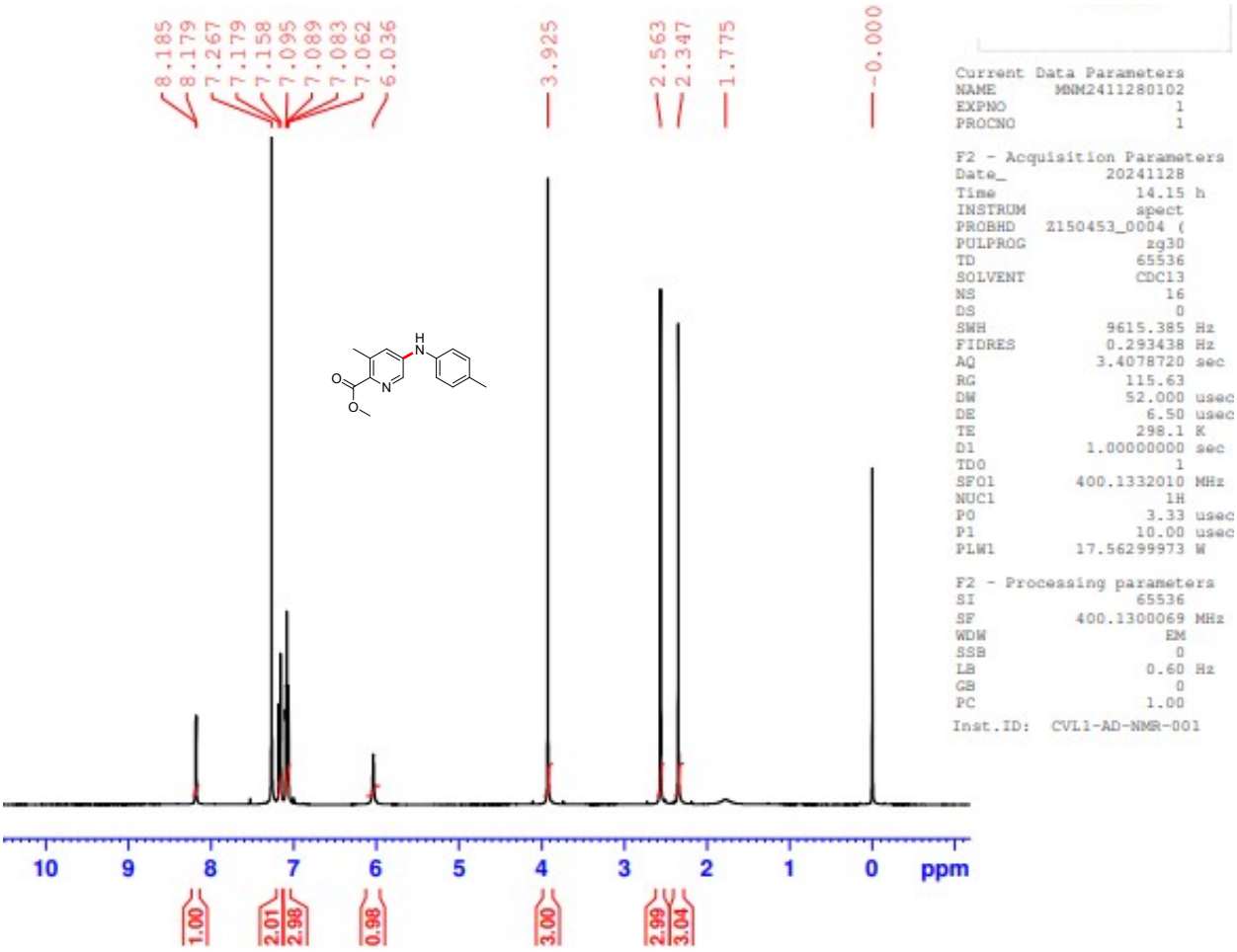
N-(p-tolyl)thiophen-3-amine (**9**) ^{13}C NMR (100 MHz, $CDCl_3$)



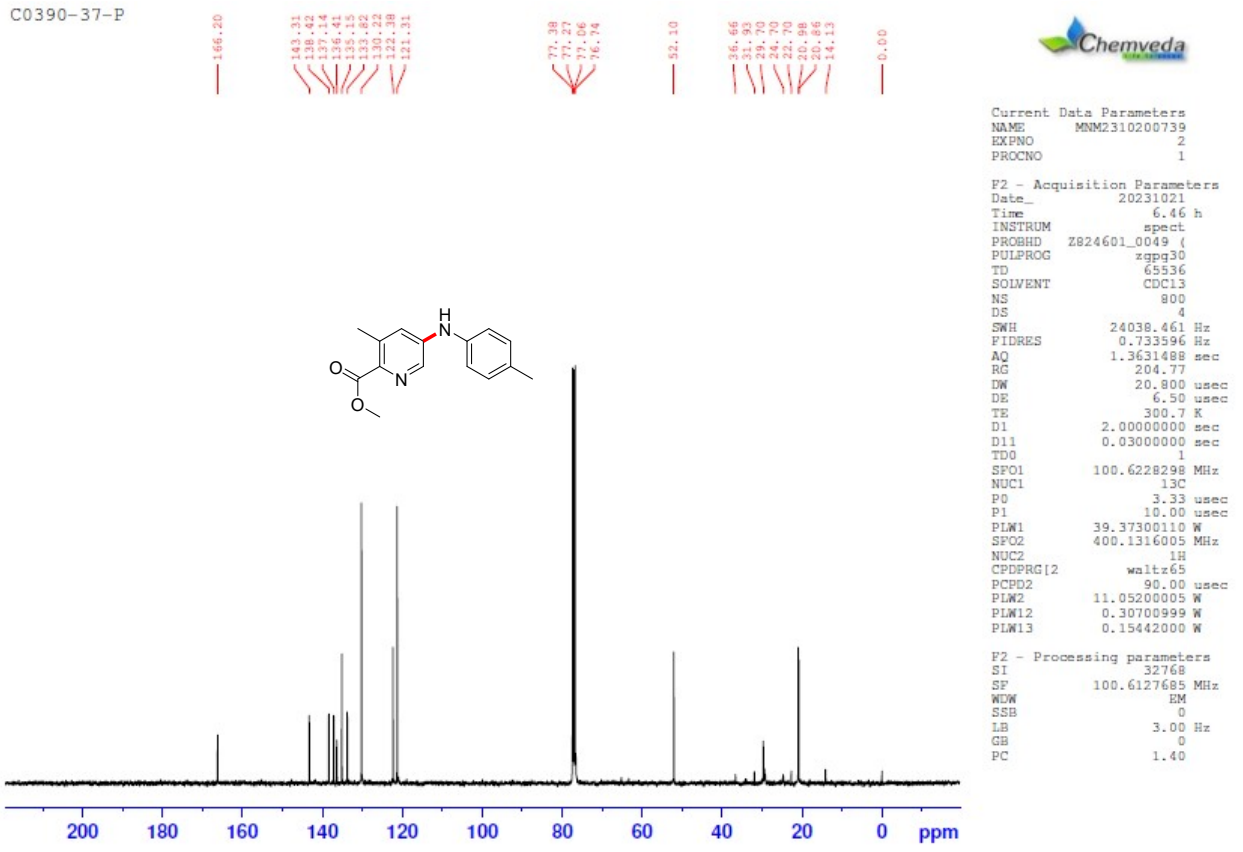
N-(p-Tolyl)pyridin-3-amine (**10**) ^{1}HNMR (400 MHz, $CDCl_3$)



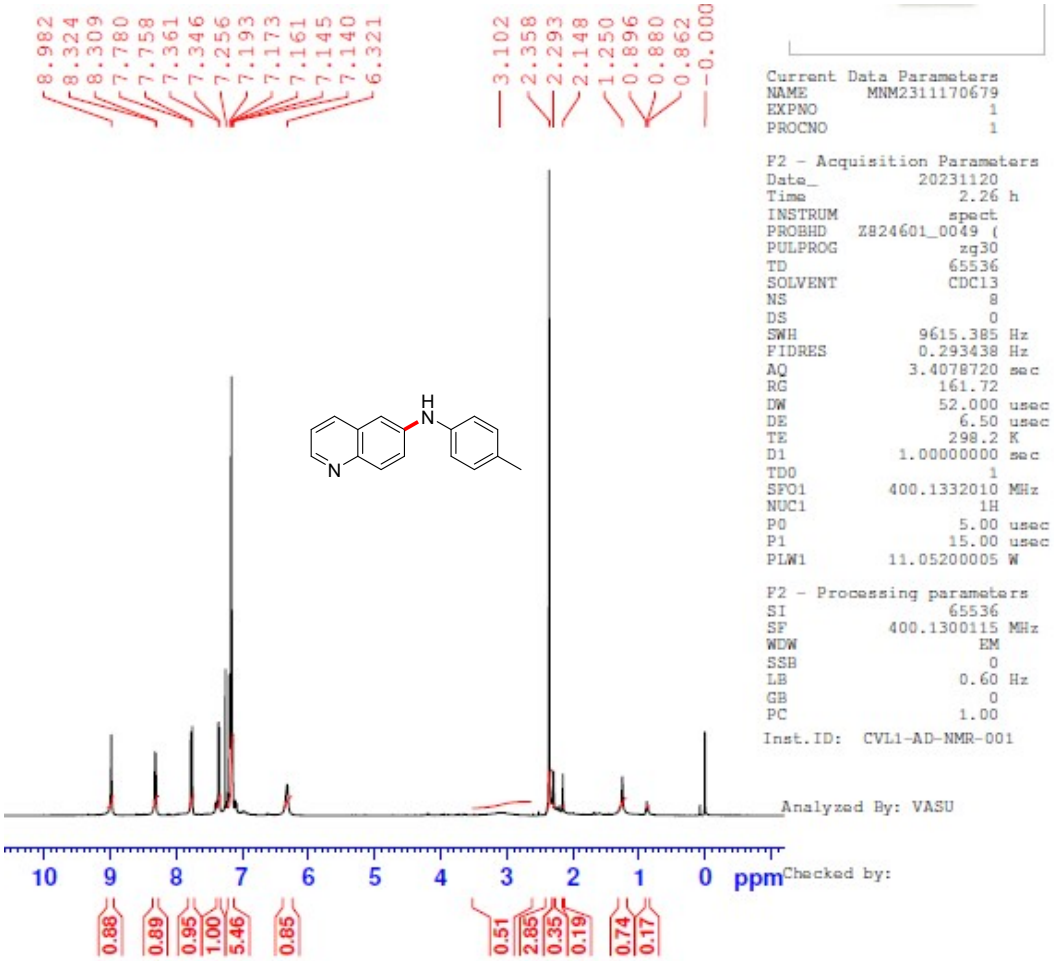
N-(p-Tolyl)pyridin-3-amine (**10**) ^{13}C NMR (100 MHz, $CDCl_3$)



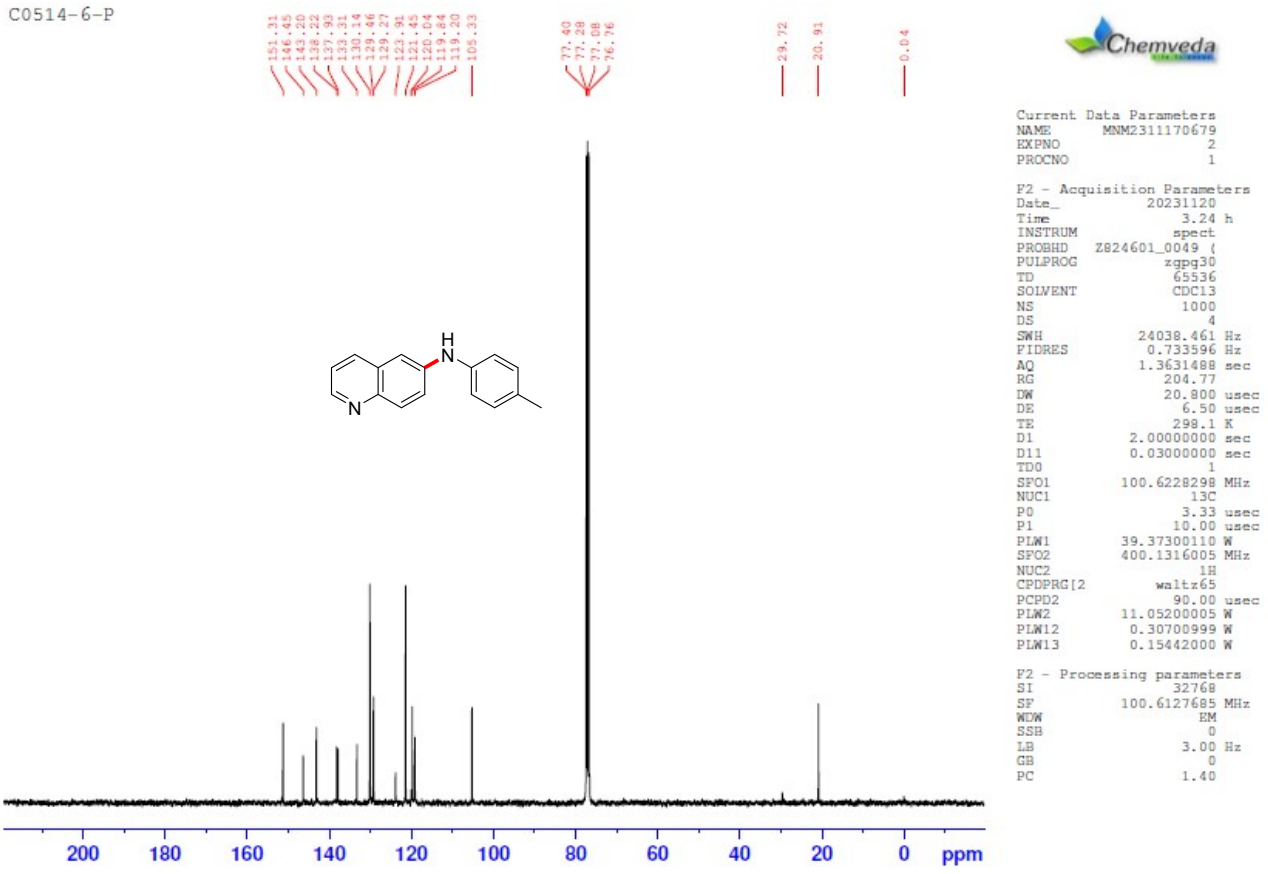
Methyl 3-methyl-5-(p-tolylamino)picolinate (**11**) ^{1}H NMR (400 MHz, $CDCl_3$)



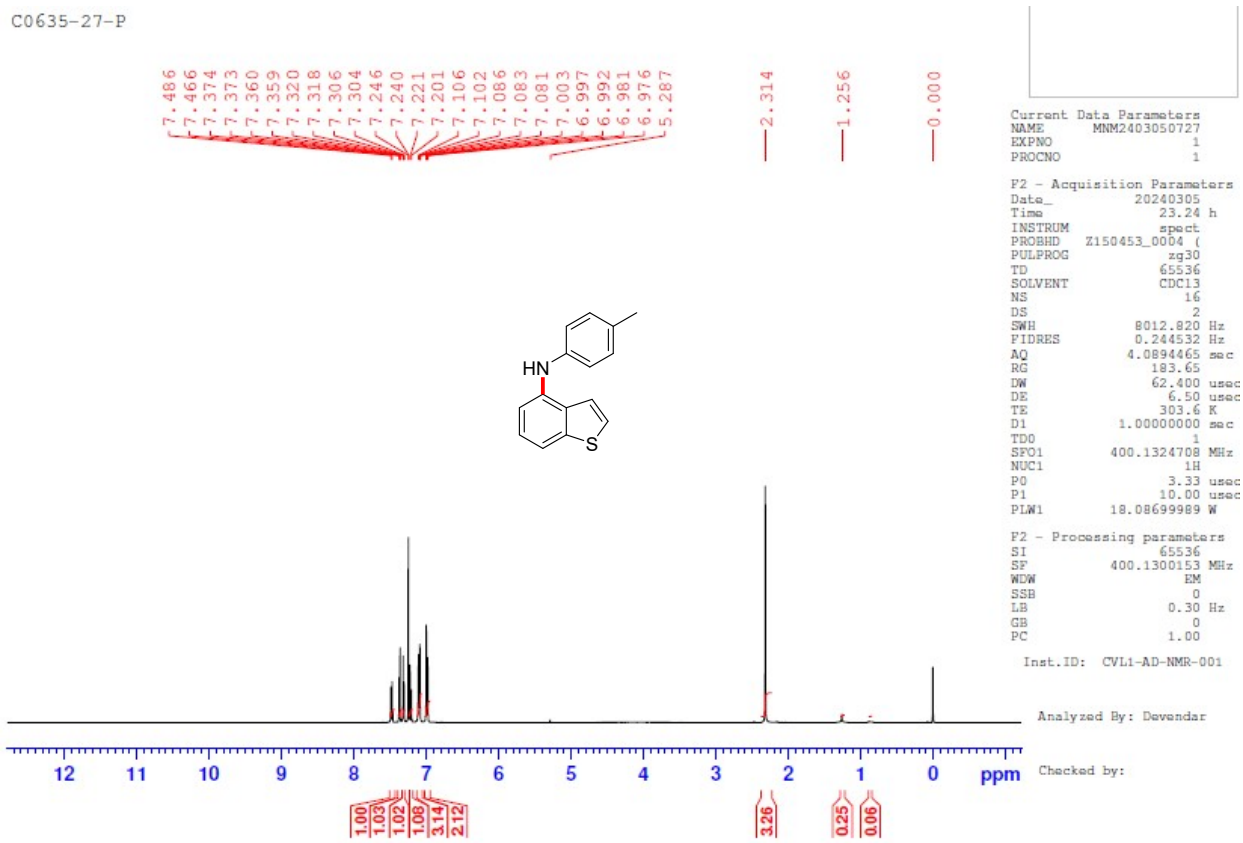
Methyl 3-methyl-5-(p-tolylamino)picolinate (**11**) ^{13}C NMR (100 MHz, $CDCl_3$)



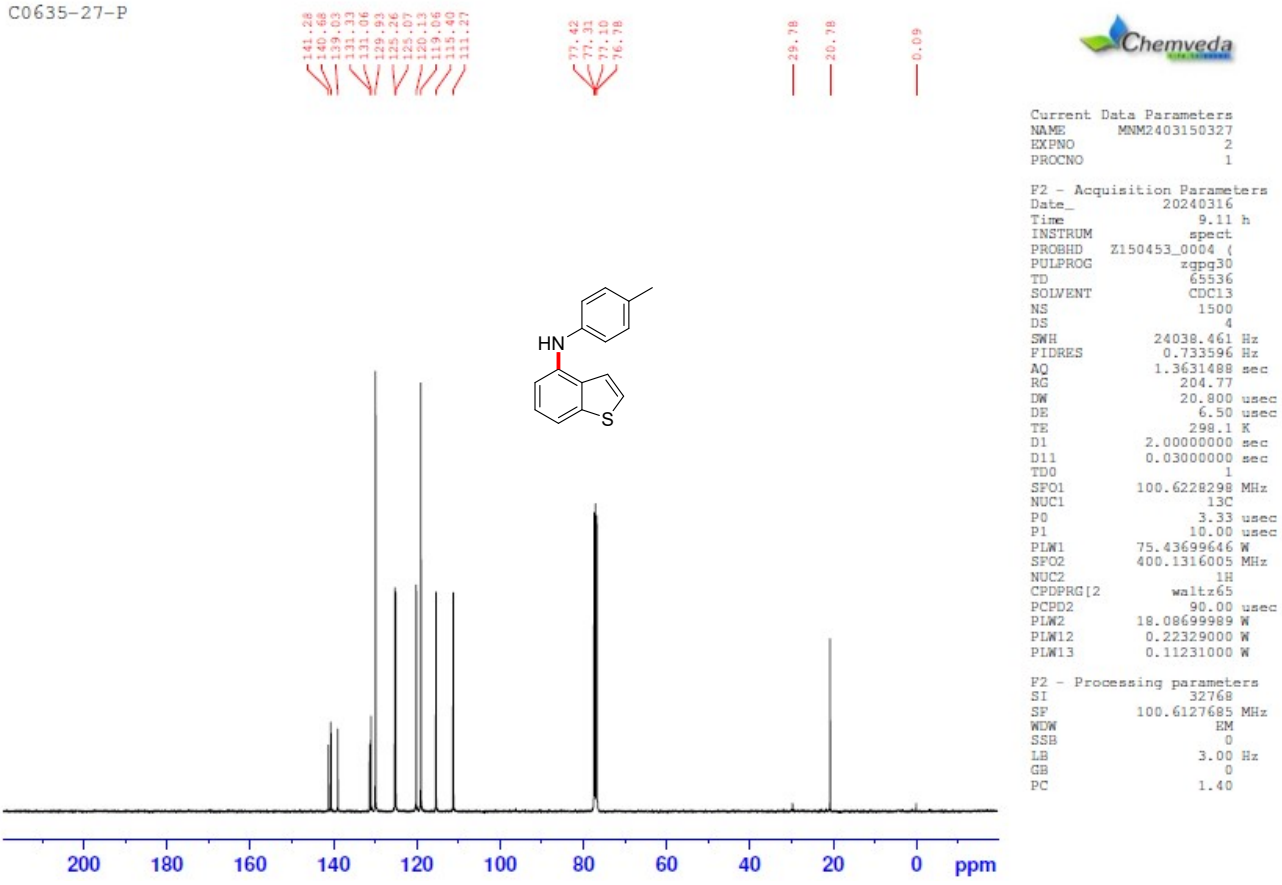
N-(p-tolyl)quinolin-6-amine (**12**) ^{1}H NMR (400 MHz, $CDCl_3$)



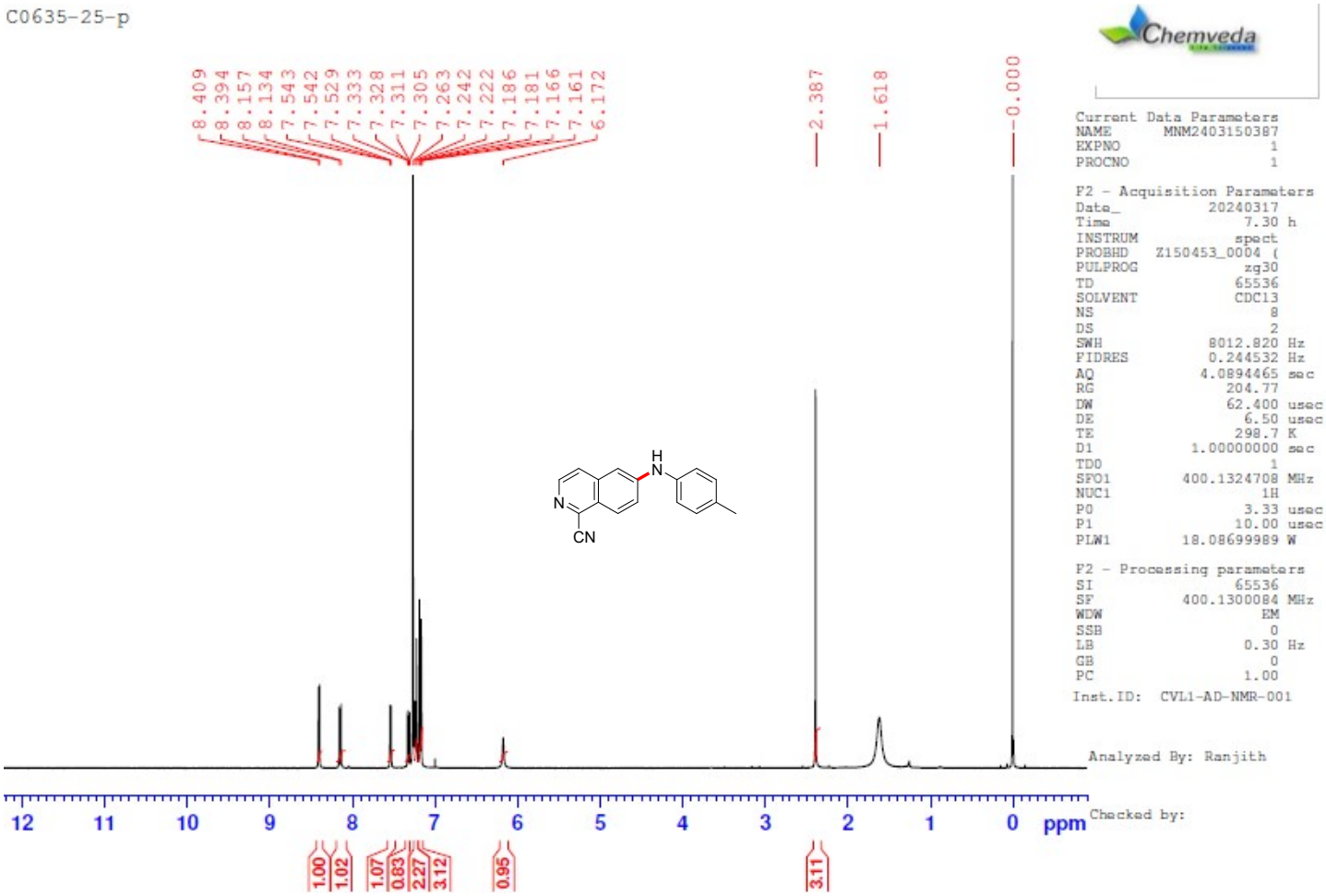
N-(p-tolyl)quinolin-6-amine (**12**) ^{13}C NMR (100 MHz, $CDCl_3$)



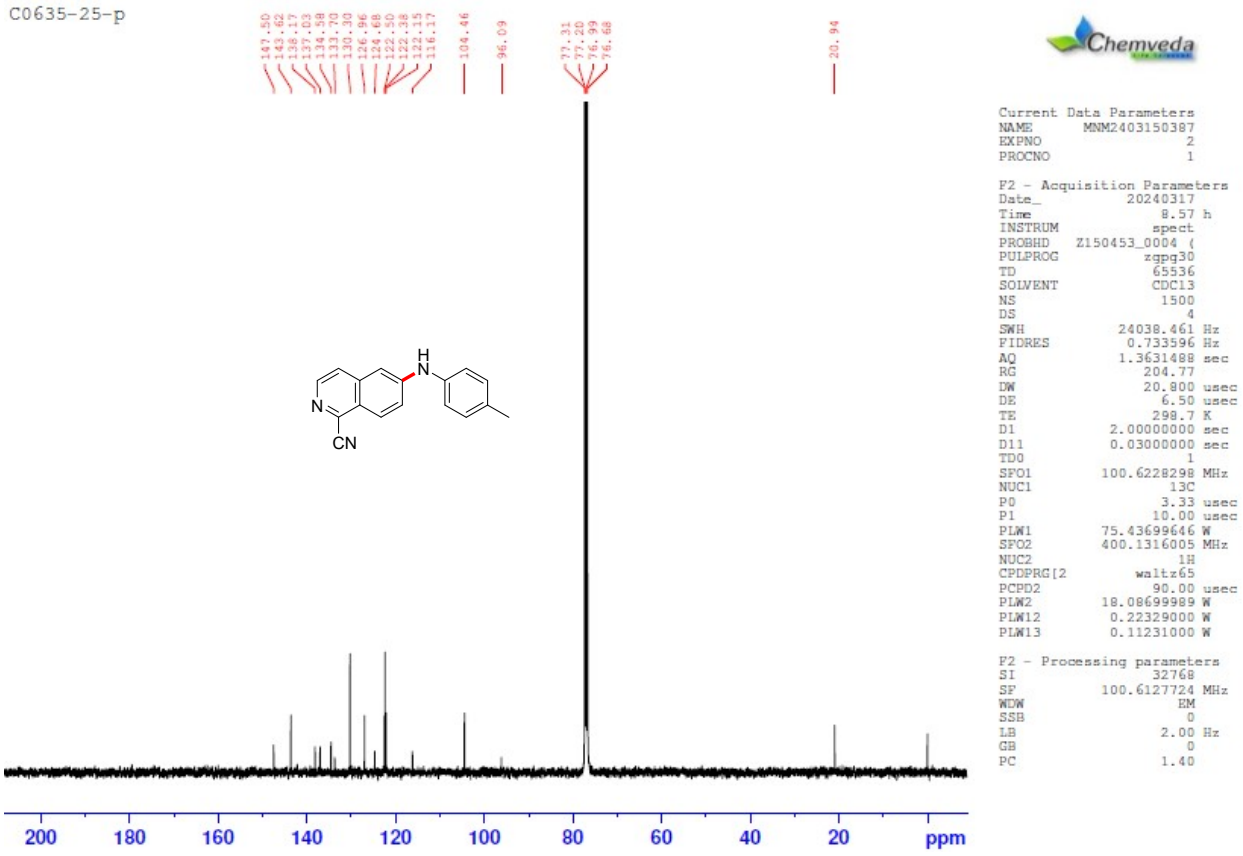
N-(p-tolyl)benzo[b]thiophen-4-amine (**13**) ^{1}H NMR (400 MHz, $CDCl_3$)



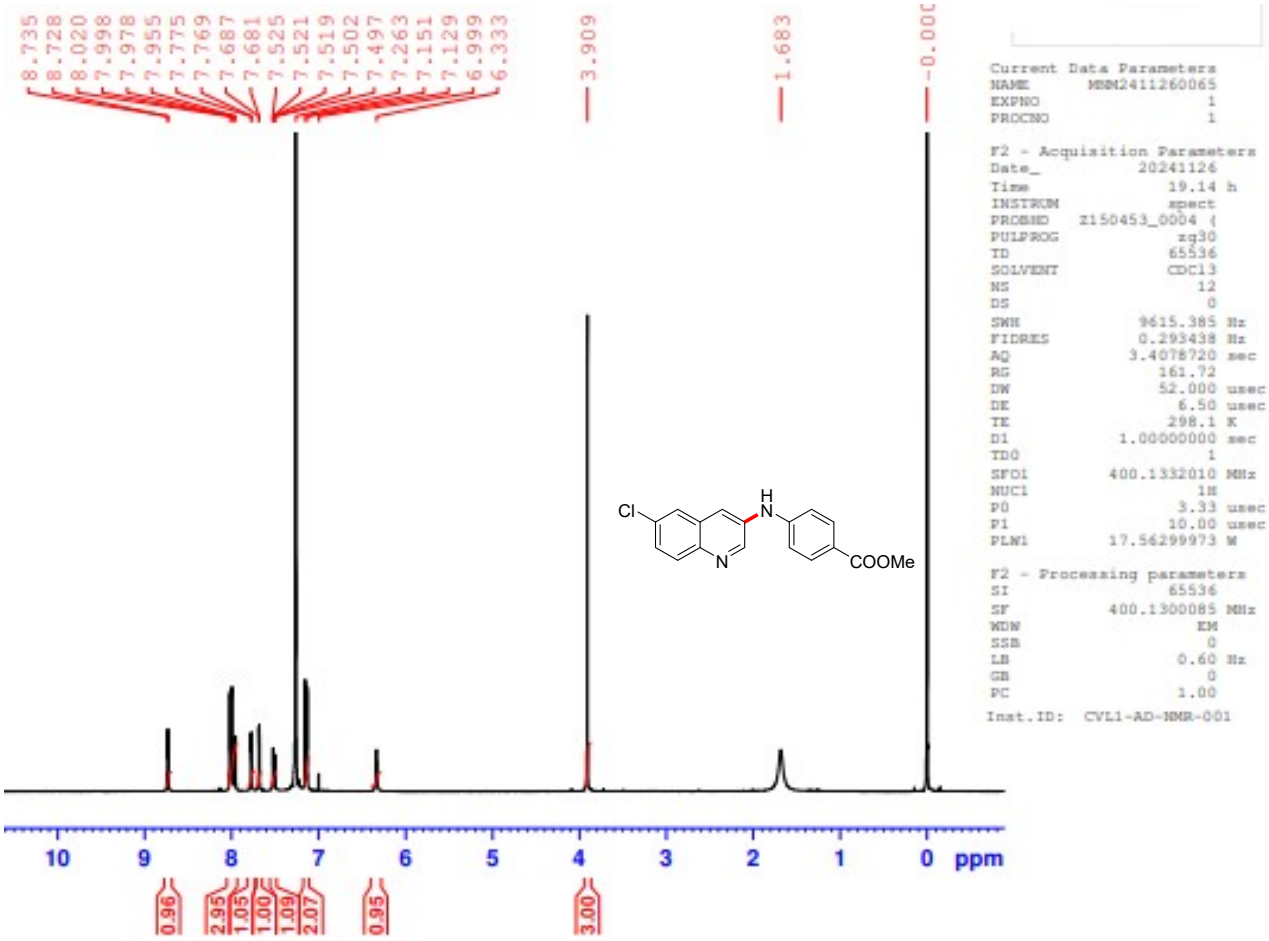
N-(p-tolyl)benzo[b]thiophen-4-amine (**13**) ^{13}C NMR (100 MHz, $CDCl_3$)



6-(p-tolylamino)isoquinoline-1-carbonitrile (**14**) ^{1}H NMR (400 MHz, $CDCl_3$)



6-(p-tolylamino)isoquinoline-1-carbonitrile (**14**) ^{13}C NMR (100 MHz, $CDCl_3$)



