# Base-Free synthesis of furfurylamines from biomass furans using Ru pincer complexes

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## Supporting Information

### 1. Monitoring the reaction of furfural with aniline using different drying agents

***Table S1.*** Monitoring the reaction of furfural and aniline using $MgSO_4$ as drying agent.

| Entry | Time | 1a (%) | 3 (%) | 2a (%) |
|---|---|---|---|---|
| **0** | 0 | 100 | - | - |
| **1** | 5 | 94 | 6 | - |
| **2** | 10 | 89 | 7 | 4 |
| **3** | 20 | 84 | 10 | 6 |
| **4** | 30 | 45 | 12 | 43 |
| **5** | 40 | 27 | 13 | 60 |
| **6** | 50 | <3 | 6 | 92 |
| **7** | 60 | - | - | 100 |

Reactions were carried out using 1.3 mmol of furfural, 1.2 equivalent aniline and 1.3 mmol of $MgSO_4$ in 7 mL *i*PrOH.

***Table S2.*** Monitoring the reaction of furfural and aniline using $Na_2SO_4$ as drying agent.

| Entry | Time | 1a (%) | 3 (%) | 2a (%) |
|---|---|---|---|---|
| **0** | 0 | 100 | - | - |
| **1** | 15 | 5 | 35 | 60 |
| **2** | 30 | 3 | 22 | 70 |
| **3** | 45 | 0 | 10 | 90 |
| **4** | 60 | 0 | 3 | 97 |

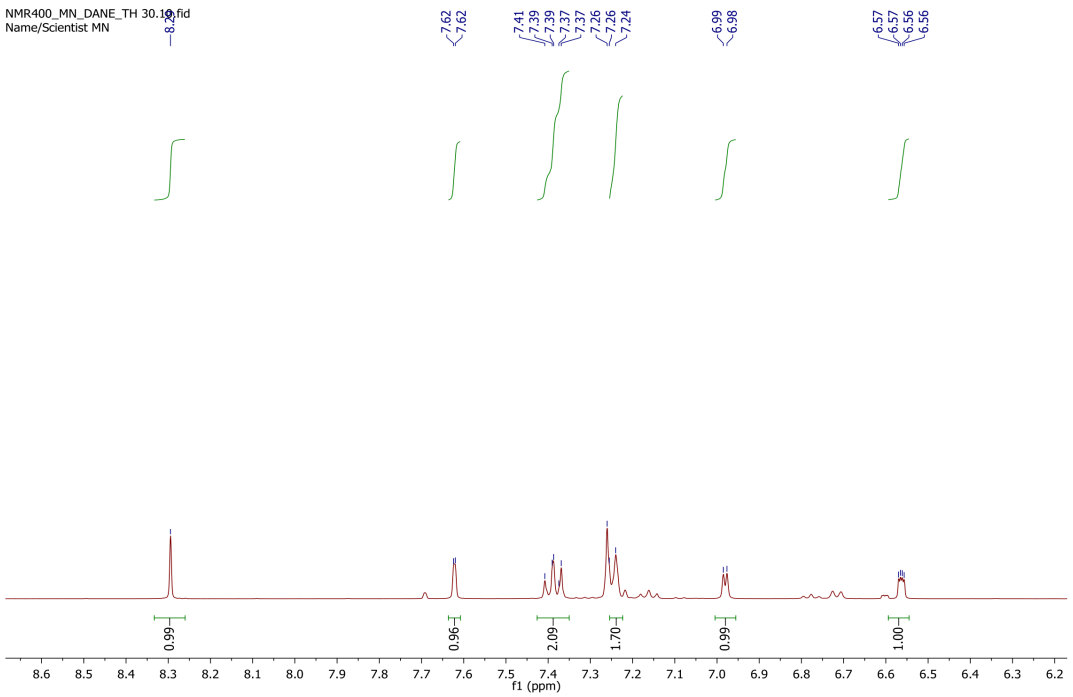
Reactions were carried out using 1.3 mmol of furfural, 1.2 equivalent aniline and 1.3 mmol of $Na_2SO_4$ in 7 mL *i*PrOH.

## 1. Product characterizations

**(E)-1-(furan-2-yl)-*N*-phenylmethanimine 1a**

$^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.29 (s, 1 H), 7.62 (s, 1 H), 7.39 (t, 2 H, *J* = 8.74 Hz), 7.26-7.24 (m, 2 H), 6.98 (d, 1 H, *J* = 3.60 Hz), 6.56 (dd, 1 H, *J* = 3.6 Hz, *J* = 1.6 Hz) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz) $\delta$: 152.1, 151.3, 147.9, 145.9, 129.4, , 126.4, 121.1, 116.6, 112.3 ppm. [64]

*1.1. $^{1}$H and $^{13}$C NMR spectra of the aldimine 1a.*




The spectrum contains approximately 5% of the starting material as impurities (furfural and aniline)

**Figure S1.$^{1}$H NMR spectrum of 1a (400 MHz, $CDCl_3$)**

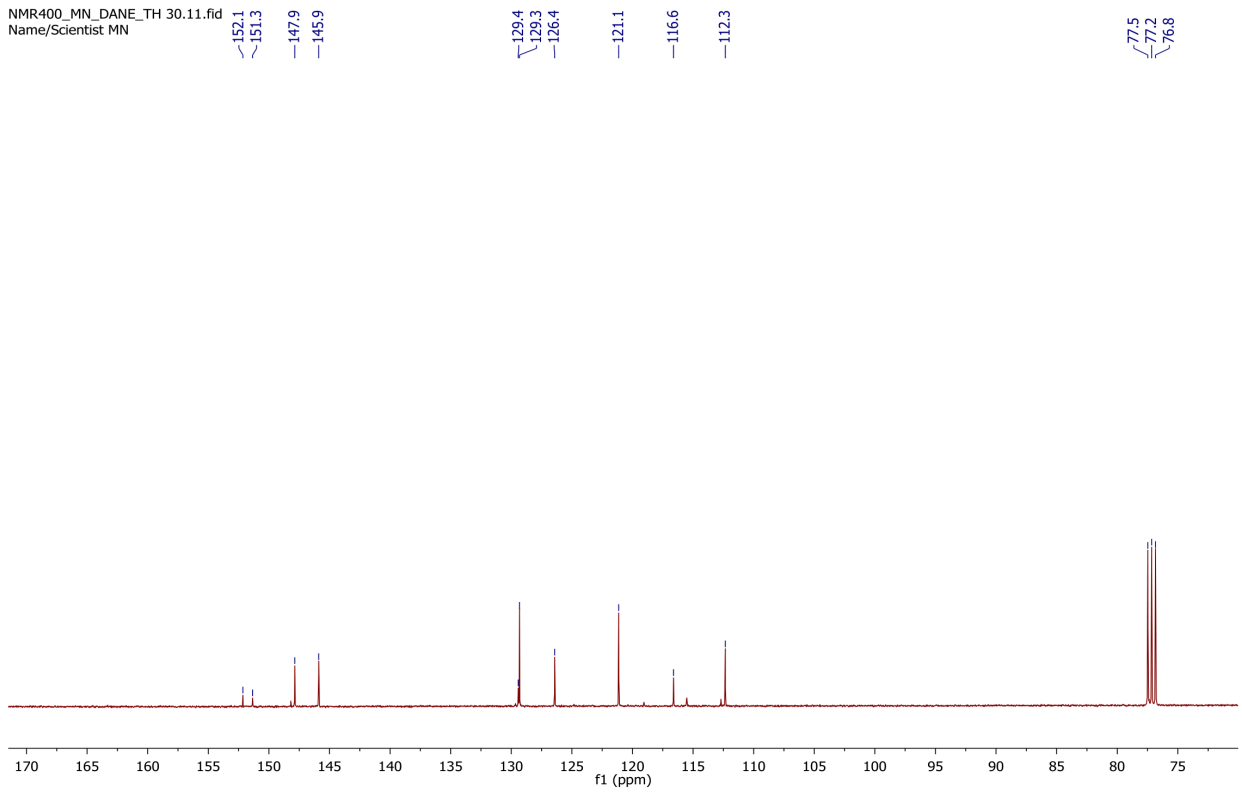



**Figure S2.$^{13}$C NMR spectrum of 1a (100 MHz, $CDCl_3$)**

*1.2. $^{1}H$ and $^{13}C$ NMR spectra of the furfurylamines.*

**_N_-(furan-2-ylmethyl)aniline 2a**

The product **2a** was obtained as a yellow oil. 209 mg, 93 %. $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.26 (s, 1 H), 7.09 (t, 2 H, $J$ = 8 Hz), 6.65 (t, 1 H, $J$ = 8 Hz), 6.57 (d, 2 H, $J$ = 8 Hz), 6.21 (dd, 1 H, $J$ = 4 Hz, $J$ = 1.6 Hz), 6.12 (dd, 1 H, $J$ = 3.2 Hz, $J$ = 1.2 Hz), 4.2 (s, 2 H), 3.97 (brs, 1 H) ppm. $^{13}C\{^{1}H\}$NMR (100 MHz) δ: 152.8, 147.6, 142.0, 129.3, 118.2, 113.3, 110.4, 107.1, 41.6 ppm.[1]

