Electronic Supplementary Material (ESI) for Chemical Science.

# Supplementary Information

# Indirect Reduction of $CO_2$ and Recycling of Polymers by Manganese-Catalyzed Transfer Hydrogenation of Amides, Carbamates, Urea Derivatives, and Polyurethanes

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## 1. General considerations

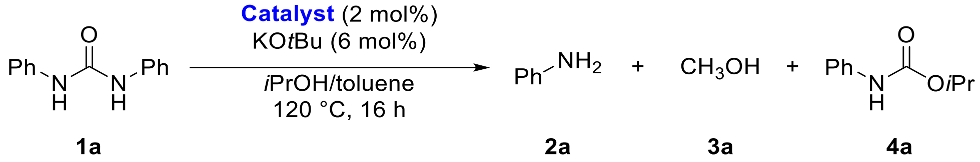
All experiments were performed under argon atmosphere by using standard Schlenk technique or in a glove box, if not stated otherwise. Dry THF, 1,4-dioxane, toluene, $CH_2Cl_2$ and *n*-hexane were purchased from *Acros Organics*, degassed and purged with argon prior to use. Chemicals were purchased from *Sigma*, *Alfa*, *Strem*, *Abcr*, *Acros* and *TCI*. Polyurethane **7a** was purchased from Sigma Aldrich and used as received, **7b** and **7c** were prepared according to the literature.[1] Deuterated solvents were ordered from *Deutero GmbH* and stored over molecular sieves. NMR spectra were received using *Bruker* 300 Fourier, *Bruker* AV 300 and *Bruker* AV 400 spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s= singlet, d= doublet, t= triplet and m= multiplet. Analytical thin layer chromatography (TLC) was carried out using commercial silica-gel plates, spots were detected with UV light and revealed with $KMnO_4$. GC analyses were performed on a Trace 1310 chromatograph with a 50m HP column. The molar masses were analyzed employing size exclusion chromatography (SEC) 1100 GPC from Agilent Technologies with a refraction index detector at 40 °C. The reported gas chromatography (GC) yields and conversions are based on a calibrated area of mesitylene as internal standard. IR spectra were recorded on a Nicolet iS10 MIR FT-IR-spectrometer from *Thermo Fisher Scientific*. The intensity of the bands is indicated by the following abbreviations: vs (very strong), s (strong), m (medium), w (weak), vw (very weak), broad signals are indexed br (broad). High Resolution Mass spectroscopy (HRMS) analysis was performed on a 6210 Time-of-Flight LC/MS (*Agilent*) at LIKAT.

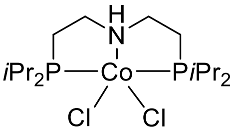
**Catalyst synthesis:** The complexes **Mn-I**[2], **Mn-II**[2], **Mn-III**[3], **Mn-IV**[4] were prepared according to the literature procedure and our report.[5] The complexes **Co-SI** and **Co-SII** were prepared according to the literature procedure[6] and our report.[7] The complexes **Fe-SI** and **Fe-SII** were prepared according to the literature procedure and our report.[8] The methanol was detected by methods reported previously by our group.[8] Note that a 50 m HP column instead of 30 m HP column was used.

## 2. Optimization Studies

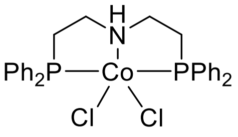
**General procedure for optimization reaction:** In a glovebox, a pressure tube equipped with a stir bar was charged with catalysts (2 mol%) and base (6 mol%). The tube was removed from the glovebox, then, the corresponding solvent was added (1.0 mL) and the mixture was stirred at room temperature (23 °C) for 5 min. Subsequently, 1,3-diphenylurea (**1a**, 106 mg, 0.500 mmol) and hydrogen donor were added in one portion. The pressure tube was placed in a preheated oil bath at the desired temperature (80–130 °C) and the mixture was stirred for 16 h. After the indicated time, the reaction mixture was cooled to room temperature (23 °C). The yields were determined by GC using mesitylene as the internal standard.

**Table S1.** Transfer hydrogenation of 1,3-diphenylurea (**1a**) with various well-known non-precious metal containing pincer type catalysts.

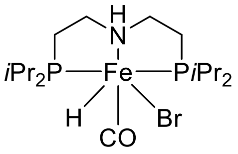




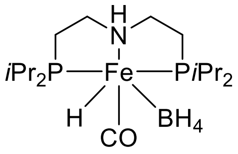
Co-**SI**



Co-**SII**



Fe-**SI**

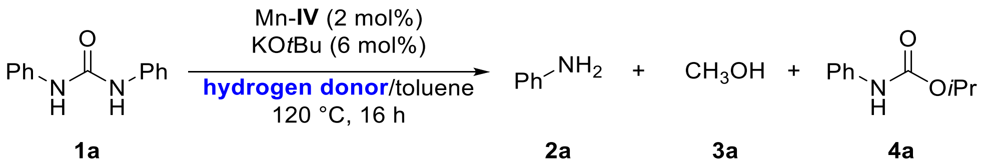


Fe-**SII**

| entry | catalyst | yield **2a** (%) | yield **3a** (%) | yield **4a** (%) |
|---|---|---|---|---|
| 1 | Co-**SI** | 49 | - | 84 |
| 2 | Co-**SII** | 51 | - | 87 |
| 3 | Fe-**SI** | 61 | 15 | 69 |
| 4 | Fe-**SII** | 63 | 20 | 65 |

Reaction conditions: **1a** (0.5 mmol), catalyst (2 mol%), KO*t*Bu (6 mol%), toluene (1 mL), *i*PrOH (1 mL), 120 °C, 16 h. The yields were determined by GC using mesitylene as the internal standard.

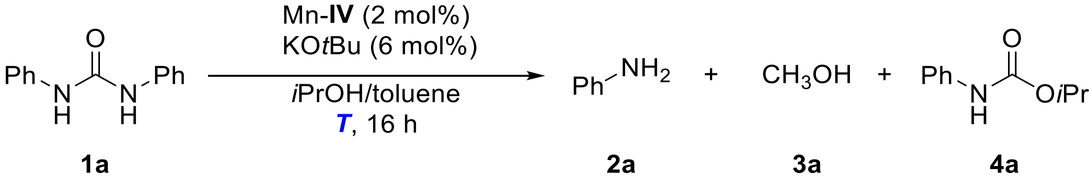
**Table S2.** Transfer hydrogenation of 1,3-diphenylurea (**1a**) with various hydrogen donors.



| entry | hydrogen donor | yield **2a** (%) | yield **3a** (%) | yield **4a** (%) |
|---|---|---|---|---|
| 1 | EtOH (1.0 mL) | 72 | 35 | 36 |
| **2** | ***i*PrOH (1.0 mL)** | **91** | **89** | **–** |
| 3 | Hantzsch ester (5.0 equiv.) | 39 | – | 76 |
| 4 | $NH_3BH_3$ (5.0 equiv.) | – | – | – |
| 5 | HCOOH/$Et_3N$ (5.0 equiv.) | – | – | – |
| 6 | Glycerol (1.0 mL) | 27 | – | 49 |

Reaction conditions: **1a** (0.5 mmol), Mn-**IV** (2 mol%), KO*t*Bu (6 mol%), toluene (1 mL), hydrogen donor, 120 °C, 16 h. The yields were determined by GC using mesitylene as the internal standard.