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PROCNO 1

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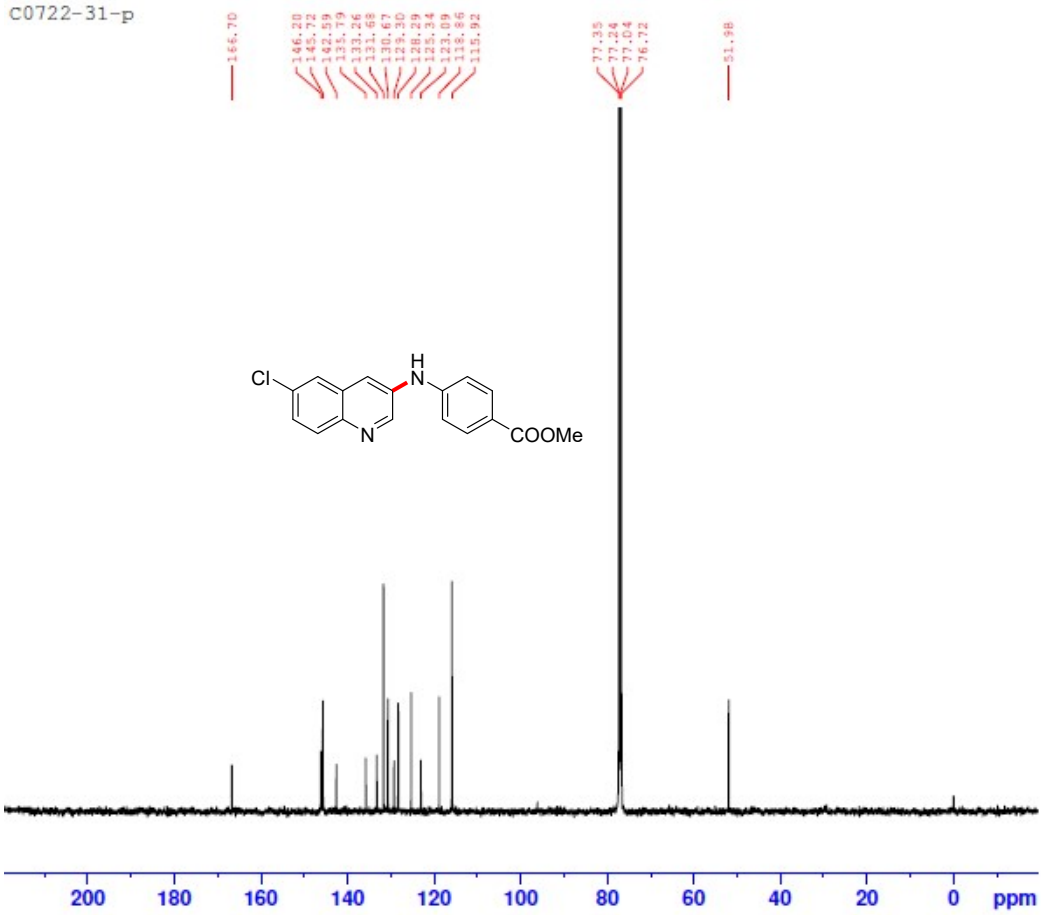
Inst.ID: CVL1-AD-NMR-001

Methyl 4-((6-chloroquinolin-3-yl)amino)benzoate (**15**) ^{1}H NMR (400 MHz, $CDCl_3$)



Chemveda

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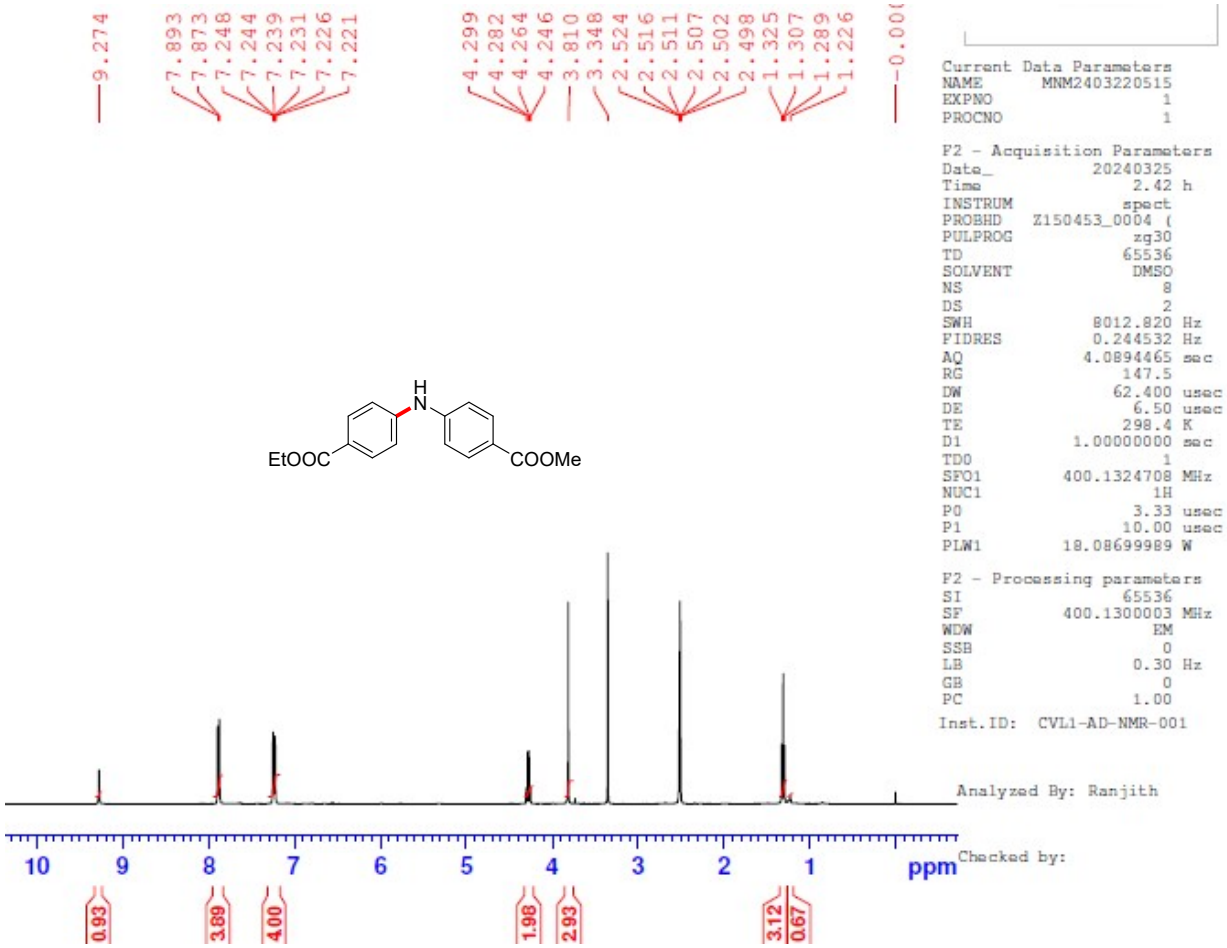
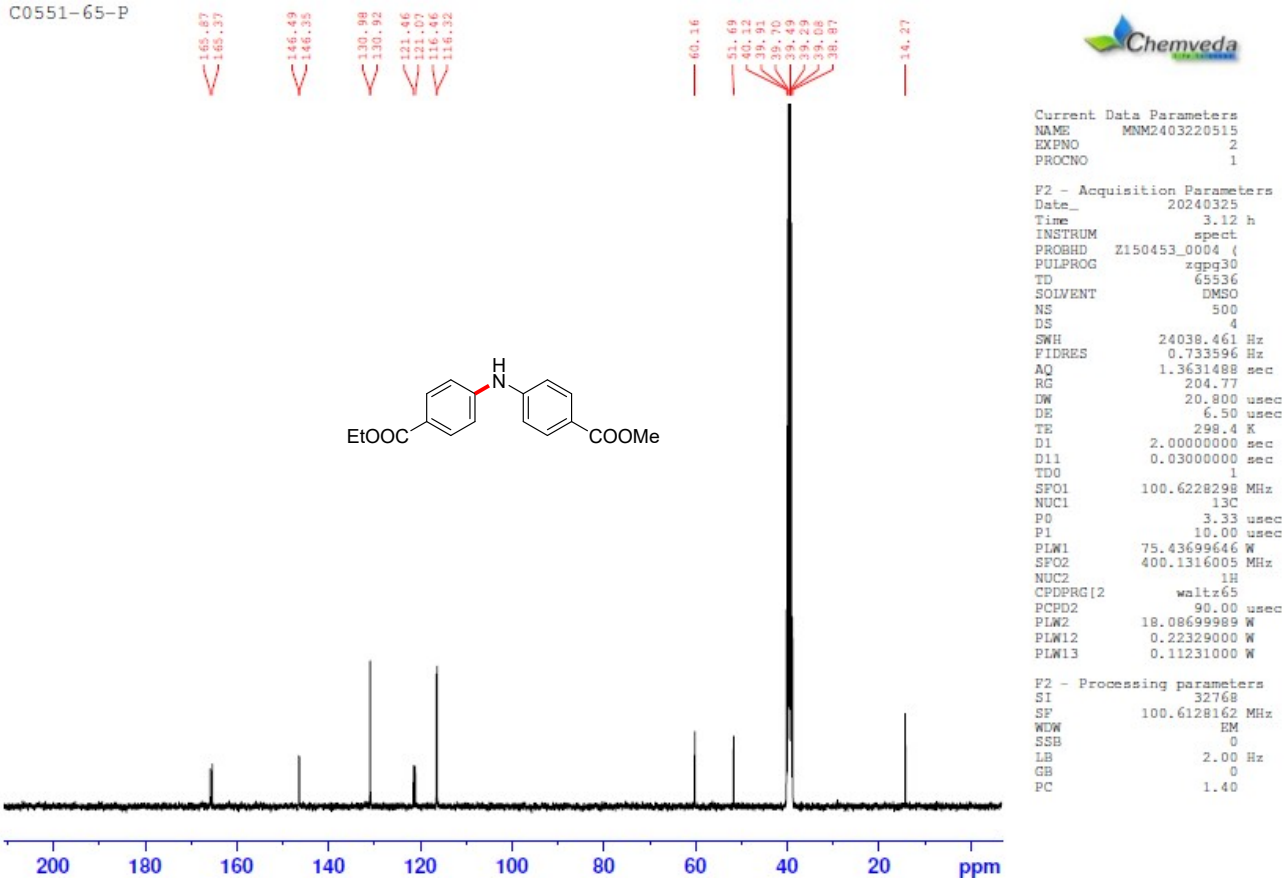
GB 0
PC 1.40

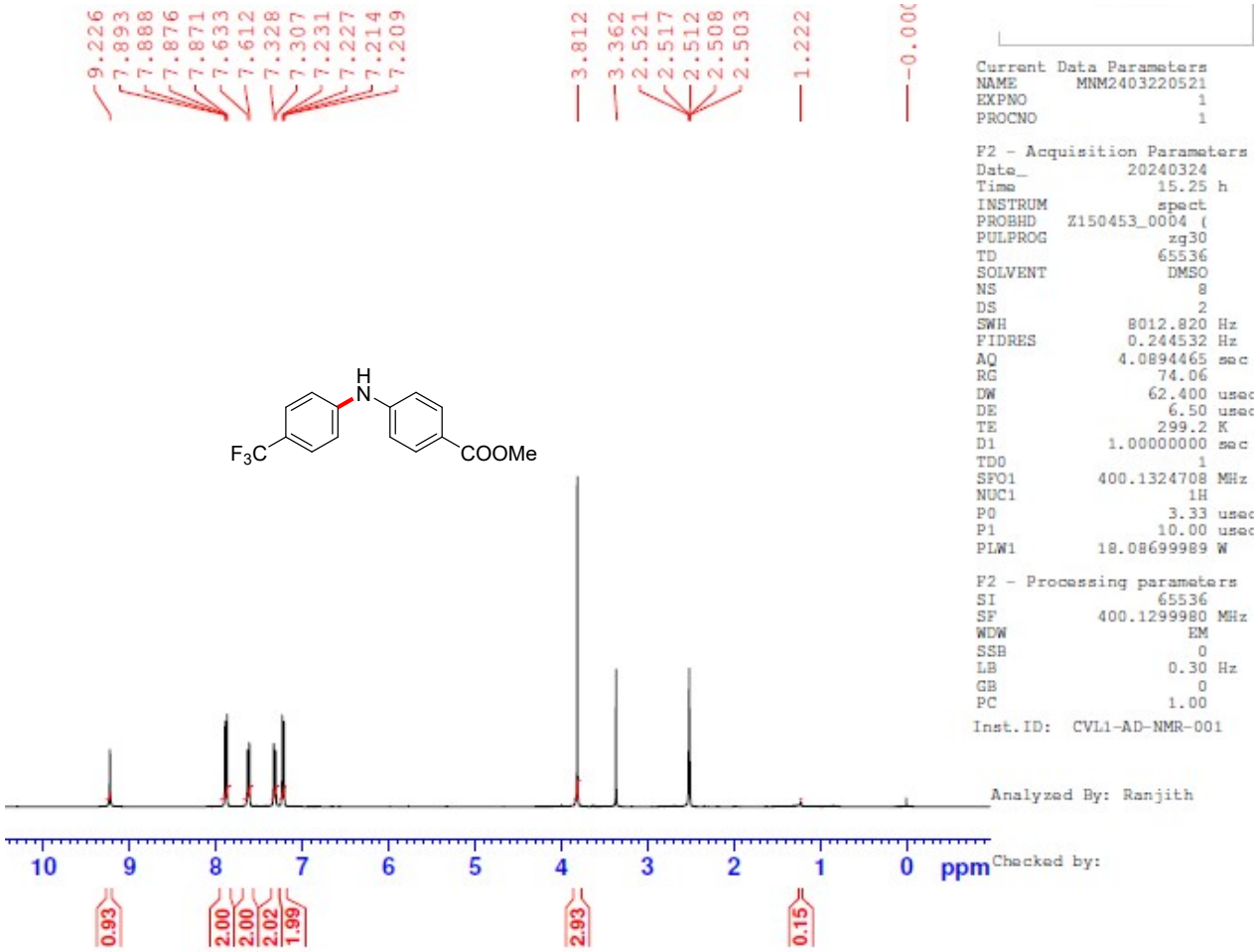
Methyl 4-((6-chloroquinolin-3-yl)amino)benzoate (**15**) ^{13}C NMR (100 MHz, $CDCl_3$)



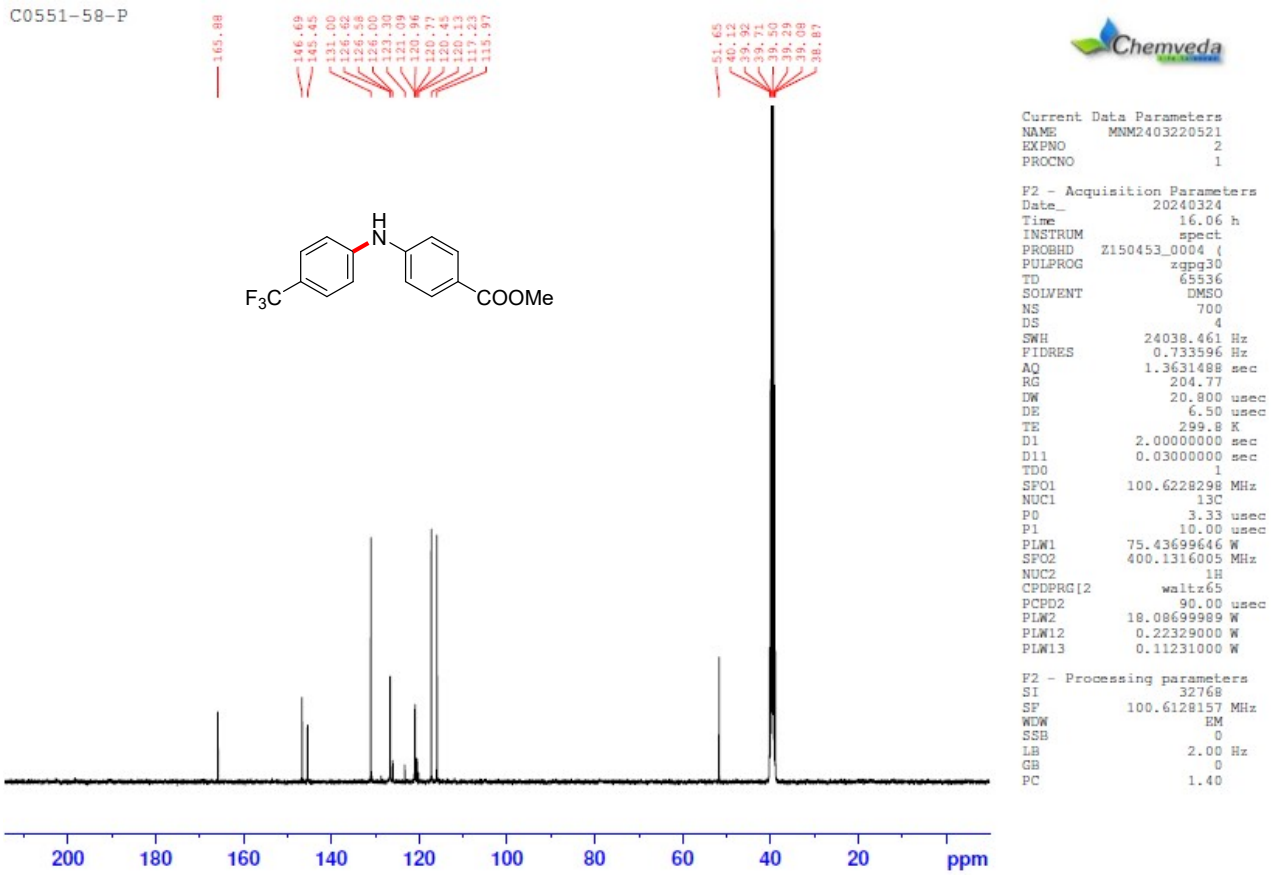
Ethyl 4-((4-(methoxycarbonyl)phenyl)amino)benzoate (**16**) ^{1}H NMR (400 MHz, DMSO-d_6)



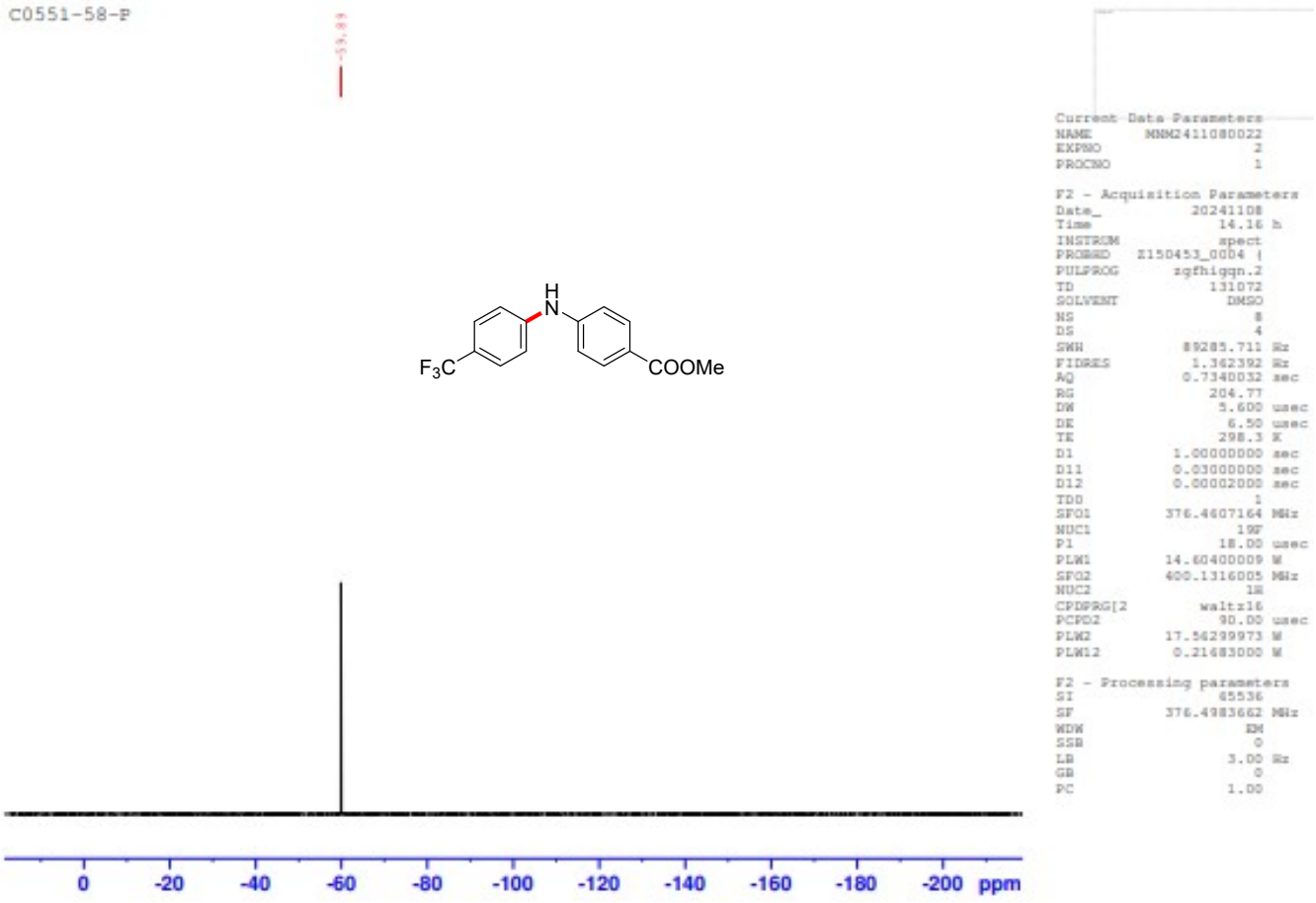
Ethyl 4-((4-(methoxycarbonyl)phenyl)amino)benzoate (**16**) ^{13}C NMR (100 MHz, DMSO-d_6)



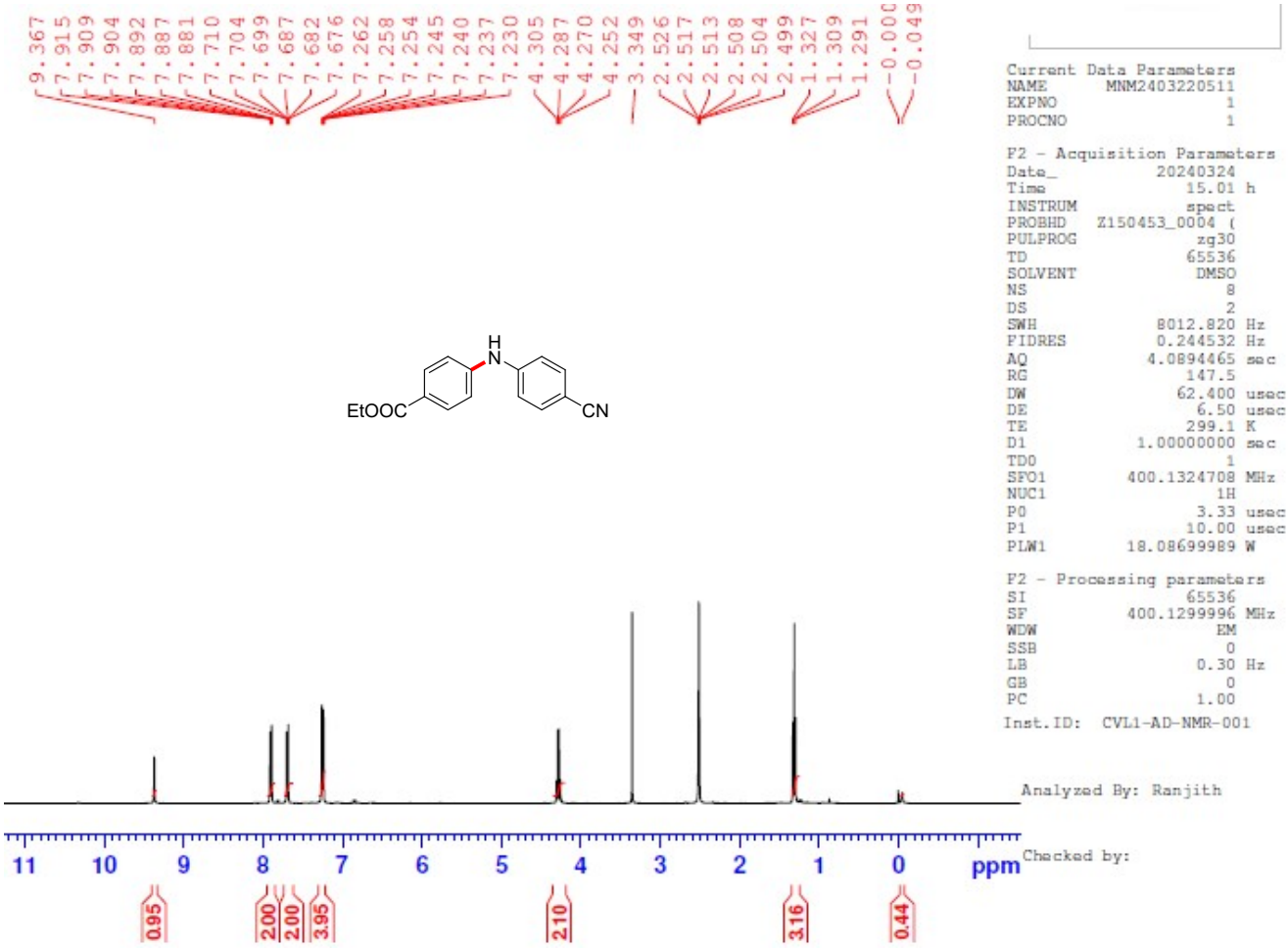
Methyl 4-((4-(trifluoromethyl)phenyl)amino)benzoate (**17**) ^{1}H NMR (400 MHz, DMSO-d_6)



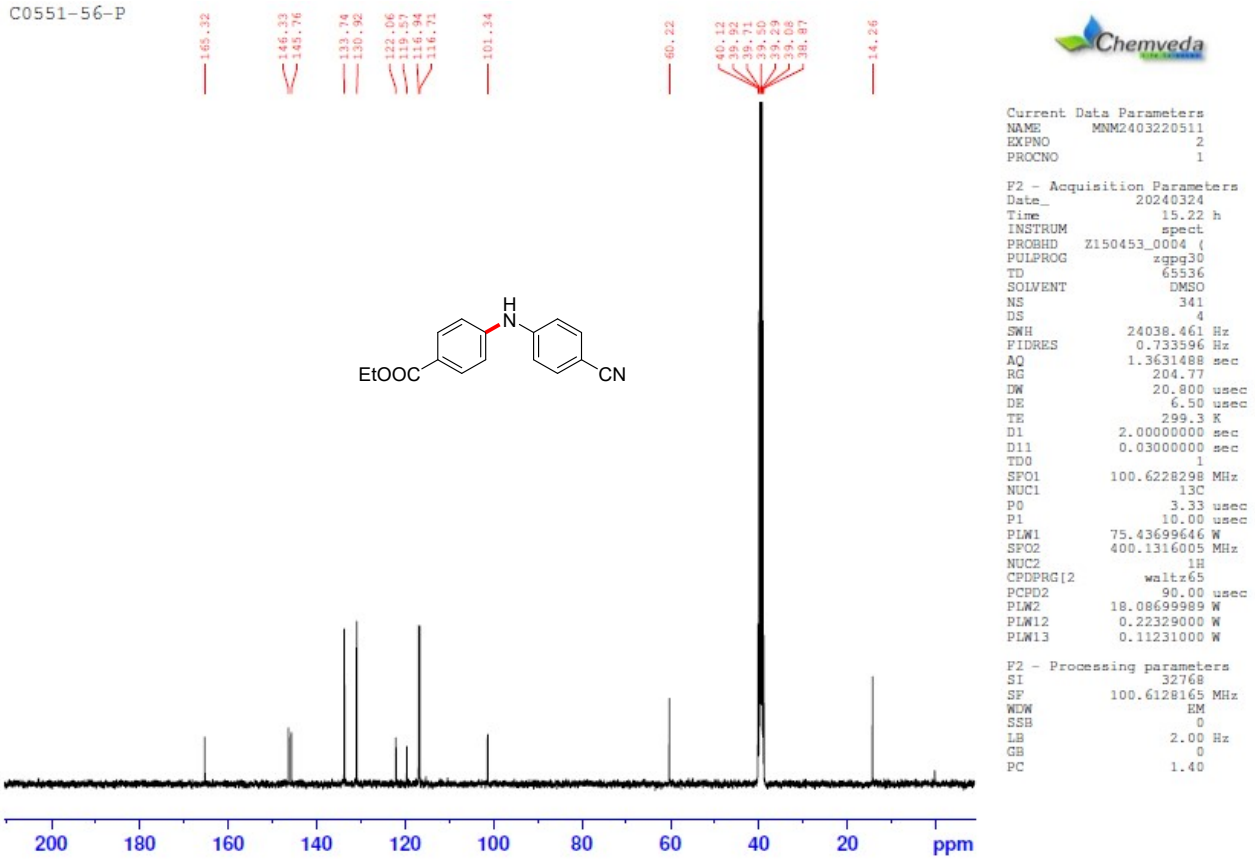
Methyl 4-((4-(trifluoromethyl)phenyl)amino)benzoate (**17**) ^{13}C NMR (376 MHz, DMSO-d_6)



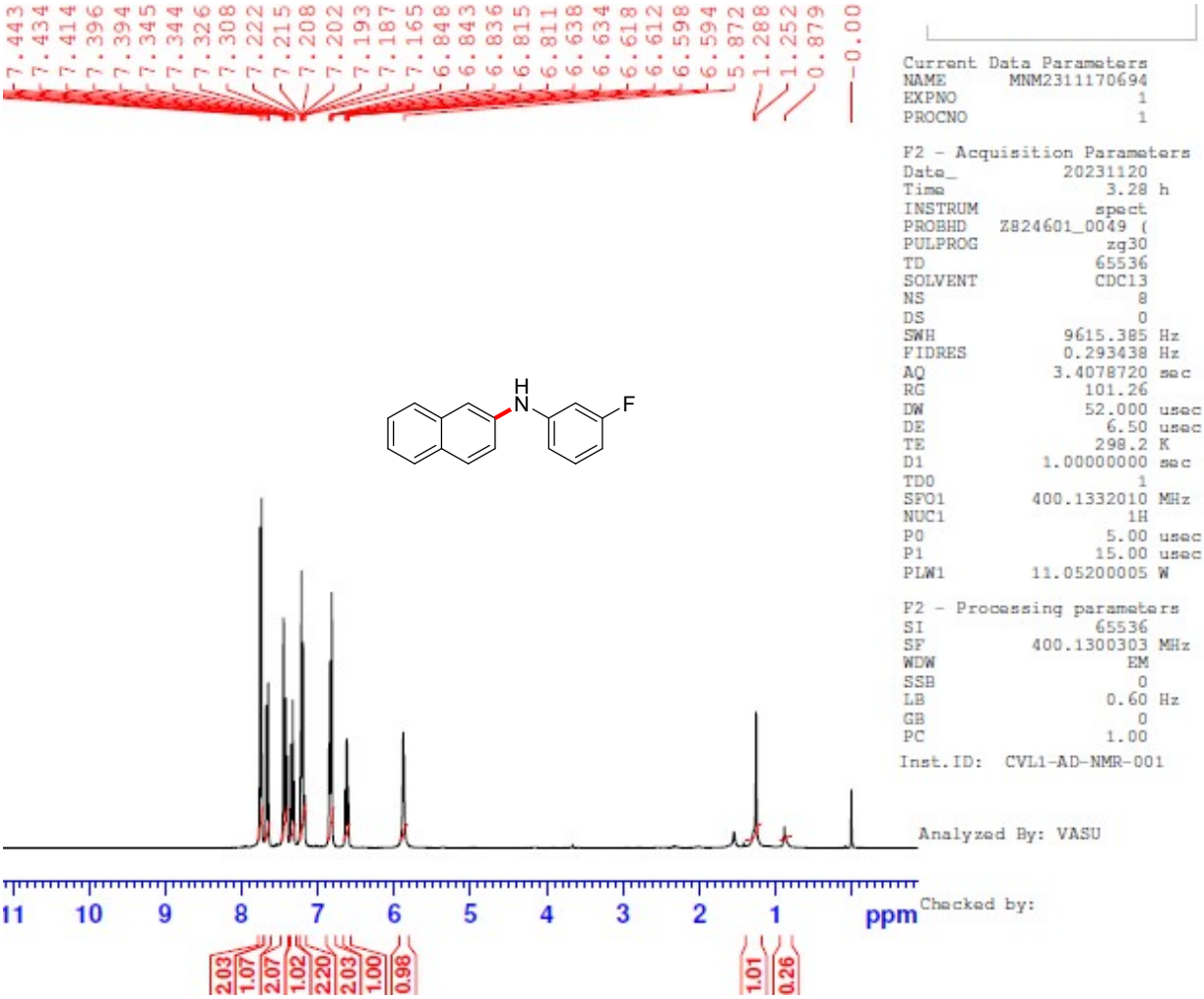
Methyl 4-((4-(trifluoromethyl)phenyl)amino)benzoate (**17**) ^{19}F NMR (100 MHz, DMSO-d_6)



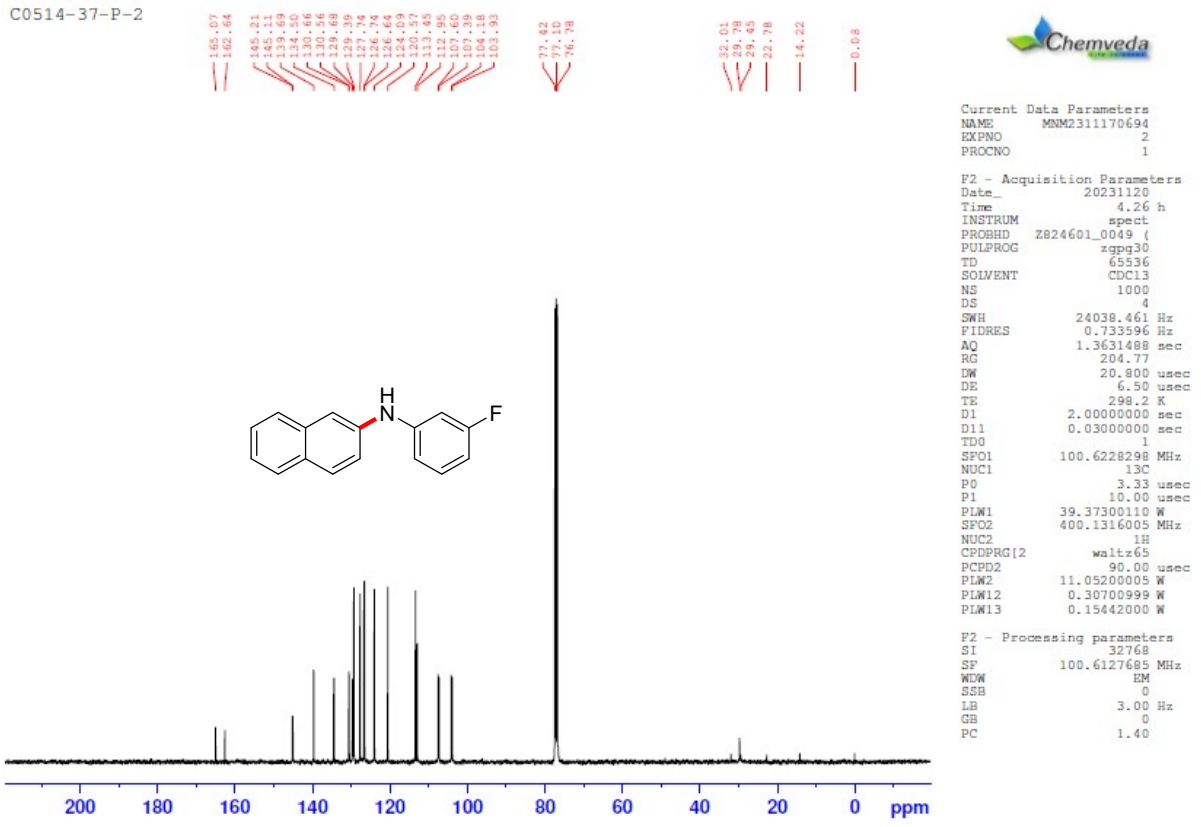
Ethyl 4-((4-cyanophenyl)amino)benzoate (**18**) ^{1}H NMR (400 MHz, DMSO-d_6)