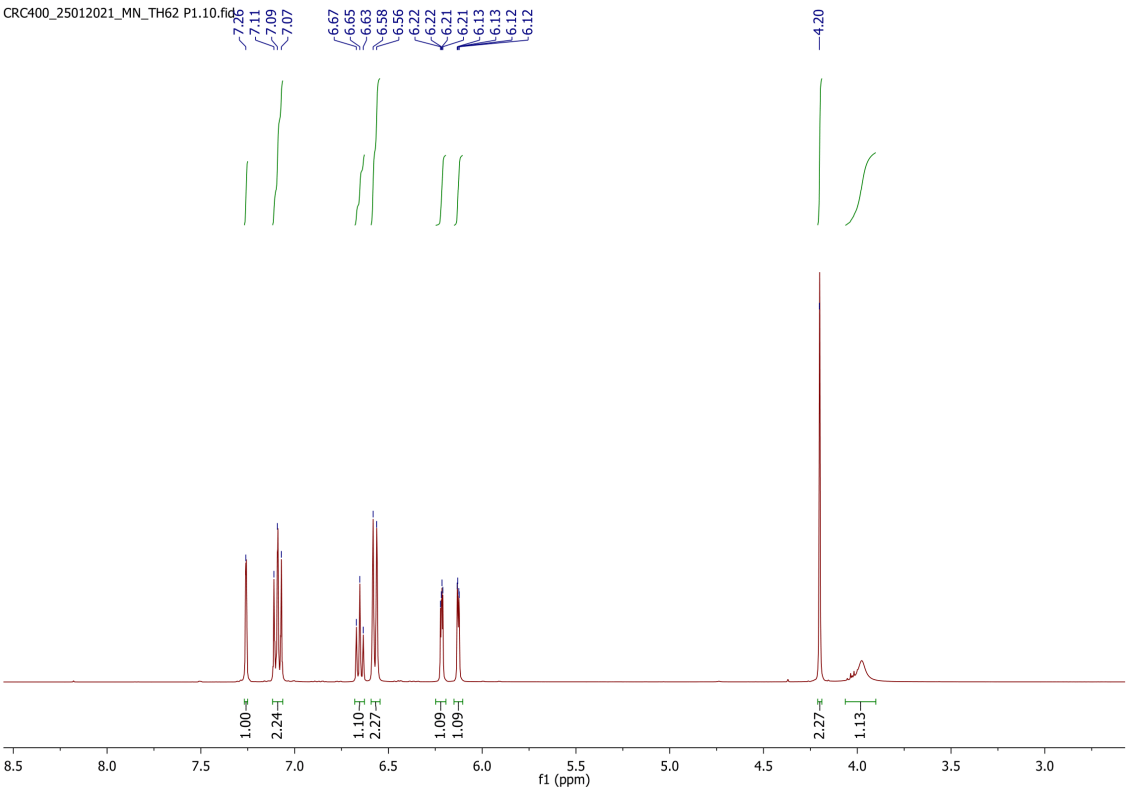



**Figure S3.$^{1}H$ NMR spectrum of 2a (400 MHz, $CDCl_3$)**

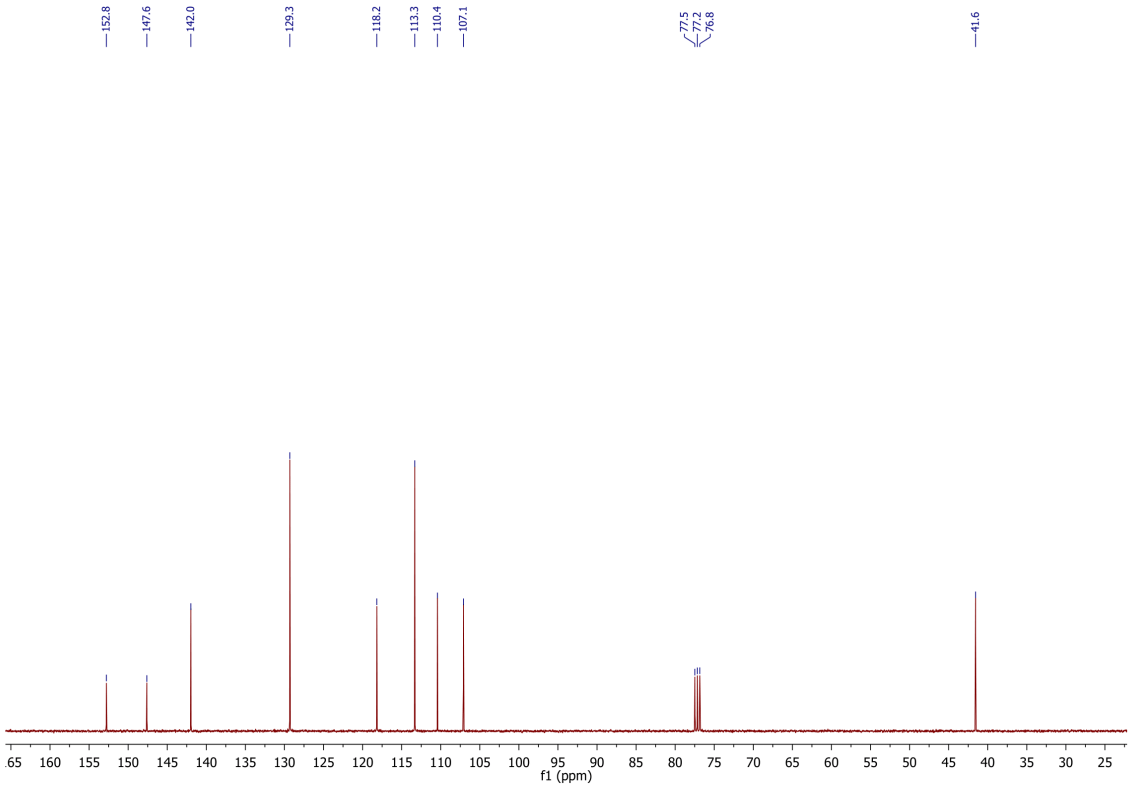



**Figure S4.$^{13}$C NMR spectrum of 2a (100 MHz, $CDCl_3$)**

**4-chloro-*N*-(furan-2-ylmethyl)aniline 2b**

The product **2b** was obtained as a yellow oil. 201 mg, 75 %. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.26 (s, 1 H), 7.02 (d, 2 H, *J* = 8 Hz), 6.49 (d, 2 H, *J* = 8 Hz), 6.22 (dd, 1 H, *J* = 3.2 Hz, *J* = 2 Hz), 6.12 (dd, 1 H, *J* = 3.2 Hz, *J* = 0.8 Hz), 4.48 (brs, 1 H), 4.17 (s, 2 H) ppm. $^{13}$C{$^{1}$H}NMR (100 MHz) $\delta$: 152.1, 145.9, 142.2, 129.1, 123.0, 114.6, 110.5, 107.4, 41.7 ppm.[65]

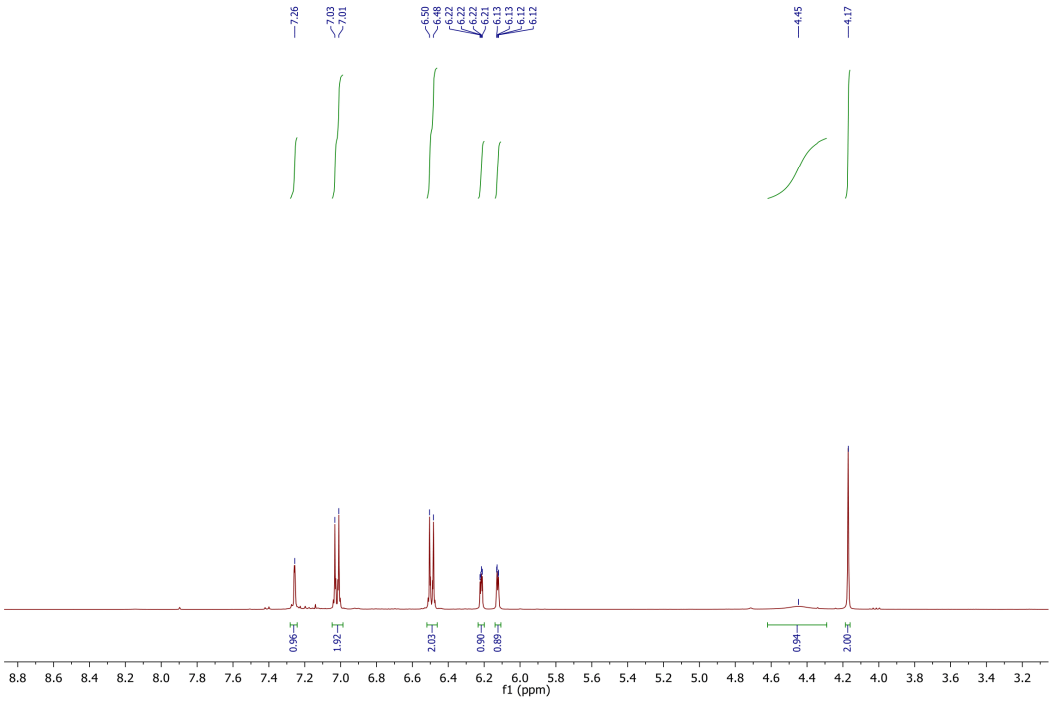



**Figure S5.$^{1}$H NMR spectrum of 2b (400 MHz, $CDCl_3$)**

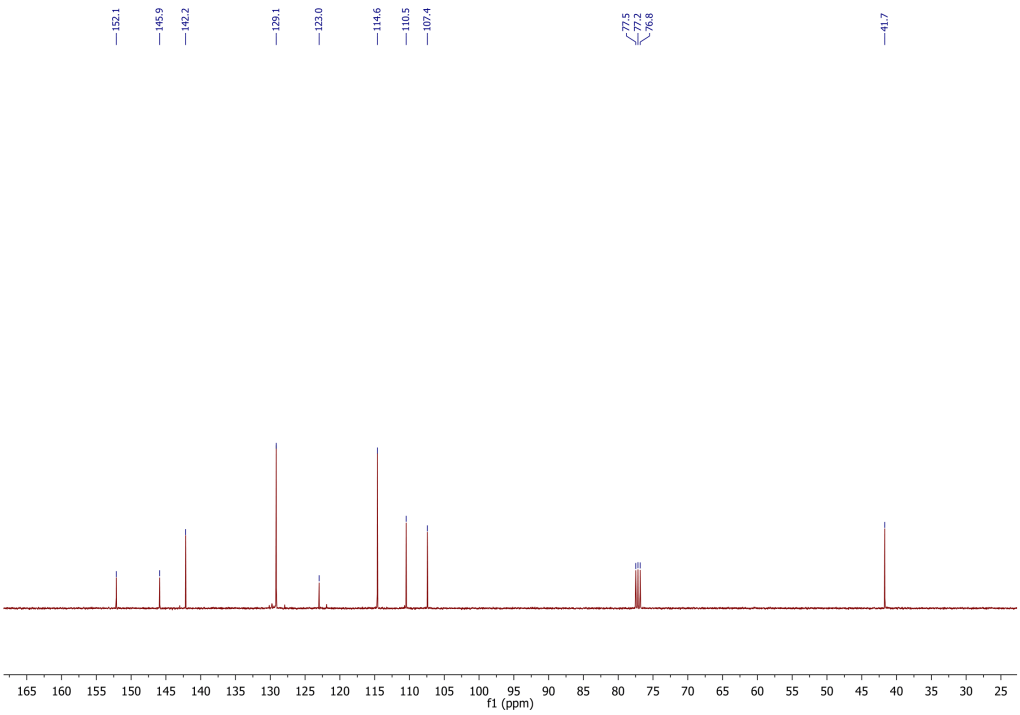



**Figure S6.$^{13}$C NMR spectrum of 2b (100 MHz, $CDCl_3$)**

**3-chloro-*N*-(furan-2-ylmethyl)aniline 2c**

The product **2c** was obtained as a yellow oil. 163.4 mg, 60 %. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.38 (s, 1 H), 7.09 (t, 1 H, $J$ = 8 Hz), 7.72 (d, 1 H, $J$ = 8 Hz), 6.67 (t, 1 H, $J$ = 2.4 Hz), 6.55 (dd, 1 H, $J$ = 8 Hz, $J$ = 2.4 Hz), 6.34 (t, 1 H, $J$ = 2.4 Hz), 6.25 (d, 1 H, $J$ = 3.2 Hz), 4.39 (brs, 1 H), 4.30 (s, 2 H) ppm. $^{13}$C{$^{1}$H}NMR (100 MHz) δ: 152.0, 148.6, 142.2, 135.1, 130.3, 118.1, 113.1, 111.7, 110.5, 107.5, 41.4 ppm.[65]