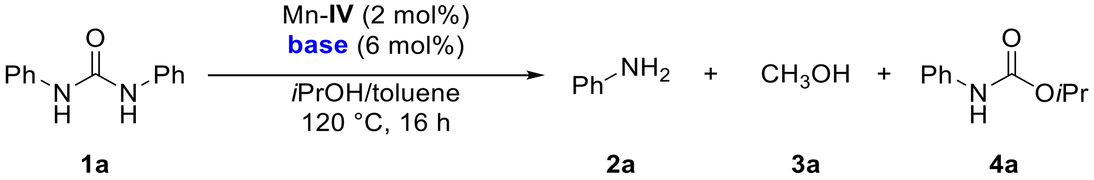
**Table S3.** Transfer hydrogenation of 1,3-diphenylurea (**1a**) at different temperatures.



| entry | T/ °C | yield **2a** (%) | yield **3a** (%) | yield **4a** (%) |
|---|---|---|---|---|
| 1 | 130 | 87 | 82 | - |
| **2** | **120** | **91** | **89** | **-** |
| 3 | 110 | 43 | 23 | 51 |
| 4 | 100 | 46 | 9 | 73 |
| 5 | 90 | 27 | - | 46 |

Reaction conditions: **1a** (0.5 mmol), Mn-**IV** (2 mol%), KO*t*Bu (6 mol%), toluene (1 mL), *i*PrOH (1 mL), *T*, 16 h. The yields were determined by GC using mesitylene as the internal standard.

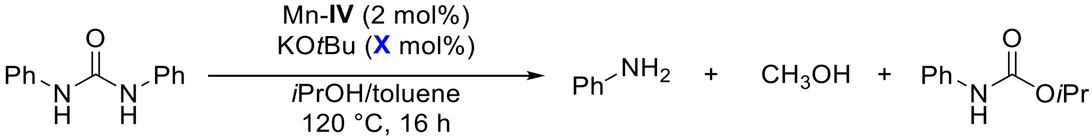
**Table S4.** Transfer hydrogenation of 1,3-diphenylurea (**1a**) with various bases.



| entry | base | yield **2a** (%) | yield **3a** (%) | yield **4a** (%) |
|---|---|---|---|---|
| 1 | KOH | - | - | - |
| 2 | $K_2CO_3$ | - | - | - |
| 3 | NaH | 7 | - | 9 |
| **4** | **KO*t*Bu** | **91** | **89** | **-** |
| 5 | $Cs_2CO_3$ | <5 | - | <5 |
| 6 | LiOH | - | - | - |
| 7 | NaOMe | - | - | - |

Reaction conditions: **1a** (0.5 mmol), Mn-**IV** (2 mol%), base (6 mol%), toluene (1 mL), *i*PrOH (1 mL), 120 °C, 16 h. The yields were determined by GC using mesitylene as the internal standard.

**Table S5.** Transfer hydrogenation of 1,3-diphenylurea (**1a**) with different amount of KO*t*Bu

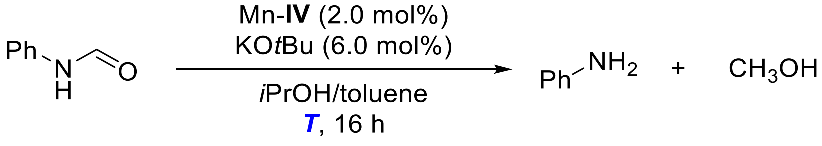


**1a** **2a** **3a** **4a**

| entry | KO*t*Bu/ mol% | yield **2a** (%) | Yield **3a** (%) | yield **4a** (%) |
|---|---|---|---|---|
| 1 | – | – | – | – |
| 2 | 2 | – | – | – |
| 3 | 4 | 63 | 48 | 43 |
| **4** | **6** | **91** | **89** | **–** |
| 5[a] | 8 | 83 | 80 | – |

Reaction conditions: **1a** (0.5 mmol), Mn-**IV** (2 mol%), base (6 mol%), toluene (1 mL), *i*PrOH (1 mL), 120 °C, 16 h. The yields were determined by GC using mesitylene as the internal standard. [a] *N*-(propan-2-ylidene)aniline and *N*-methylaniline were detected as by-products

**Table S6.** Transfer hydrogenation of formanilide (**5a**) at different temperatures.

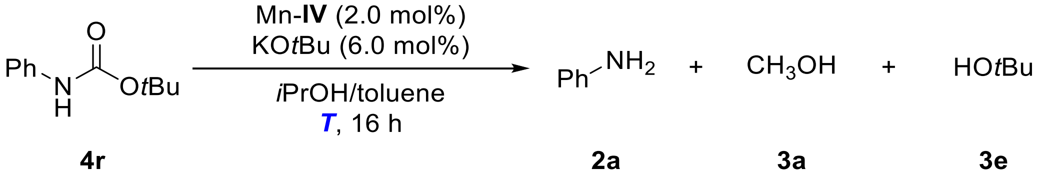


**5a** **2a** **3a**

| entry | T/ °C | yield **2a** (%) | yield **3a** (%) |
|---|---|---|---|
| 1 | 130 | 82 | 75 |
| 2 | 120 | 89 | 83 |
| 3 | 110 | 91 | 84 |
| **4** | **100** | **93** | **86** |
| 5 | 90 | 82 | 75 |
| 6 | 80 | 54 | 42 |

Reaction conditions: **5a** (0.5 mmol), Mn-**IV** (2 mol%), KO*t*Bu (6 mol%), toluene (1 mL), *i*PrOH (1 mL), *T*, 16 h. The yields were determined by GC using mesitylene as the internal standard.