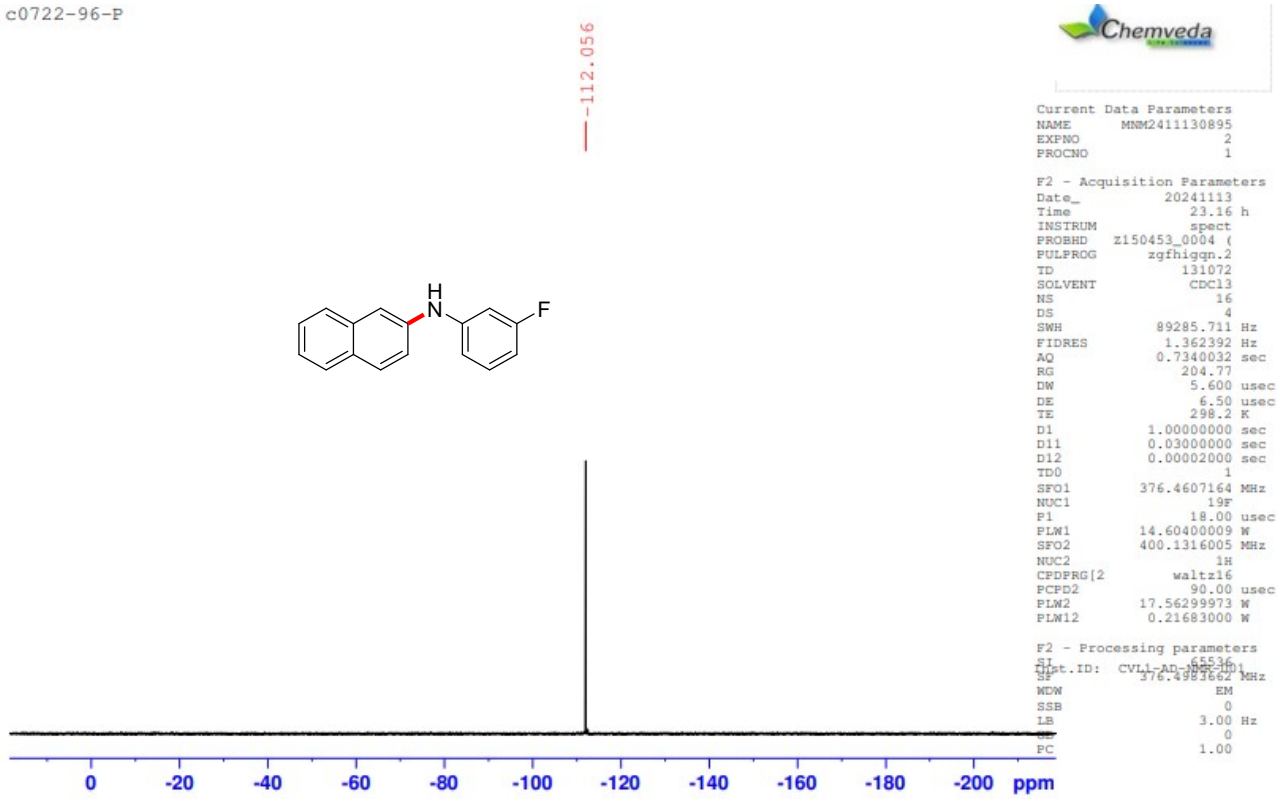
Ethyl 4-((4-cyanophenyl)amino)benzoate (**18**) ^{13}C NMR (100 MHz, DMSO-d_6)



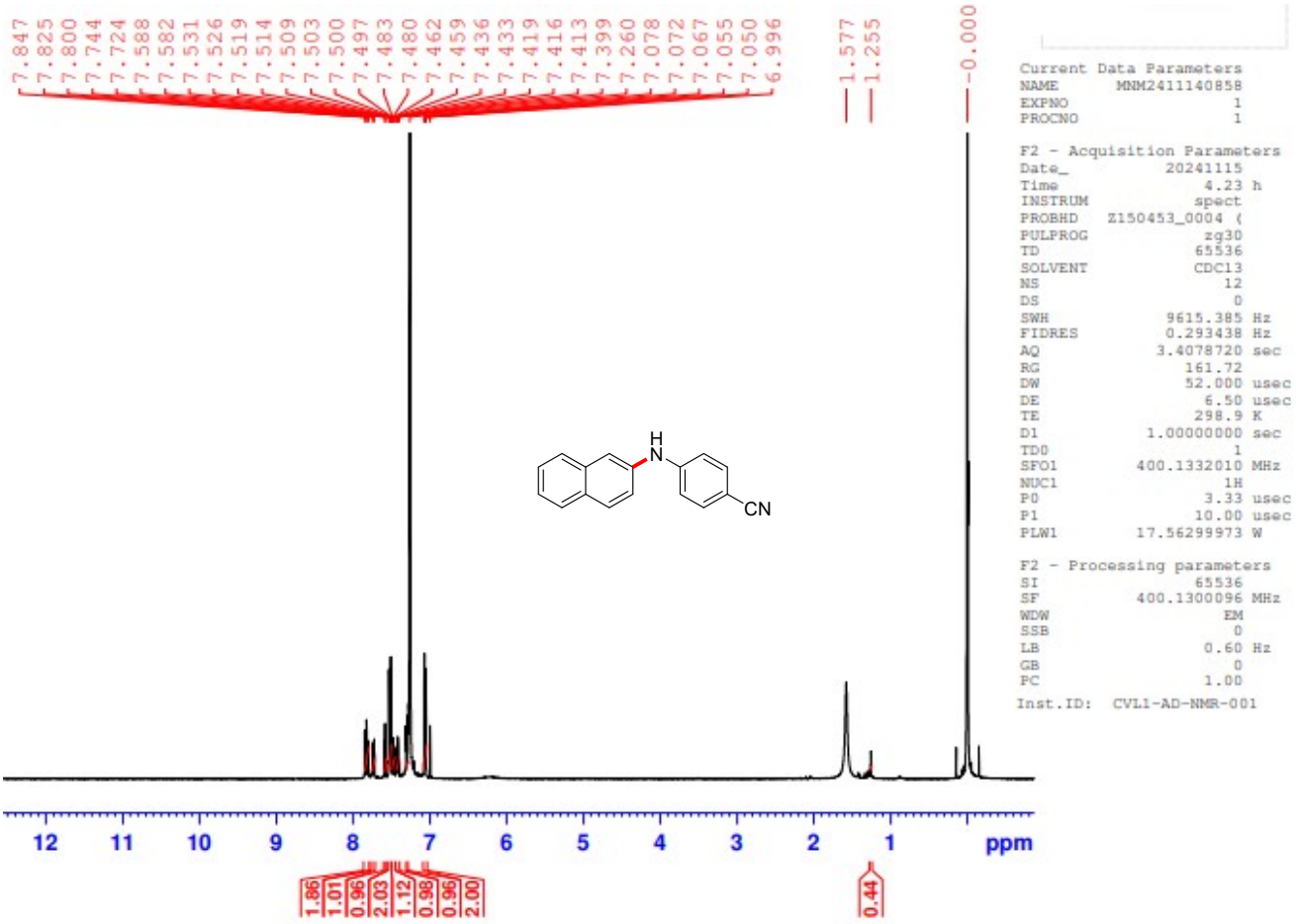
N-(3-Fluorophenyl)naphthalen-2-amine (**19**) ^{1}H NMR (400 MHz, $CDCl_3$)



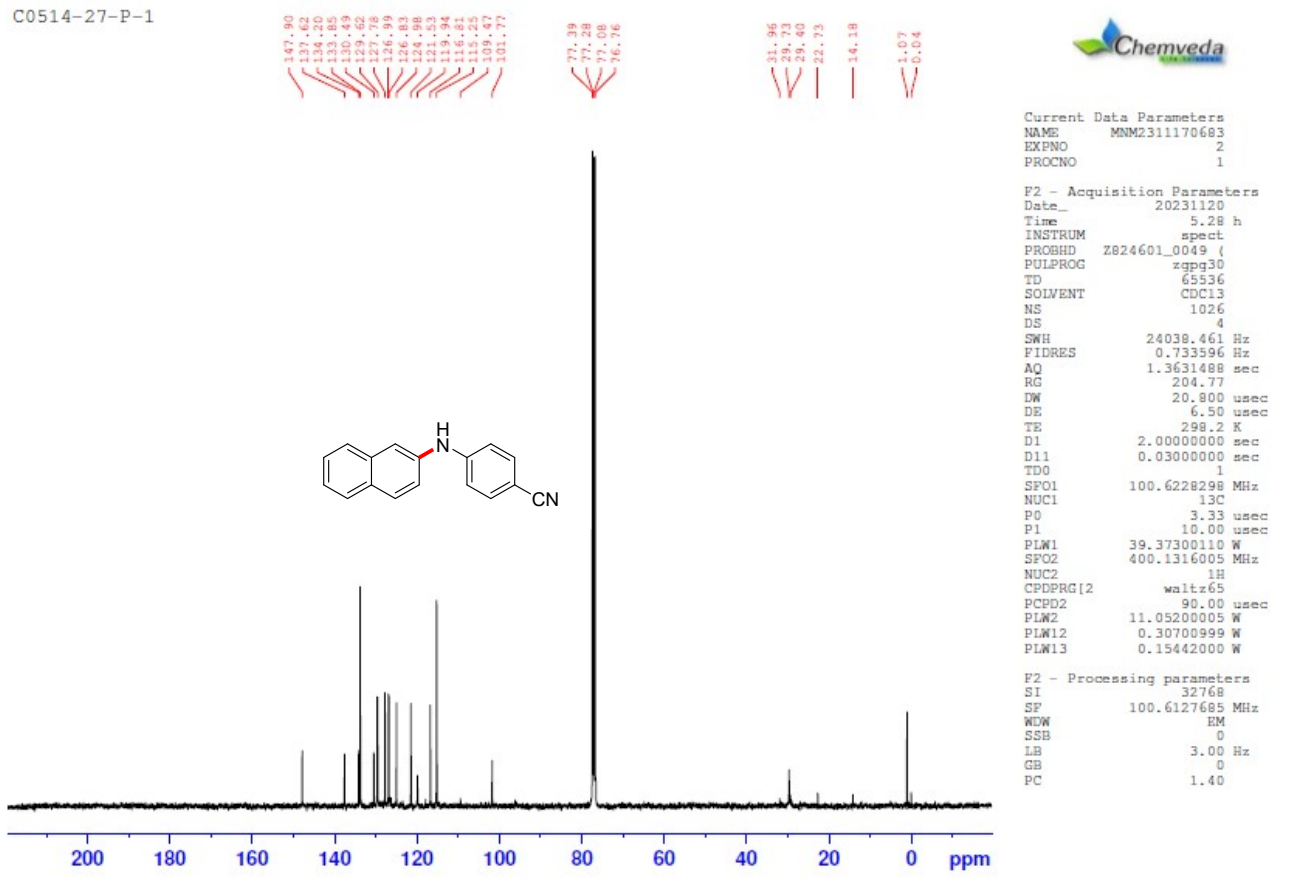
N-(3-Fluorophenyl)naphthalen-2-amine (**19**) ^{13}C NMR (100 MHz, $CDCl_3$)



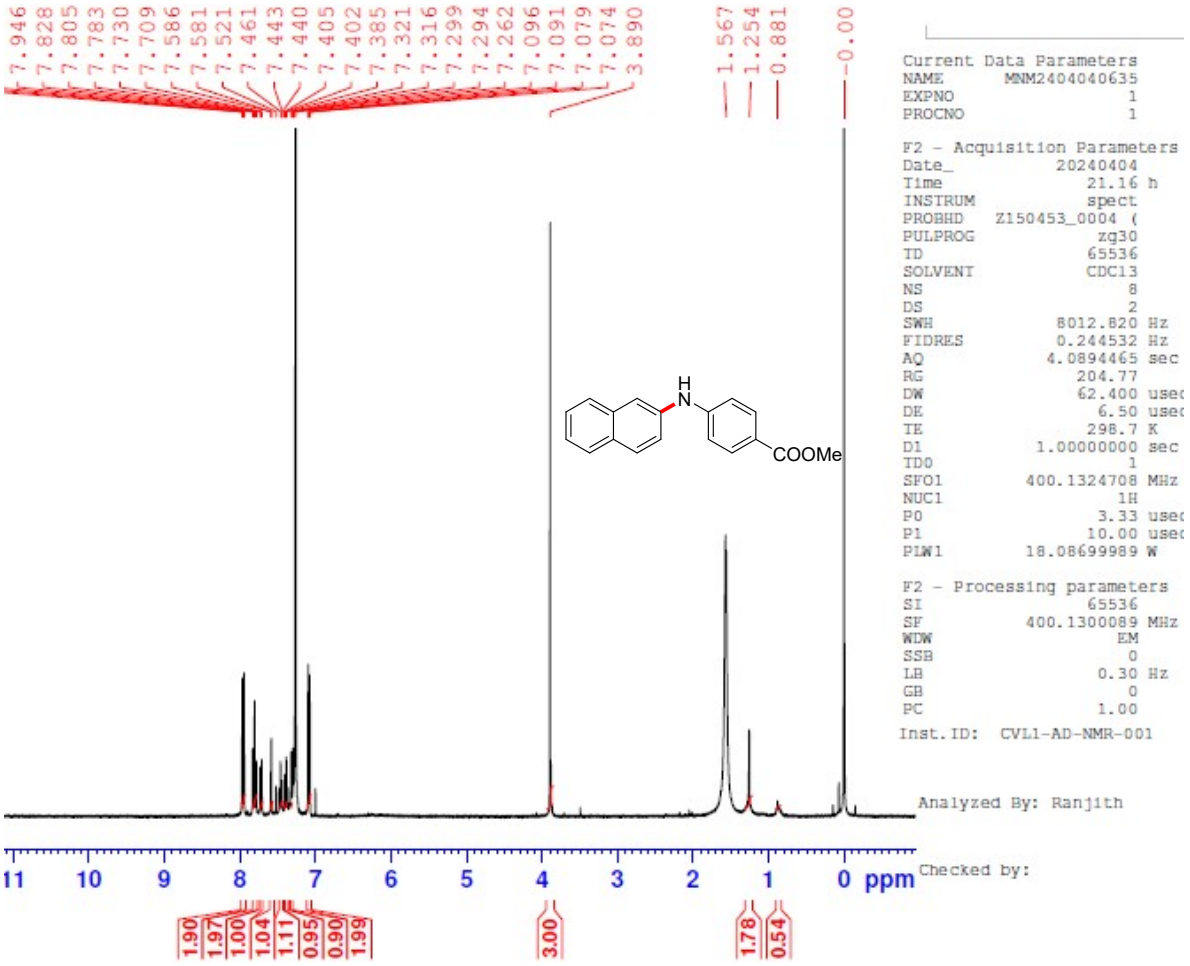
N-(3-Fluorophenyl)naphthalen-2-amine (**19**) ^{19}F NMR (376 MHz, $CDCl_3$)



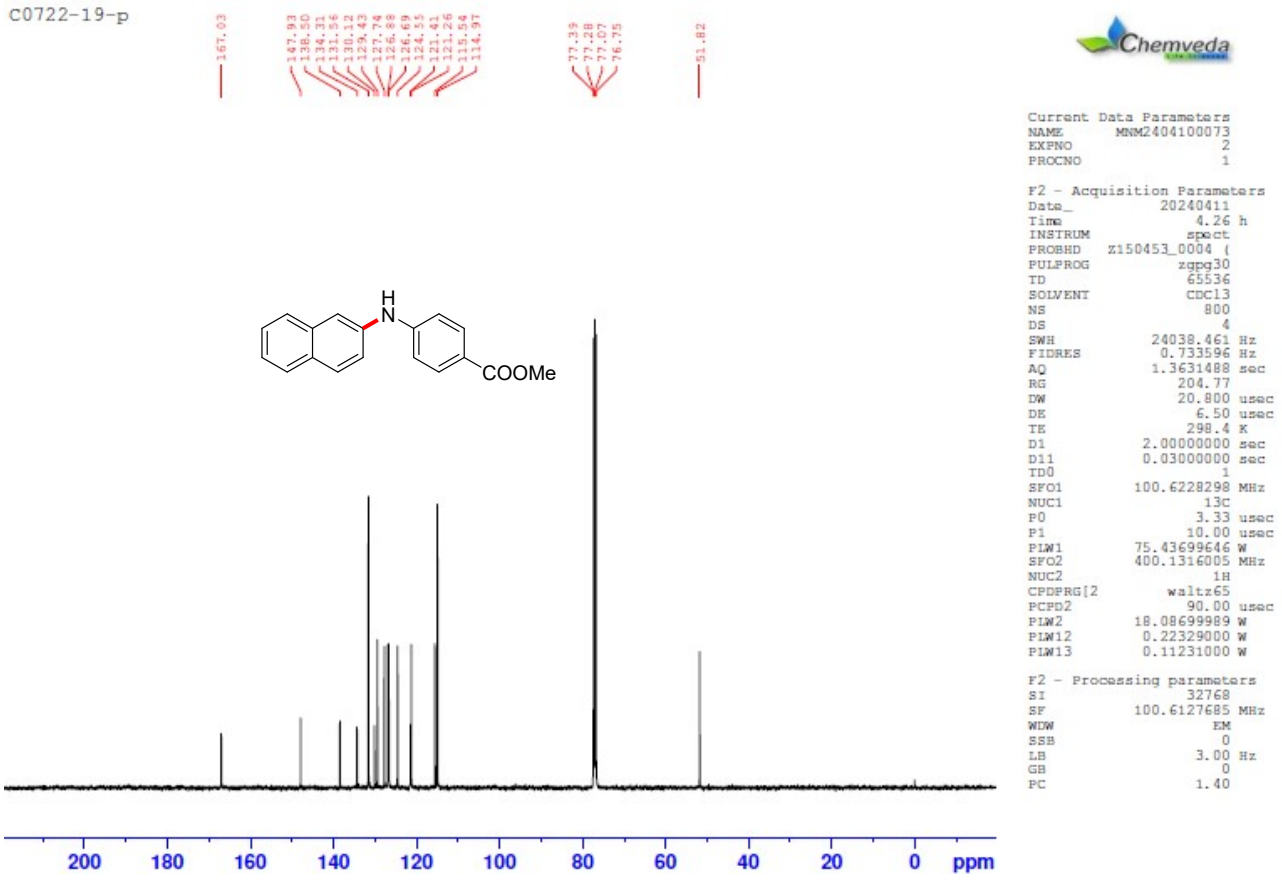
4-(Naphthalen-2-ylamino)benzonitrile (**20**) ^{1}H NMR (400 MHz, $CDCl_3$)



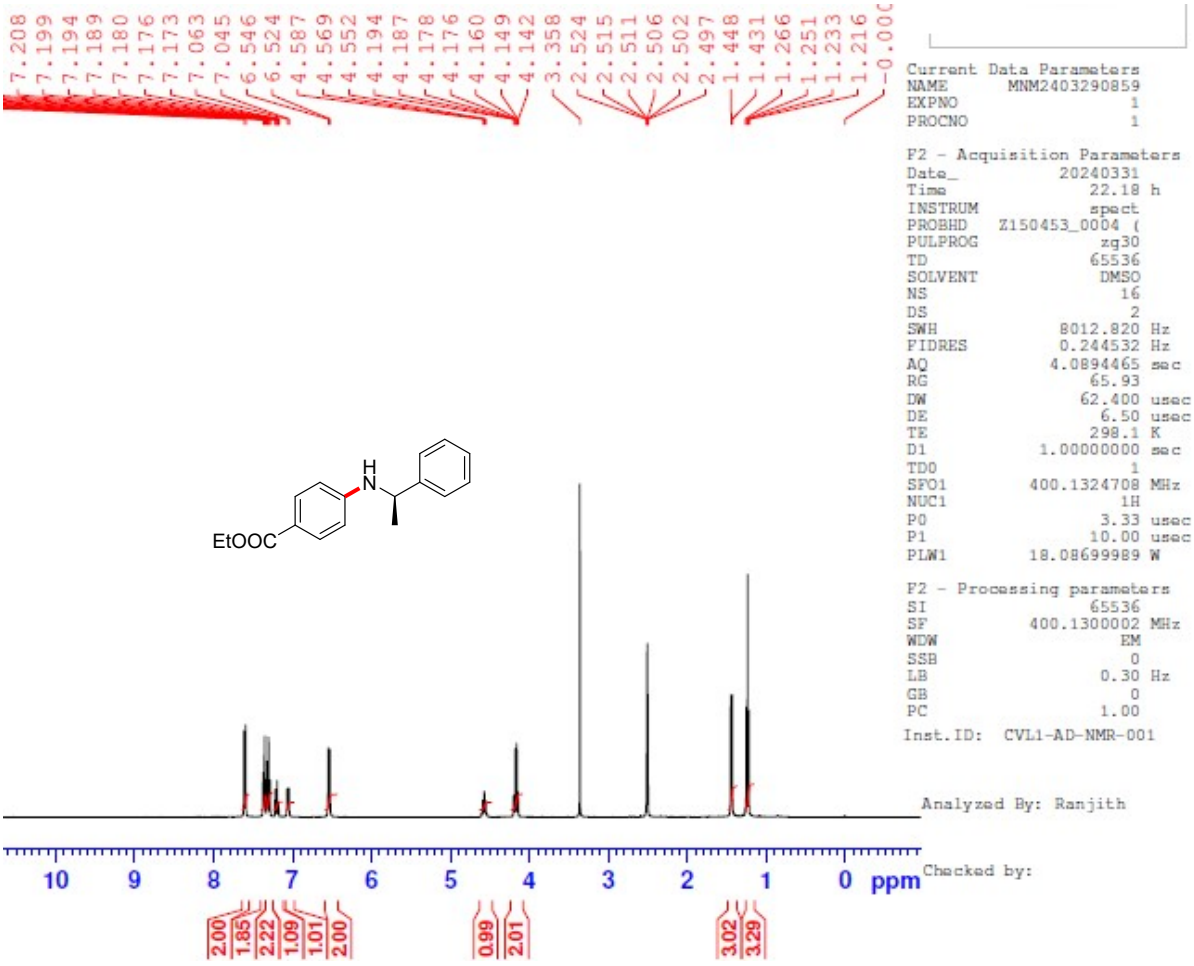
4-(Naphthalen-2-ylamino)benzonitrile (**20**) ^{13}C NMR (100 MHz, $CDCl_3$)



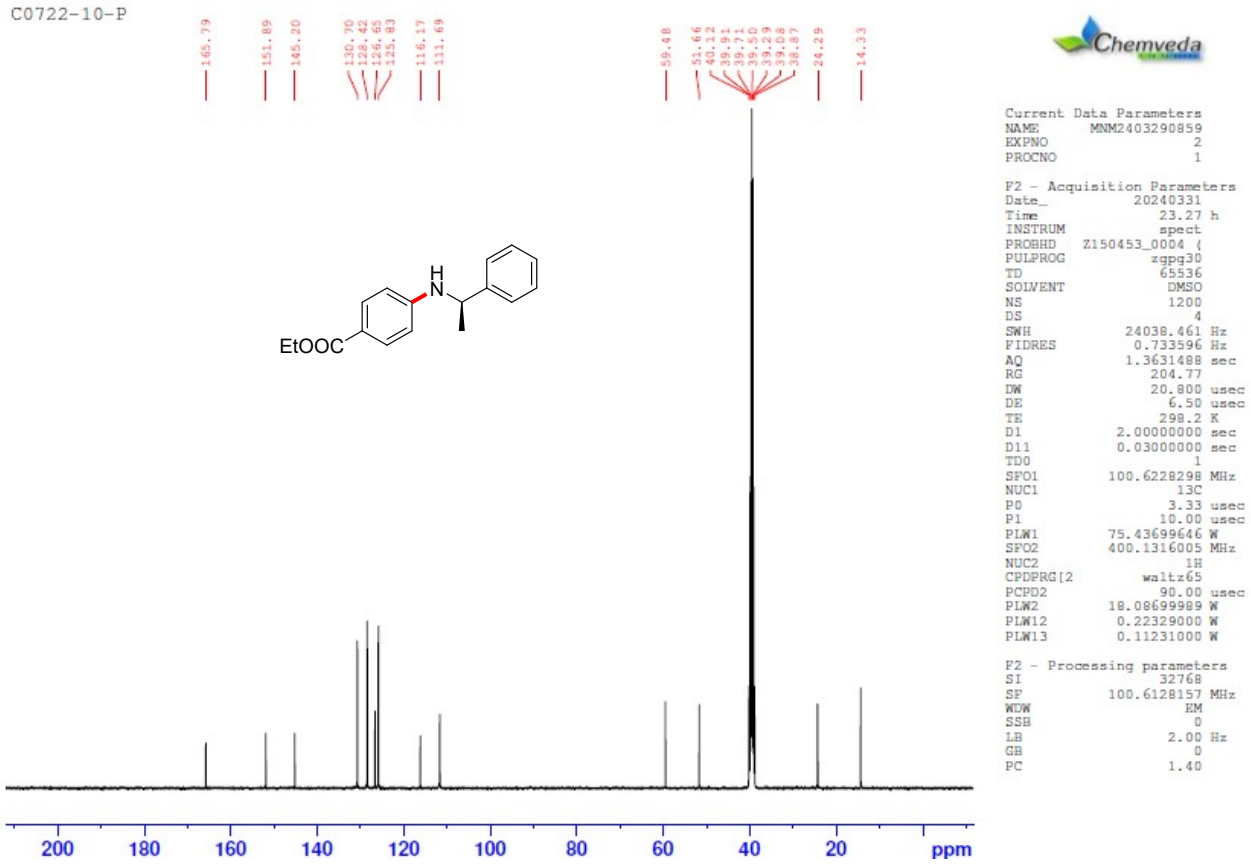
Methyl 4-(naphthalen-2-ylamino)benzoate (**21**) ^{1}H NMR (400 MHz, $CDCl_3$)



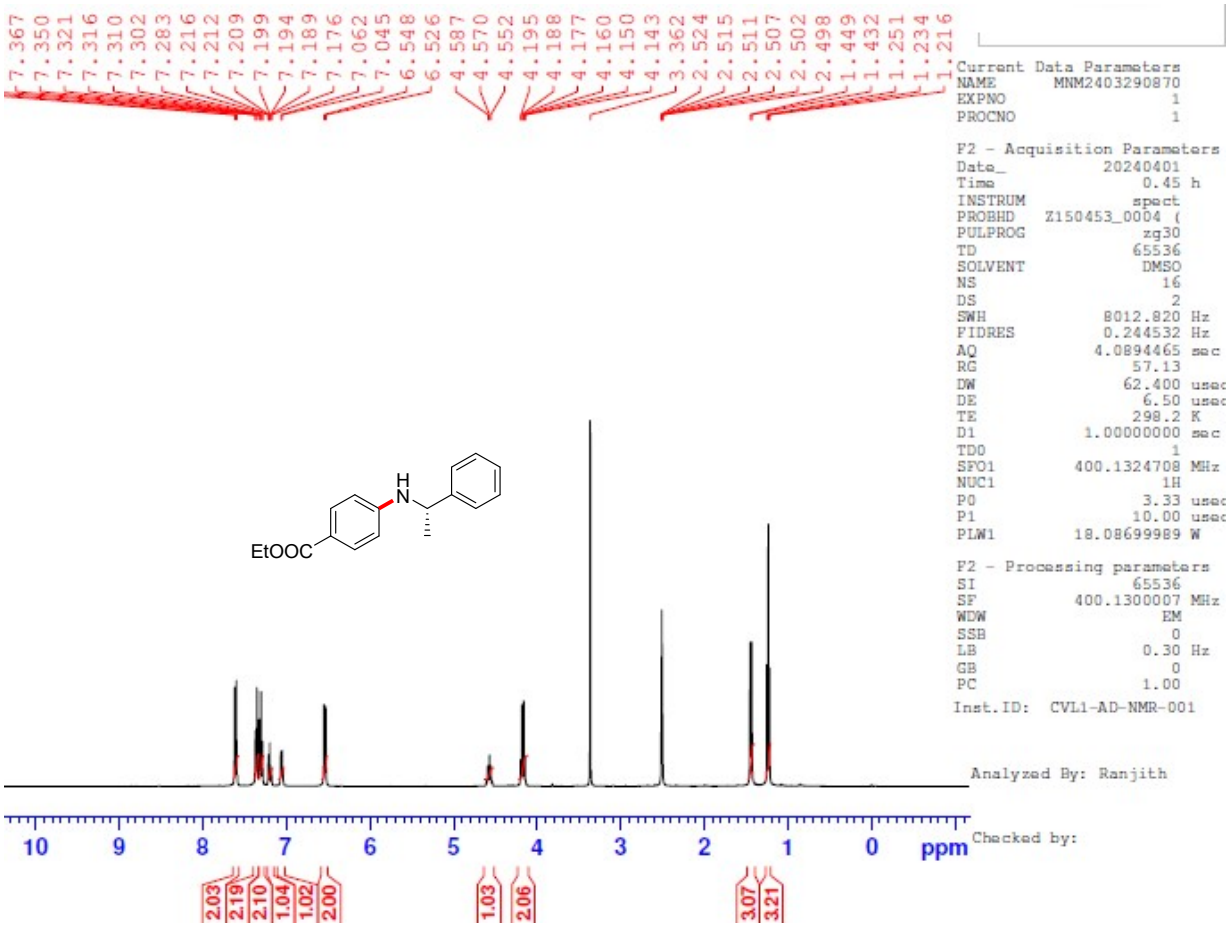
Methyl 4-(naphthalen-2-ylamino)benzoate (**21**) ^{13}C NMR (100 MHz, $CDCl_3$)



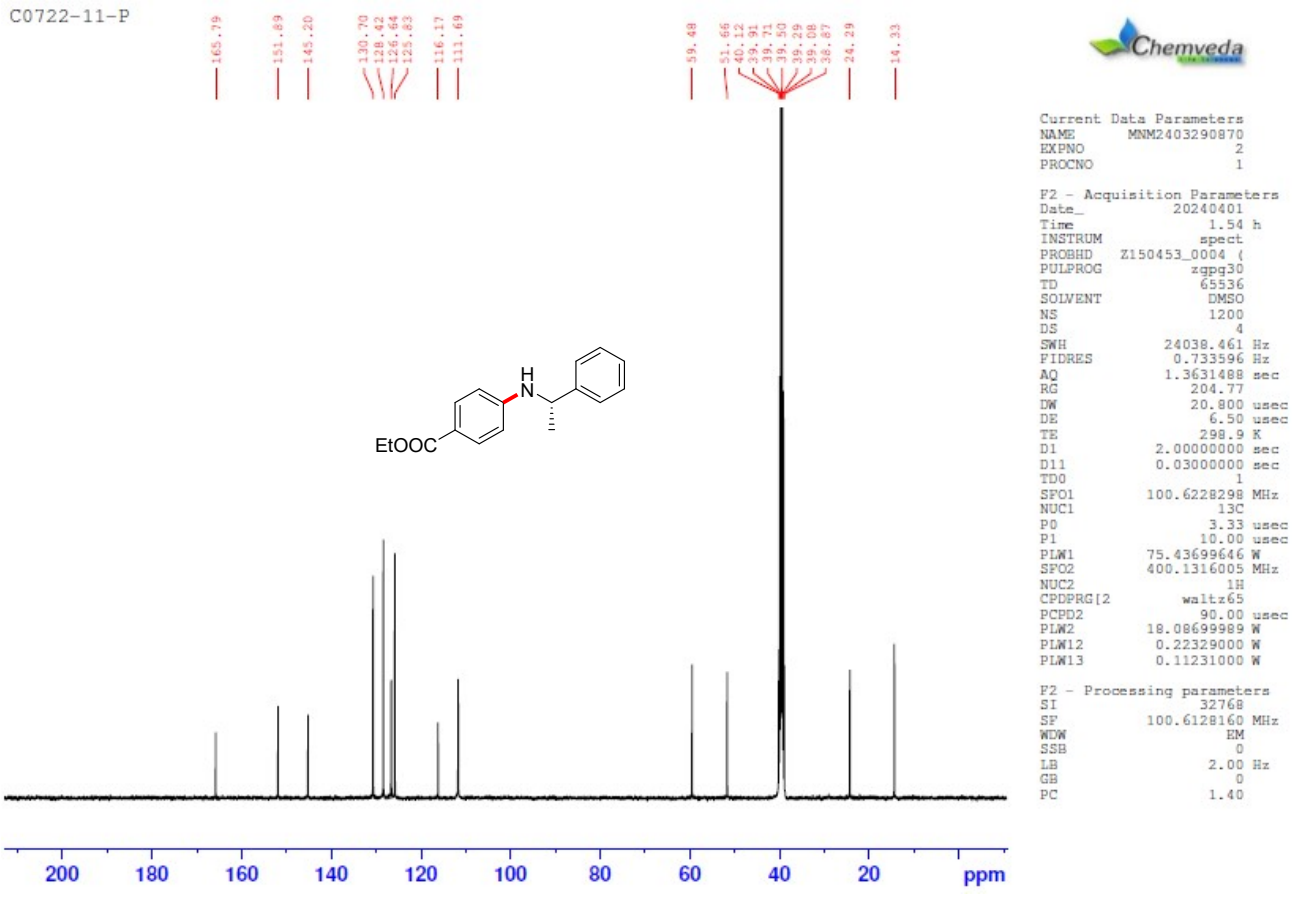
Ethyl (R)-4-((1-phenylethyl)amino)benzoate (**22**) ^{1}H NMR (400 MHz, DMSO-d_6)