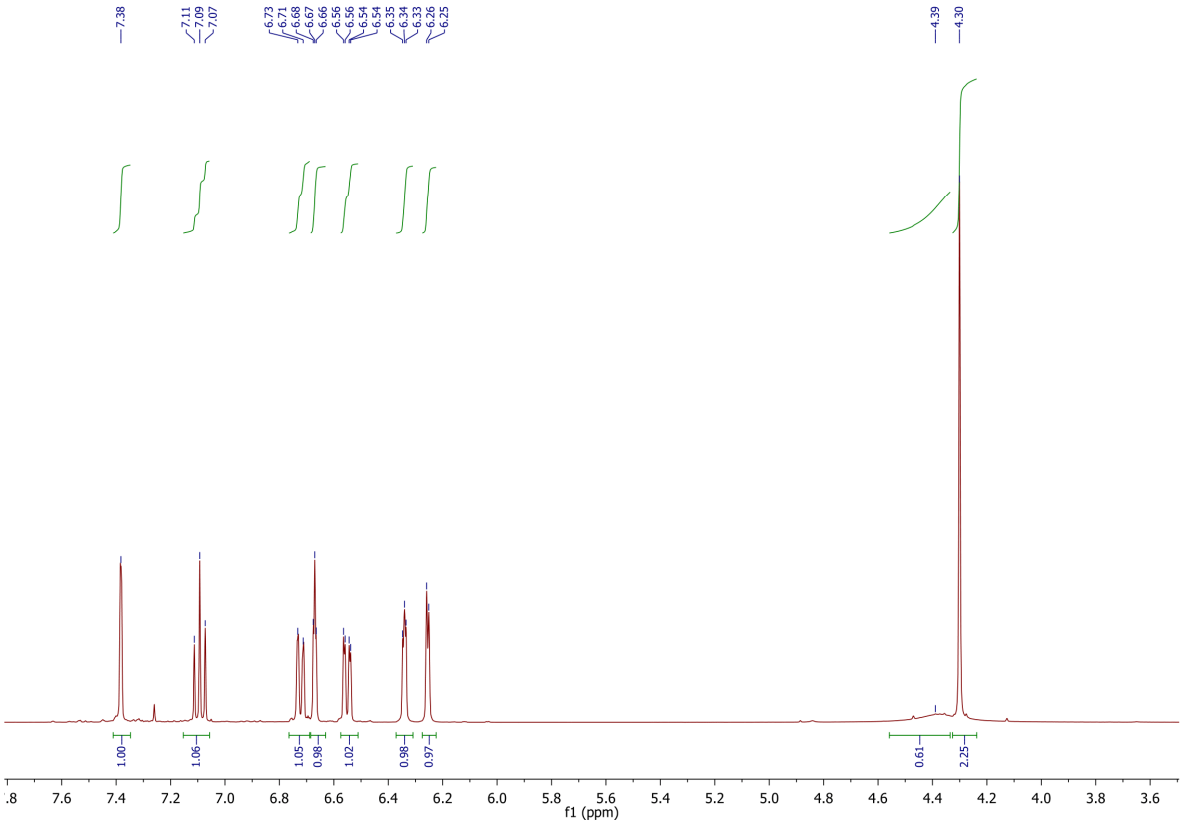



**Figure S7.$^{1}$H NMR spectrum of 2c (400 MHz, $CDCl_3$)**

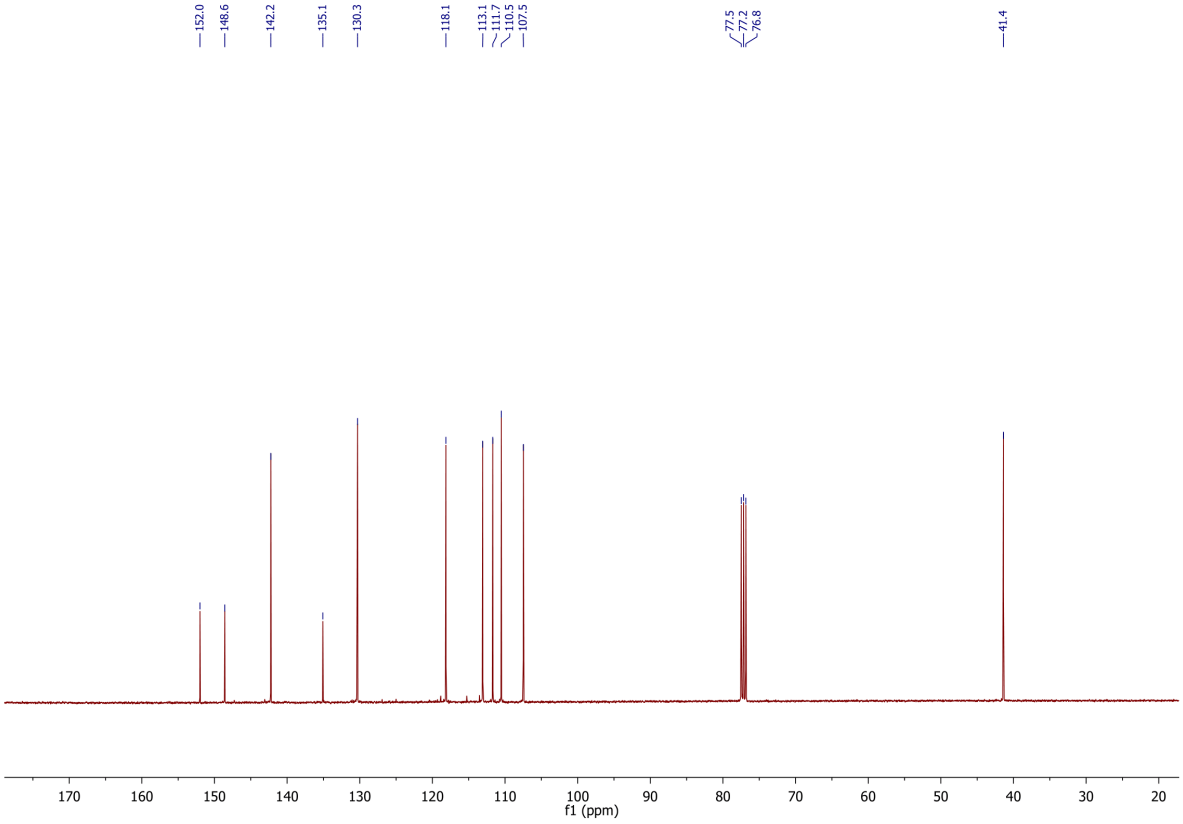



**Figure S8.$^{13}$C NMR spectrum of 2c (100 MHz, $CDCl_3$)**

***N*-(furan-2-ylmethyl)-4-methylaniline 2d**

The product **2d** was obtained as a yellow oil. 127 mg, 61 %. $^{1}$H NMR (400 MHz, $CDCl_3$) *δ*: 7.26 (s, 1 H), 6.91 (d, 2 H, *J* = 8 Hz), 6.51 (d, 2 H, *J* = 8 Hz), 6.22 (dd, 1 H, *J* = 3.2 Hz, *J* = 2 Hz), 6.13 (dd, 1 H, *J* = 3.6 Hz, *J* = 1.2 Hz), 4.19 (s, 2 H), 3. 87 (brs, 1 H), 2.15 (s, 3 H) ppm. $^{13}$C{$^{1}$H}NMR (100 MHz) δ: 153.1, 145.4, 141.9, 129.8, 127.4, 113.5, 110.4, 107.0, 41.9, 20.5 ppm.[66]

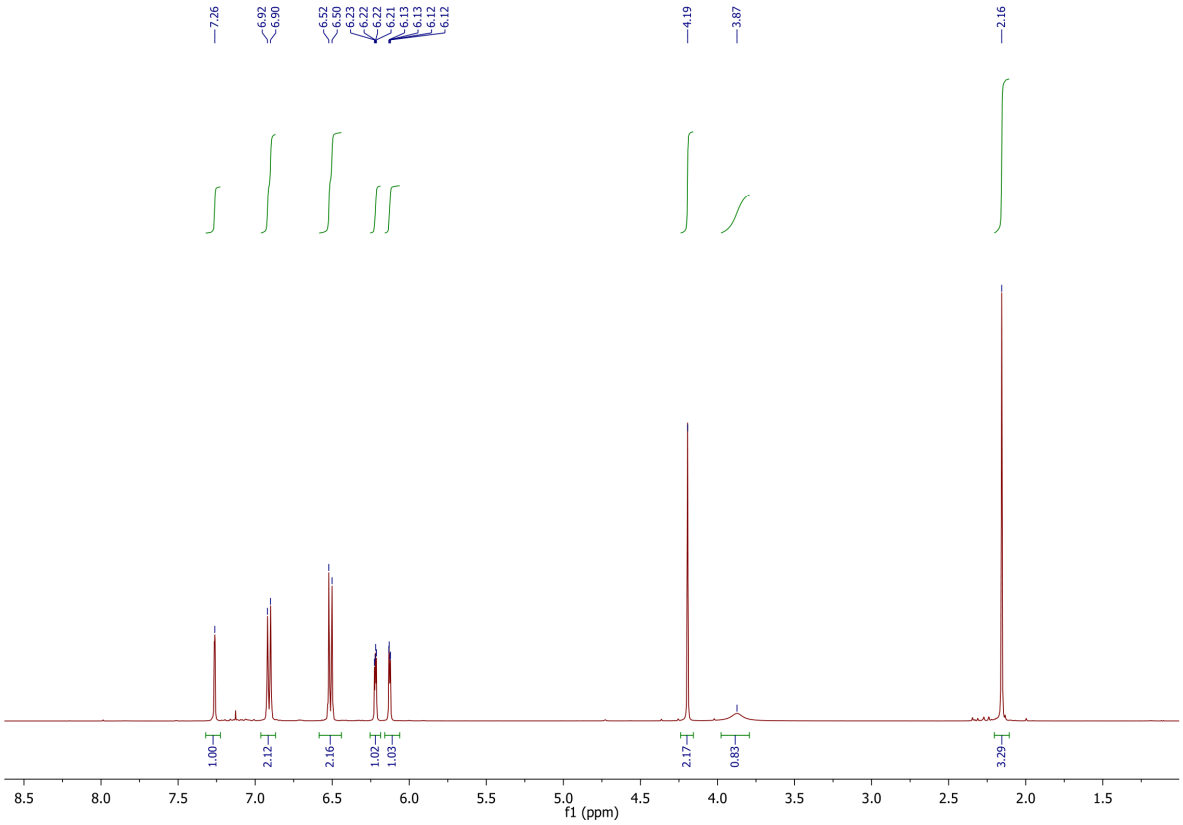



**Figure S9.$^{1}$H NMR spectrum of 2d (400 MHz, $CDCl_3$)**

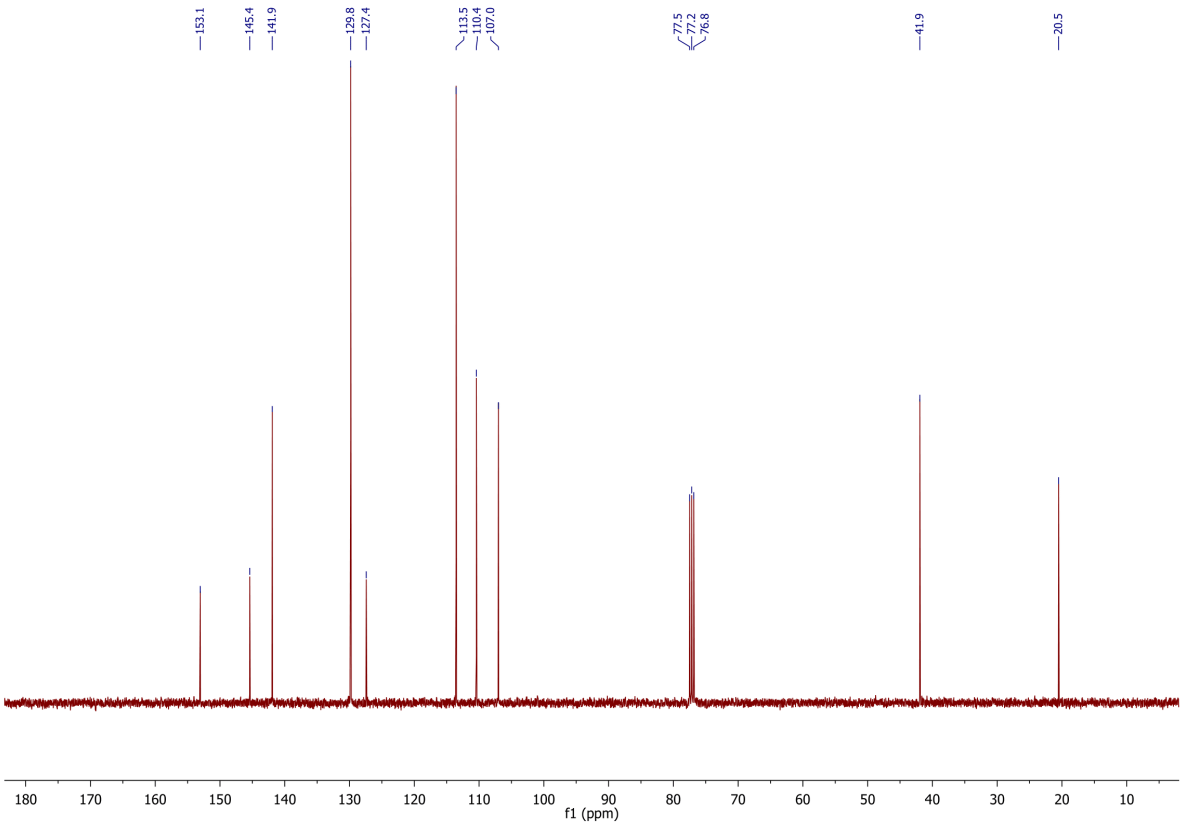



**Figure S10.$^{13}$C NMR spectrum of 2d (100 MHz, $CDCl_3$)**

**4-bromo-*N*-(furan-2-ylmethyl)aniline 2e**

The product **2e** was obtained as a yellow oil. 222 mg, 69 %. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.39 (s, 1 H), 7.29 (d, 2 H, *J* = 8.8 Hz), 6.59 (d, 2 H, *J* = 8.8 Hz), 6.34 (dd, 1 H, *J* = 3.2 Hz, *J* = 2 Hz), 6.26 (d, 1 H, *J* = 3.2 Hz), 4.31 (s, 2 H) ppm. $^{13}$C{$^{1}$H}NMR (100 MHz) $\delta$: 151.9, 146.1, 142.2, 132.0, 115.1, 110.4, 110.2, 107.4, 41.6 ppm.[65]