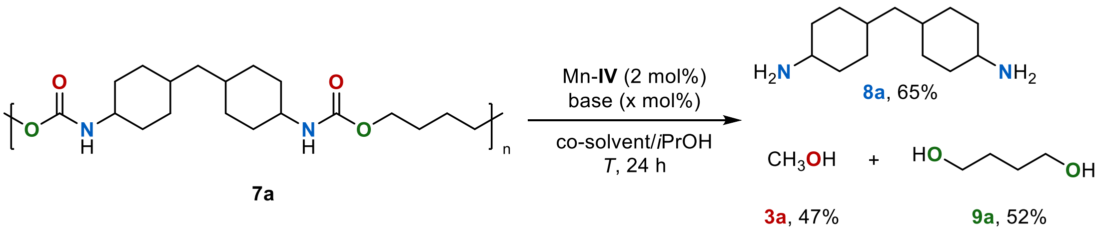
**Table S7.** Transfer hydrogenation of *tert*-butyl phenylcarbamate (**4r**) at different temperatures.



| entry | T/ °C | yield **2a** (%) | yield **3a** (%) | yield **3e** (%)[a] |
|---|---|---|---|---|
| 1 | 100 | 33 | 25 | 32 |
| 2 | 120 | 56 | 47 | 49 |
| **3** | **140** | **78** | **70** | **71** |
| 4 | 150 | 74 | 68 | 66 |

Reaction conditions: **4r** (0.5 mmol), Mn-**IV** (2 mol%), KO*t*Bu (6 mol%), toluene (1 mL), *i*PrOH (1 mL), *T*, 16 h. The yields were determined by GC using mesitylene as the internal standard. [a] The yield was determined by $^1$H-NMR using mesitylene as the internal standard.

**Table S8.** Transfer hydrogenation of polyurethane **7** with different conditions.



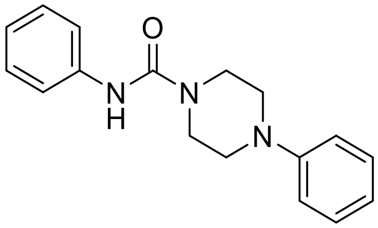
| entry | T/ °C | co-solvent | base (x mol%) | yield **3a** (%) | yield **8a** (%) | yield **9a** (%)[a] |
|---|---|---|---|---|---|---|
| 1 | 100 | toluene | KO*t*Bu (6 mol%) | – | – | – |
| 2 | 120 | toluene | KO*t*Bu (6 mol%) | – | – | – |
| 3 | 130 | toluene | KO*t*Bu (6 mol%) | <5 | 7 | 8 |
| 4 | 140 | toluene | KO*t*Bu (6 mol%) | 14 | 30 | 23 |
| 5 | 150 | toluene | KO*t*Bu (6 mol%) | 23 | 42 | 31 |
| **6** | **150** | **THF** | **KO*t*Bu (6 mol%)** | **47** | **65** | **52** |
| 7 | 150 | 1,4-dioxane | KO*t*Bu (6 mol%) | 39 | 55 | 46 |
| 8 | 150 | DMSO | KO*t*Bu (6 mol%) | 9 | 16 | 13 |
| 9 | 150 | *n*-hexane | KO*t*Bu (6 mol%) | 29 | 34 | 36 |
| 10 | 150 | $CH_2Cl_2$ | KO*t*Bu (6 mol%) | 11 | 17 | 15 |
| 11 | 150 | THF | KO*t*Bu (2 mol%) | 17 | 22 | 20 |
| 12 | 150 | THF | KO*t*Bu (4 mol%) | 21 | 26 | 19 |
| 13 | 150 | THF | KO*t*Bu (8 mol%) | 39 | 58 | 51 |
| 14 | 150 | THF | KO*t*Bu (12 mol%) | 28 | 45 | 40 |
| 15 | 150 | THF | KOH (6 mol%) | trace | <5 | <5 |
| 16 | 150 | THF | $K_3PO_4$ (6 mol%) | 23 | 31 | 32 |

Reaction conditions: **7a** (167 mg), Mn-**IV** (2 mol%), base (x mol%), co-solvent (1 mL), *i*PrOH (1 mL), *T*, 24 h. The yields were determined by GC using mesitylene as the internal standard.

## 3. Synthesis of substrates

### 3.1 Carbamates and urea derivatives

*N*-4-Diphenylpiperazine-1-carboxamide (**1i**)[9]



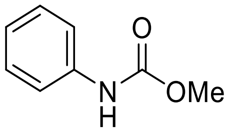
A flame-dried flask was degassed, flushed with argon, and charged with 4-phenyl-1-piperazine (810 mg, 5.00 mmol), $CH_2Cl_2$ (5 mL) and $Et_3N$ (1.01 g, 10.0 mmol). Then, phenyl isocyanate (595 mg, 5.00 mmol) added as dropwise. The reaction mixture was stirred at 23 °C overnight. The reaction mixture was then diluted with $CH_2Cl_2$ (10 mL), washed with 1M HCl (3 x 20 mL), water (10 mL), and then dried with $Na_2SO_4$. The crude product was purified by column chromatography ($CH_2Cl_2$/methanol = 80:1) to afford the desired product **1i** (1.04 g, 3.71 mmol, 74 %).

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.46 – 7.25 (m, 6H), 7.18 – 6.84 (m, 4H), 6.61 (br s, 1H), 3.68 (m, 4H), 3.24 (m, 4H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 155.22, 151.02, 139.02, 129.38, 129.04, 123.42, 120.58, 120.30, 116.65, 49.33, 44.17 ppm.

The spectroscopic data correspond to those reported in the literature.[9]

*N*-Phenyl methyl carbamate (**4b**)[10]



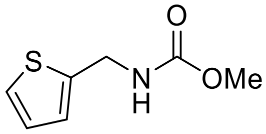
A flame-dried flask was degassed, flushed with argon, and charged with aniline (465 mg, 5.00 mmol), $CH_2Cl_2$ (5 mL) and $Et_3N$ (1.52 g, 15.0 mmol). Then, methyl chloroformate (940 mg, 10.0 mmol) added as dropwise. The reaction mixture was stirred at 23 °C overnight. The reaction mixture was then diluted with $CH_2Cl_2$ (10 mL), washed with 1M HCl (3 x 20 mL), water (10 mL), and then dried over $Na_2SO_4$. The crude product was purified by column chromatography (pentane/ethyl acetate = 20:1) to afford the desired product **4b** (611 mg, 4.05 mmol, 81 %) as light yellow solid.

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.61 – 7.20 (m, 4H), 7.17 – 6.96 (m, 1H), 6.78 (br s, 1H), 3.80 (s, 3H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 154.23, 137.97, 129.15, 123.57, 118.85, 52.44 ppm.