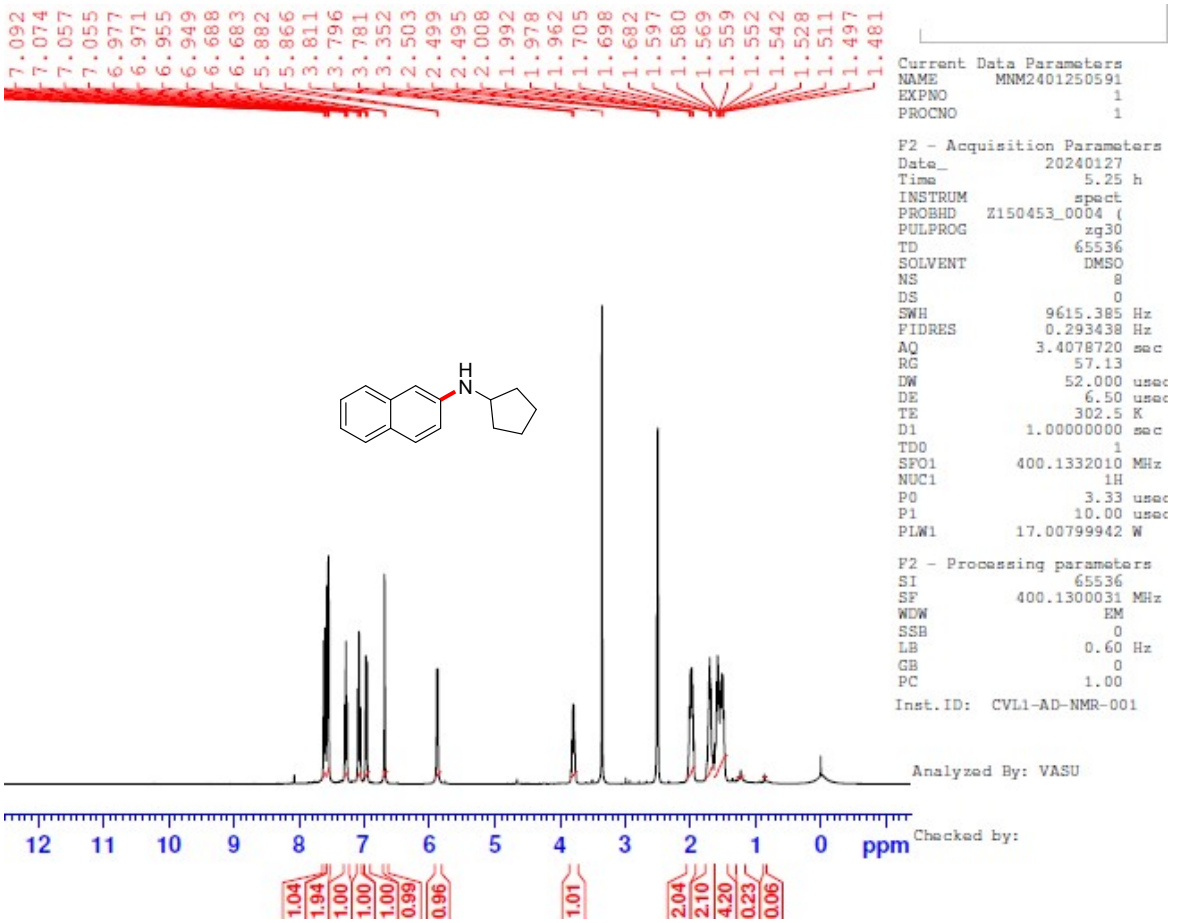
Ethyl (R)-4-((1-phenylethyl)amino)benzoate (**22**) ^{13}C NMR (100 MHz, DMSO-d_6)



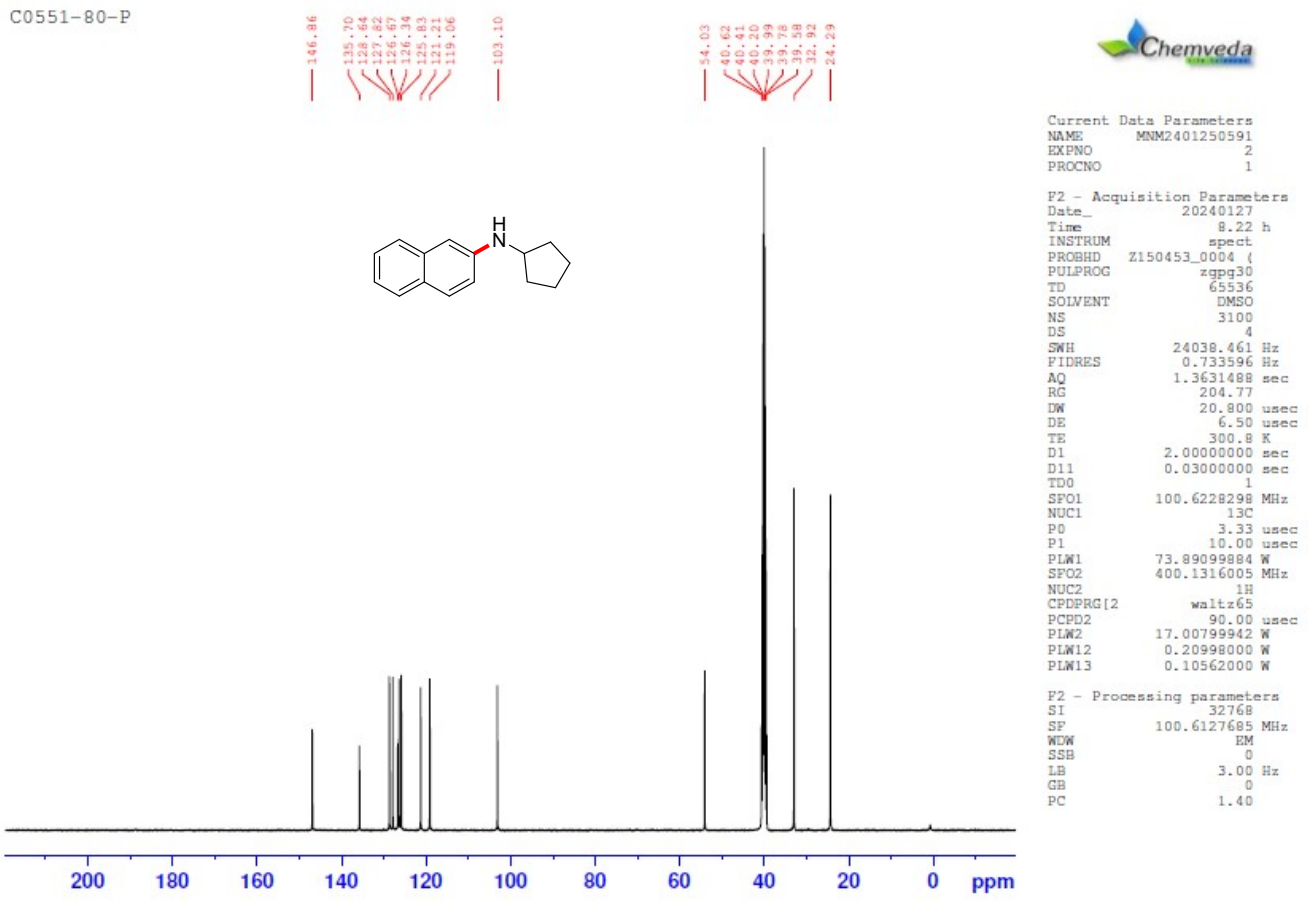
Ethyl (S)-4-((1-phenylethyl)amino)benzoate (**23**) ^{1}H NMR (400 MHz, DMSO-d_6)



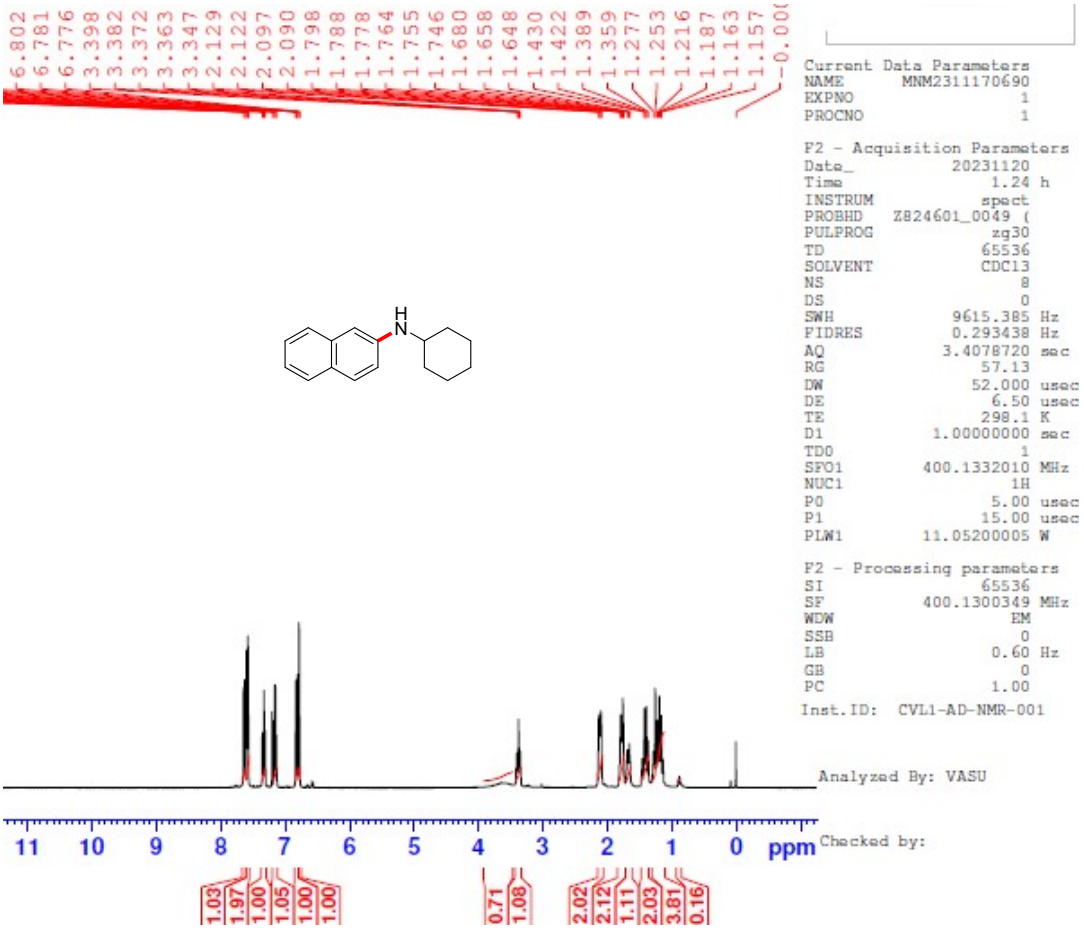
Ethyl (S)-4-((1-phenylethyl)amino)benzoate (**23**) ^{13}C NMR (100 MHz, DMSO-d_6)



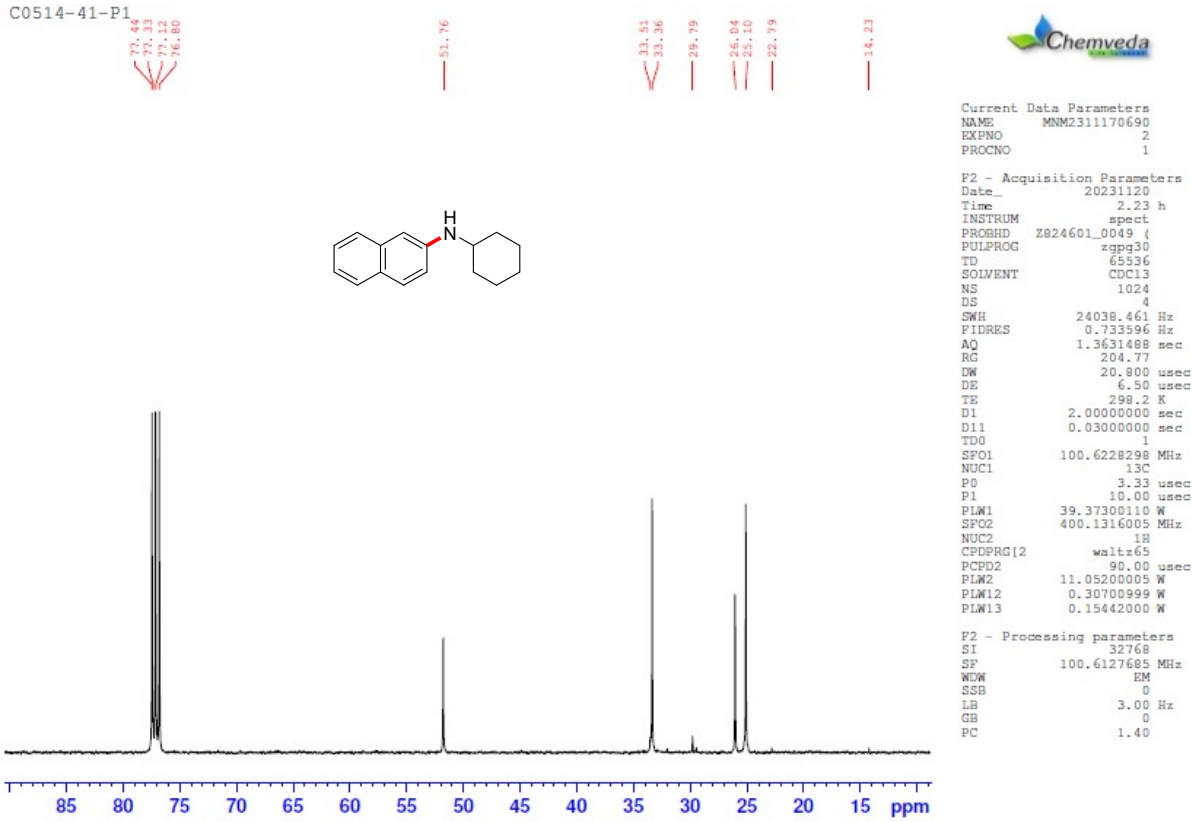
N-Cyclopentylnaphthalen-2-amine (**24**) ^{1}H NMR (400 MHz, DMSO-d_6)



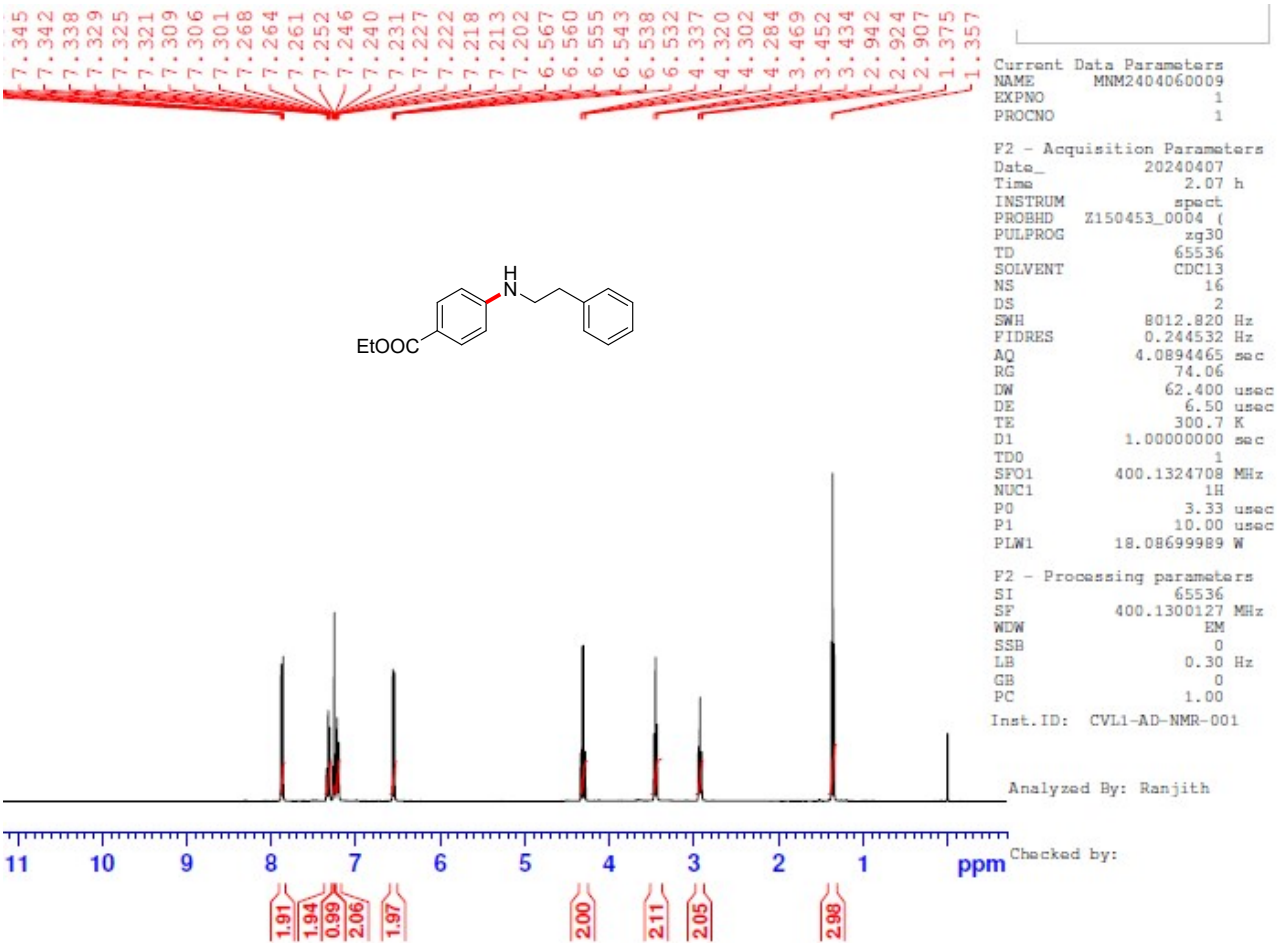
N-Cyclopentylnaphthalen-2-amine (**24**) ^{13}C NMR (100 MHz, DMSO-d_6)



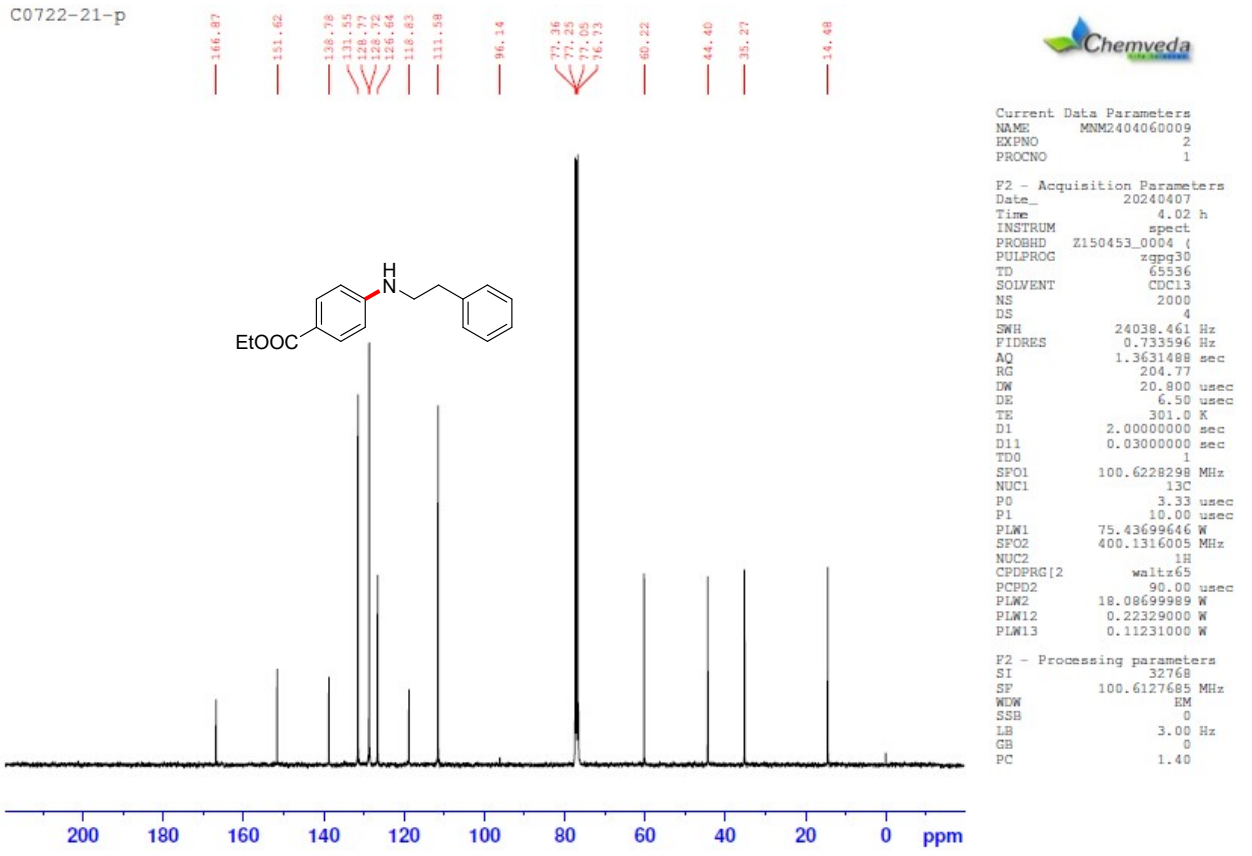
N-Cyclohexylnaphthalen-2-amine (**25**) ^{1}H NMR (400 MHz, $CDCl_3$)



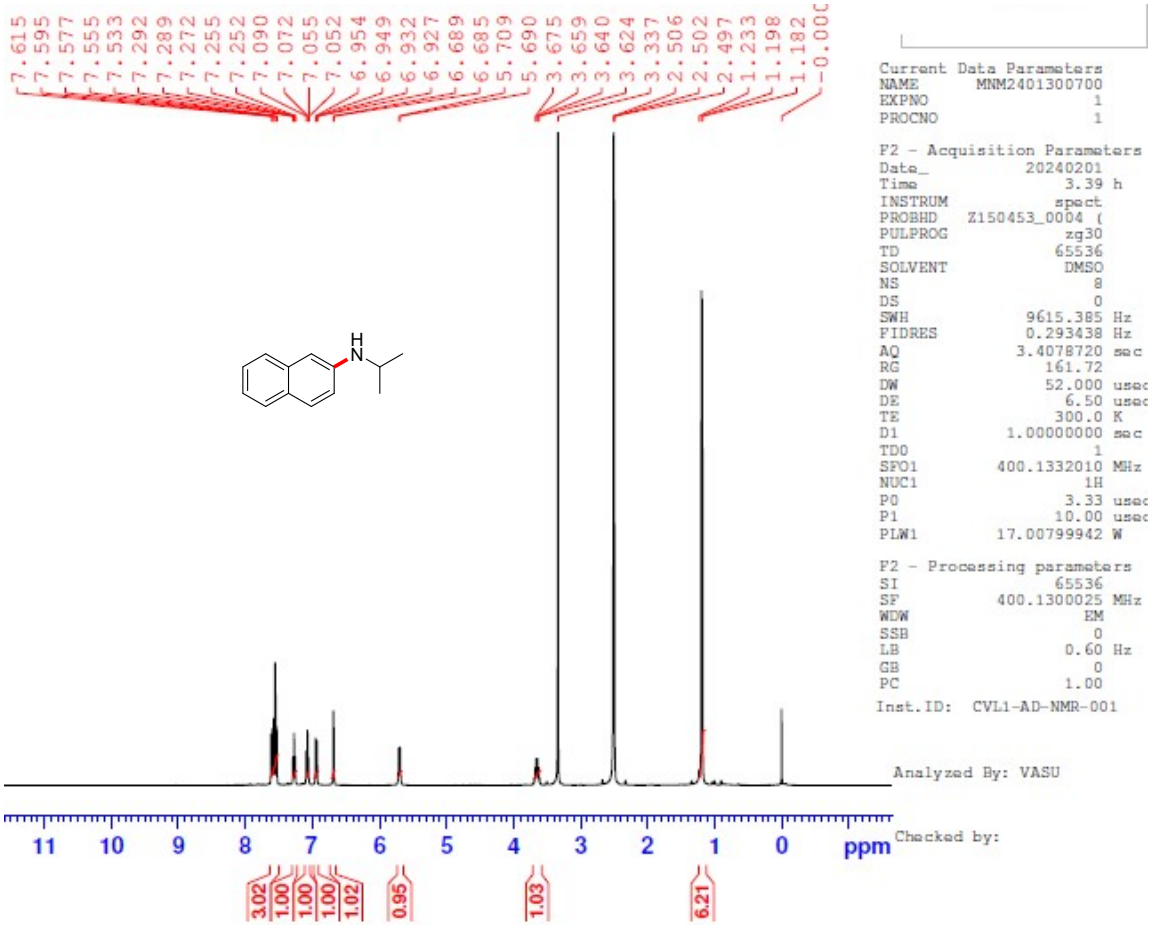
N-Cyclohexylnaphthalen-2-amine (**25**) ^{13}C NMR (100 MHz, $CDCl_3$)



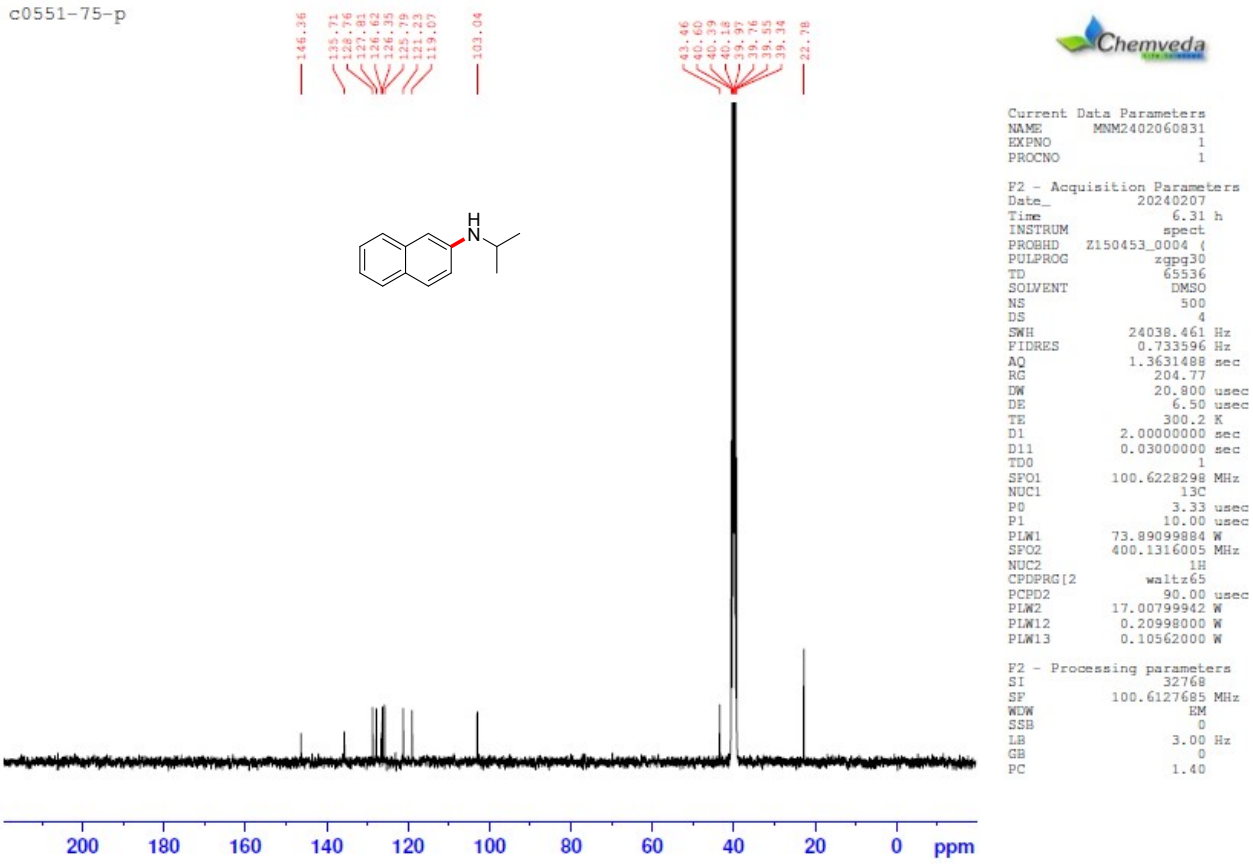
Ethyl 4-(phenethylamino)benzoate (**26**) ^{1}H NMR (400 MHz, $CDCl_3$)



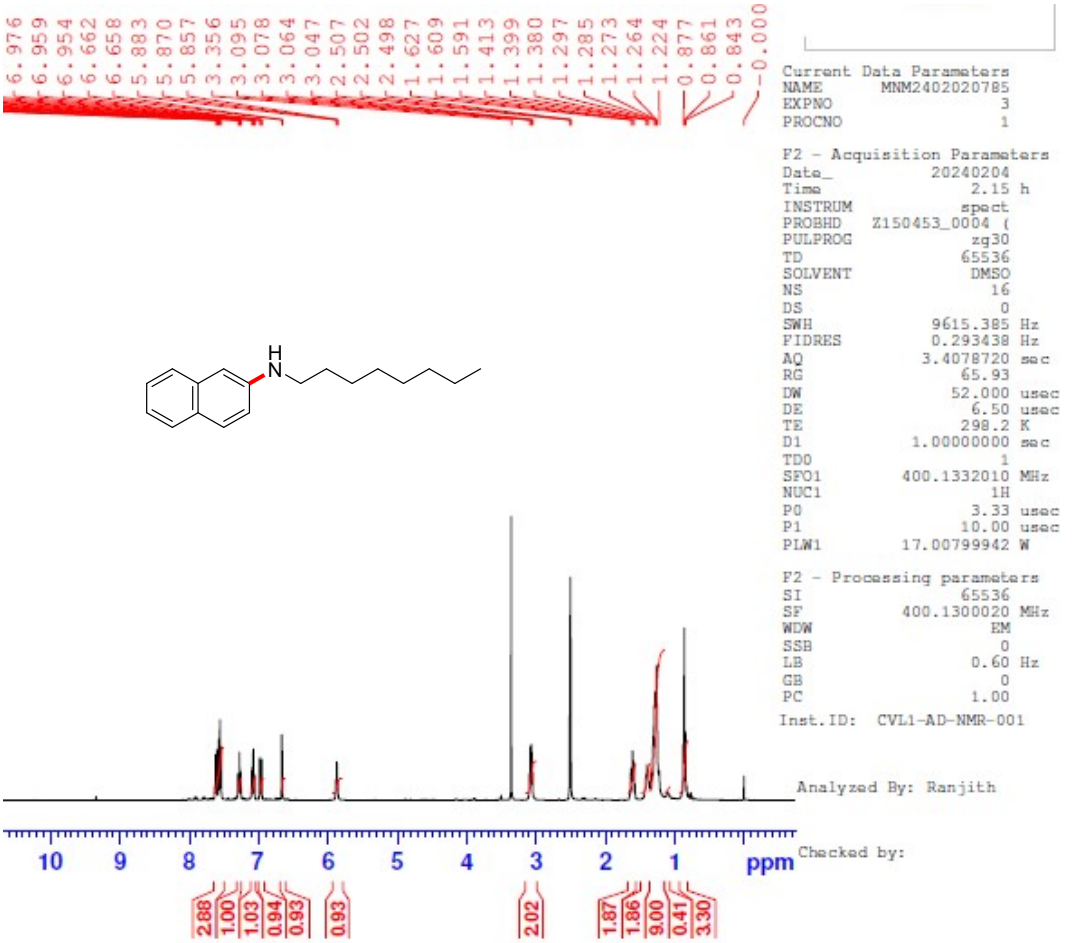
Ethyl 4-(phenethylamino)benzoate (**26**) ^{13}C NMR (100 MHz, $CDCl_3$)



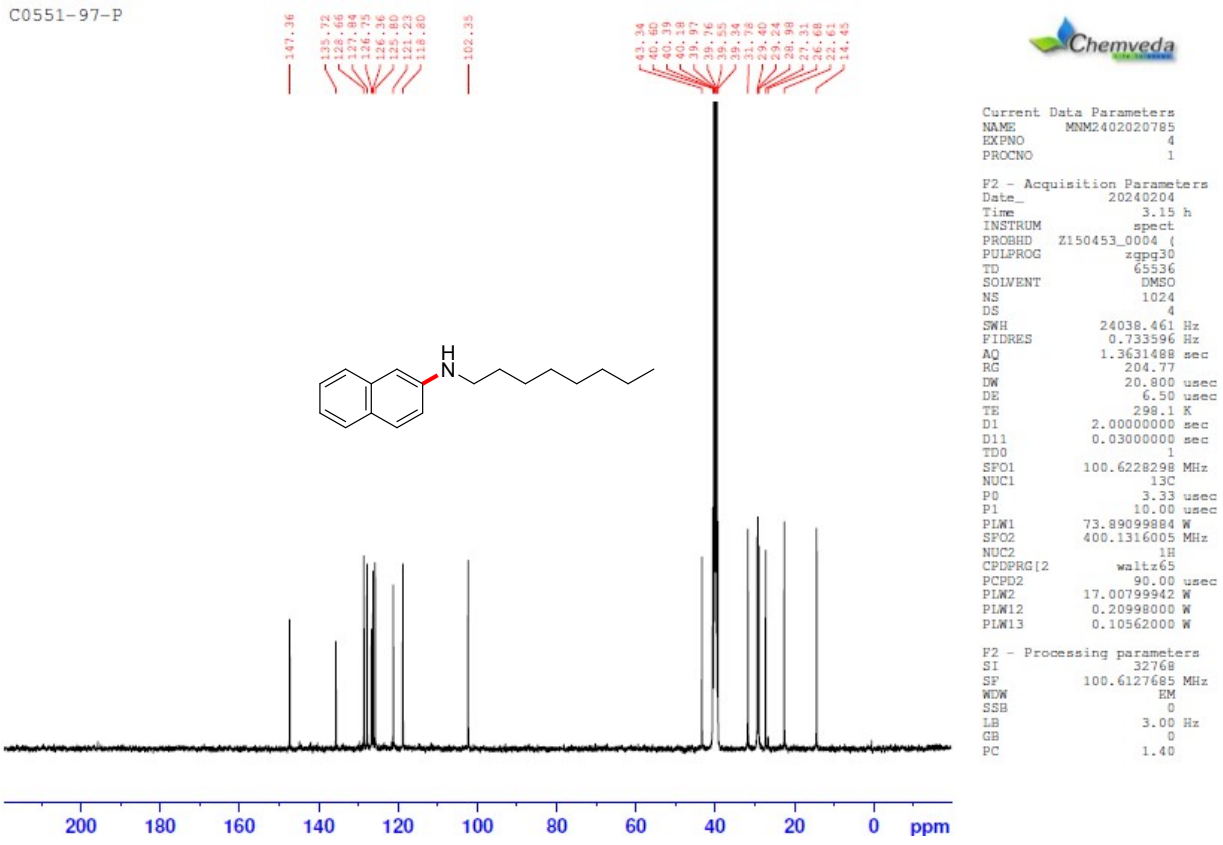
N-Isopropylnaphthalen-2-amine (**27**) ^{1}H NMR (400 MHz, DMSO-d_6)