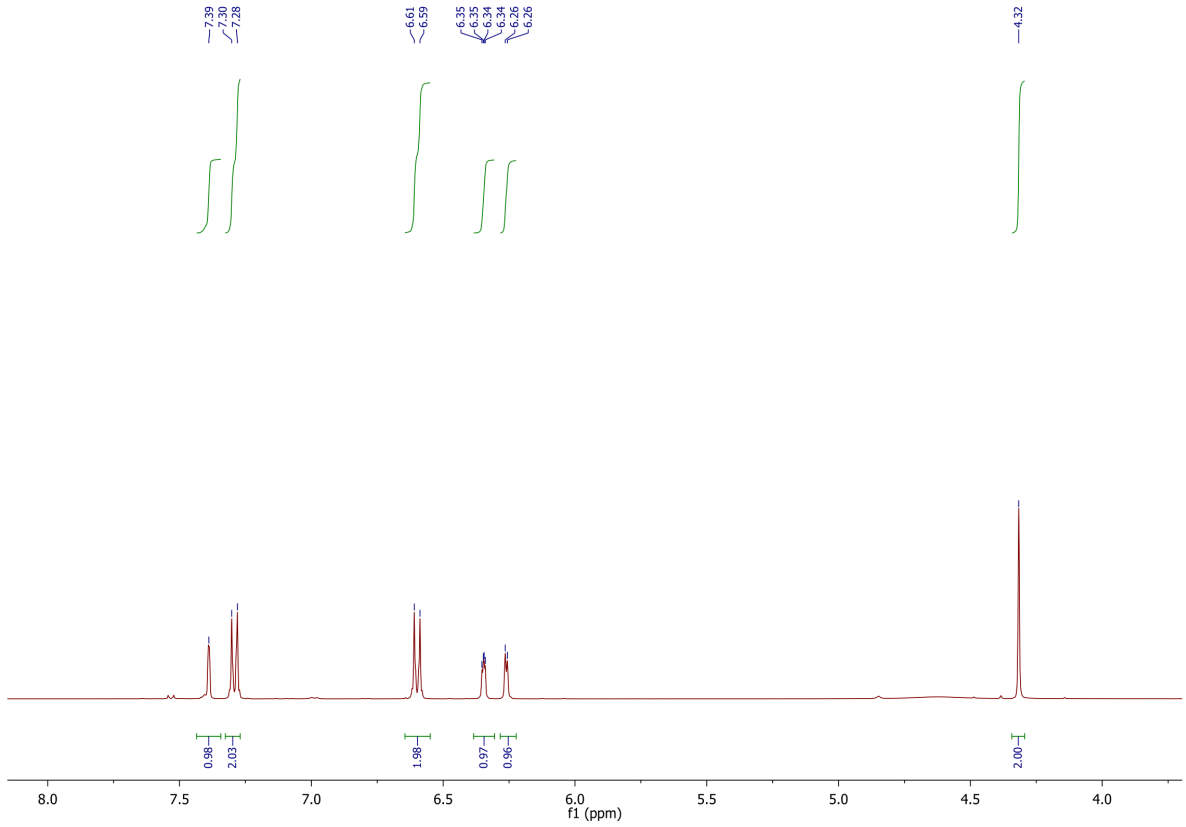



**Figure S11.$^{1}$H NMR spectrum of 2e (400 MHz, $CDCl_3$)**

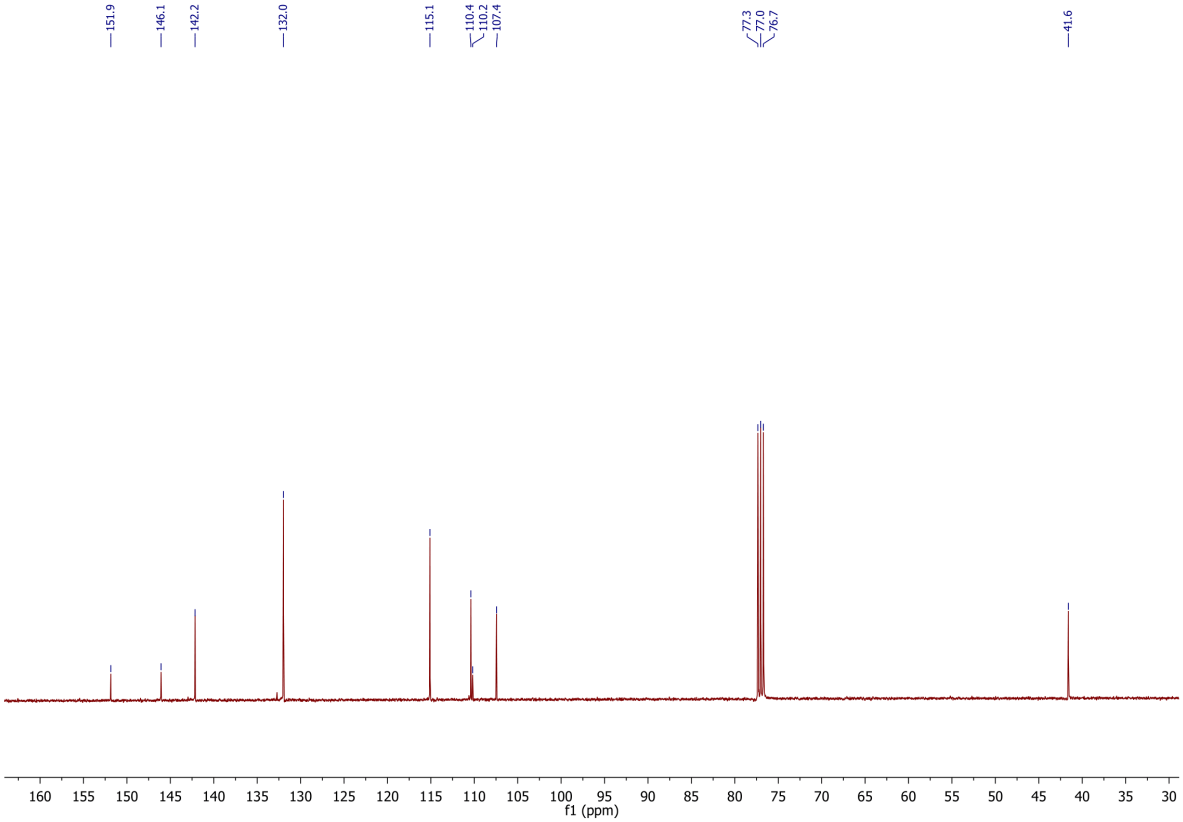



**Figure S12.$^{13}$C NMR spectrum of 2e (100 MHz, $CDCl_3$)**

**2-fluoro-*N*-(furan-2-ylmethyl)aniline 2f**

The product 2f was obtained as a yellow oil. 137 mg, 56 %. 1H NMR (400 MHz, CDCl3) $\delta$: 7.37 (s, 1 H), 7.02-6.95 (m, 2 H), 6.80 (t, 1 H, $J$ = 8.4 Hz), 6.70-6.66 (m, 1 H), 6.32 (dd, 1 H, $J$ = 3.2 Hz, $J$ = 2 Hz), 6.26 (dd, 1 H, $J$ = 3.2 Hz, $J$ = 0.8 Hz), 4.37 (s, 2 H) ppm. $^{13}C\{^1H\}$NMR (100 MHz) δ: 152.2, 152.0 (d, $J_{CF}$ = 240 Hz), 142.3, 124.7 (d, $J_{CF}$ = 4 Hz), 117.9 (d, $J_{CF}$ = 7 Hz), 114.8, 113.1, 110.5, 107.5, 41.3 ppm.[67]