The spectroscopic data correspond to those reported in the literature.[10]

Thiophene-2-methylamine methyl carbamate (**4f**)[11]



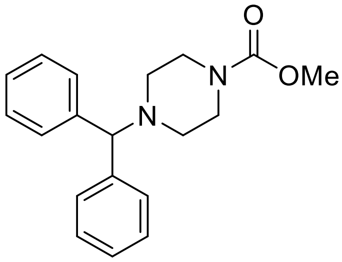
A flame-dried flask was degassed, flushed with argon, and charged with 2-aminomethylthiophene (565 mg, 5.00 mmol), $CH_2Cl_2$ (5 mL) and $Et_3N$ (1.52 g, 15.0 mmol). Then, methyl chloroformate (940 mg, 10.0 mmol) was added dropwise and the reaction mixture was stirred at 23 °C overnight. The reaction mixture was then diluted with $CH_2Cl_2$ (10 mL), washed with 1M HCl (3 x 20 mL), water (10 mL), and then dried with $Na_2SO_4$. The crude product was purified by column chromatography (pentane/ethyl acetate = 20:1) to afford the desired product **4f** (607 mg, 3.55 mmol, 71%) as yellow oil.

**$^1$H-NMR** (400 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.14 (d, $J$ = 4.9, Hz, 1H), 6.93 – 6.83 (m, 2H), 5.26 – 4.99 (br s, 1H), 4.56 – 4.30 (m, 2H), 3.61 (s, 3H) ppm.

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 25 °C) $\delta$ = 156.86, 141.45, 126.95, 125.80, 125.17, 52.37, 39.97 ppm.

The spectroscopic data correspond to those reported in the literature.[11]

Methyl 4-benzhydrylpiperazine-1-carboxylate (**4m**)



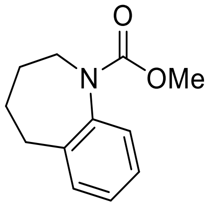
A flame-dried flask was degassed, flushed with argon, and charged with diphenylmethylpiperazine (1.26 g, 5.00 mmol), $CH_2Cl_2$ (5 mL) and $Et_3N$ (1.52 g, 15.0 mmol). Then, methyl chloroformate (940 mg, 10.0 mmol) added as dropwise. The reaction mixture was stirred at 23 °C overnight. The reaction mixture was then diluted with $CH_2Cl_2$ (10 mL), washed with 1M HCl (3 x 20 mL), water (10 mL), and then dried with $Na_2SO_4$. The crude product was purified by column chromatography (pentane/ethyl acetate = 20:1) to afford the desired product **4m** as white solid (1.18 g, 3.80 mmol, 76 %).

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.53 – 7.44 (m, 4H), 7.37 – 7.27 (m, 4H), 7.26 – 7.17 (m, 2H), 4.30 (br s, 1H), 3.71 (s, 3H), 3.57 – 3.48 (m, 4H), 2.51 – 2.38 (m, 4H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 156.86, 142.13, 128.44, 127.74, 126.95, 75.87, 52.32, 51.45, 43.77 ppm.

HRMS (EI) calculated for $C_{15}H_{22}O_2$: 310.1676; found $C_{15}H_{22}O_2$: 310.1681.

Methyl 2,3,4,5-tetrahydro-1H-benzo[b]azepine-1-carboxylate (**4n**)[12]



A flame-dried flask was degassed, flushed with argon, and charged with 2,3,4,5-tetrahydro-1Hbenzo[b]azepine (735 mg, 5.00 mmol), DMF (10 mL) and $K_2CO_3$ (2.08 g, 15.0 mmol). Then, methyl chloroformate (940 mg, 15.0

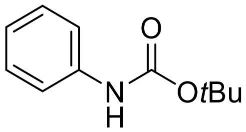
mmol) added as dropwise. The reaction mixture was stirred at 23 °C overnight. The reaction mixture was then diluted with mixture of toluene and ethyl acetate (1:1, 20 mL), washed with 1M HCl (3 x 20 mL), water (10 mL), and then dried with $Na_2SO_4$. The crude product was purified by column chromatography (pentane/ethyl acetate = 20:1) to afford the desired product **4n** as white solid (625 mg, 3.05 mmol, 61 %).

**$^1$H-NMR** (400 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.12 – 7.04 (m, 4H), 4.34 (br s, 1H), 3.69 (br s, 1H), 3.55 (s, 3H), 2.69 – 2.62 (m, 2H), 1.81 – 1.69 (m, 4H) ppm.

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 25 °C) $\delta$ = 155.34, 142.15, 139.83, 129.78, 127.97, 127.14, 126.67, 52.76, 48.96, 34.61, 29.48, 26.29 ppm.

The spectroscopic data correspond to those reported in the literature.[12]

### *tert*-Butyl phenylcarbamate (**4r**)[13]



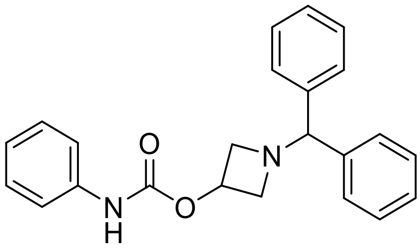
A flame-dried flask was degassed, flushed with argon, and charged with aniline (465 mg, 5.00 mmol), THF (5.0 mL) and di-tert-butyl dicarbonate (1.09 g, 5.00 mmol). The reaction mixture was stirred at 23 °C overnight. The reaction mixture was then diluted with $CH_2Cl_2$ (10 mL), water (10 mL), and then dried with $Na_2SO_4$. The crude product was purified by column chromatography (pentane/ethyl acetate = 20:1) to afford the desired product **4r** (858 mg, 4.45 mmol, 89 %) as white solid.

**$^1$H-NMR** (400 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.45 – 7.36 (m, 2H), 7.36 – 7.27 (m, 2H), 7.05 (d, $J$ = 8.5 Hz, 1H), 6.49 (br s, 1H), 15.4 (s, 9H) ppm.

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 25 °C) $\delta$ = 152.89, 138.46, 129.12, 123.17, 118.66, 80.65, 28.49 ppm.

The spectroscopic data correspond to those reported in the literature.[13]

### (1-Benzhydrylazetidin-3-yl) *N*-phenylcarbamate (**4p**)



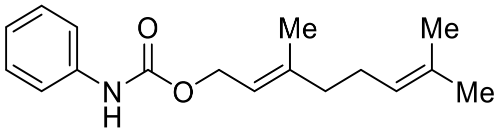
A flame-dried flask was degassed, flushed with argon, and charged with phenyl isocyanate (595 mg, 5.00 mmol), $CH_2Cl_2$ (10 mL), $K_2CO_3$ (2.08 g, 15.0 mmol) and 1-(diphenylmethyl)-3-hydroxyazetidine (1.19 g, 5.00 mmol). The reaction mixture was stirred at 23 °C overnight. The reaction mixture was then diluted with $CH_2Cl_2$ (10 mL), washed with 1M HCl (3 x 20 mL), water (10 mL), and then dried with $Na_2SO_4$. The crude product was purified by column chromatography ($CH_2Cl_2$/methanol = 20:1) to afford the desired product **4p** (966 mg, 2.70 mmol, 54 %) as white solid.