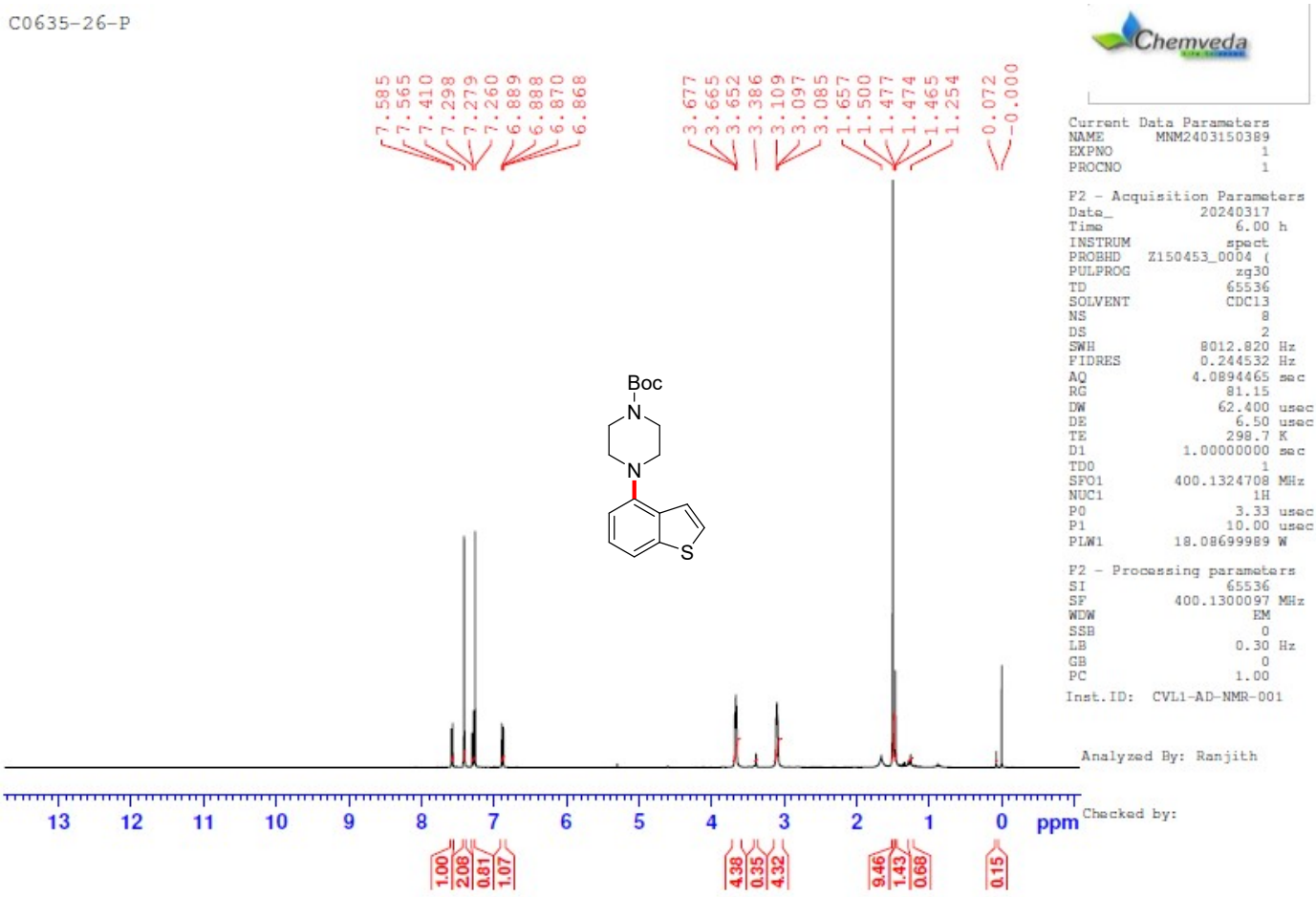
N-Isopropylnaphthalen-2-amine (**27**) ^{13}C NMR (100 MHz, DMSO-d_6)



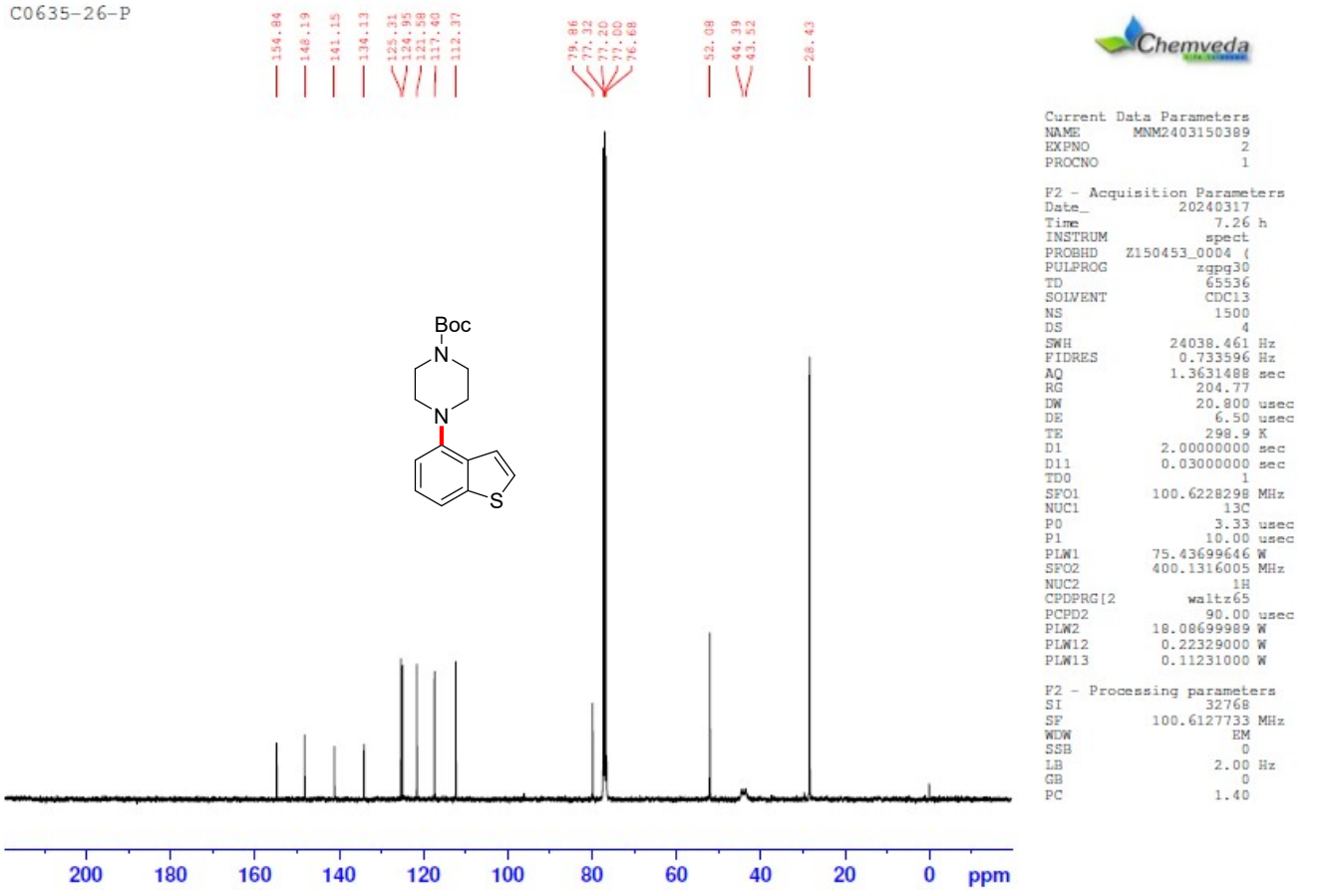
N-Octylnaphthalen-2-amine (**28**) ^{1}H NMR (400 MHz, DMSO-d_6)



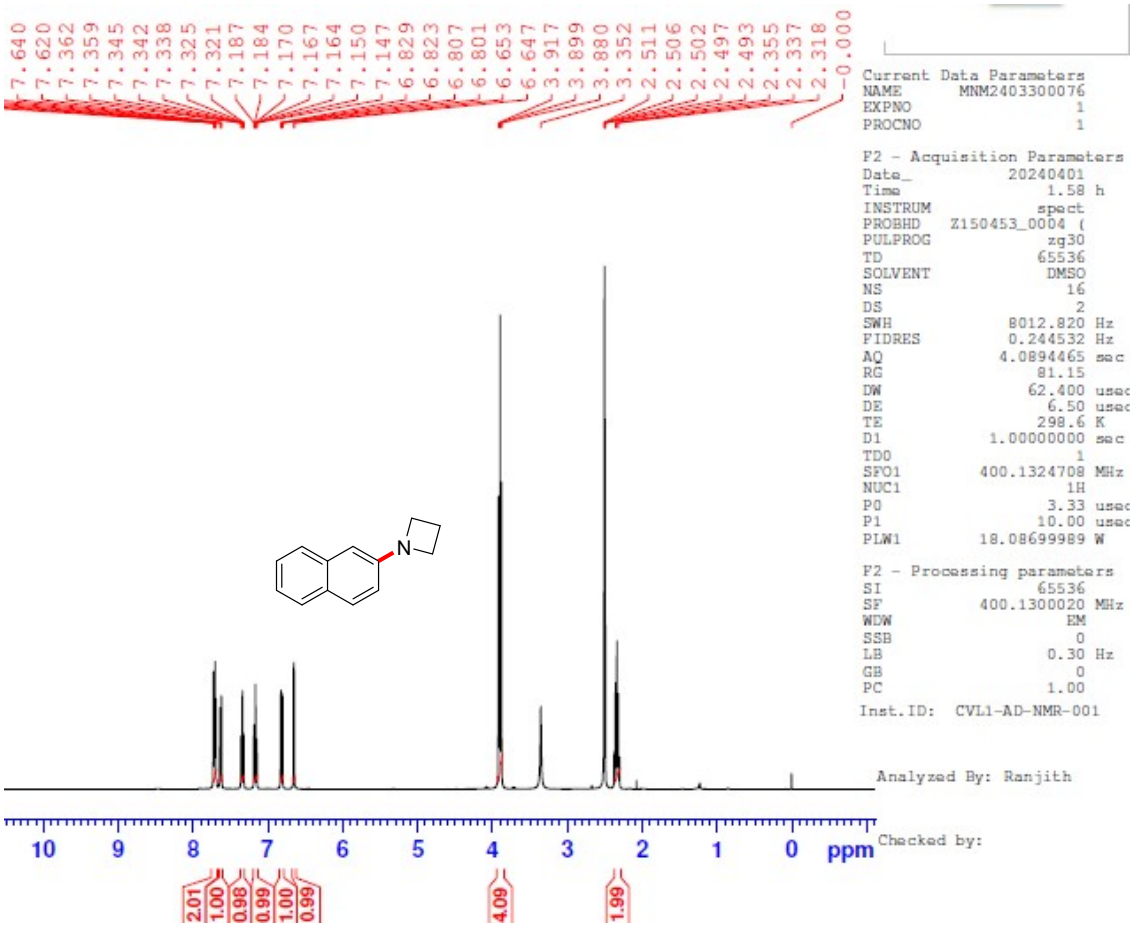
N-Octylnaphthalen-2-amine (**28**) ^{13}C NMR (100 MHz, DMSO-d_6)



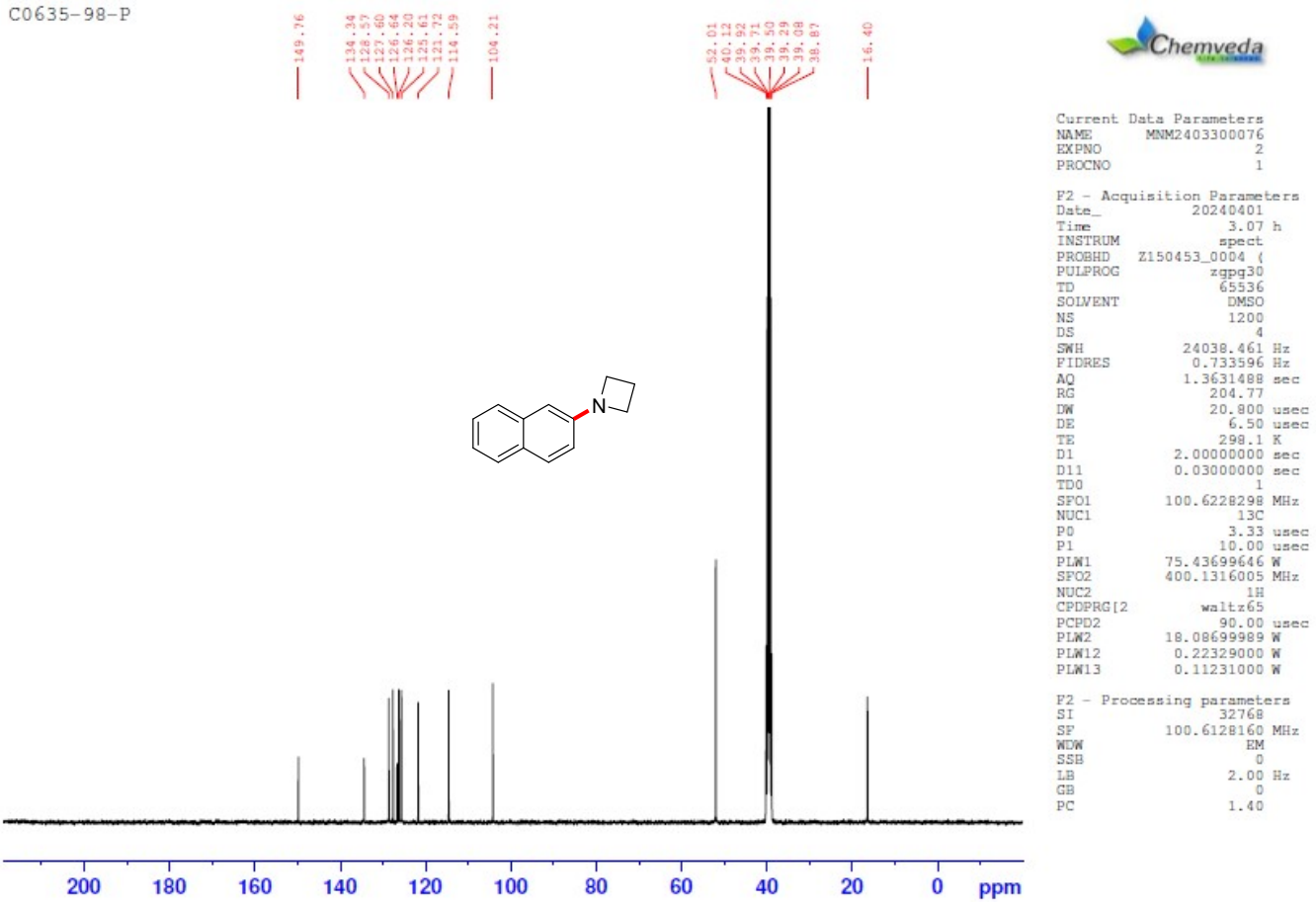
tert-Butyl 4-(benzo[b]thiophen-4-yl)piperazine-1-carboxylate (**29**) ^{1}H NMR (400 MHz, $CDCl_3$)



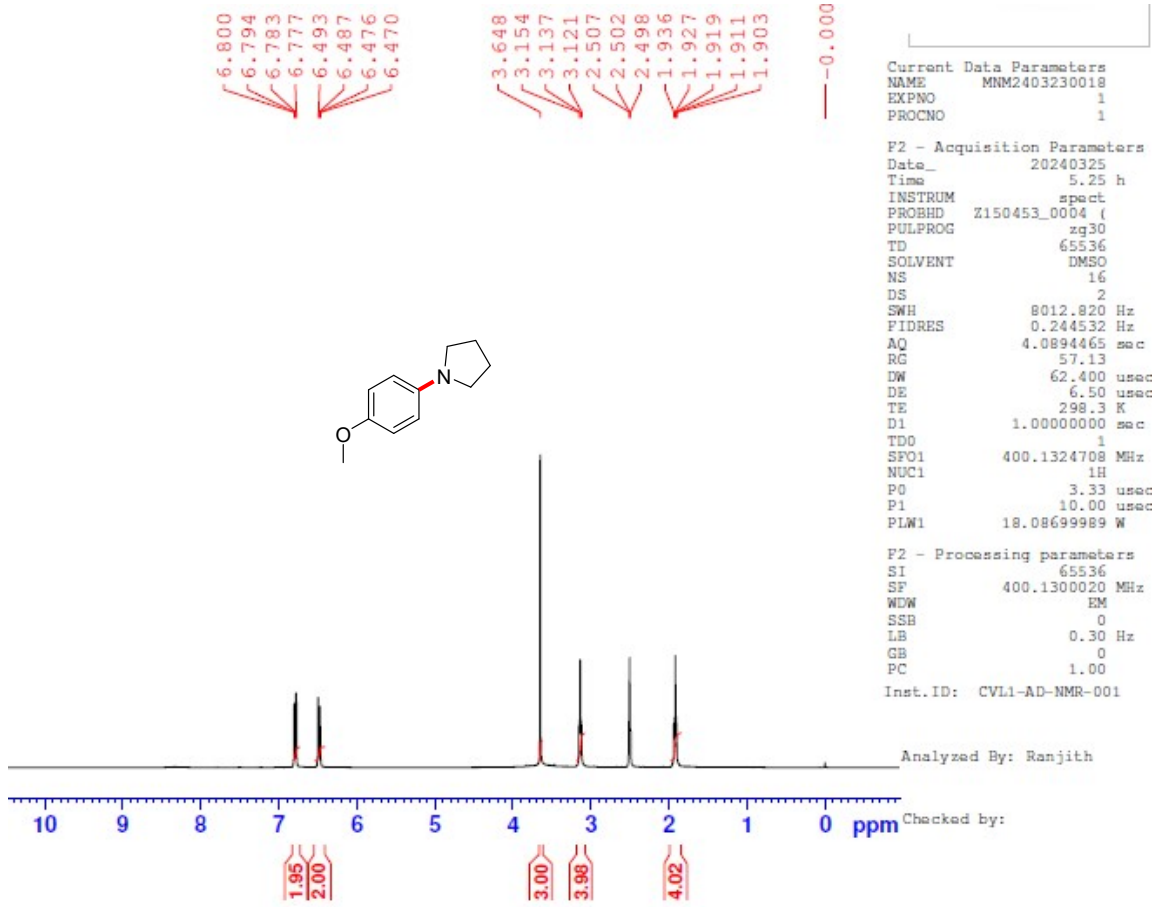
tert-Butyl 4-(benzo[b]thiophen-4-yl)piperazine-1-carboxylate (**29**) ^{13}C NMR (100 MHz, $CDCl_3$)



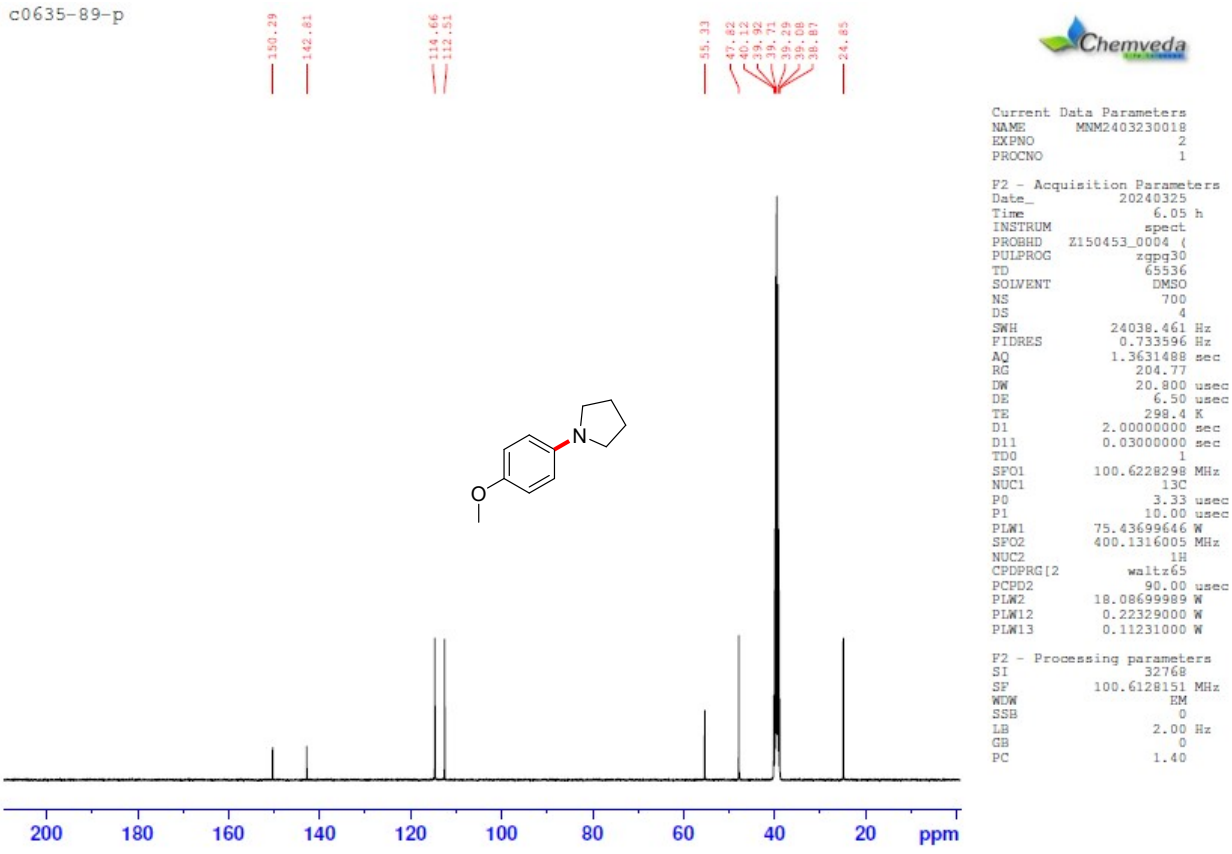
1-(Naphthalen-2-yl)azetidine (**30**) ^{1}H NMR (400 MHz, DMSO-d_6)



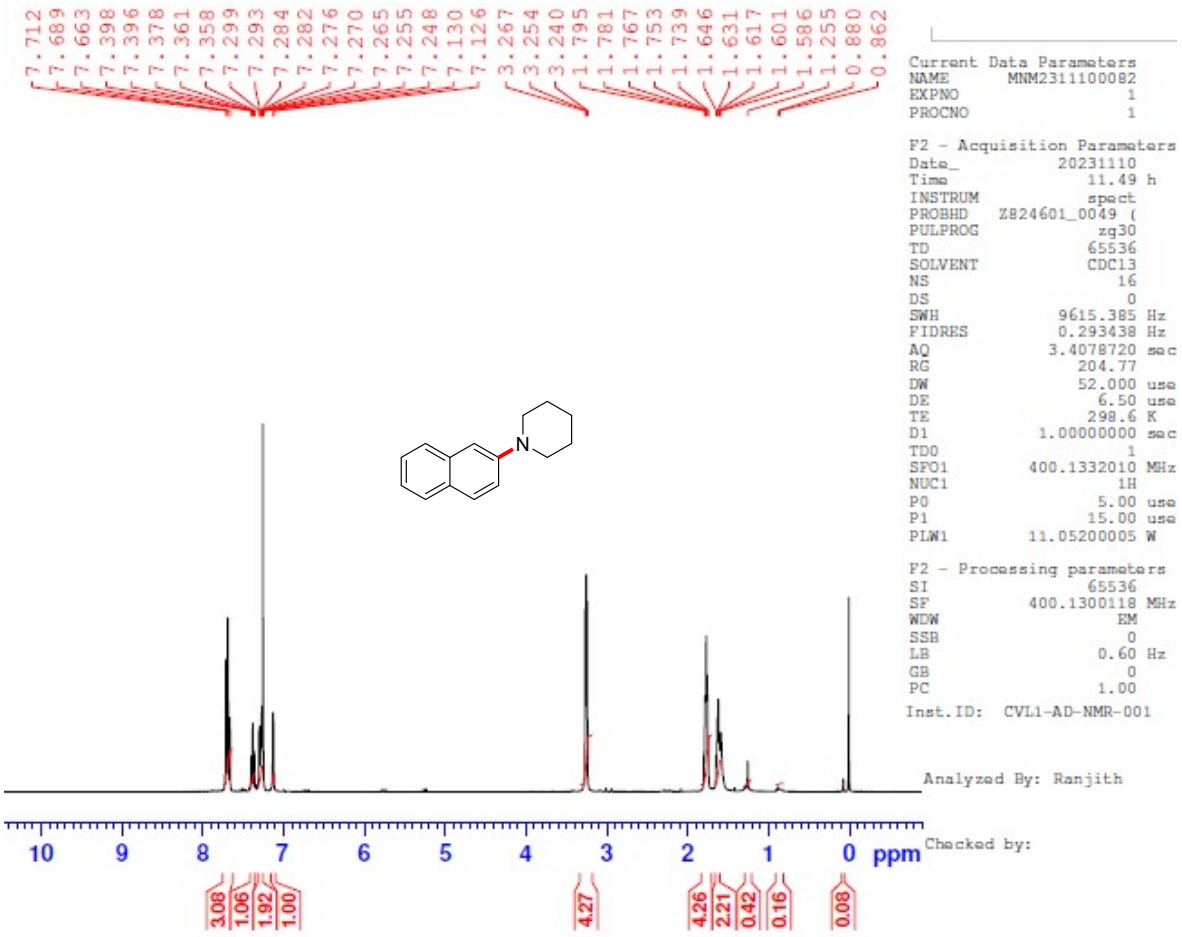
1-(Naphthalen-2-yl)azetidine (**30**) ^{13}C NMR (100 MHz, DMSO-d_6)



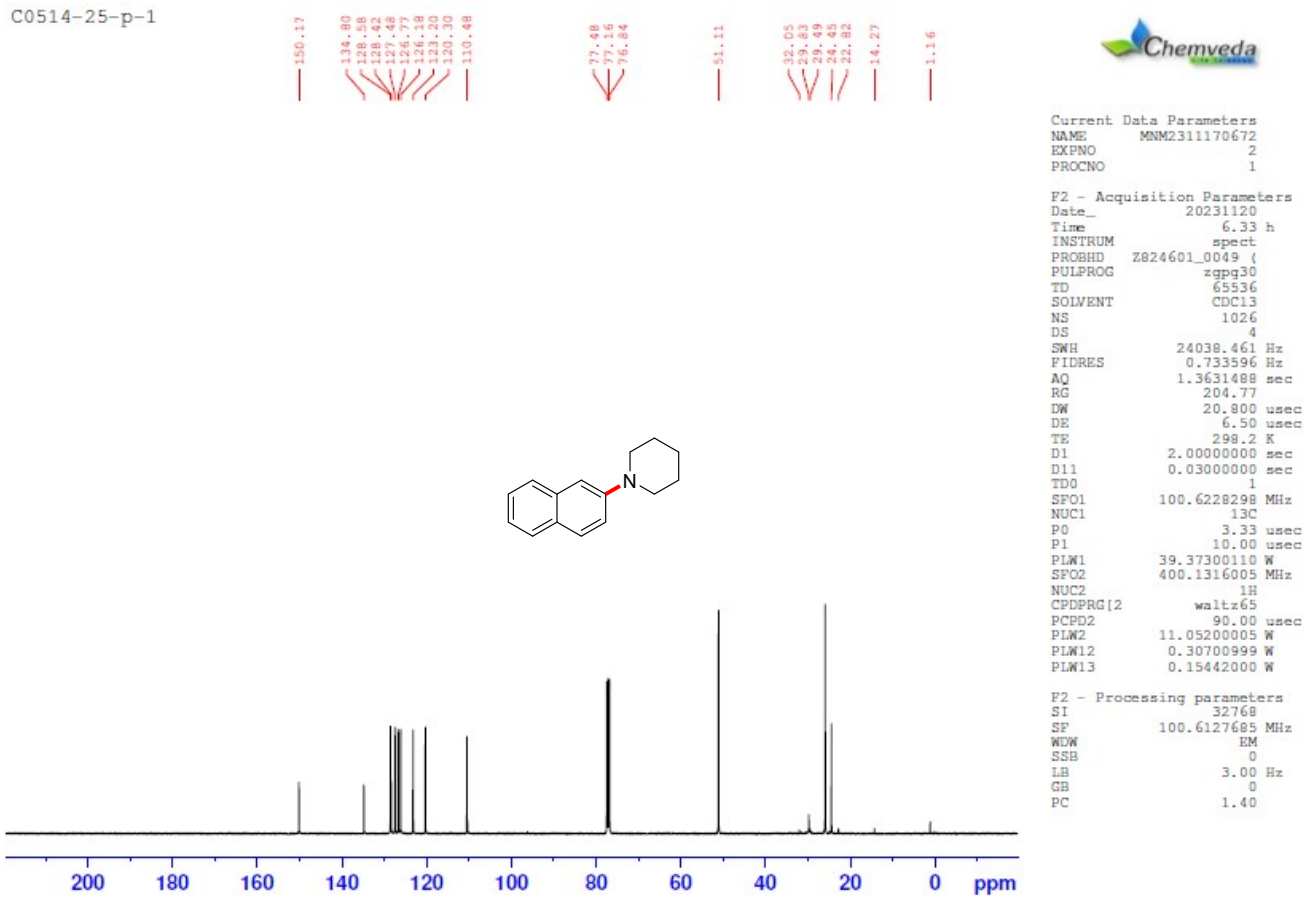
1-(4-Methoxyphenyl)pyrrolidine (**31**) ^{1}H NMR (400 MHz, DMSO-d_6)



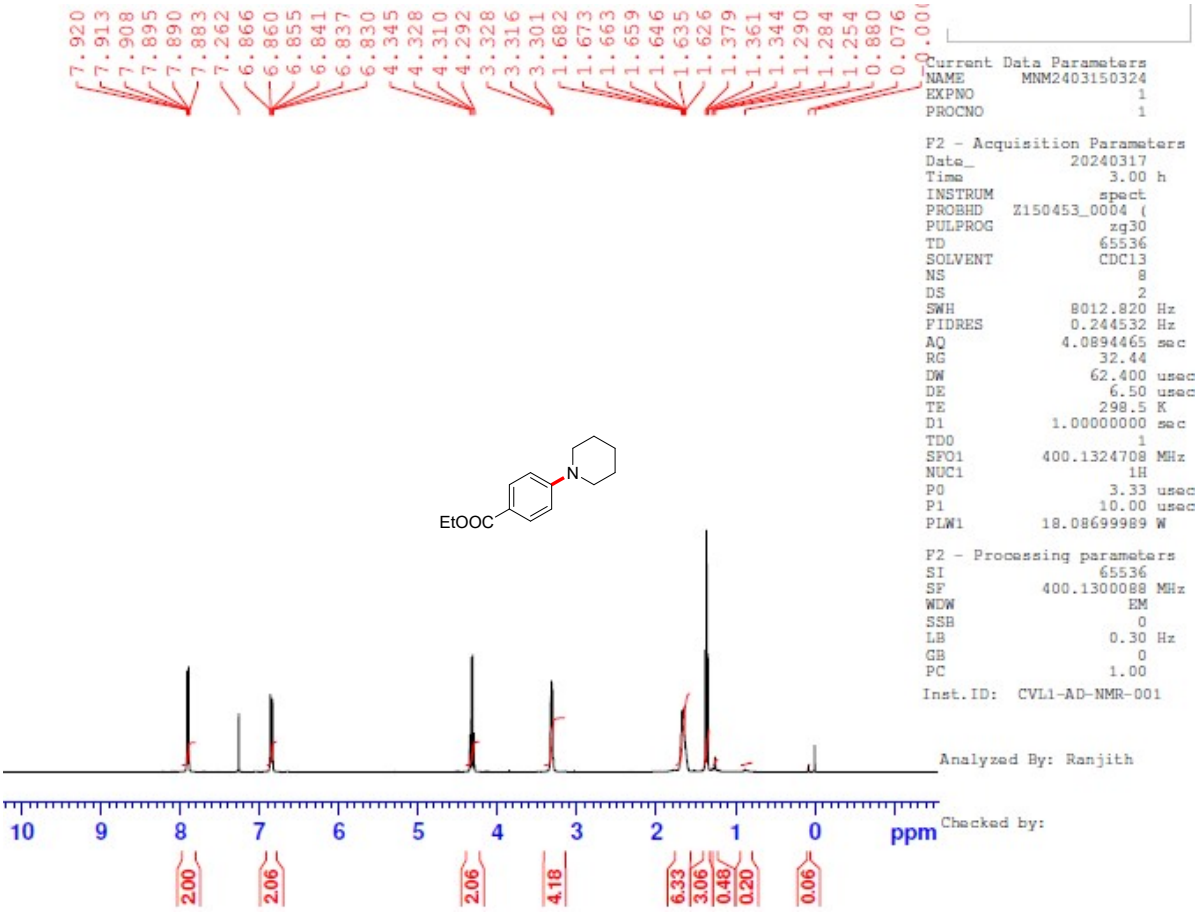
1-(4-Methoxyphenyl)pyrrolidine (**31**) ^{13}C NMR (100 MHz, DMSO-d_6)