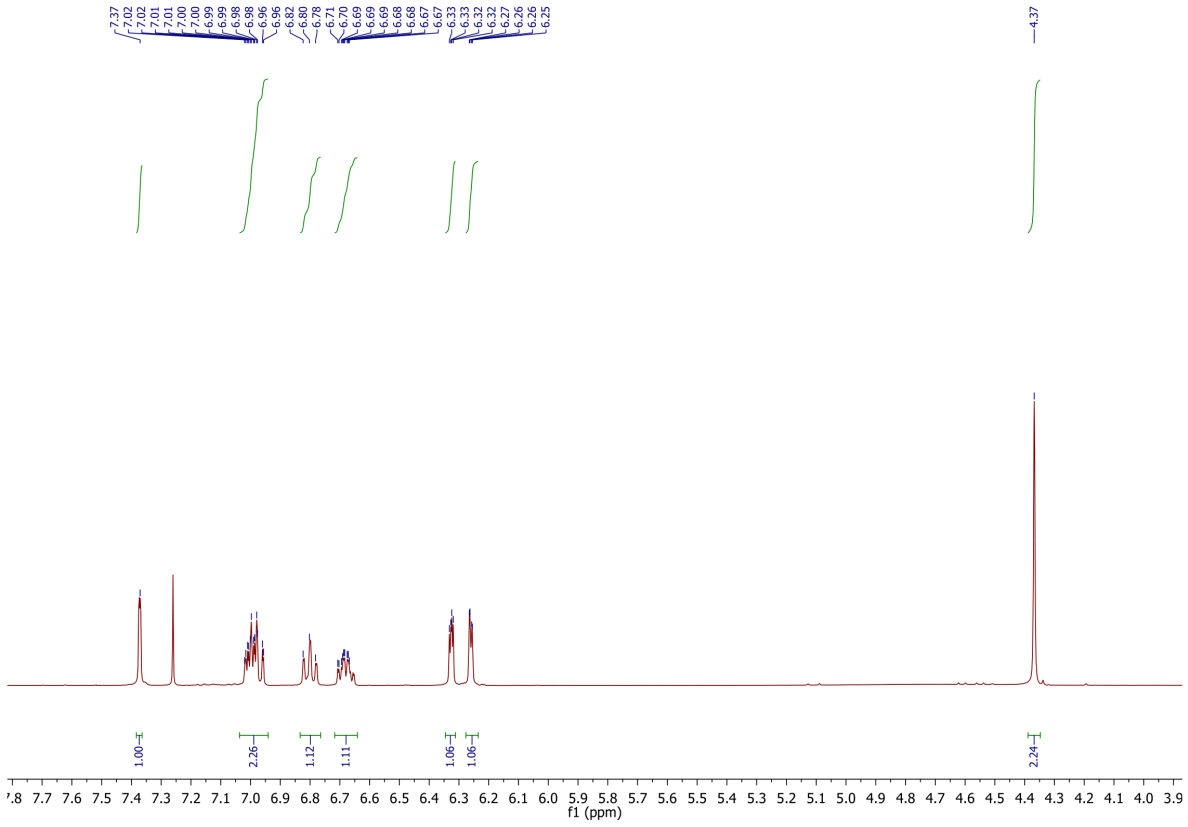



**Figure S13.$^1$H NMR spectrum of 2f (400 MHz, $CDCl_3$)**

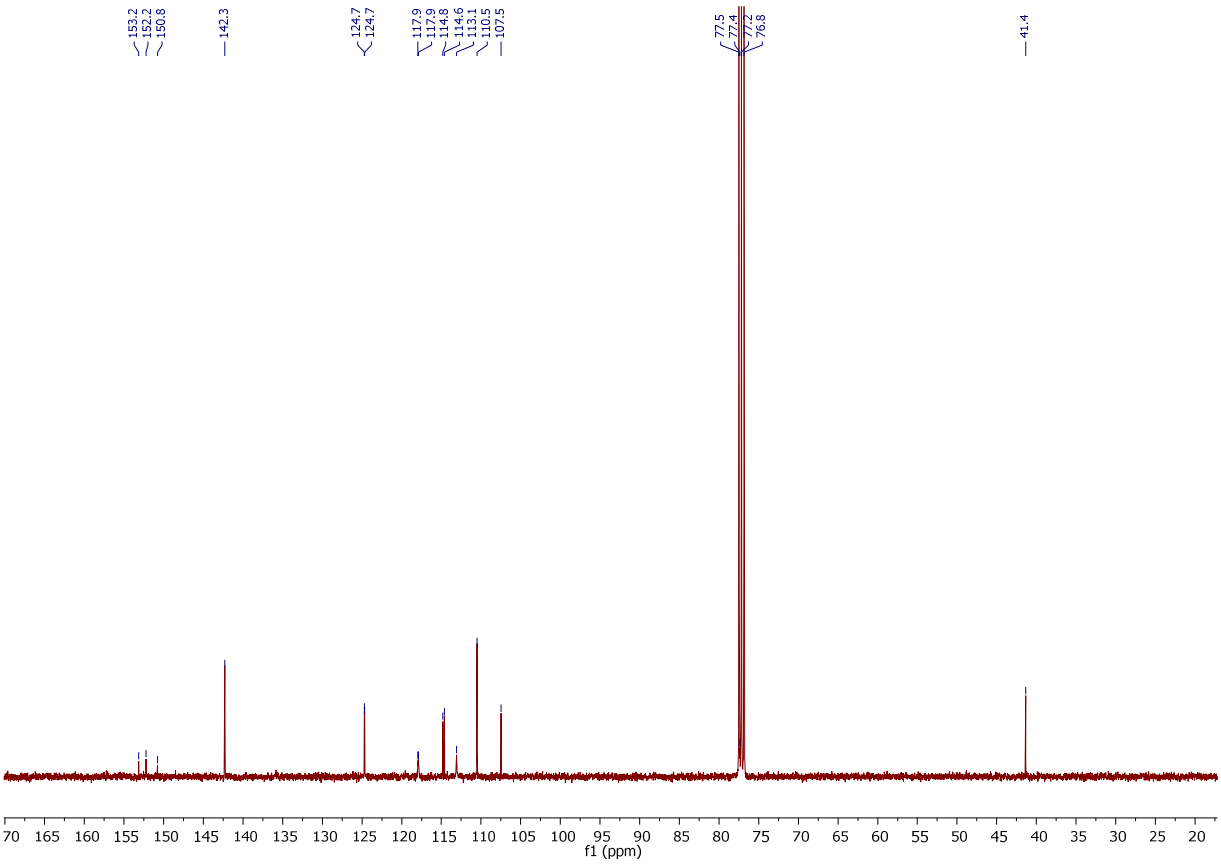



**Figure S14.$^{13}$C NMR spectrum of 2f (100 MHz, $CDCl_3$)**

***N*-(furan-2-ylmethyl)-N-methylaniline 2g**

The product **2g** was obtained as a yellow oil. 214 mg, 89 %. $^{1}$H NMR (400 MHz, $CDCl_3$) *δ*: 7.36 (s, 1 H), 7.18 (t, 2 H, *J* = 7.4 Hz), 6.70 (t, 2 H, *J* = 8 Hz), 6.59 (d, 1 H, *J* = 7.6 Hz), 6.30 (dd, 1 H, *J* = 3.2 Hz, *J* = 2 Hz), 6.23 (d, 1 H, 3.2 Hz), 4.52 (s, 2 H), 2.78 (3 H) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz) δ: 154.2, 149.3, 142.5, 129.2, 117.4, 112.6, 110.4, 107.7, 57.3, 30.8 ppm.[1]

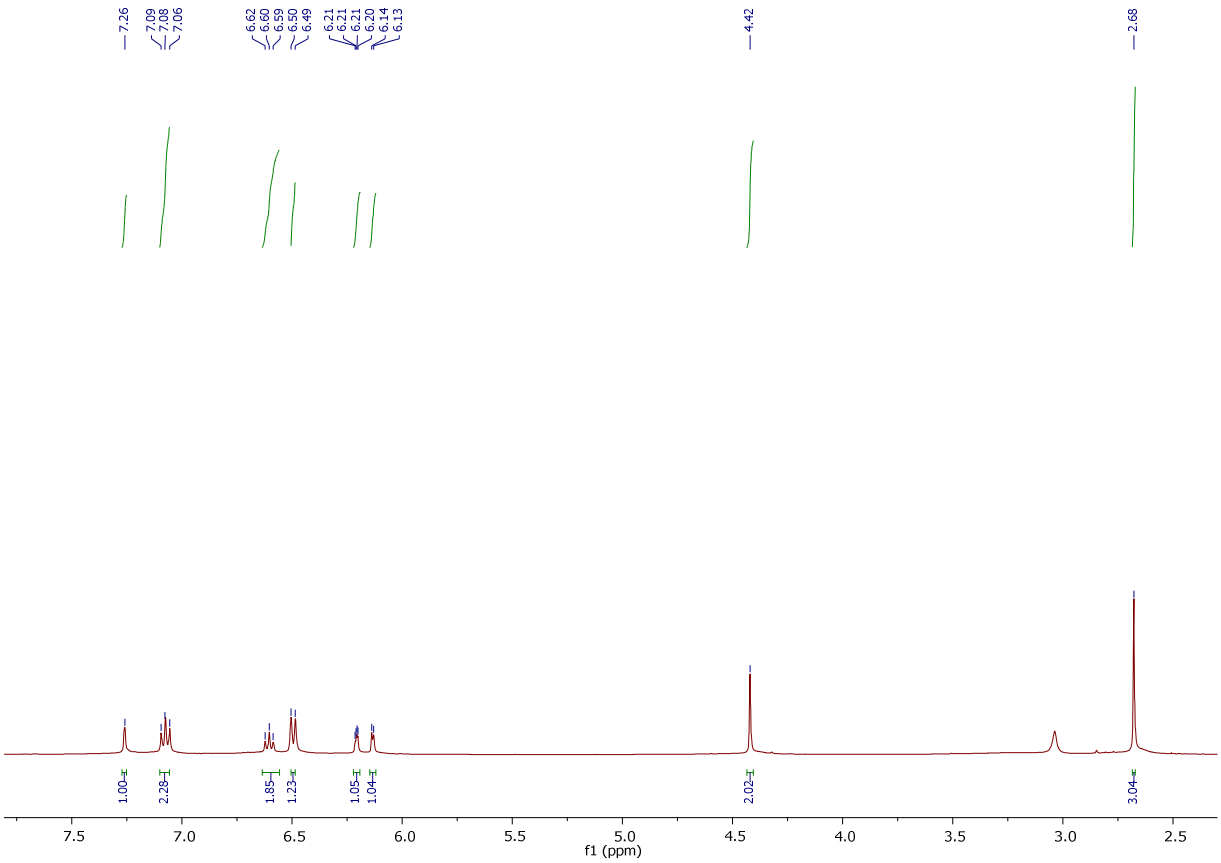



**Figure S15.$^{1}$H NMR spectrum of 2g (400 MHz, $CDCl_3$)**

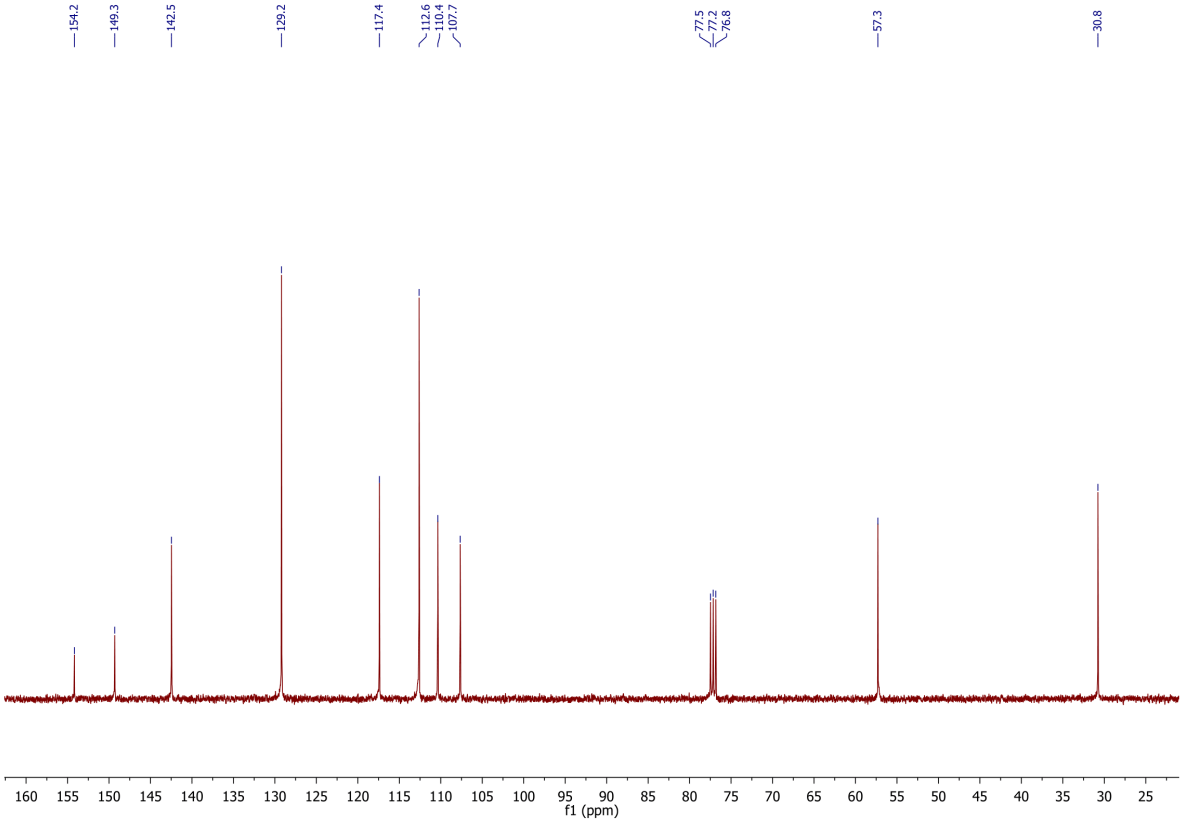



**Figure S16.$^{13}$C NMR spectrum of 2g (100 MHz, $CDCl_3$)**

**4-fluoro-*N*-(furan-2-ylmethyl)aniline 2h**

The product **2h** was obtained as a white powder. 182 mg, 74 %. $^{1}$H NMR (400 MHz, MeOD) $\delta$: 7.65 (d, 1 H, $J$ = 1.2 Hz), 7.41-7.37 (m, 2 H), 7.29 (t, 2 H, $J$ = 8.4 Hz), 6.52 (d, 1 H, $J$ = 3.2 Hz), 6.48 (dd, 1 H, $J$ = 3.6 Hz, $J$ = 2 Hz), 4.68 (s, 3 H) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz) δ: 156.2 (d, $J_{CF}$ = 260 Hz), 152.6, 143.9 (d, $J_{CF}$ = 1 Hz), 142.0, 115.7 (d, $J_{CF}$ = 23 Hz), 114.2 (d, $J_{CF}$ = 7 Hz), 110.4, 107.2, 42.1 ppm.[1]