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.54 – 7.43 (m, 4H), 7.43 – 7.28 (m, 8H), 7.28 – 7.20 (m, 2H), 7.16 – 7.03 (m, 1H), 6.81 (s, 1H), 5.21 (q, $J$ = 6.2 Hz, 1H), 4.44 (s, 1H), 3.83 – 3.54 (m, 2H), 3.32 – 3.02 (m, 2H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 152.74, 141.88, 137.67, 129.17, 128.61, 127.52, 127.36, 123.71, 118.78, 78.38, 64.52, 60.27 ppm.

HRMS (EI) calculated for $C_{15}H_{22}O_2$: 358.1676; found $C_{15}H_{22}O_2$: 358.1672.

(*E*)-3,7-Dimethylocta-2,6-dien-1-yl phenylcarbamate (**4q**)[11]



A flame-dried flask was degassed, flushed with argon, and charged with phenyl isocyanate (595 mg, 5.00 mmol), $CH_2Cl_2$ (5 mL), $Et_3N$ (15.2 mg, 15.0 mmol) and Geraniol (770 mg, 5.00 mmol). The reaction mixture was stirred at 23 °C overnight. The mixture was then diluted with $CH_2Cl_2$ (10 mL), washed with 1M HCl (3 x 20 mL), water (10 mL), and dried with $Na_2SO_4$. The crude product was purified by column chromatography (hexanes/ethyl acetate = 50:1) to afford the desired product **4q** (859 mg, 3.15 mmol, 63 %) as white solid.

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.40 – 7.24 (m, 2H), 7.22 – 7.07 (m, 2H), 7.01 – 6.81 (m, 2H), 5.29 (t, *J* = 7.1, 1H), 5.06 – 4.93 (m, 1H), 4.59 (d, *J* = 7.1 Hz, 2H), 2.09 – 1.87 (m, 4H), 1.66 – 1.55 (m, 6H), 1.50 (s, 3H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 153.90, 142.36, 138.16, 131.84, 129.00, 123.81, 123.30, 118.81, 118.56, 62.06, 39.58, 26.35, 25.72, 17.73, 16.51 ppm.

The spectroscopic data correspond to those reported in the literature.[14]

## 3.2 Polyurethanes

MDI based polyurethane (**7b**)[1]

A flame-dried flask was degassed, flushed with argon, and charged with 4,4'-methylenebis(phenyl isocyanate) (MDI) (5.00 g, 20.0 mmol) and DMF (20 mL). 1,6-hexanediol (2.36 g, 20.0 mmol) was dissolved in DMF (20 mL) and added slowly. The reaction mixture was stirred for 2 h at 23°C and subsequently heated to 60 °C and stirred for another 2 h. The mixture was poured into 100 mL of water. The formed precipitate was filtered off, washed with $H_2O$ and $Et_2O$ and dried at 60 °C in an oven. The product was obtained as a white solid (6.34 g).

**GPC:** $M_n$ = 3100 g·mol$^{-1}$, $M_w$ = 11000 g·mol$^{-1}$

TDI based polyurethane (**7c**)[1]

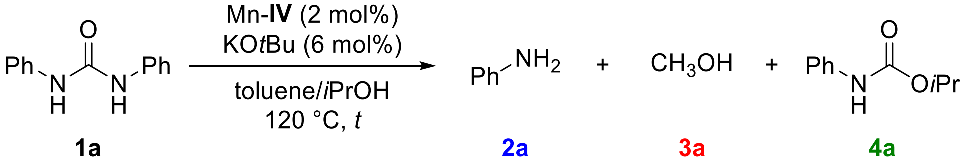
A flame-dried flask was degassed, flushed with argon, and charged with 2,4-diisocyanato-1-methyl-benzene (TDI) (3.50 g, 20.0 mmol) and DMF (20 mL). 1,6-hexanediol (2.36 g, 20.0 mmol) was dissolved in DMF (20 mL) and added slowly. The reaction mixture was stirred for 2 h at 23°C and subsequently heated to 60 °C and stirred for another 2 h. The mixture was poured into 100 mL of water. The formed precipitate was filtered off, washed with $H_2O$ and $Et_2O$ and dried at 60 °C in an oven. The product was obtained as a white solid (4.74 g).

**GPC:** $M_w$ = 2200 g·mol$^{-1}$, $M_n$ = 9600 g·mol$^{-1}$

## 4. Mechanistic experiments

**Representative protocol:** In a glovebox, a pressure tube equipped with a stir bar was charged with Mn-**IV** (6.2 mg, 0.01 mmol, 2 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 6 mol%). The tube was removed from the glovebox, then, toluene (1 mL) was added, and the mixture was stirred at room temperatures (23°C) for 5 min. Subsequently, urea derivative 1 (0.5 mmol) and *i*PrOH (1 mL) was added in one portion. The pressure tube was placed in a preheated oil bath at 120 °C and stirred for the corresponding times. After cooling down the reaction mixture to room temperatures (23°C), mesitylene was added as internal standard and the product distribution was determined by GC at the respective time.