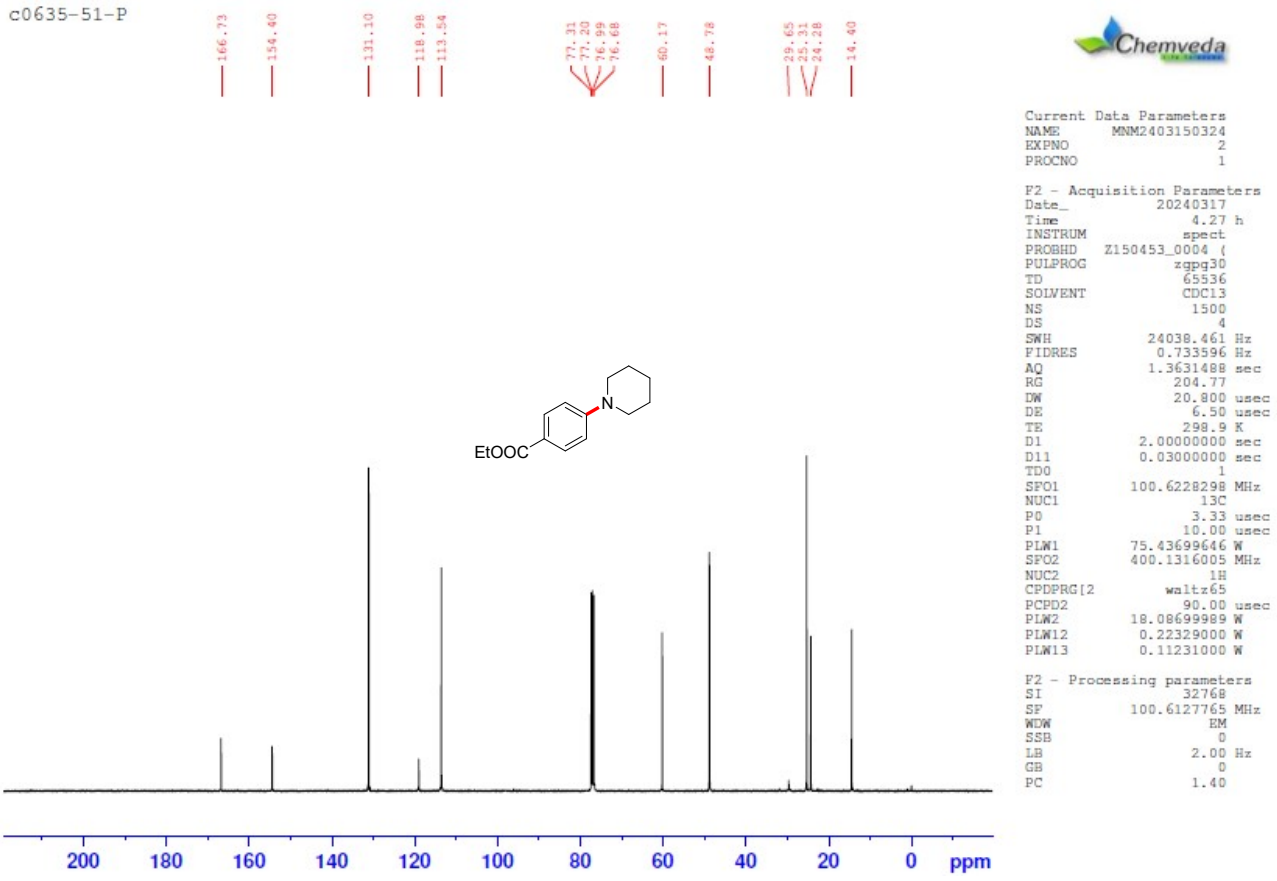
1-(Naphthalen-2-yl)piperidine (**32**) ^{1}H NMR (400 MHz, $CDCl_3$)



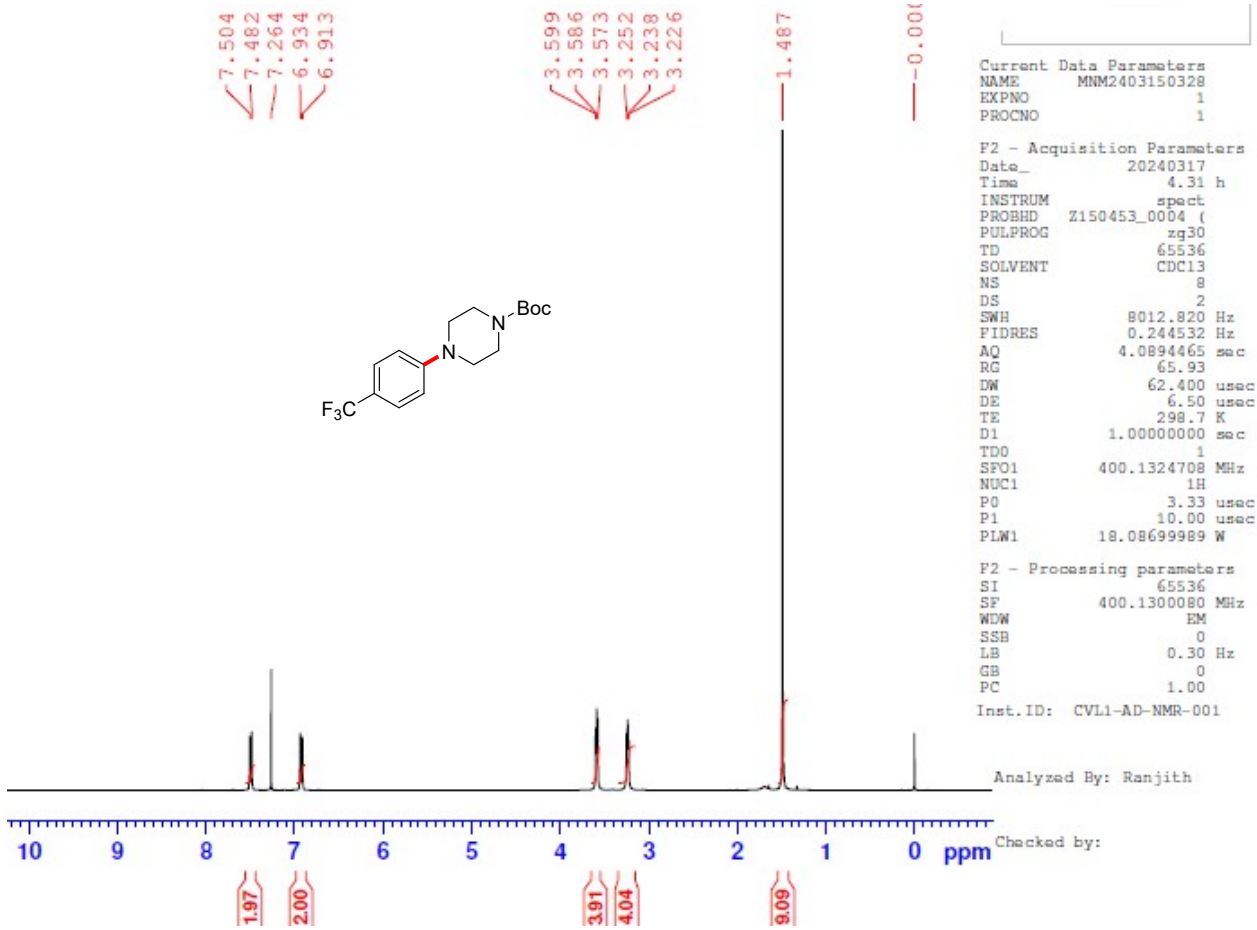
1-(Naphthalen-2-yl)piperidine (**32**) ^{13}C NMR (100 MHz, $CDCl_3$)



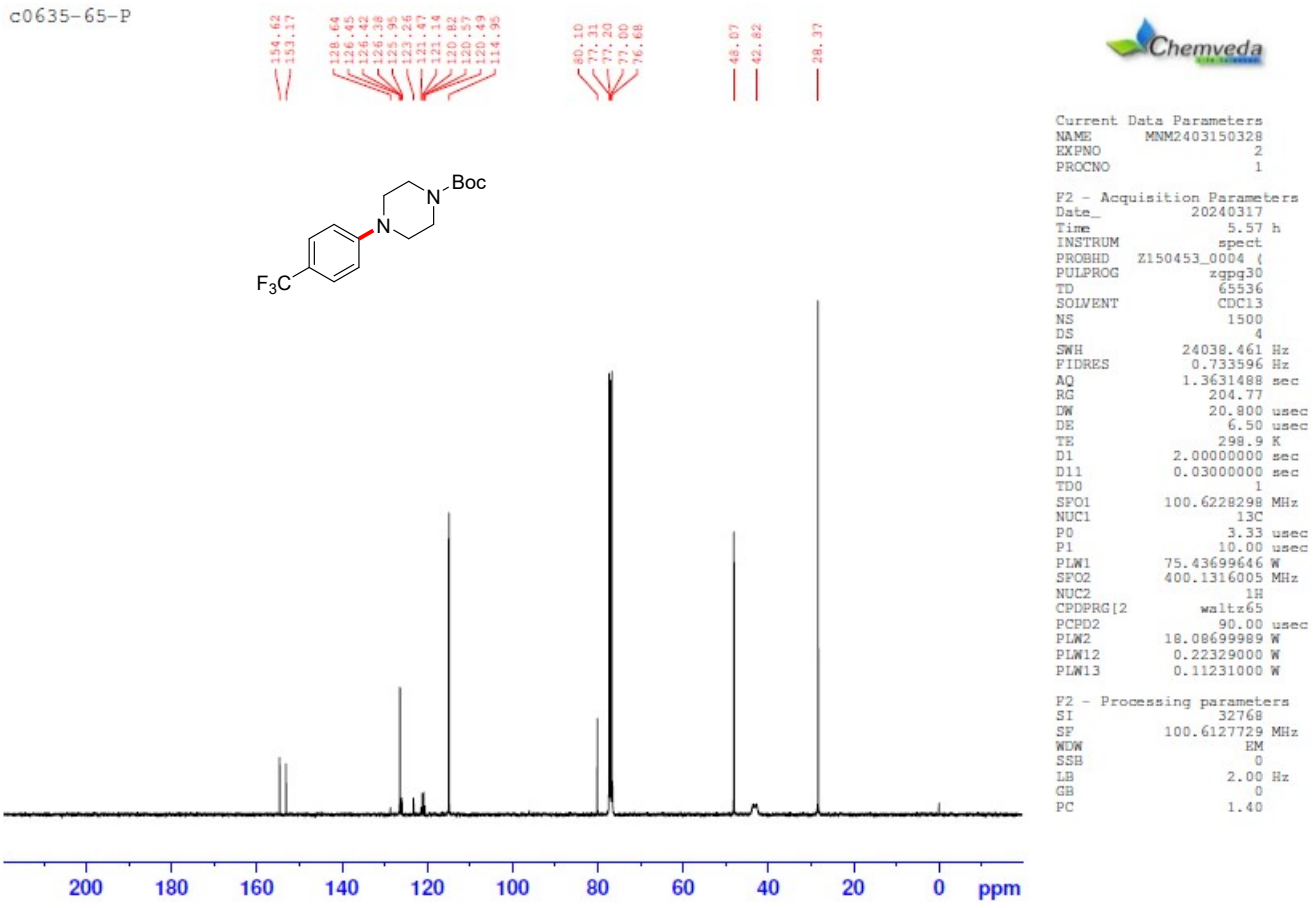
Ethyl 4-(piperidin-1-yl)benzoate (**33**) ^{1}H NMR (400 MHz, $CDCl_3$)



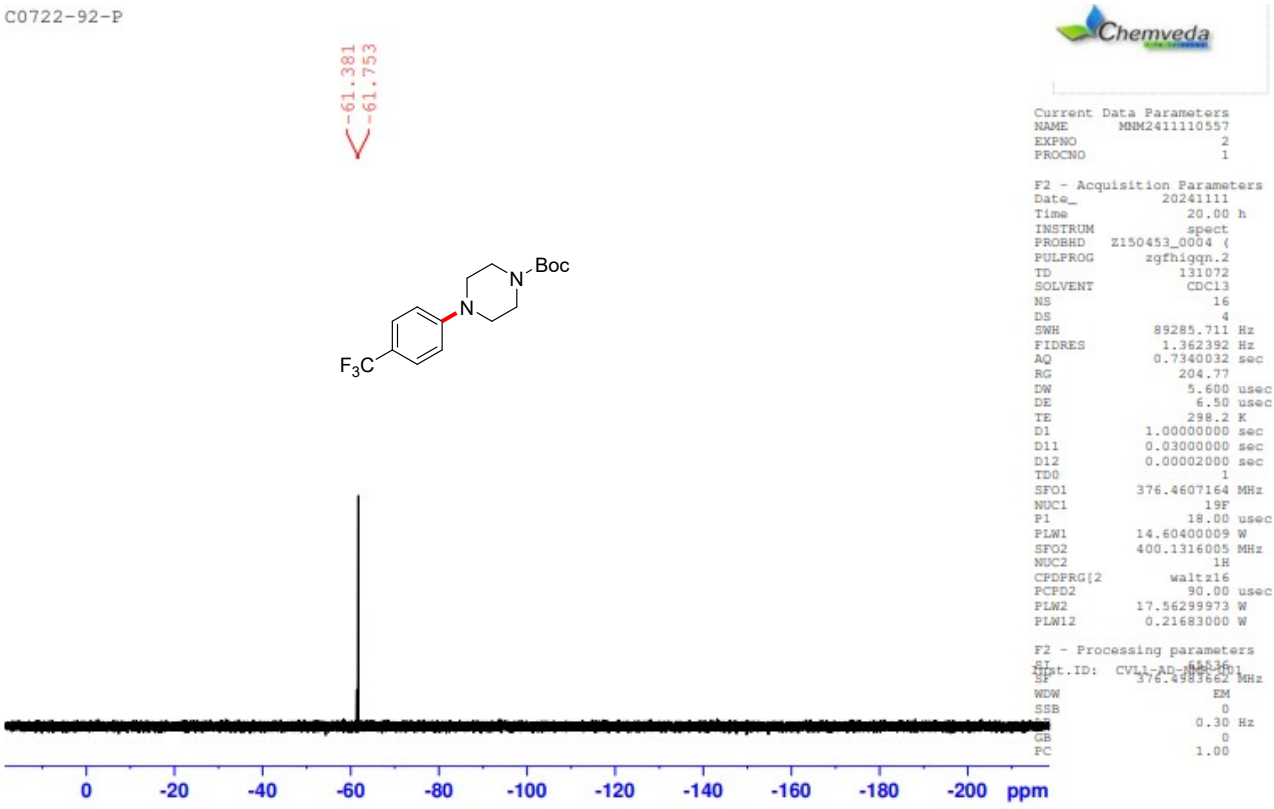
Ethyl 4-(piperidin-1-yl)benzoate (**33**) ^{13}C NMR (100 MHz, $CDCl_3$)



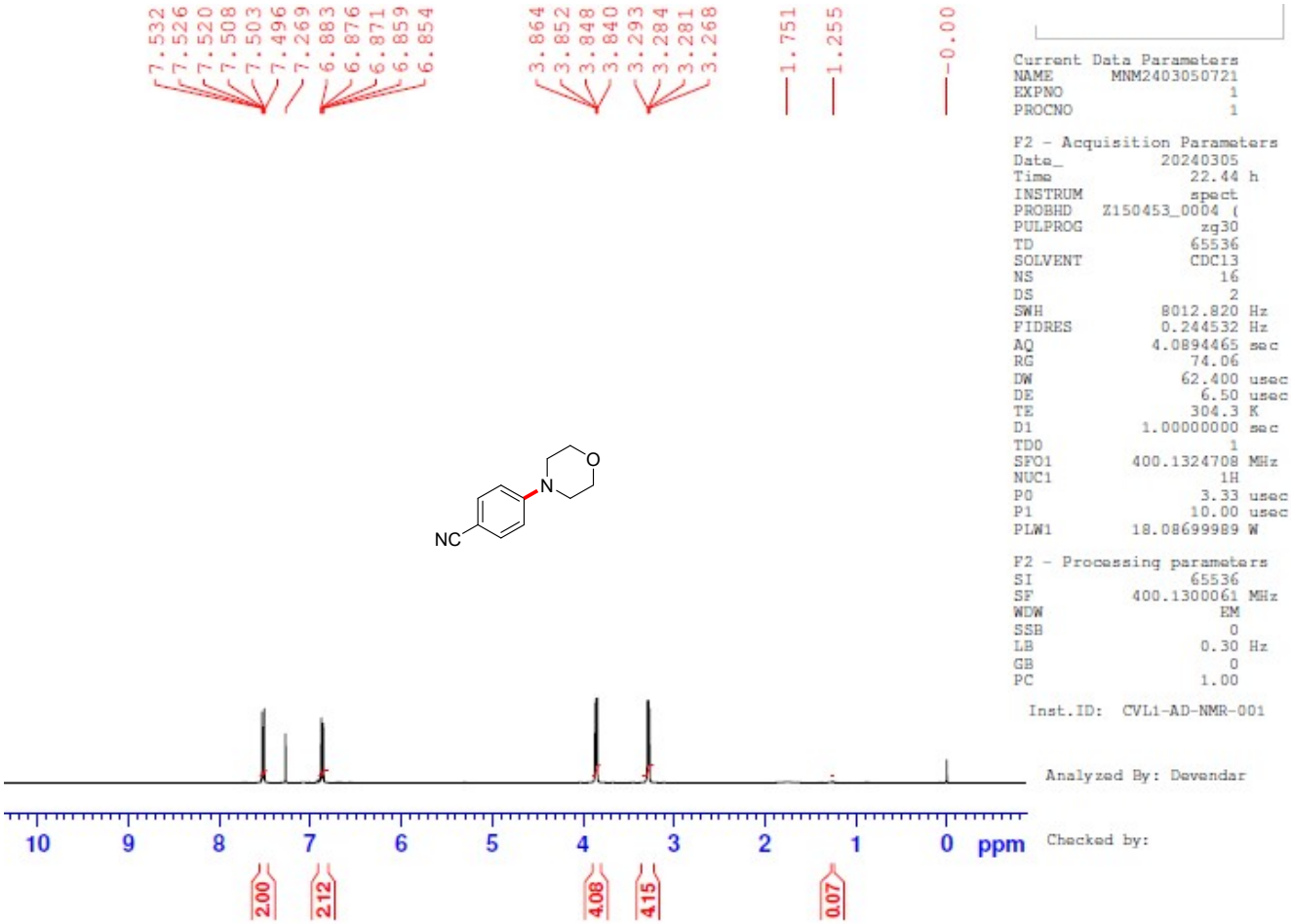
tert-Butyl 4-(4-(trifluoromethyl)phenyl)piperazine-1-carboxylate (**34**) ^{1}H NMR (400 MHz, $CDCl_3$)



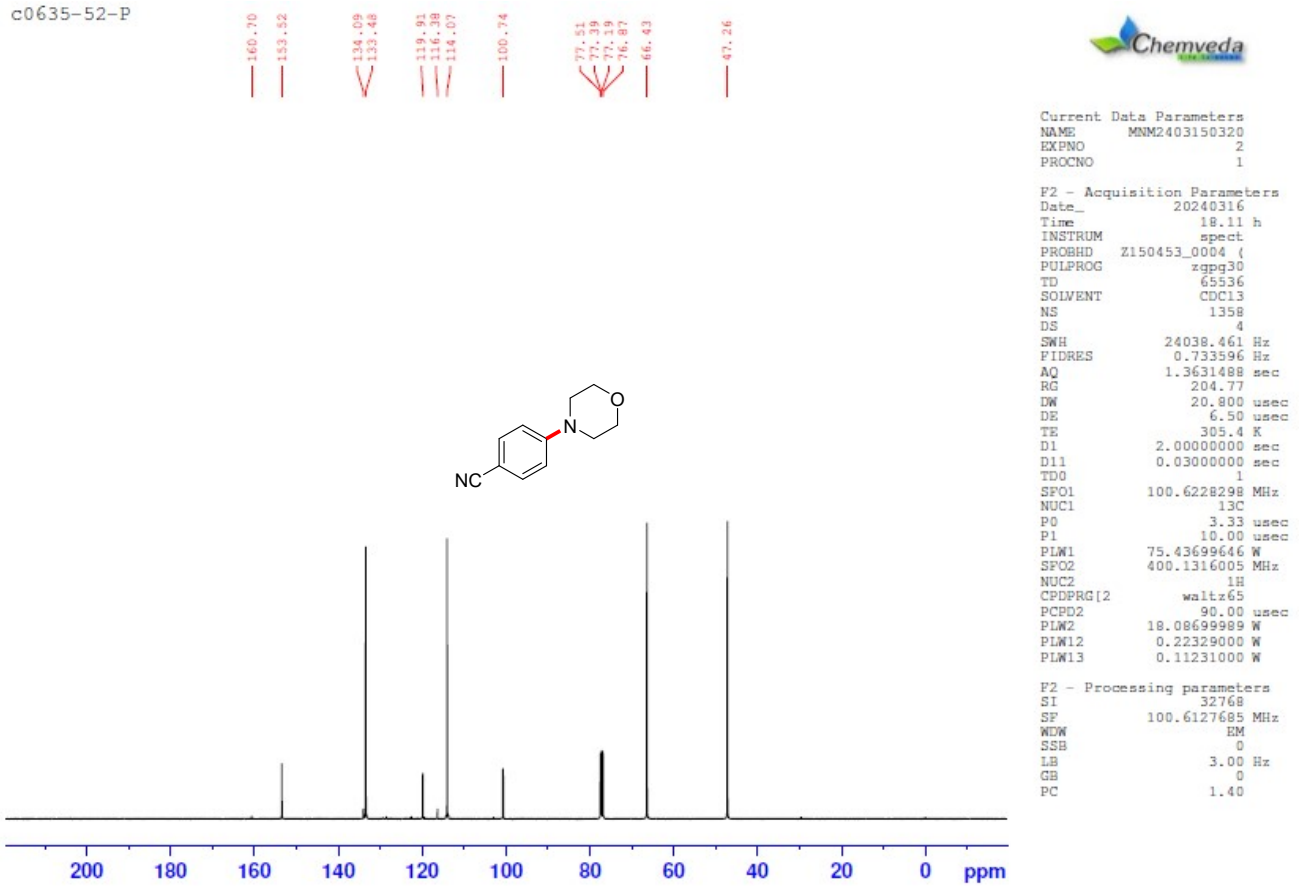
tert-Butyl 4-(4-(trifluoromethyl)phenyl)piperazine-1-carboxylate (**34**) ^{13}C NMR (100 MHz, $CDCl_3$)



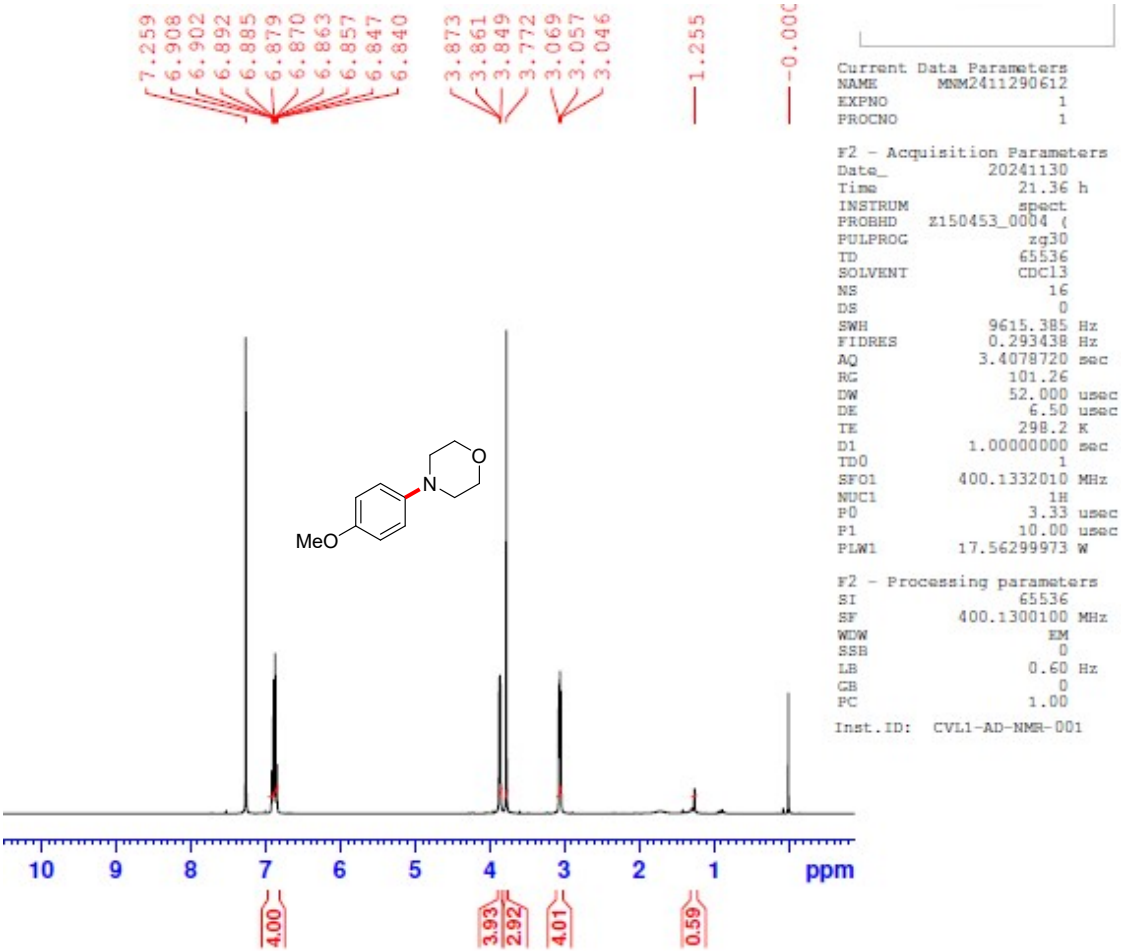
tert-Butyl 4-(4-(trifluoromethyl)phenyl)piperazine-1-carboxylate (**34**) ^{19}F NMR (376 MHz, $CDCl_3$)



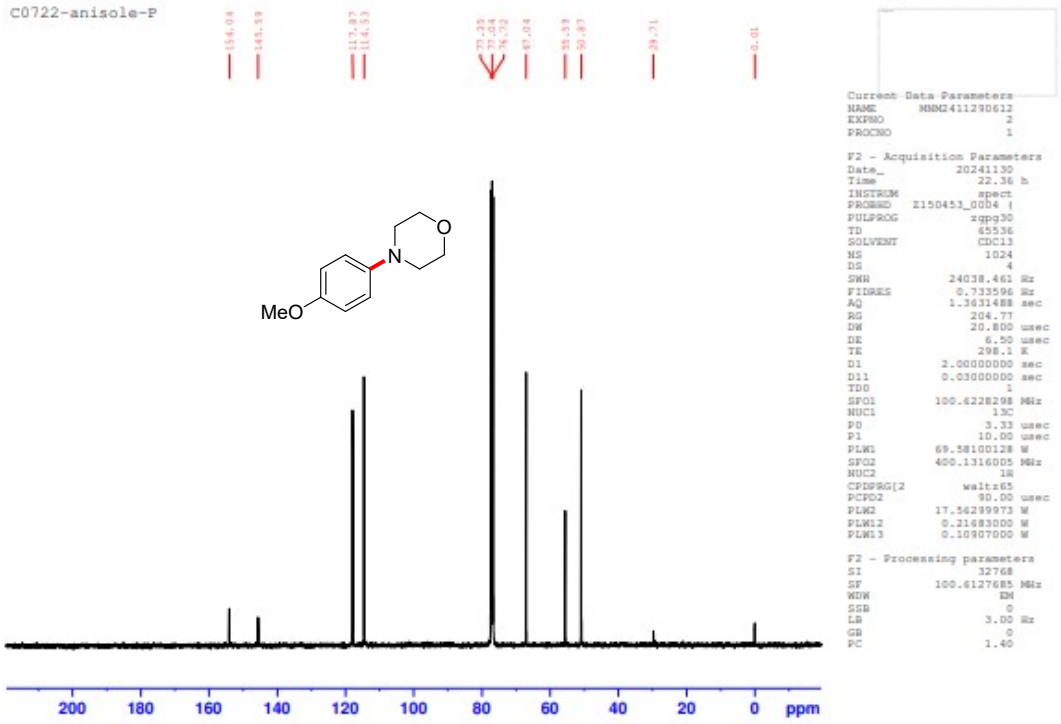
4-Morpholinobenzonitrile (**35**) ^{1}H NMR (400 MHz, $CDCl_3$)



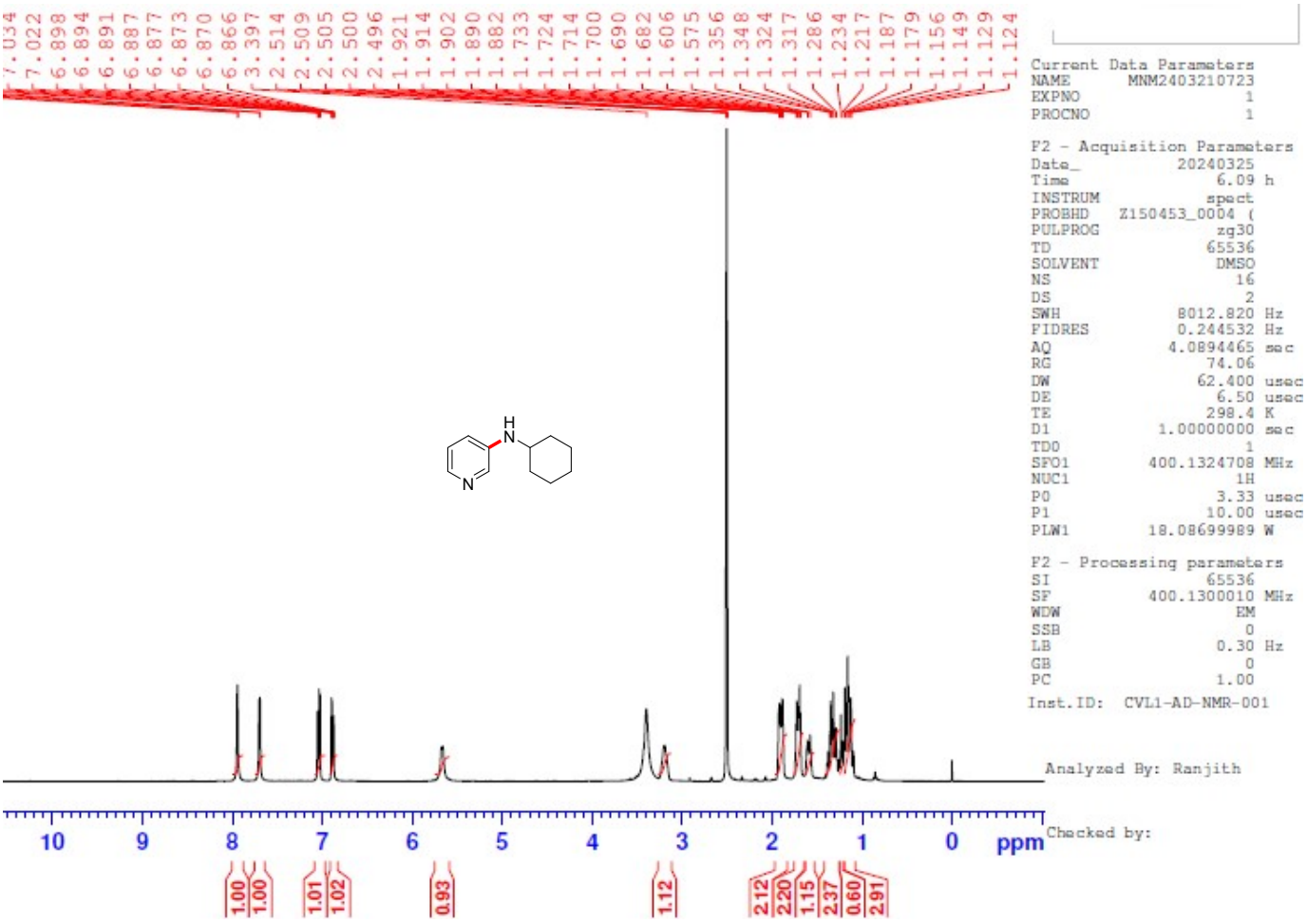
4-Morpholinobenzonitrile (**35**) ^{13}C NMR (100 MHz, $CDCl_3$)



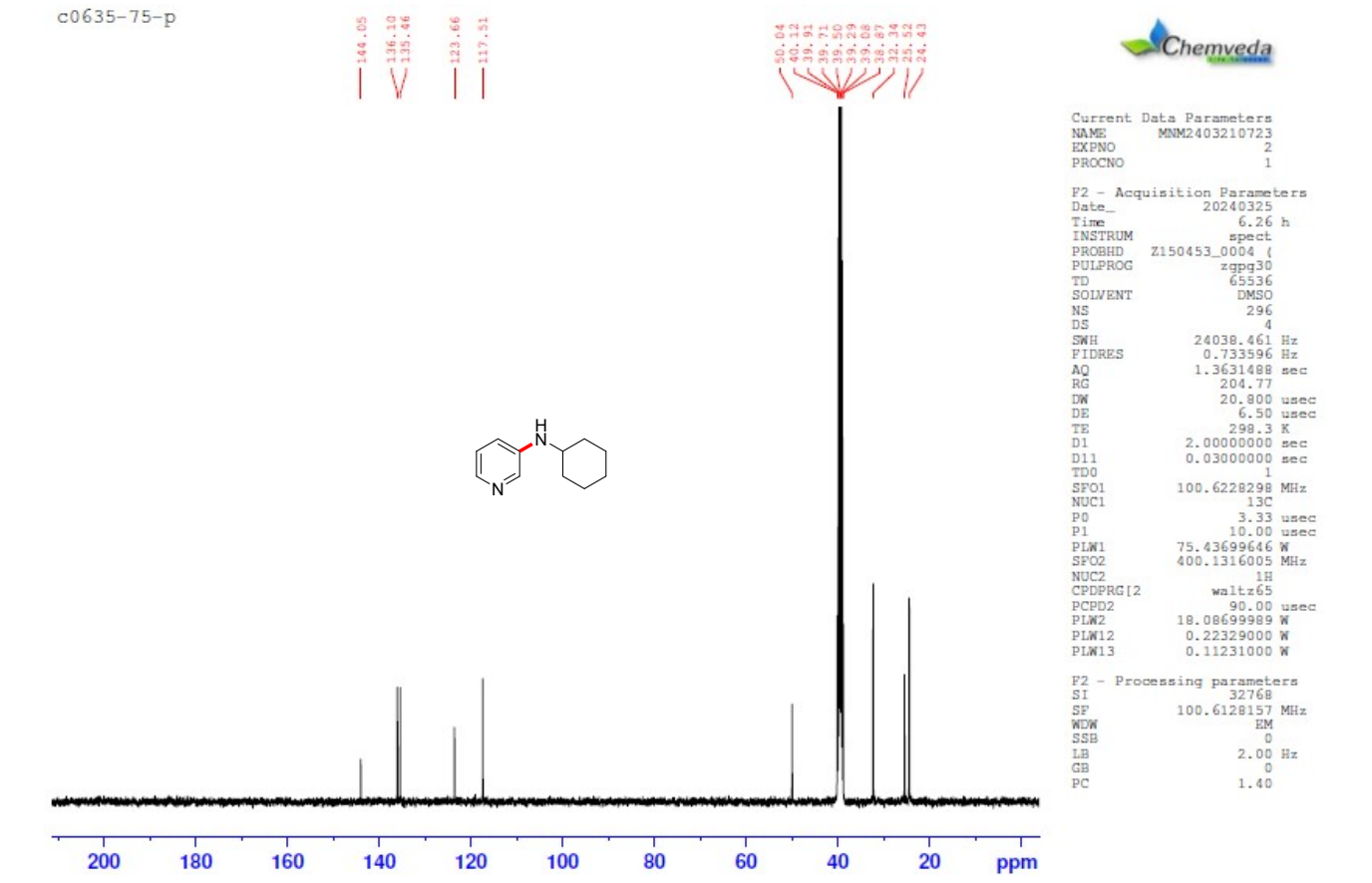
4-(4-methoxyphenyl)morpholine (**36**) ^{1}H NMR (400 MHz, $CDCl_3$)