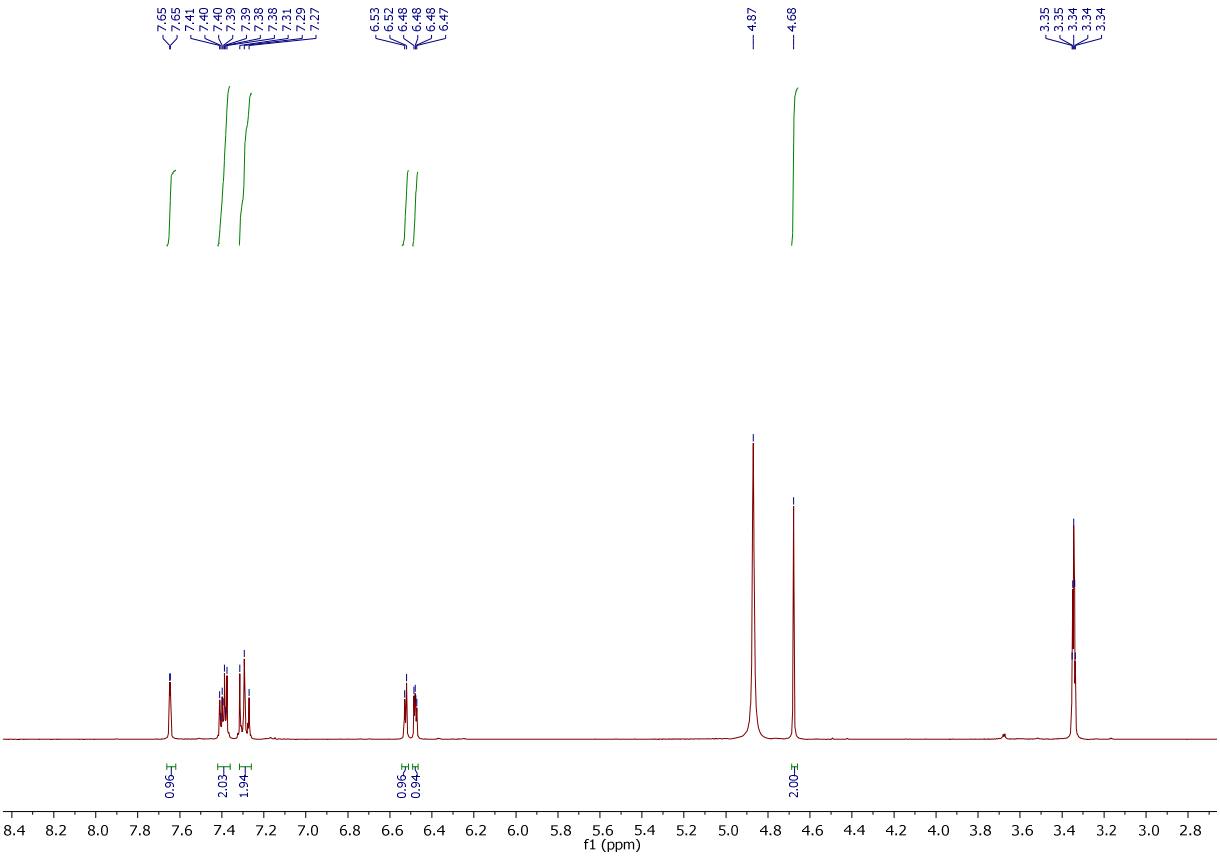



**Figure S17.$^{1}$H NMR spectrum of 2h (400 MHz, $CD_3OD$)**

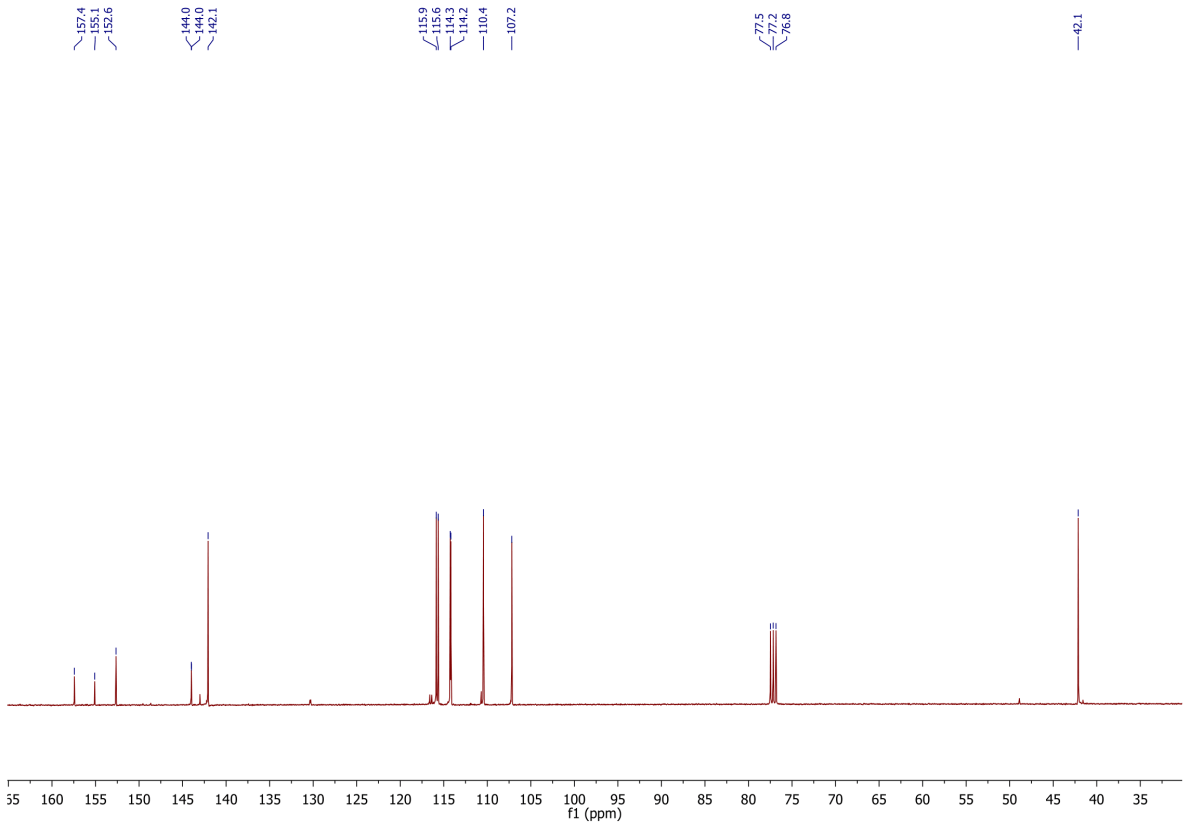



**Figure S18.$^{13}$C NMR spectrum of 2h (100 MHz, $CDCl_3$)**

***N*-(furan-2-ylmethyl)-4-(trifluoromethyl)aniline 2i**

The product **2i** was obtained as a yellow oil. 239 mg, 77 %. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.44 (d, 2 H, $J$ = 8.4 Hz), 7.40 (s, 1 H), 6.70 (d, 2 H, $J$ = 8.4 Hz), 6.35 (dd, 1 H, $J$ = 3.2 Hz, $J$ = 2 Hz), 6.27 (d, 1 H, $J$ = 3.2 Hz) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz) δ: 151.7, 149.8, 142.4, 126.7 (q, $J_{CF}$ = 3 Hz), 124.0 (q, $J_{CF}$ = 270 Hz),( 119.8 (q, $J_{CF}$ = 32 Hz), 112.6, 110.5, 107.6, 41.1 ppm.[68]