### 4.1 Kinetic profile for the transfer hydrogenation of 1a



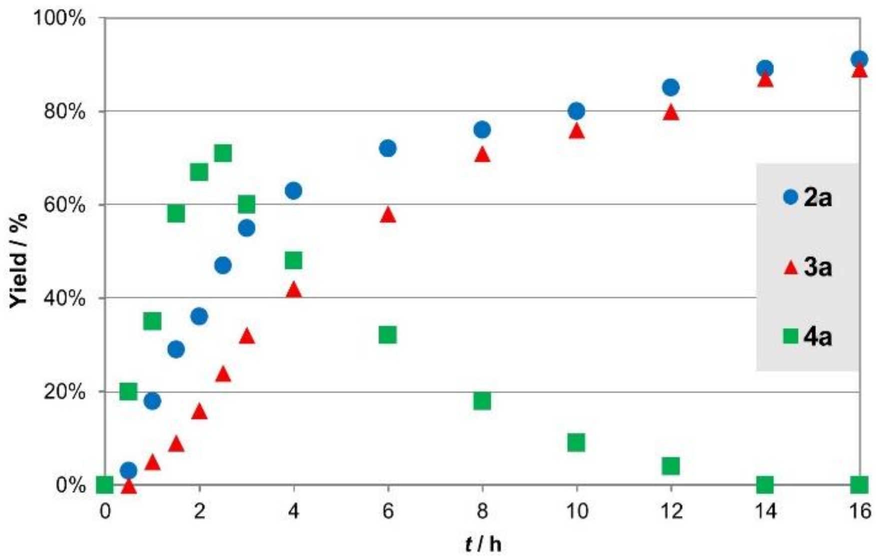


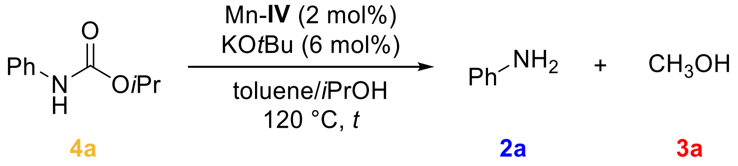
**Figure S1**. Kinetic profile for the transfer hydrogenation of **1a**

**Table S9.** Yield of products **2a** and **3a** as well as intermediate **4a** in the transfer hydrogenation of **1a** at different reaction times.

| entry | *t*/ h | yield **2a** (%)[a] | yield **3a** (%)[a] | yield **4a** (%)[a] |
|---|---|---|---|---|
| 1 | 0.5 | 3 | 0 | 20 |
| 2 | 1.0 | 18 | 5 | 35 |
| 3 | 1.5 | 29 | 9 | 58 |
| 4 | 2.0 | 36 | 16 | 67 |
| 5 | 2.5 | 47 | 24 | 71 |
| 6 | 3 | 55 | 32 | 60 |
| 7 | 4 | 63 | 42 | 48 |
| 8 | 6 | 72 | 58 | 32 |
| 9 | 8 | 76 | 71 | 18 |
| 10 | 10 | 80 | 76 | 9 |
| 11 | 12 | 85 | 80 | 4 |
| 12 | 14 | 89 | 87 | 0 |
| 13 | 16 | 91 | 89 | 0 |

Reaction conditions: **1a** (0.5 mmol), Mn-**IV** (2 mol%), KO*t*Bu (6 mol%), toluene (1 mL), *i*PrOH (1 mL), 120 °C, *t*. [a]The yields were determined by GC using mesitylene as the internal standard. The yield is the average of two duplicate experiments.

### 4.2 Kinetic profile for the transfer hydrogenation of 4a



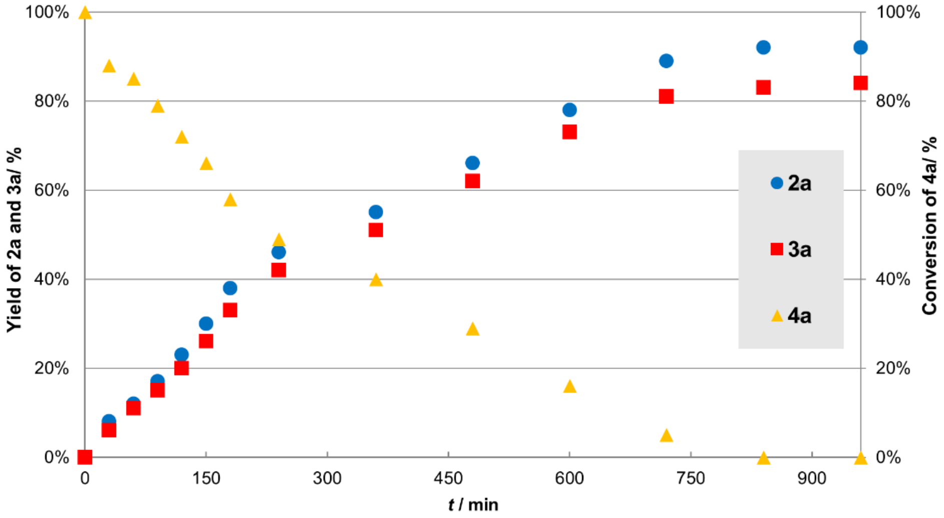


**Figure S2**. Kinetic profile for the transfer hydrogenation of **4a**

**Table S10.** Conversion of **4a** and yields of products **2a** and **3a** in the transfer hydrogenation of **4a** at different reaction times.

| entry | *t*/ min | conversion **4a** (%) | yield **2a** (%) | yield **3a** (%) |
|---|---|---|---|---|
| 1 | 30 | 12 | 8 | 6 |
| 2 | 60 | 15 | 12 | 11 |
| 3 | 90 | 21 | 17 | 15 |
| 4 | 120 | 28 | 23 | 20 |
| 5 | 150 | 34 | 30 | 26 |
| 6 | 180 | 42 | 38 | 33 |
| 7 | 240 | 51 | 46 | 42 |
| 8 | 360 | 60 | 55 | 51 |
| 9 | 480 | 71 | 66 | 62 |
| 10 | 600 | 84 | 78 | 73 |
| 11 | 720 | 95 | 89 | 81 |
| 12 | 840 | 100 | 92 | 83 |
| 13 | 960 | 100 | 92 | 84 |

Reaction conditions: **1a** (0.5 mmol), Mn-**IV** (2 mol%), KO*t*Bu (6 mol%), toluene (1 mL), *i*PrOH (1 mL), 120 °C, *t*. The yields were determined by GC using mesitylene as the internal standard.