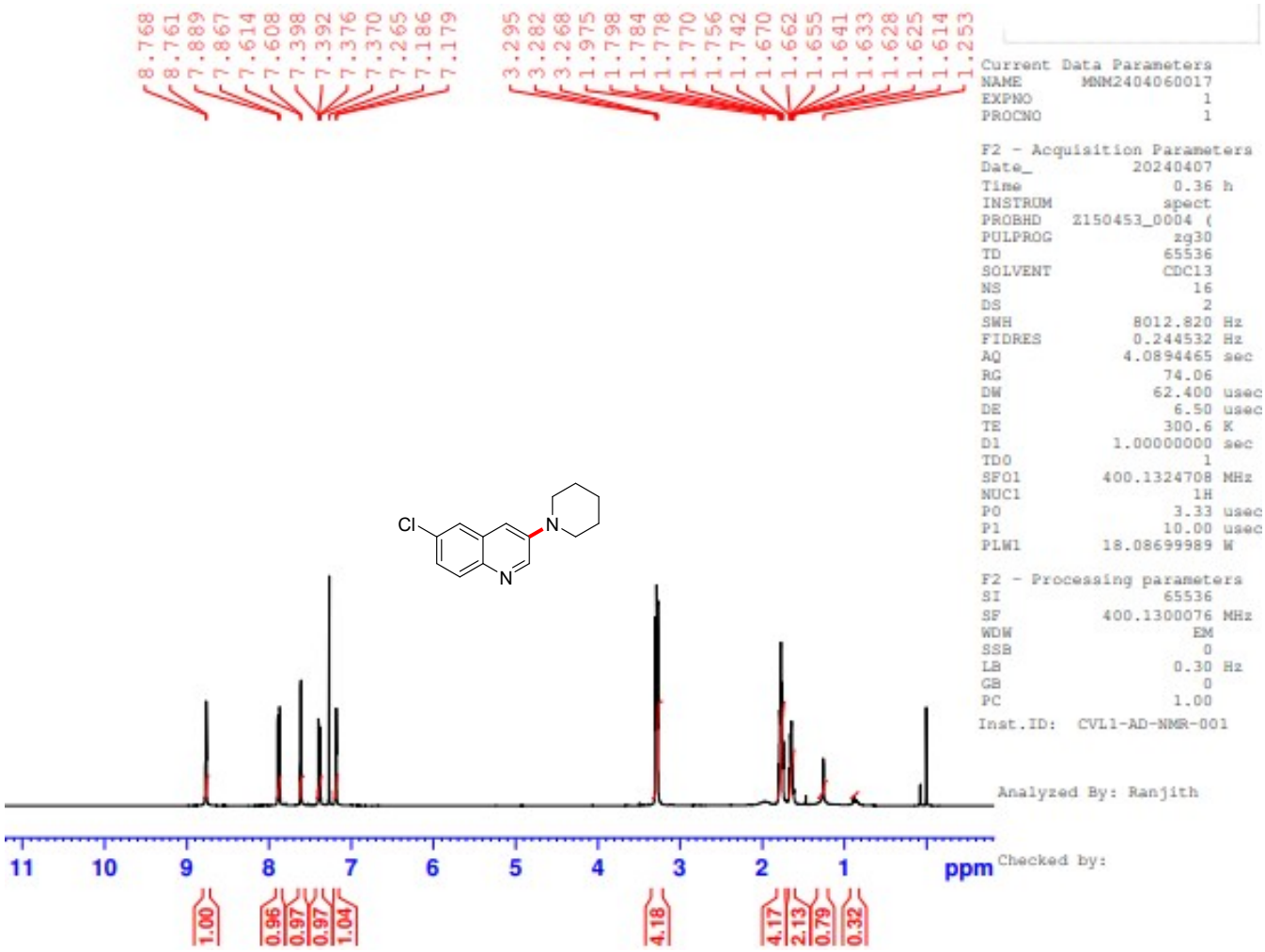
4-(4-methoxyphenyl)morpholine (**36**) ^{13}C NMR (100 MHz, $CDCl_3$)



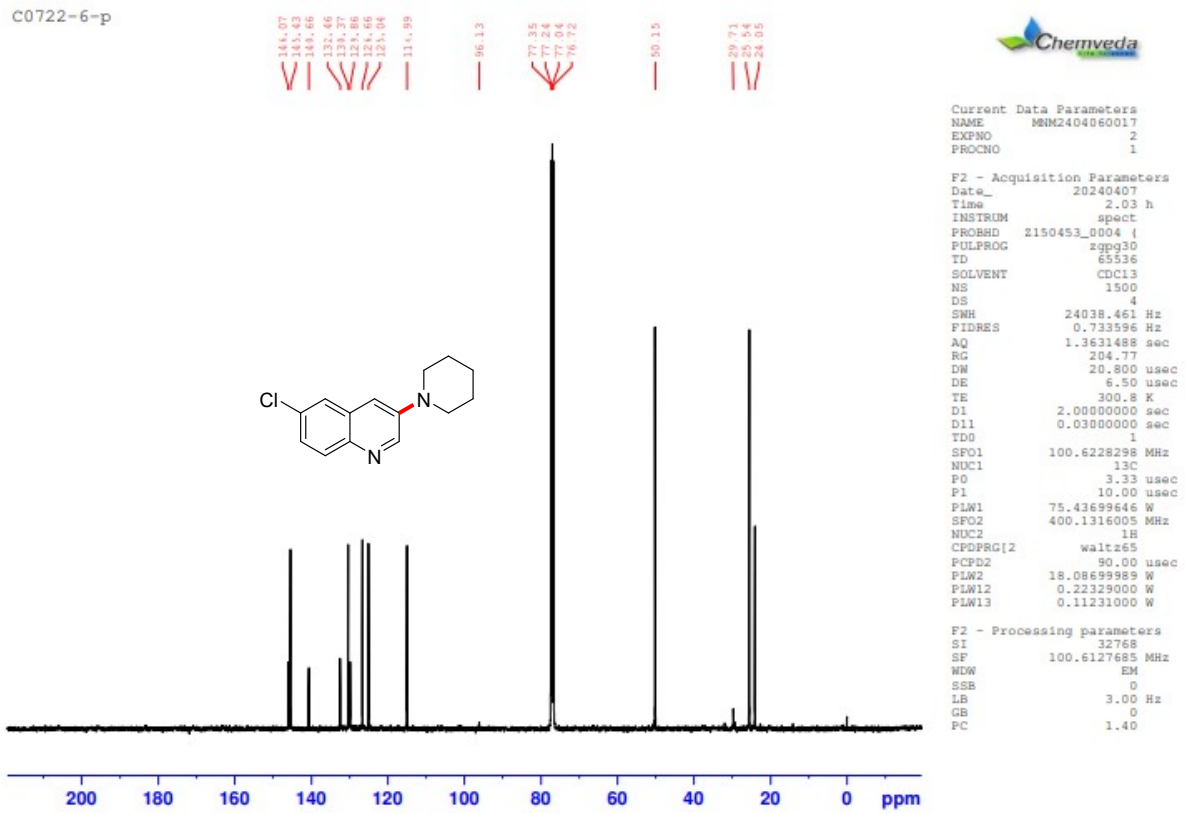
N-Cyclohexylpyridin-3-amine (**37**) ^{1}H NMR (400 MHz, DMSO-d_6)



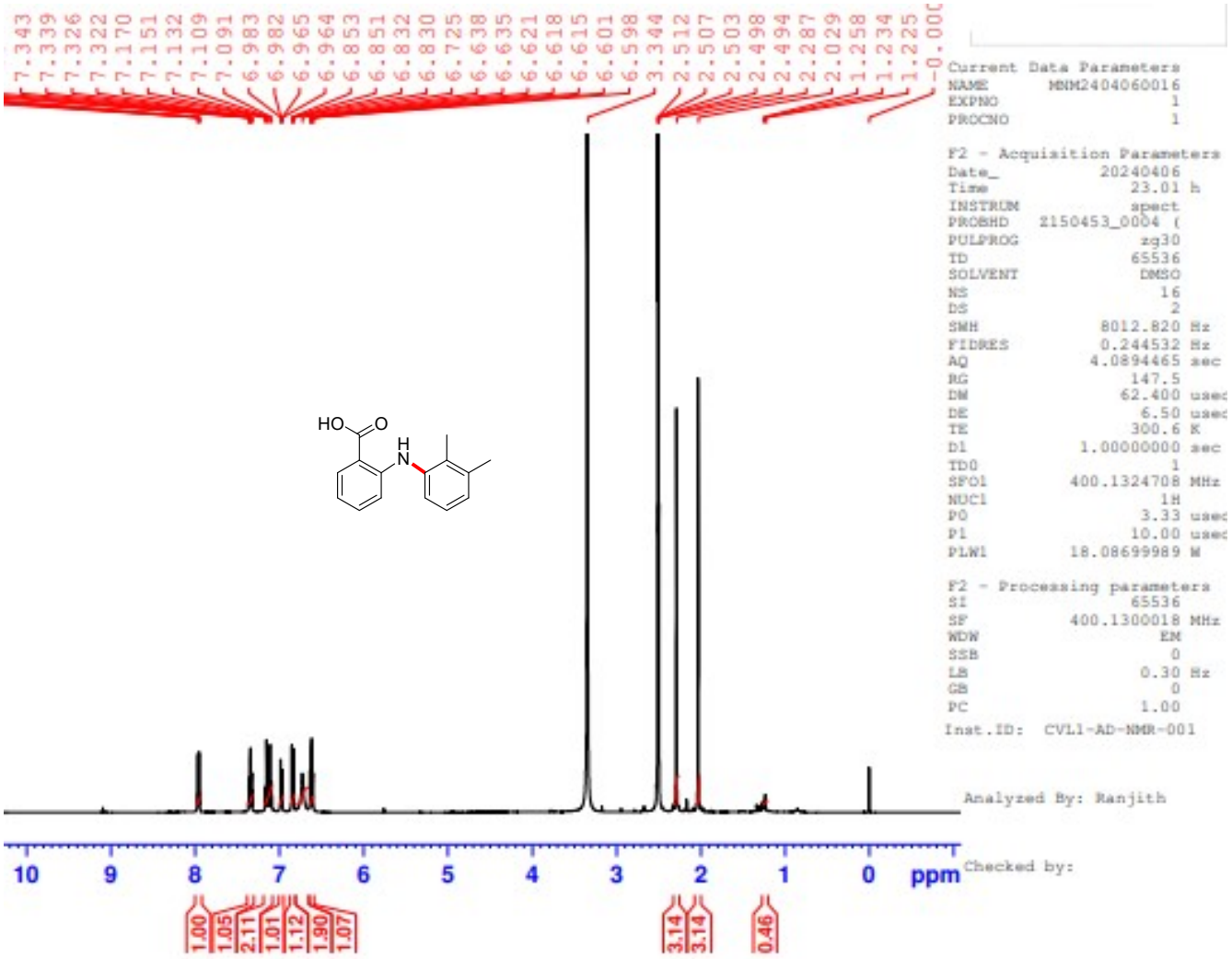
N-Cyclohexylpyridin-3-amine (**37**) ^{13}C NMR (100 MHz, DMSO-d_6)



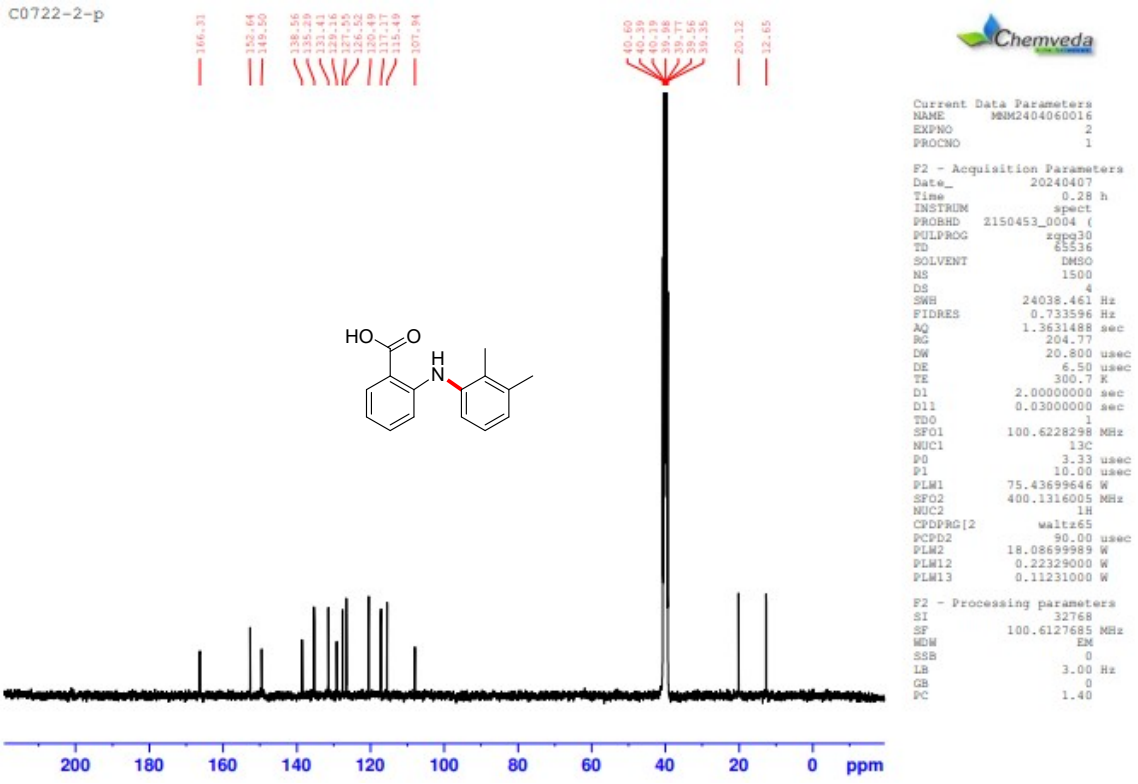
6-Chloro-3-(piperidin-1-yl)quinoline (**38**) ^{1}H NMR (400 MHz, $CDCl_3$)



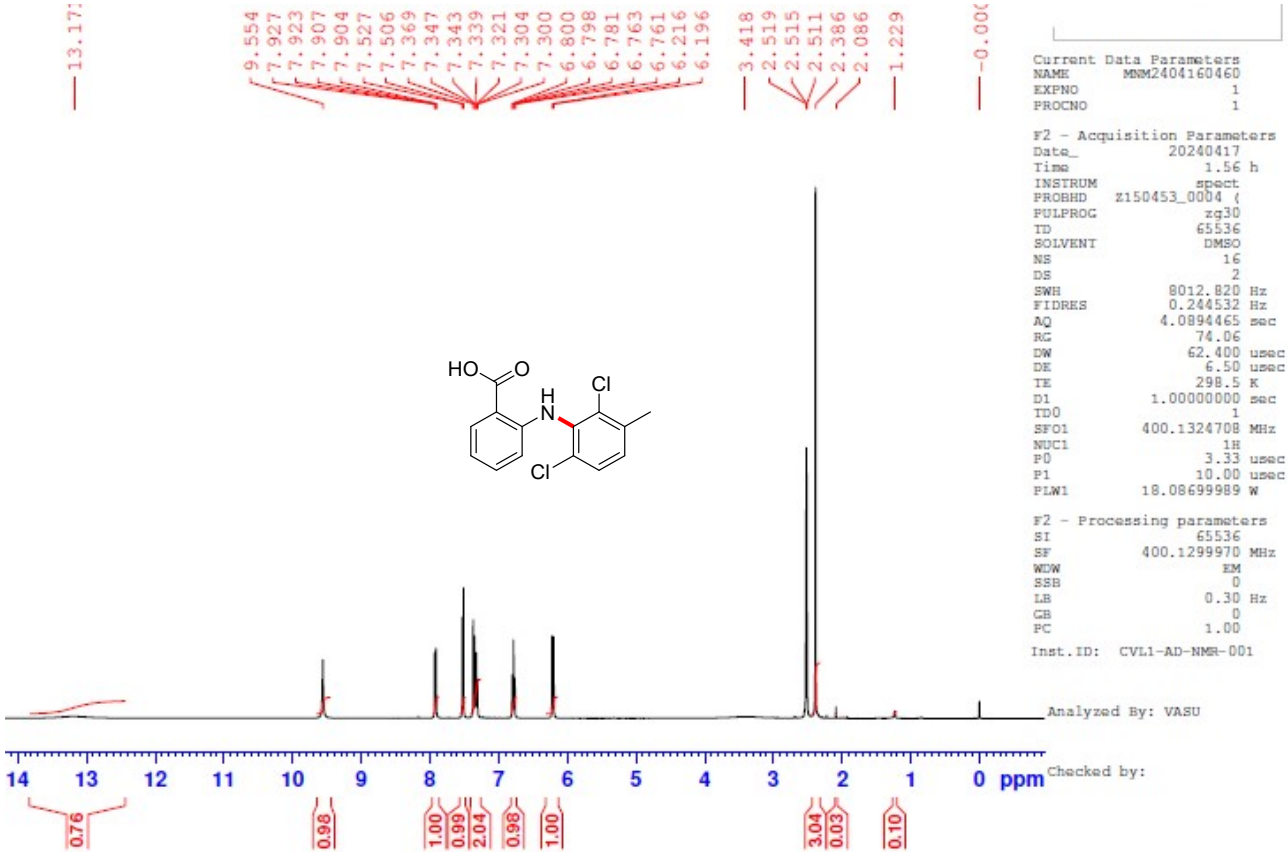
6-Chloro-3-(piperidin-1-yl)quinoline (**38**) ^{13}C NMR (100 MHz, $CDCl_3$)



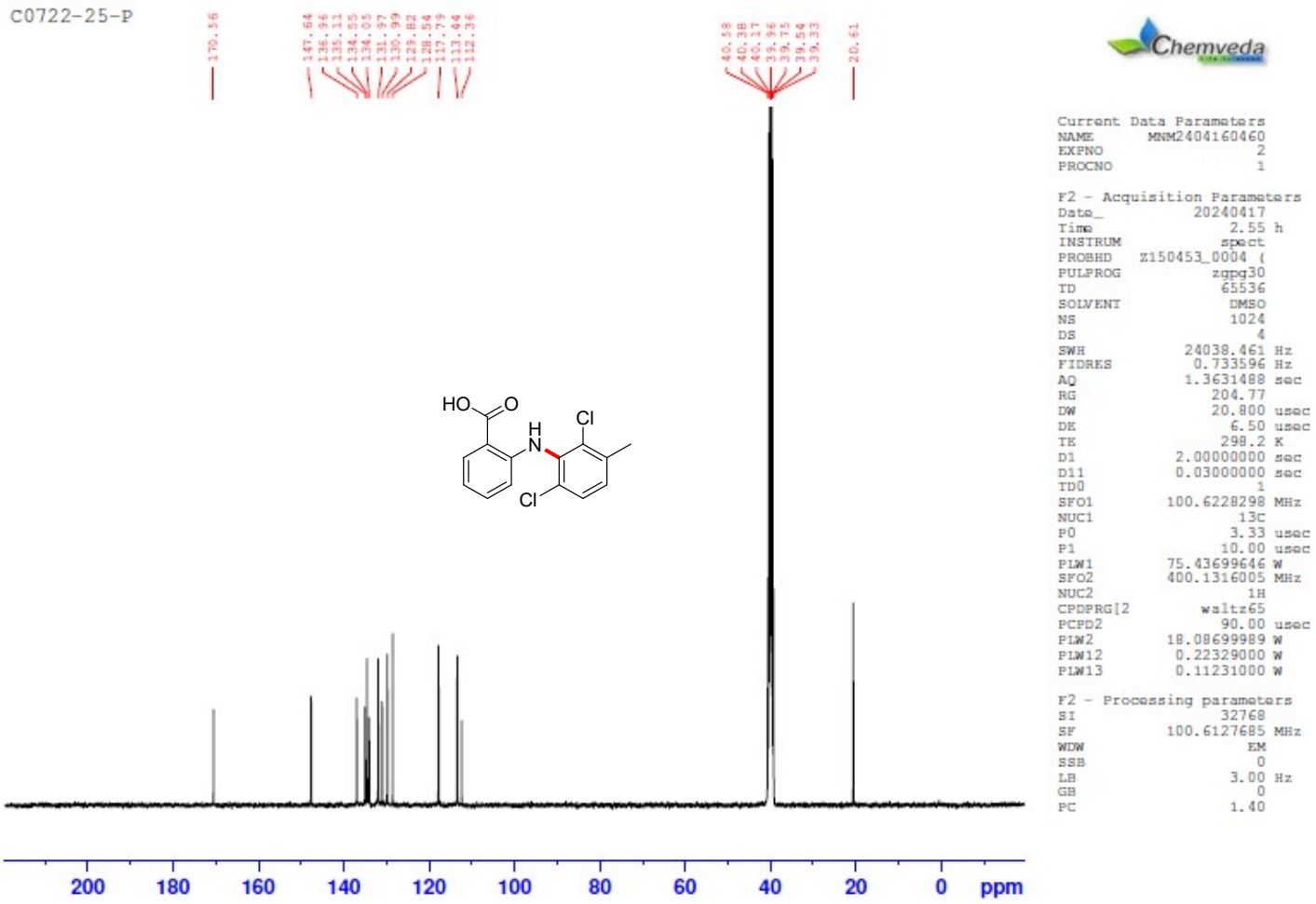
Mefenamic acid ^{1}H NMR (400 MHz, DMSO-d_6)



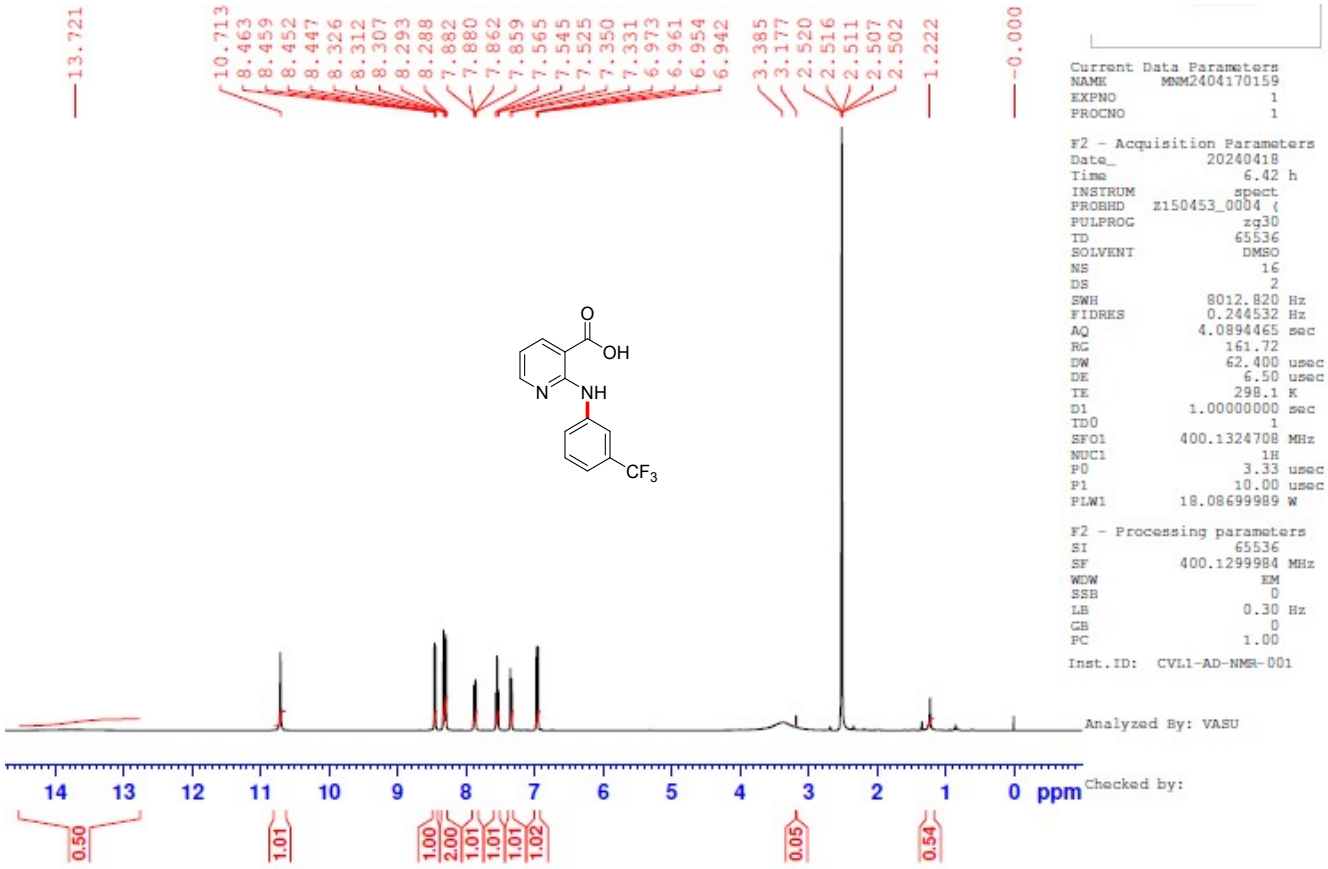
Mefenamic acid ^{13}C NMR (100 MHz, DMSO-d_6)



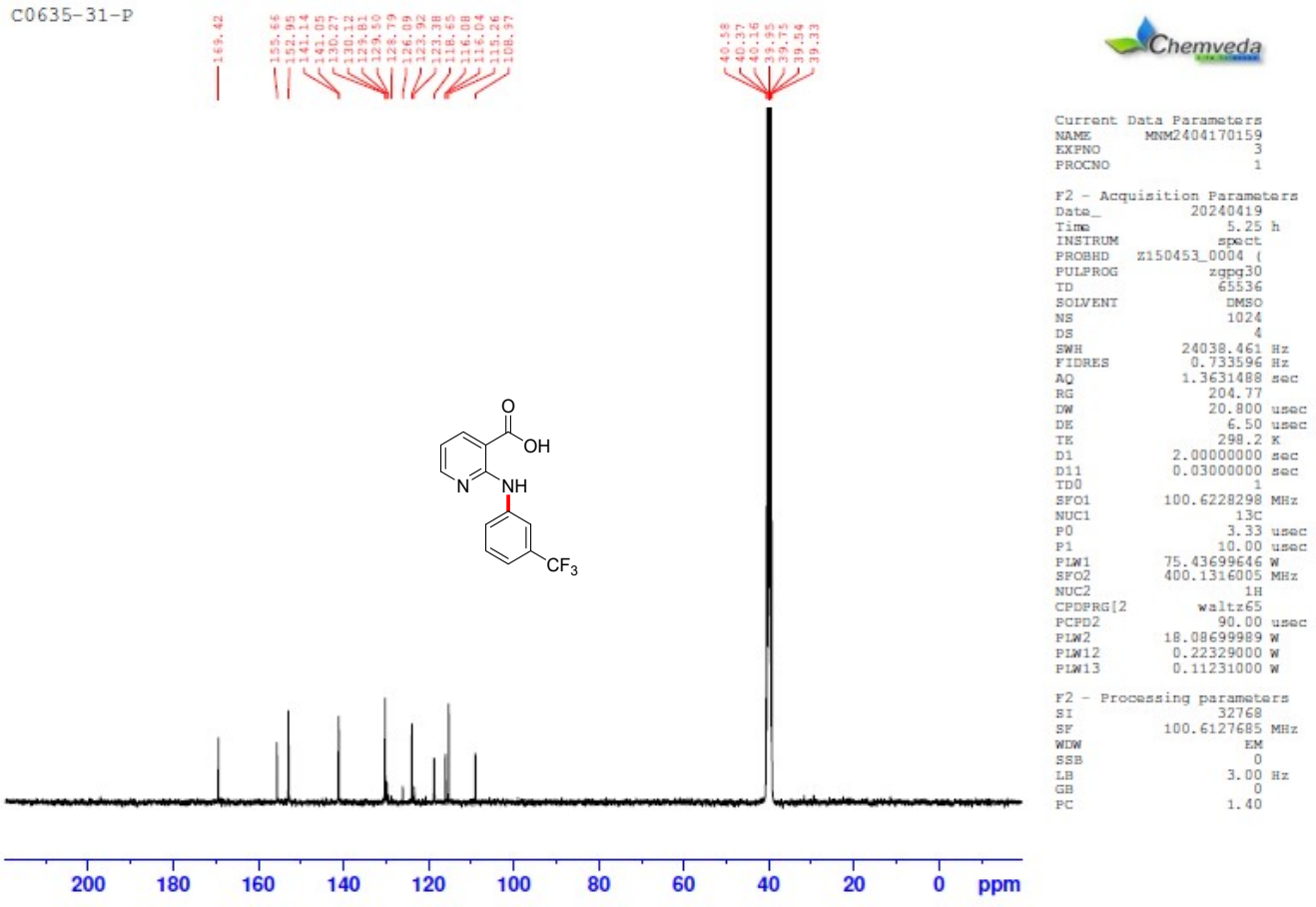
Meclofenac ^{1}H NMR (400 MHz, DMSO-d_6)



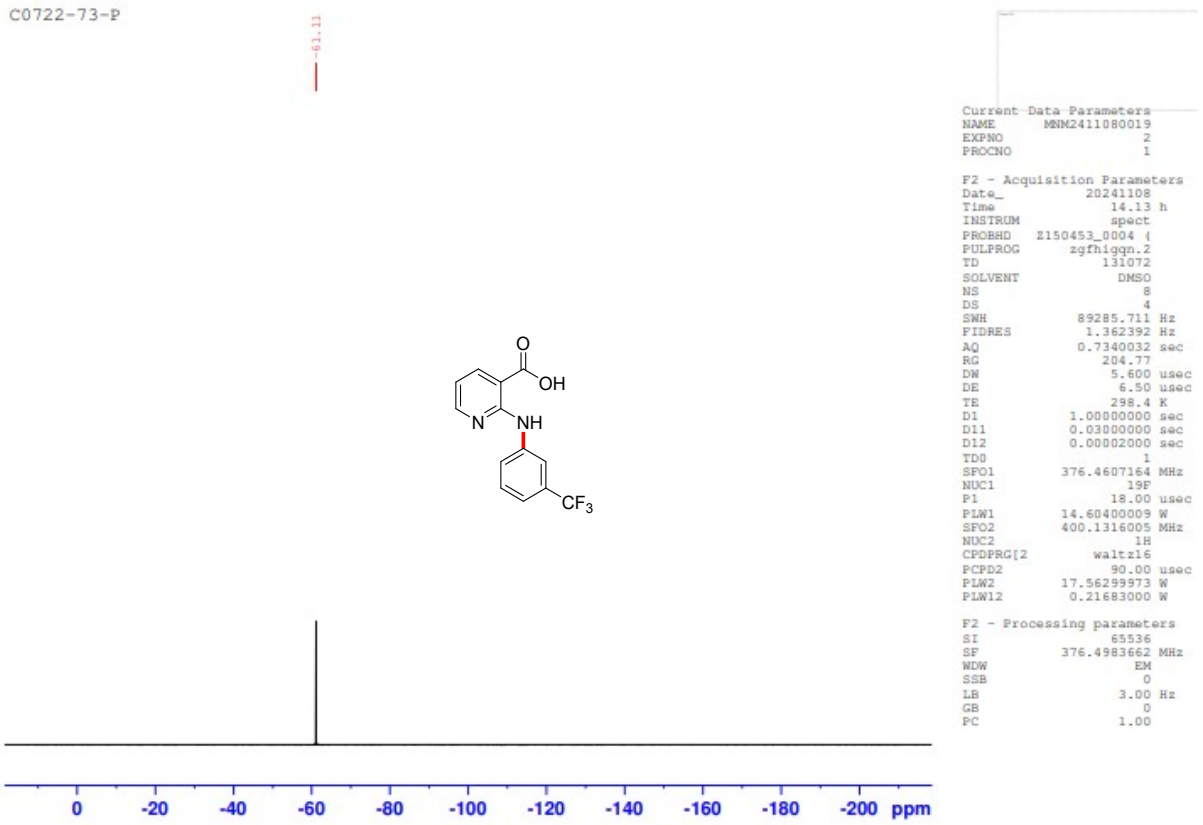
Meclofenac ^{13}C NMR (100 MHz, DMSO-d_6)



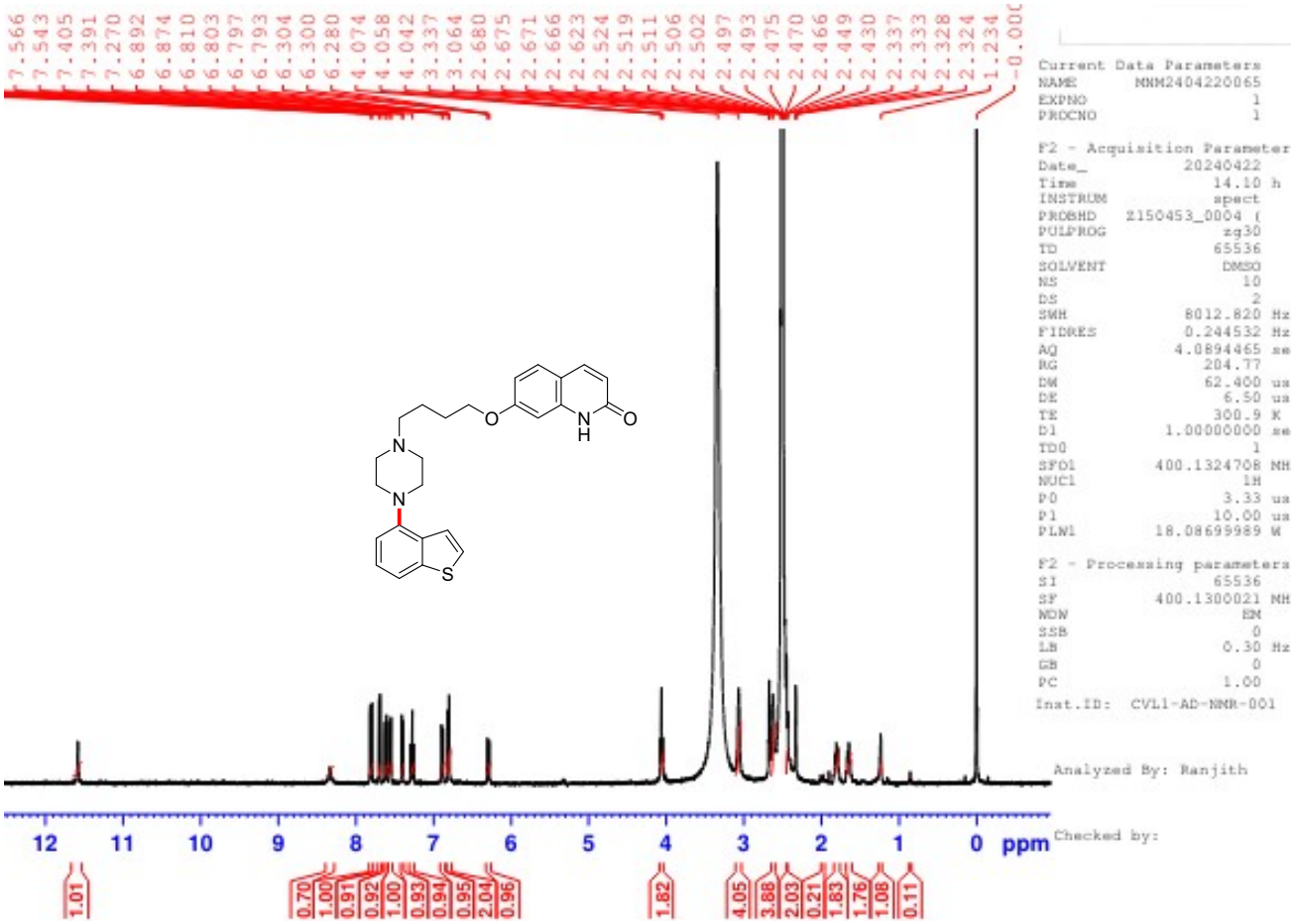
Niflumic acid ^{1}H NMR (400 MHz, DMSO-d_6)