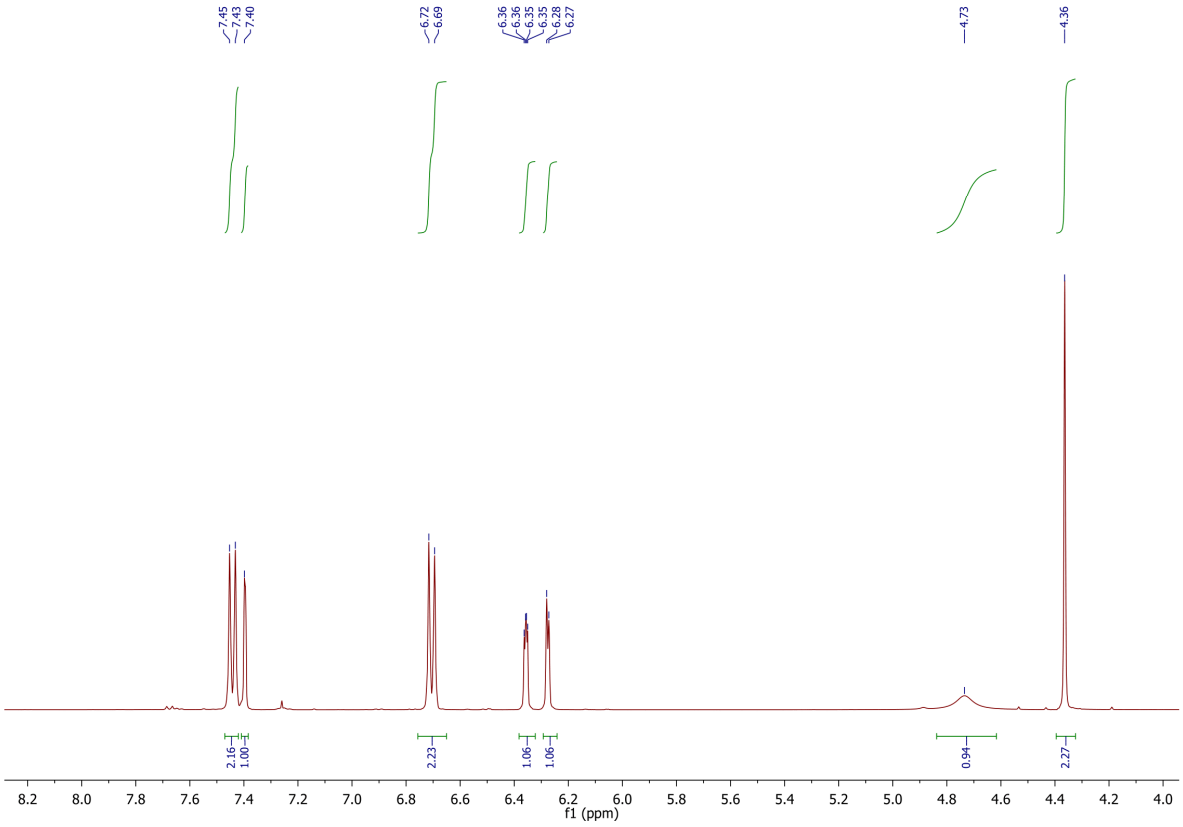



**Figure S19.$^{1}$H NMR spectrum of 2i (400 MHz, $CDCl_3$)**

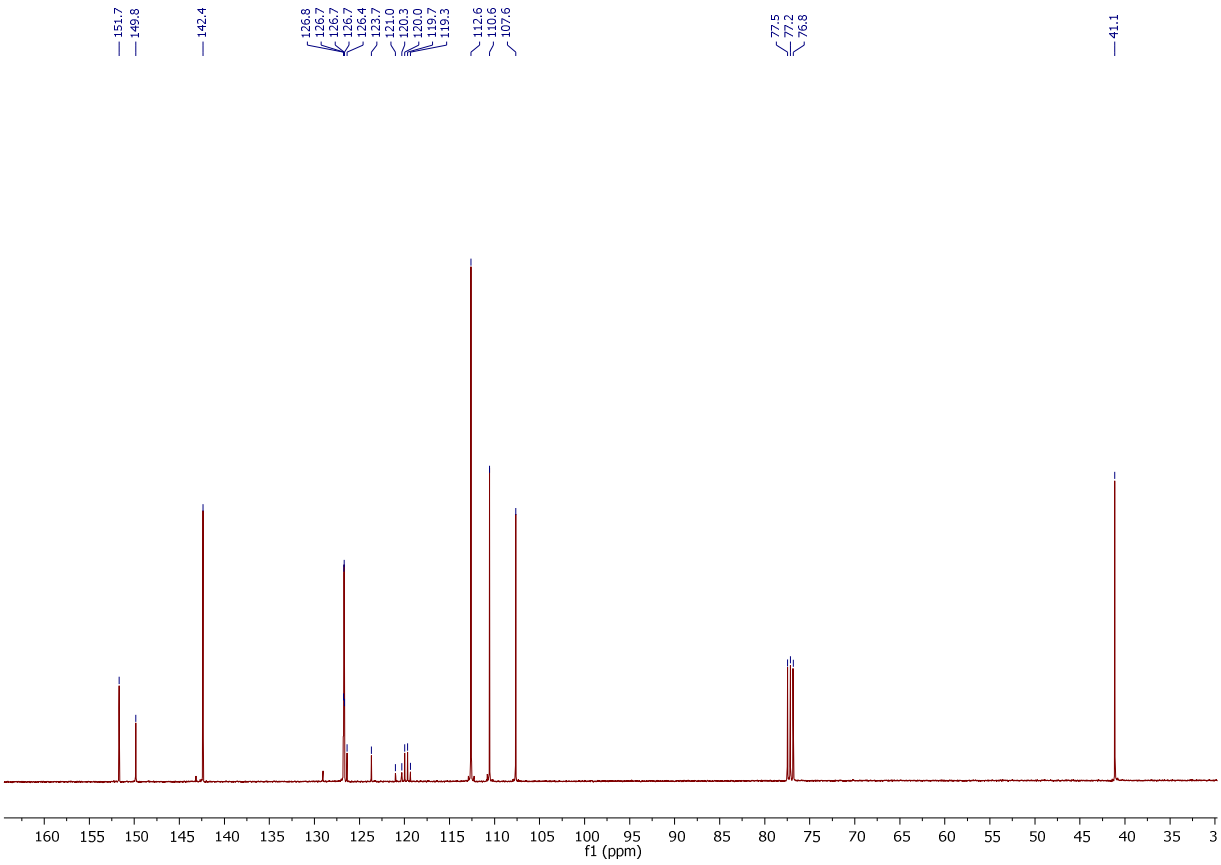



**Figure S20.$^{13}$C NMR spectrum of 2i (100 MHz, $CDCl_3$)**

***N*-(furan-2-ylmethyl)pyridin-4-amine 2j**

The product **2i** was obtained as a yellow oil. 212 mg, 95 %. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.13 (d, 2 H, *J* = 6.4 Hz), 7.37 (d, 1 H, *J* = 0.8 Hz), 6.49 (d, 2 H, *J* = 6 Hz), 6.31 (dd, 1 H, *J* = 5.2 Hz, *J* = 1.6 Hz), 6.25 (d, 1 H, *J* = 2.4 Hz), 4.60 (s, 2 H), 4.29 (s, 1 H) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz) $\delta$: 151.7, 150.8, 147.8, 129.3, 181.1, 113.3, 108.0, 106.3, 41.7, 13.7 ppm.[69]

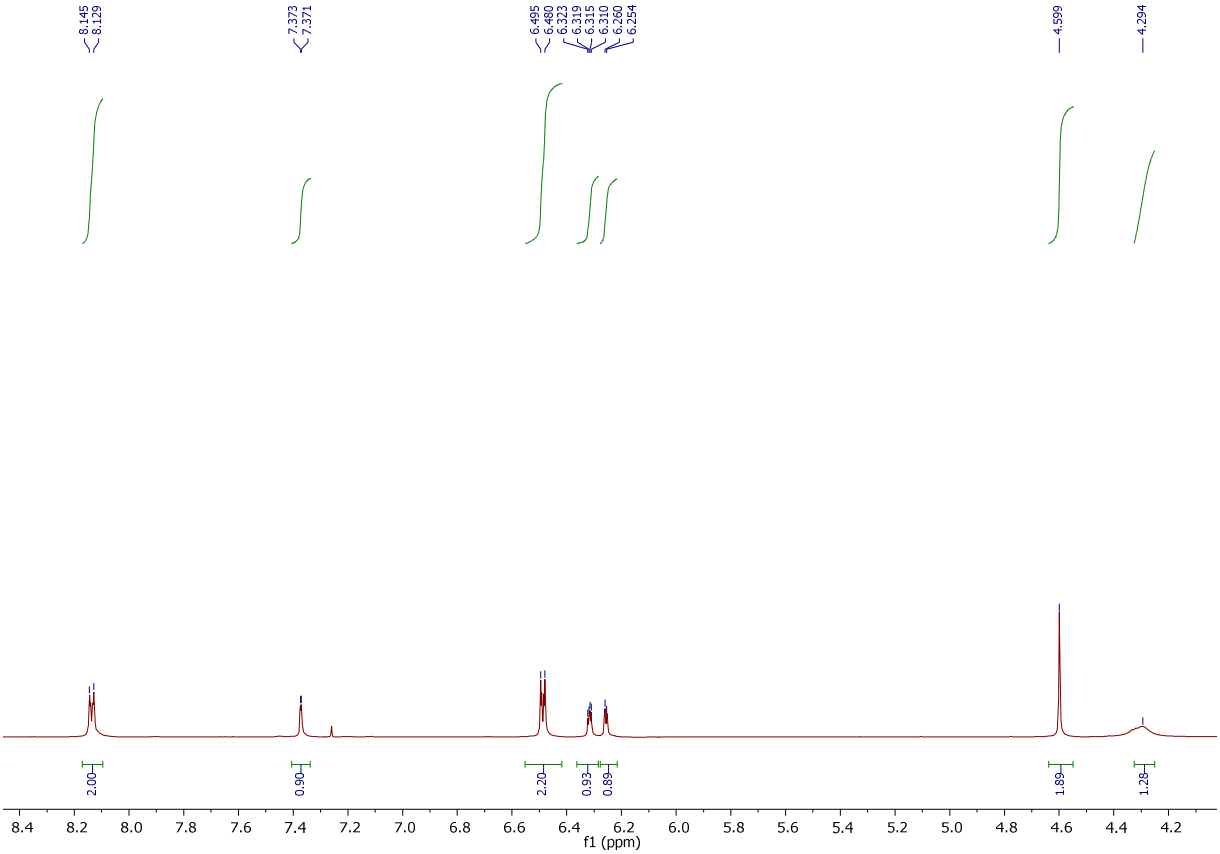



**Figure S21.$^{1}$H NMR spectrum of 2j (400 MHz, $CDCl_3$)**

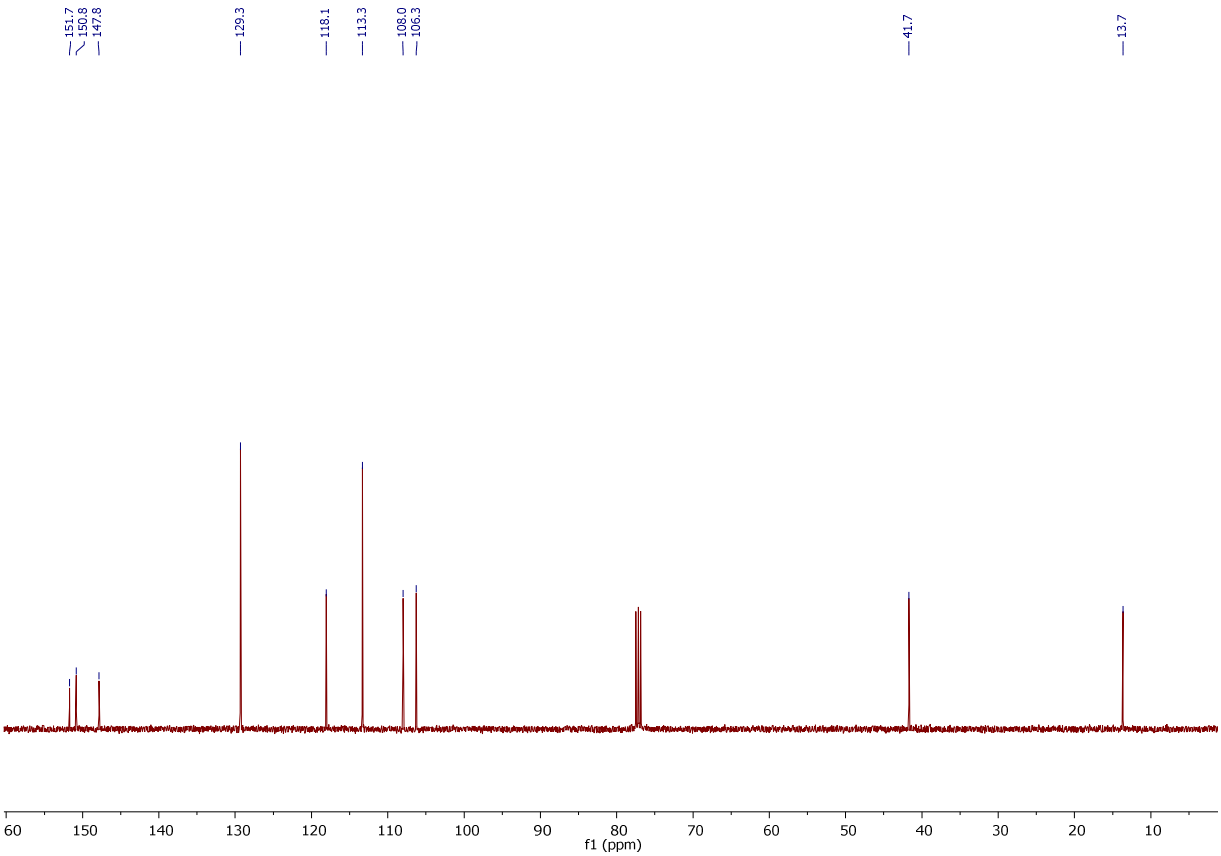



**Figure S22.$^{13}$C NMR spectrum of 2j (100 MHz, $CDCl_3$)**

**(5-((phenylamino)methyl)furan-2-yl)methanol 4**

The product **4** was obtained as a yellow oil. 230 mg, 87 %. $^{1}$H NMR (400 MHz, $CDCl_3$) *δ*: 7.19 (t, 2 H, *J* = 7.2 Hz), 6.75 (t, 1 H, *J* = 7.2 Hz), 6.67 (d, 2 H, *J* = 8 Hz), 6.21-6.17 (m, 2 H), 4.55 (s, 2 H), 4.29 (s, 2 H) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz) δ: 153.6, 153.0, 147.6, 129.2, 118.2, 113.4, 108.7, 107.9, 57.5, 41.6 ppm.[70]