### 4.3 Kinetic profile for the transfer hydrogenation of 5a

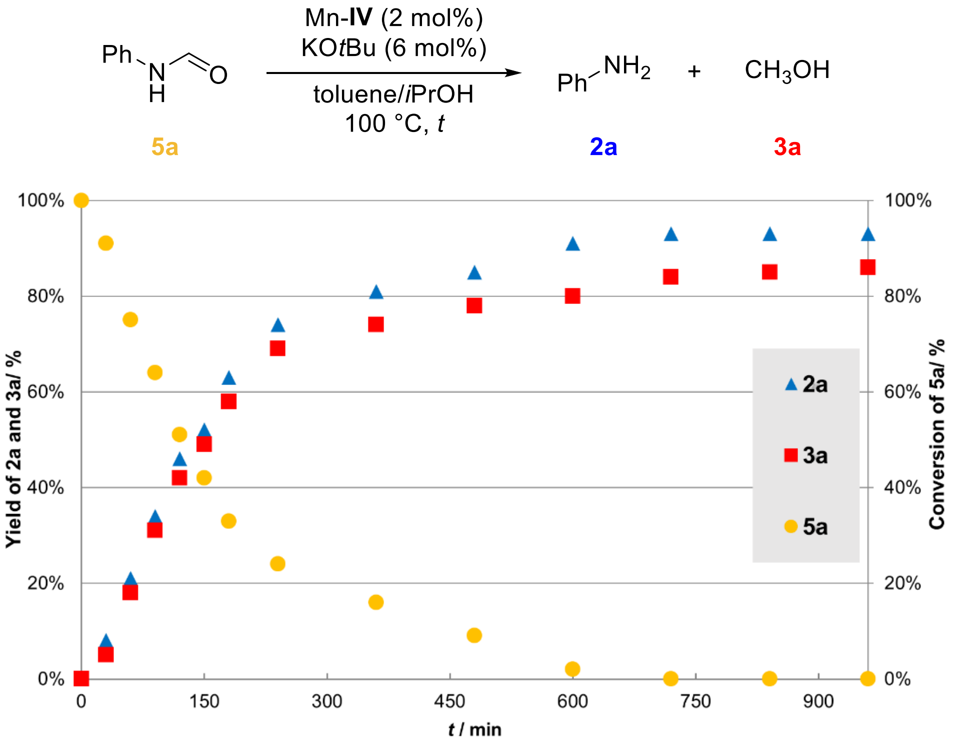


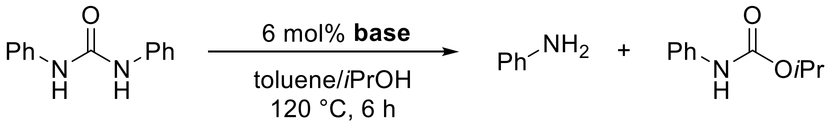
**Figure S3**. Kinetic profile for the transfer hydrogenation of **5a**

**Table S11.** Conversion of **5a** and yields of products **2a** and **3a** in the transfer hydrogenation of **5a** at different reaction times.

| entry | *t*/ min | conversion **5a** (%) | yield **2a** (%) | yield **3a** (%) |
|---|---|---|---|---|
| 1 | 30 | 9 | 8 | 5 |
| 2 | 60 | 25 | 21 | 18 |
| 3 | 90 | 36 | 34 | 31 |
| 4 | 120 | 49 | 46 | 42 |
| 5 | 150 | 58 | 52 | 49 |
| 6 | 180 | 67 | 63 | 58 |
| 7 | 240 | 76 | 74 | 69 |
| 8 | 360 | 84 | 81 | 74 |
| 9 | 480 | 91 | 85 | 78 |
| 10 | 600 | 98 | 89 | 80 |
| 11 | 720 | 100 | 90 | 84 |
| 12 | 840 | 100 | 90 | 85 |
| 13 | 960 | 100 | 91 | 85 |

Reaction conditions: **1a** (0.5 mmol), Mn-**IV** (2 mol%), KO*t*Bu (6 mol%), toluene (1 mL), *i*PrOH (1 mL), 120 °C, *t*. The yields were determined by GC using mesitylene as the internal standard.

### 4.4 Control experiments for base-catalzyed synthesis of carbamates 4a from urea derivatives 1a

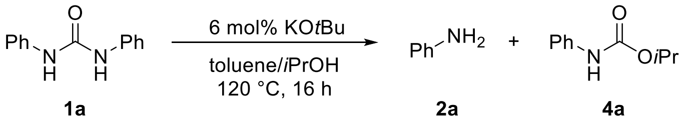


**1a** **2a** **4a**

| | | | | |
|---|---|---|---|---|
| NaH | $Cs_2CO_3$ | **KO*t*Bu** | KOH | $K_2CO_3$ |
| **2a**: 7 % | **2a**: 0 % | **2a**: 90 % | **2a**: 0 % | **2a**: 0 % |
| **4a**: 9 % | **4a**: 0 % | **4a**: 94 % | **4a**: 0 % | **4a**: 0 % |
| NaOMe | LiOH | LiHMDS | TBD | DABCO |
| **2a**: 0 % | **2a**: 0 % | **2a**: 0 % | **2a**: 0 % | **2a**: 0 % |
| **4a**: 0 % | **4a**: 0 % | **4a**: 0 % | **4a**: 0 % | **4a**: 0 % |

**Scheme S1**. Base-catalyzed synthesis carbamates from urea derivatives.

### 4.5 Selected GC and GC-MS studies



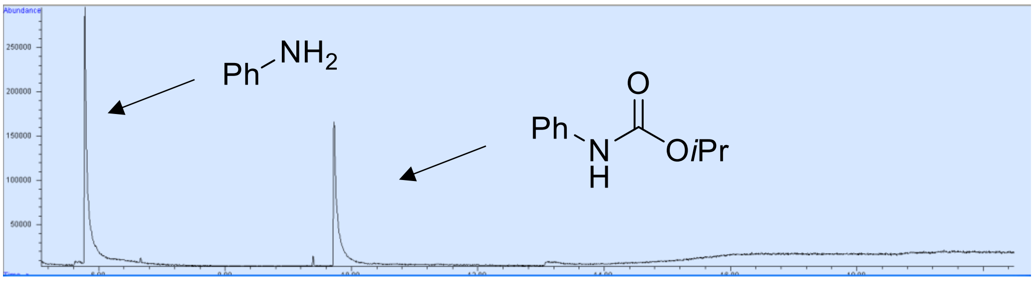
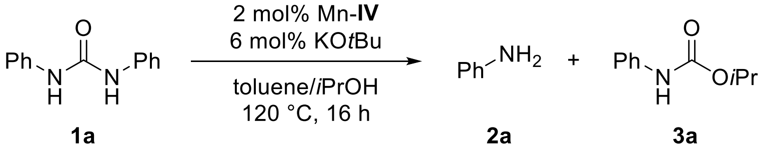


**Figure S4**. GC-MS chromatogram of crude reaction mixture: KO*t*Bu catalyzed synthesis **4a** from **1a**



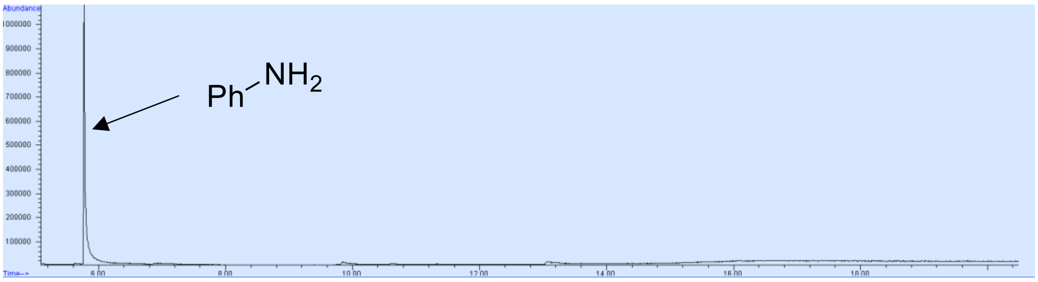
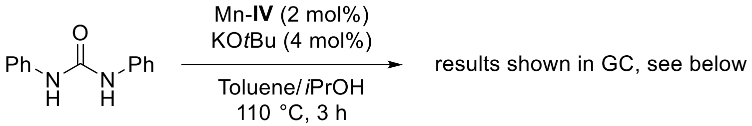