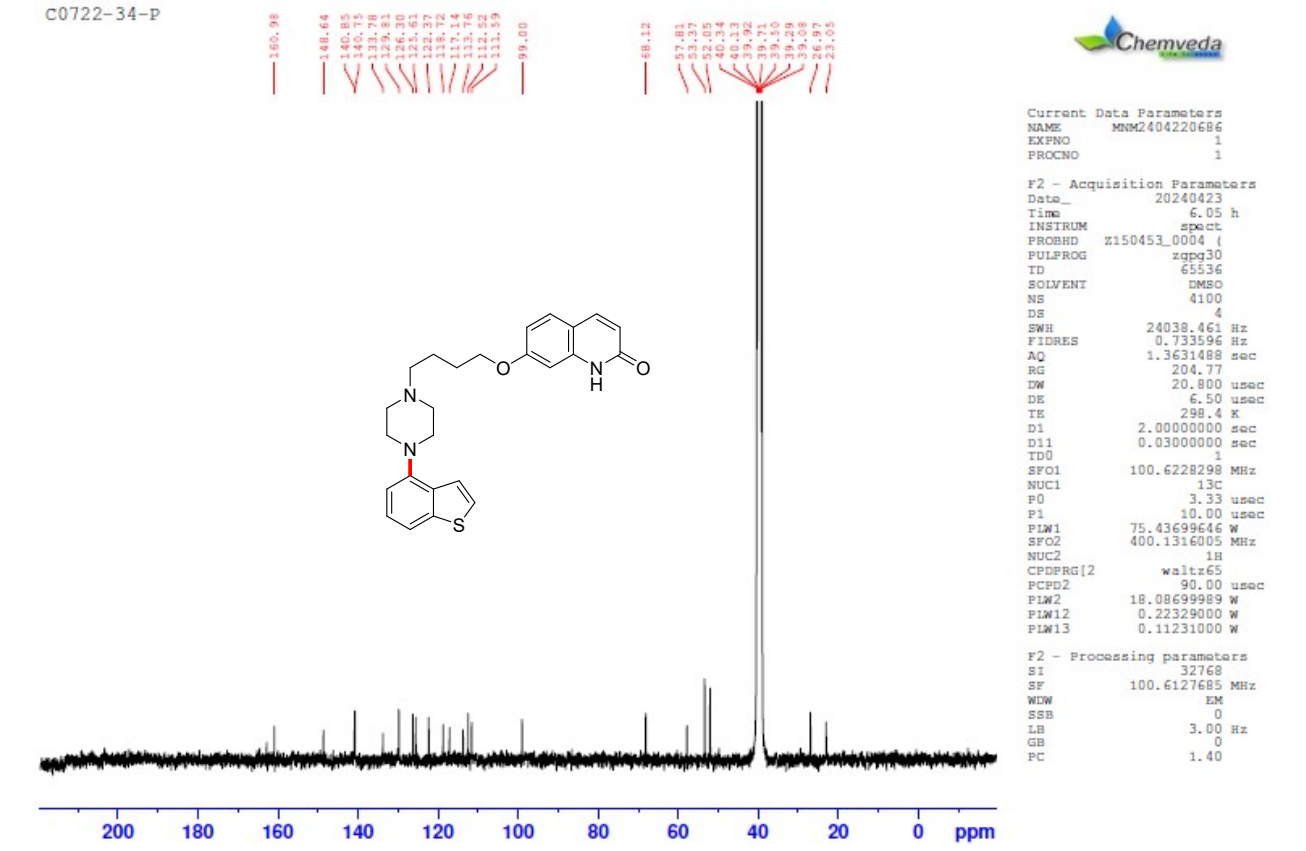
Niflumic acid ^{13}C NMR (100 MHz, DMSO-d_6)



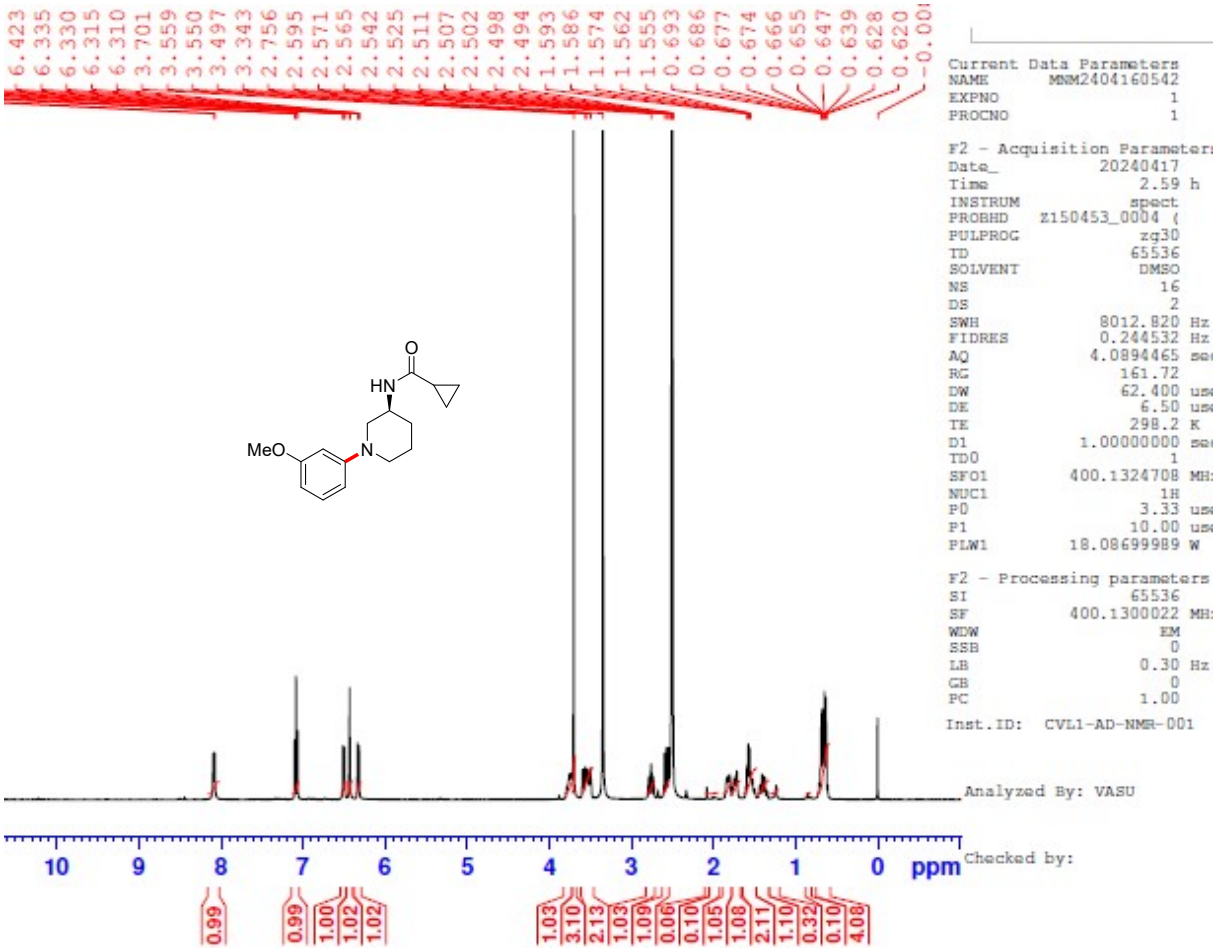
Niflumic acid ^{19}F NMR (376 MHz, DMSO-d_6)



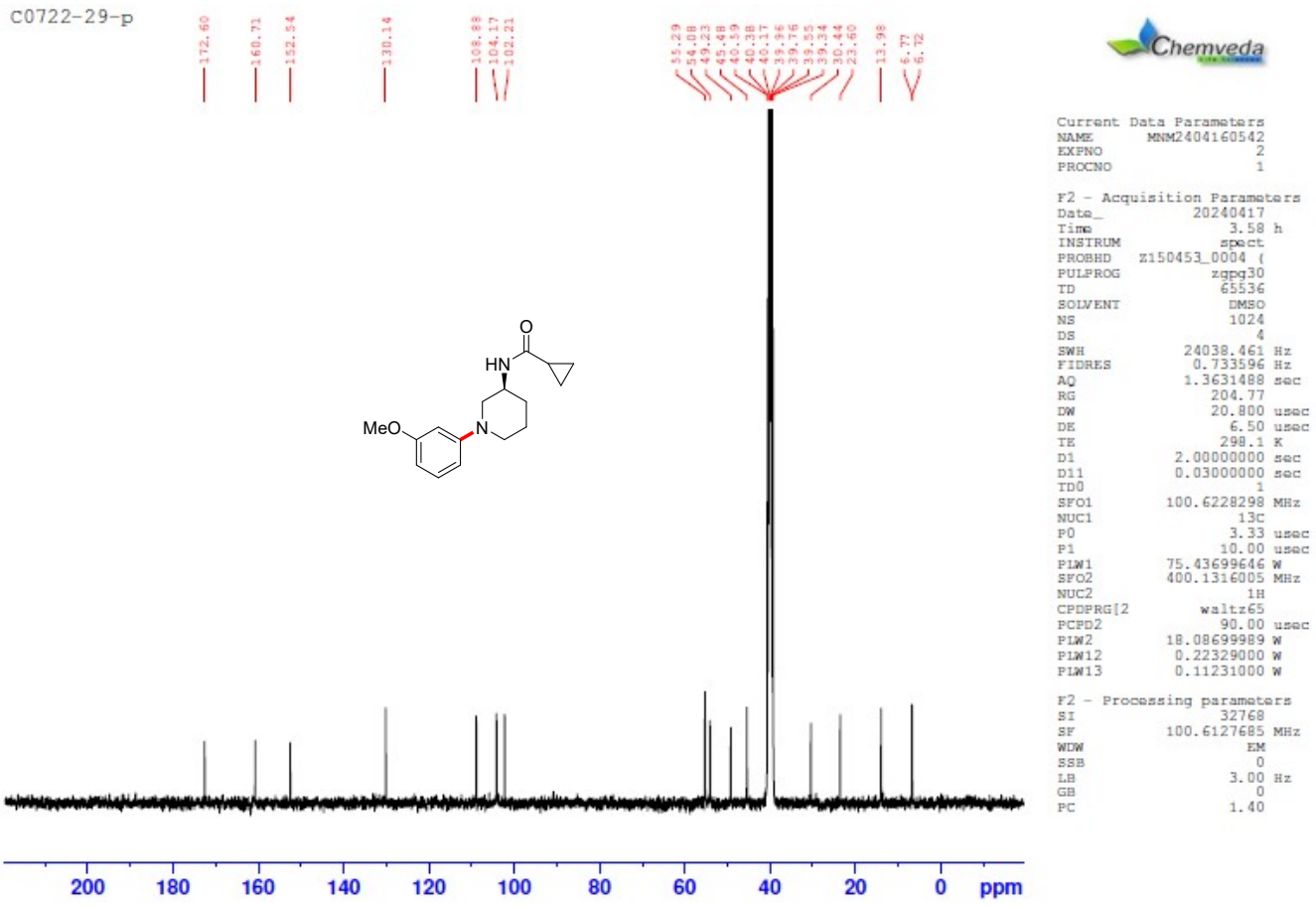
Brexpiprazole ^{1}H NMR (400 MHz, DMSO-d_6)



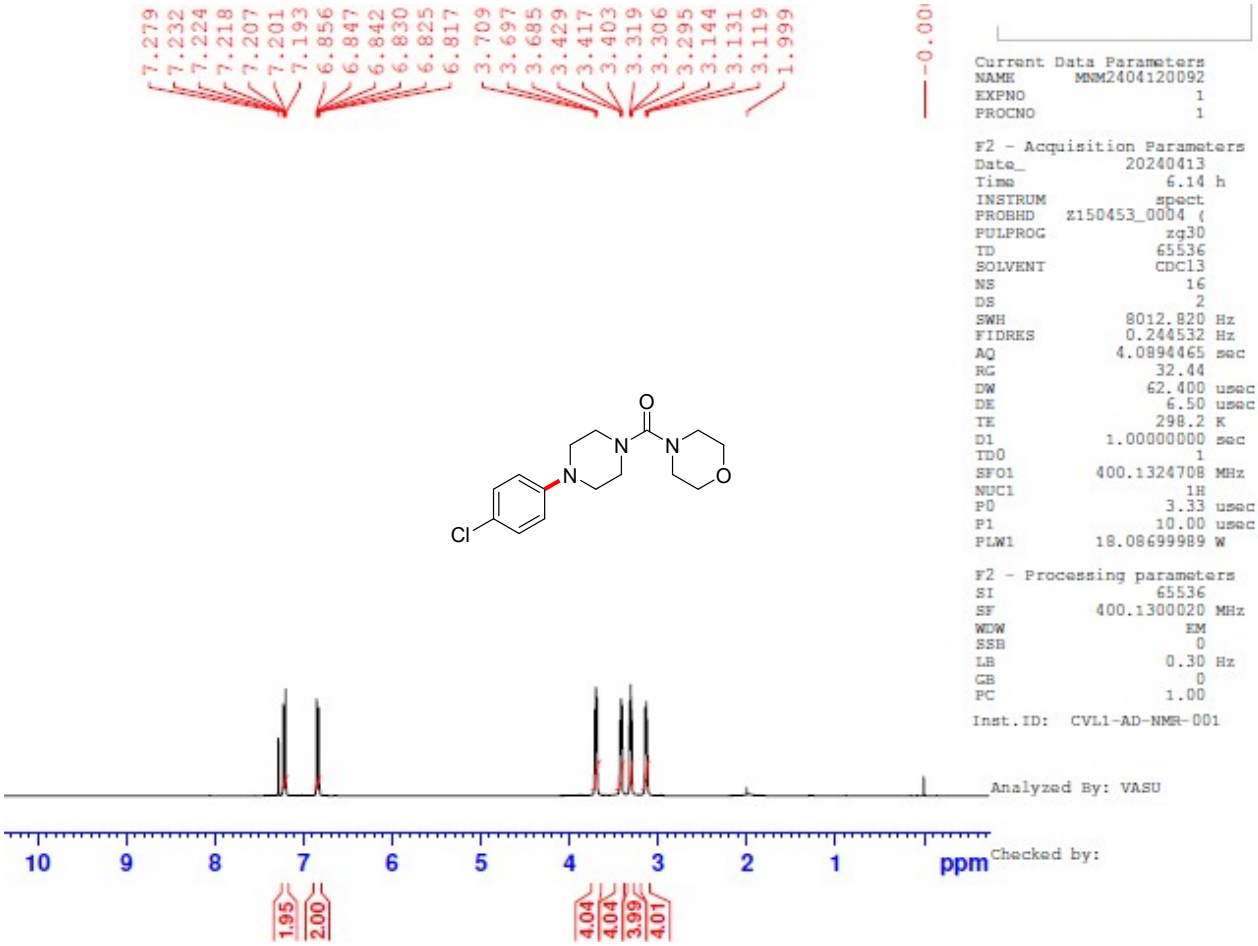
Brexpiprazole ^{13}C NMR (100 MHz, DMSO-d_6)



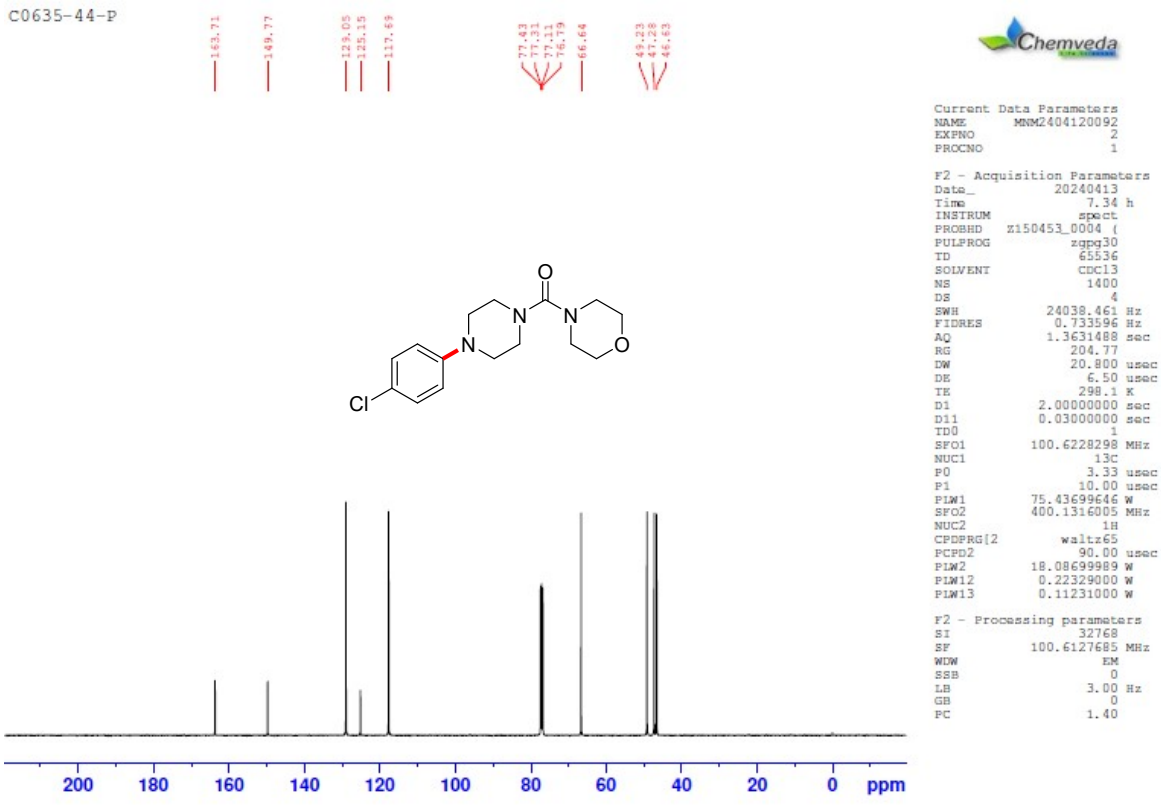
Melatonin receptor ligand ^{1H} NMR (400 MHz, DMSO-d_6)



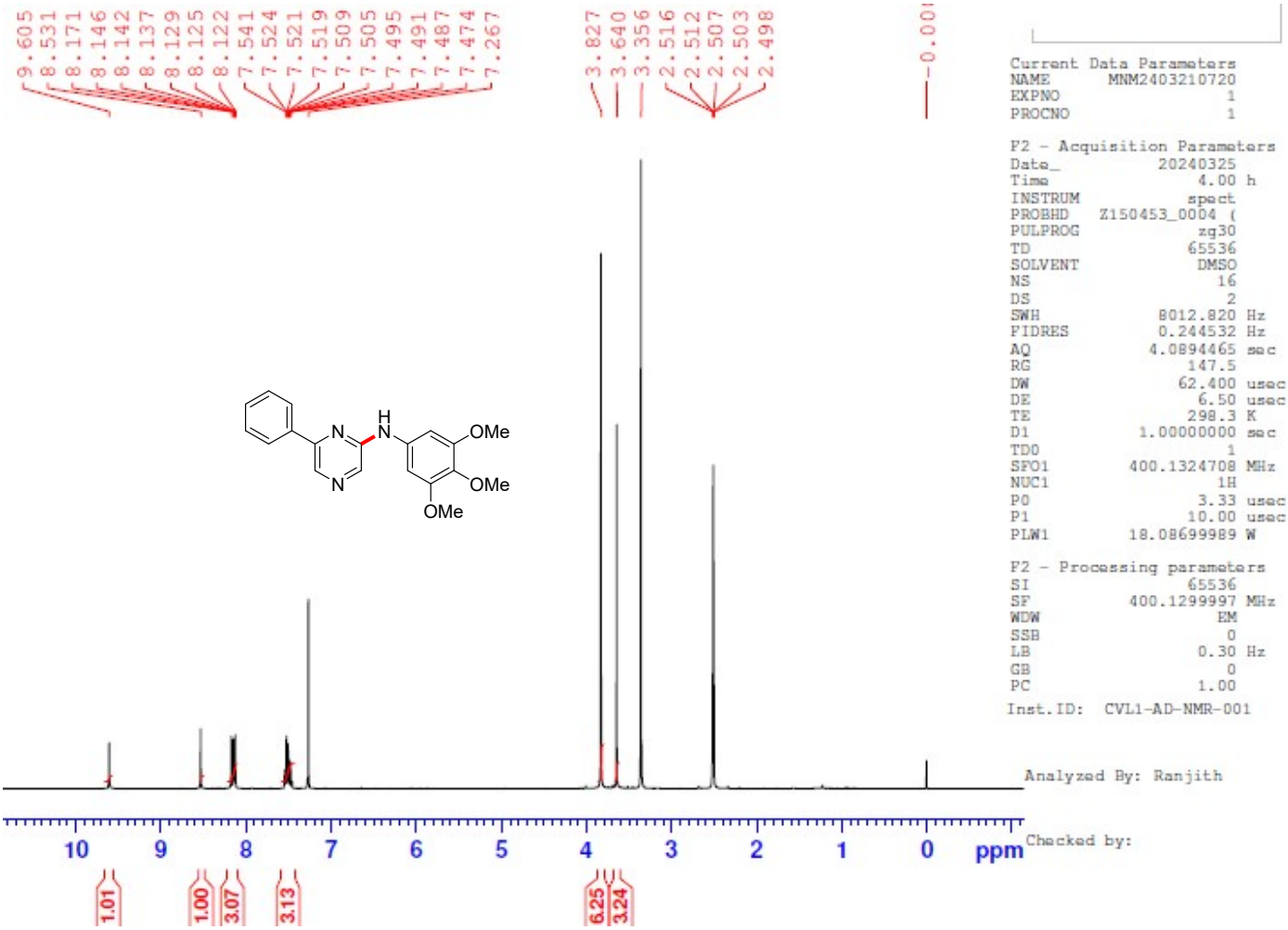
Melatonin receptor ligand ^{13}C NMR (100 MHz, DMSO-d_6)



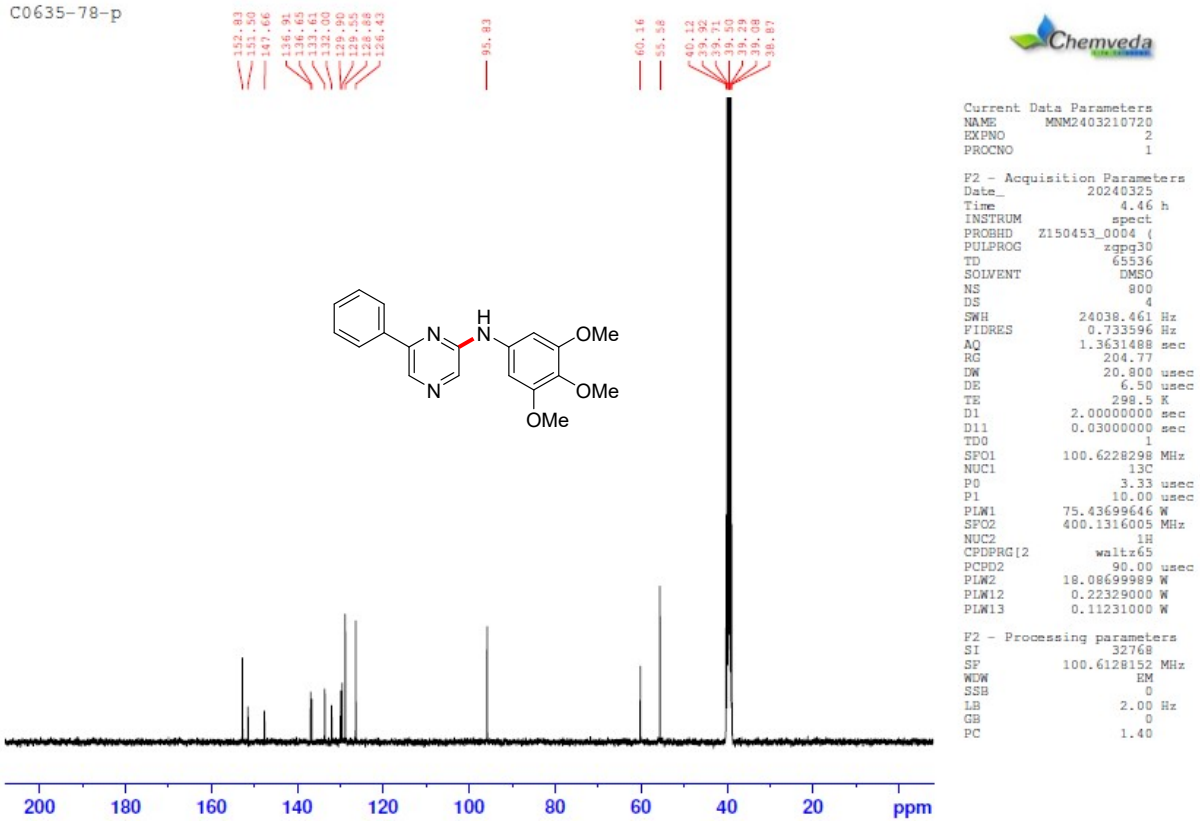
β-hyroxysteroid degydrogenase inhibitor ^{1}H NMR (400 MHz, $CDCl_3$)



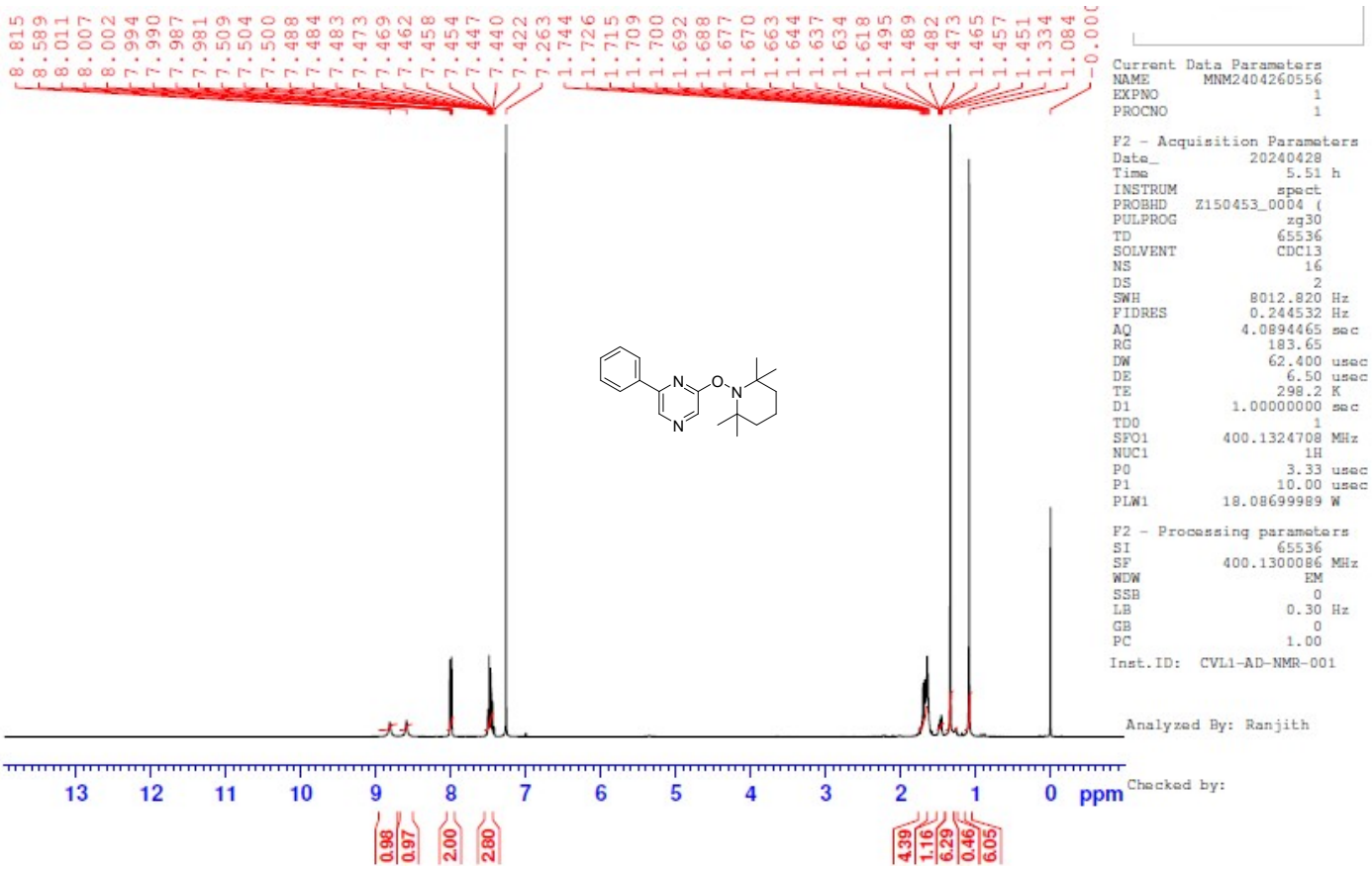
β-hyroxysteroid degydrogenase inhibitor ^{13}C NMR (100 MHz, $CDCl_3$)



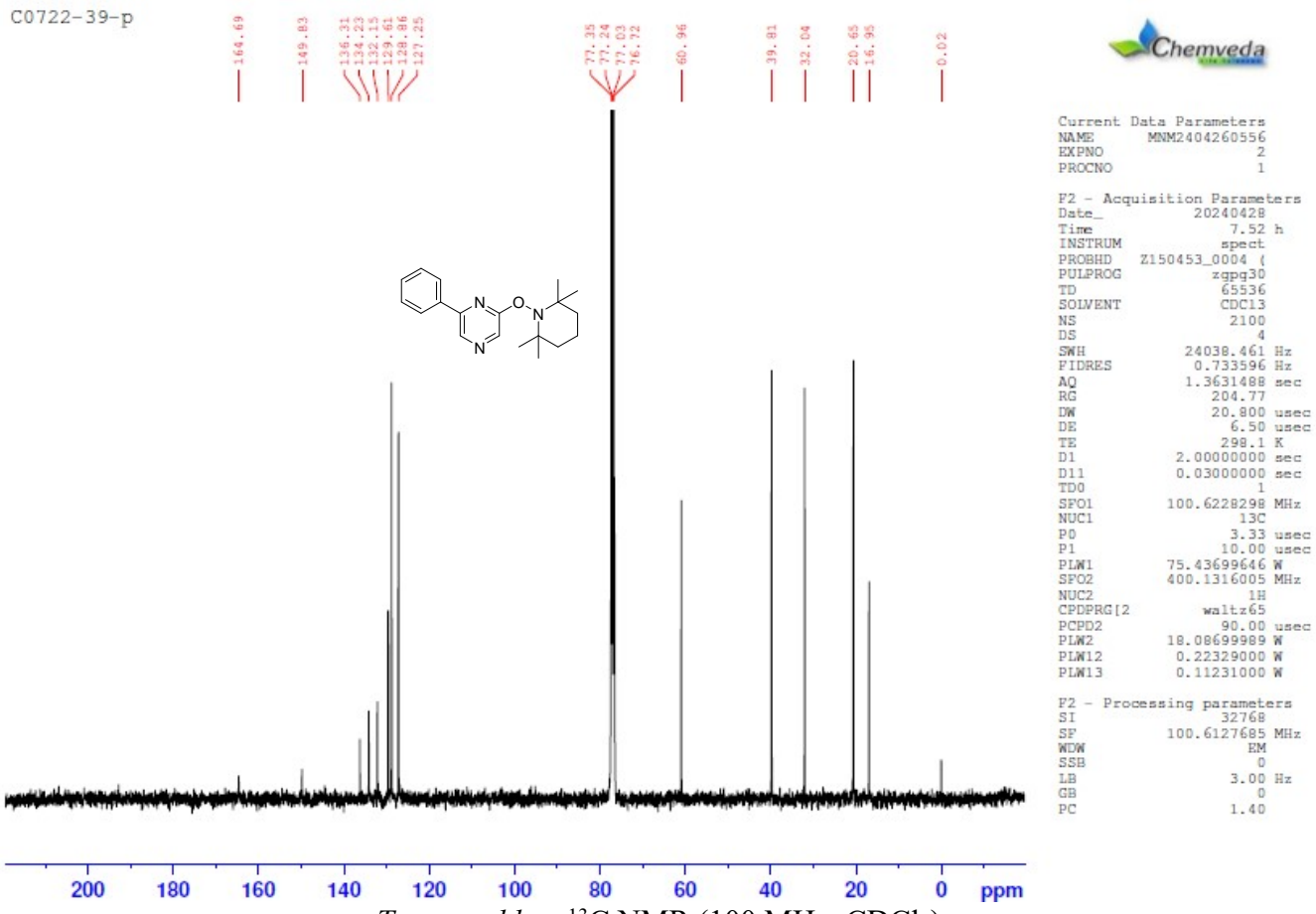
BRAF inhibitor ^{1}H NMR (400 MHz, DMSO-d_6)



BRAF inhibitor ^{13}C NMR (100 MHz, DMSO-d_6)



Tempo-adduct ^{1}H NMR (400 MHz, $CDCl_3$)



Tempo-adduct ^{13}C NMR (100 MHz, $CDCl_3$)