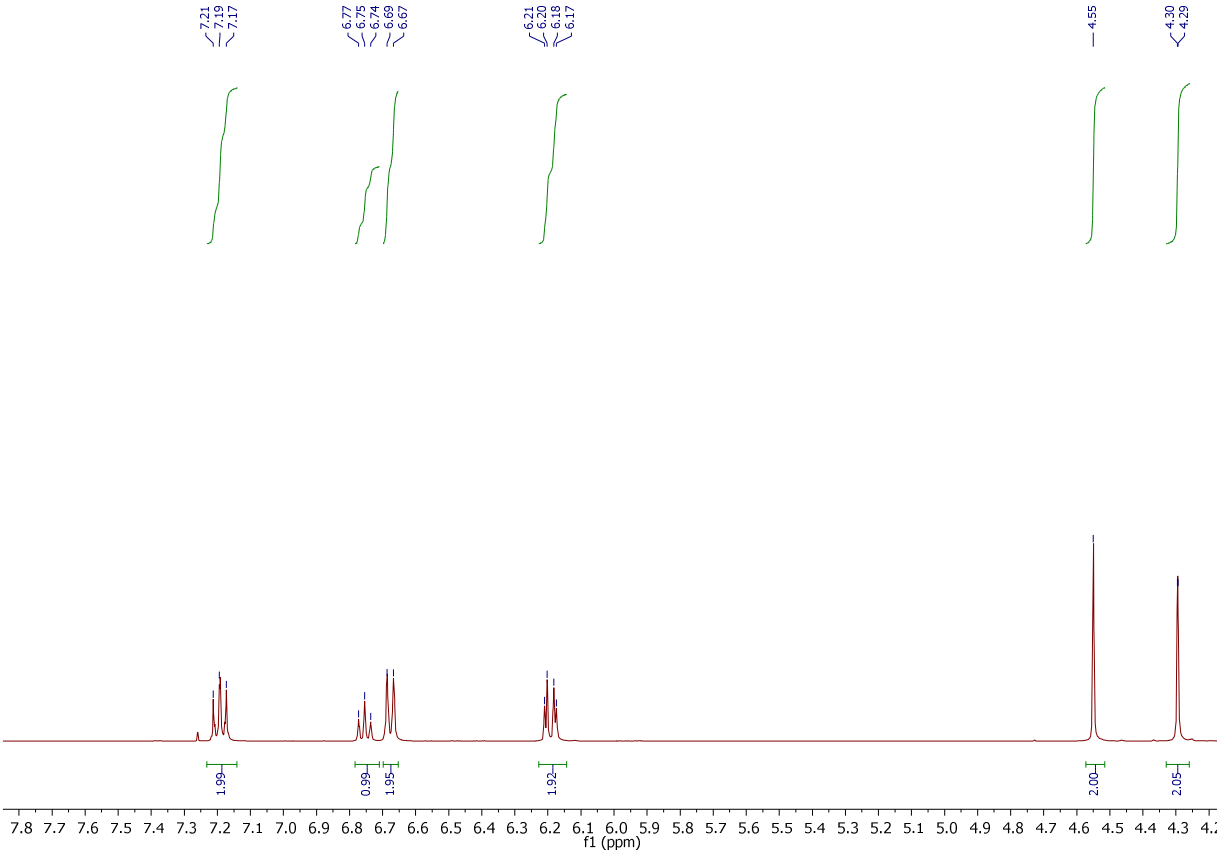



**Figure S23.$^{1}$H NMR spectrum of 4 (400 MHz, $CDCl_3$)**

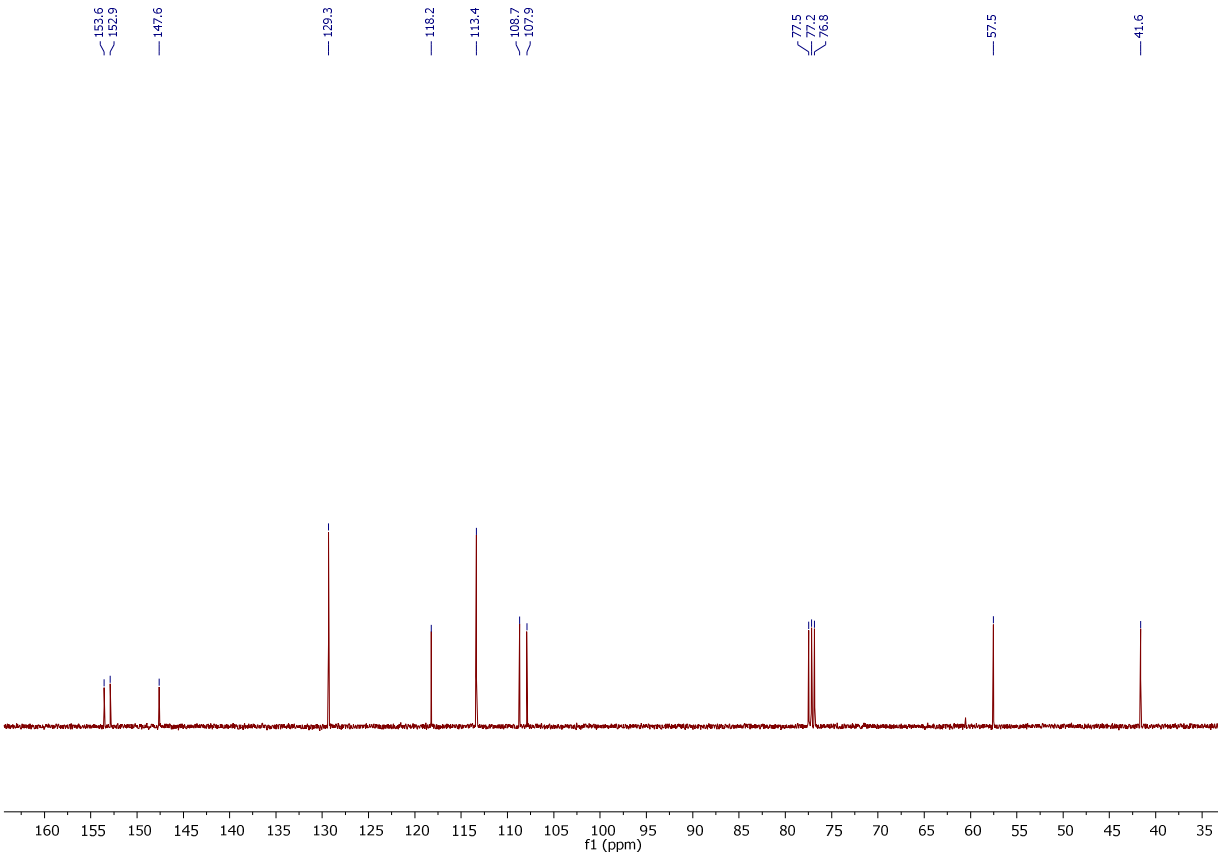



**Figure S24.$^{13}$C NMR spectrum of 4 (100 MHz, $CDCl_3$)**

***N*-((5-methylfuran-2-yl)methyl)aniline 5**

The product **5** was obtained as a colorless oil. 230 mg, 54 %. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.21 (t, 2 H, $J$ = 8 Hz), 6.76 (t, 1 H, $J$ = 7.2 Hz), 6.70 (2 H, $J$ = 8.8 Hz), 6.13 (d, 1 H, 2.8 Hz), 5.92 (d, 1 H, $J$ = 2.4 Hz), 4.27 (s, 2 H), 4.06 (s, 1 H), 2.30 (s, 3 H) ppm. $^{13}$C{$^{1}$H} NMR (100 MHz) δ: 154.8, 153.2, 149.9, 149.8, 142.3, 110.4, 109.7, 107.4, 57.1, 57.0 ppm.[62]

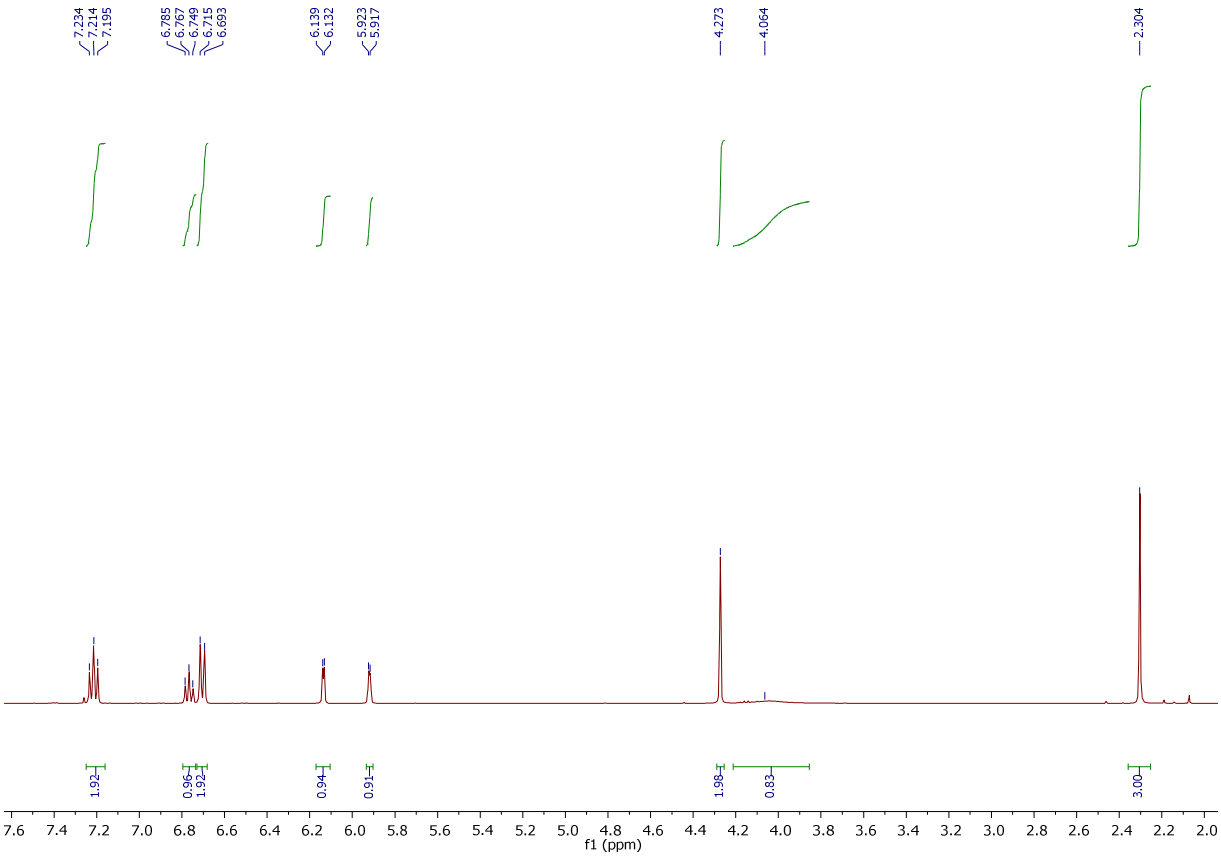



**Figure S25.$^{1}$H NMR spectrum of 5 (400 MHz, $CDCl_3$)**

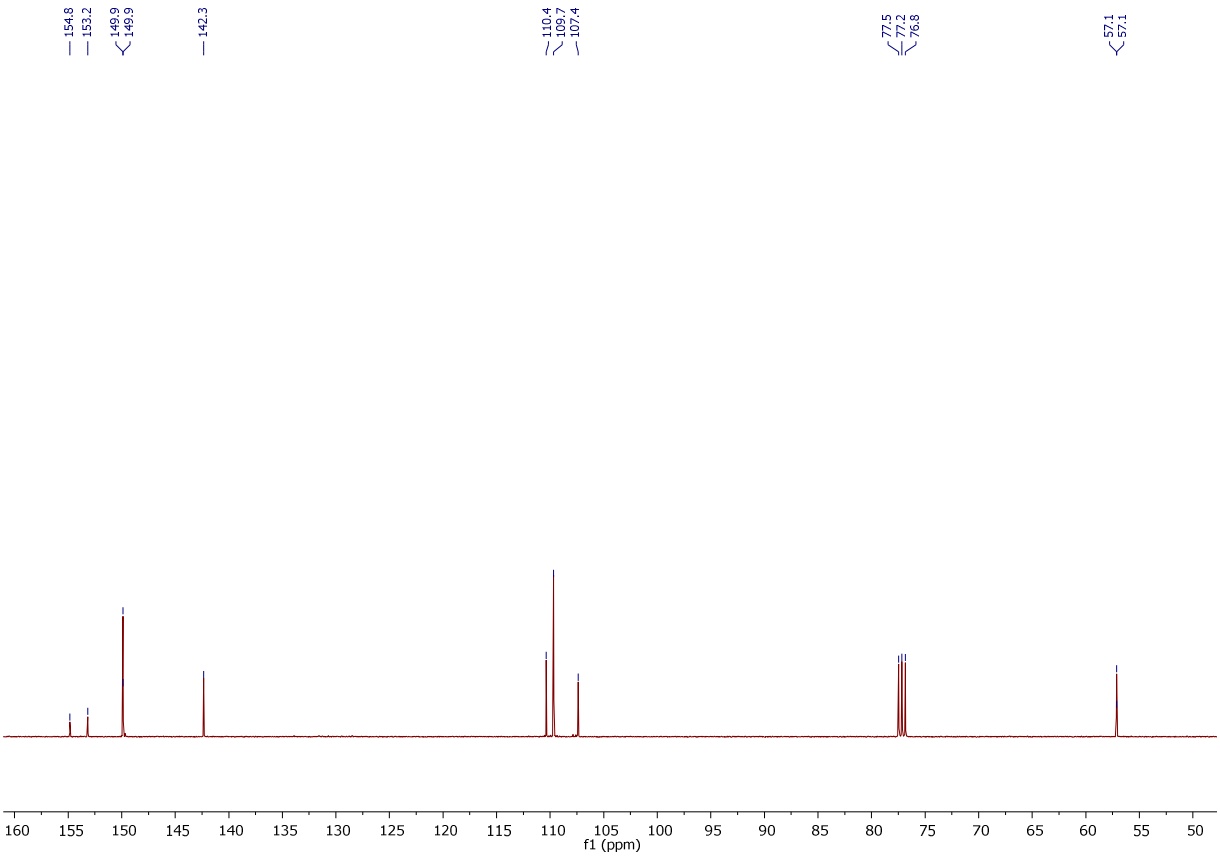



**Figure S26.$^{13}$C NMR spectrum of 5 (100 MHz, $CDCl_3$)**