**Figure S5**. GC-MS chromatogram of crude reaction mixture: Manganese-catalyzed transfer hydrogenation of **1a** under our standard conditions (Table 1, entry 8)

### 4.6 Control experiments for transfer hydrogenation of 1a



**1a** (0.5 mmol)

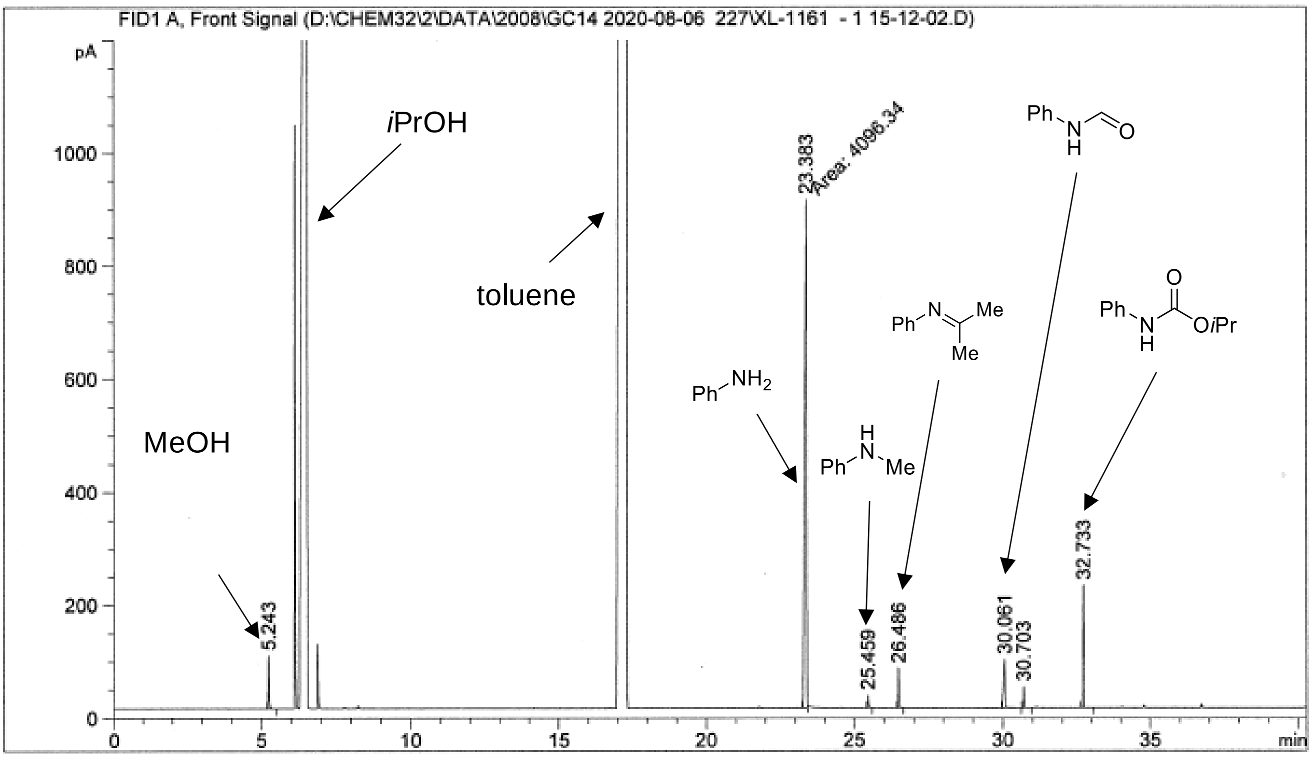
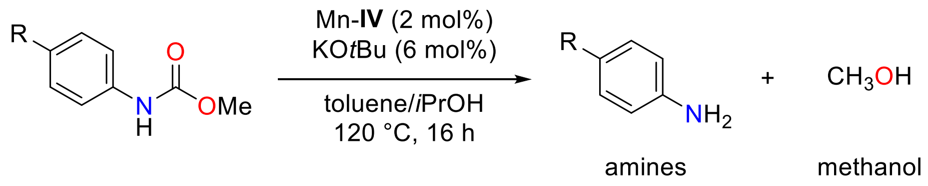
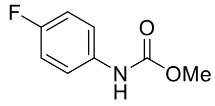
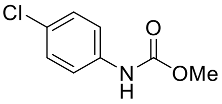
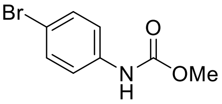
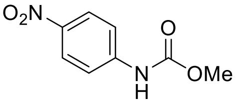
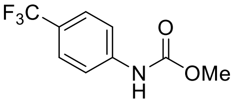
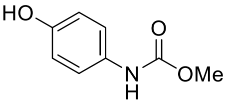


**Figure S6**. Control experiments for the transfer hydrogenation of **1a** (50 m HP column used for GC)

## 5. Functional group tolerance test (including failed examples)

**Table S12.** Transfer hydrogenation of carbamates **4** with different functional groups.



| substrates | amines/ % | methanol/ % |
|---|---|---|
|  | 76 | 60 |
|  | 79 | 74 |
|  | 63 | 56 |
|  | 0 | 31[a] |
|  | 67 | 60 |
|  | traces | 27[a] |

Reaction conditions: **4** (0.5 mmol), Mn-**IV** (2 mol%), KO*t*Bu (6 mol%), toluene (1 mL), *i*PrOH (1 mL), 120 °C, 16 h. The yields were determined by GC using mesitylene as the internal standard. [a]Methanol is derived from the transesterification of *i*PrOH.

## 6. Transfer hydrogenation of amides, carbamates, urea derivatives and polyurethanes

### 6.1 General method of transfer hydrogenation reaction

**General Procedure 1:** Transfer hydrogenation of urea derivatives **1**

In a glovebox, a pressure tube equipped with a stir bar was charged with Mn-**IV** (6.2 mg, 0.01 mmol, 2 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 6 mol%). The tube was removed from the glovebox, then, toluene (1 mL) was added, and the mixture was stirred at room temperatures (23°C) for 5 min. Subsequently, urea derivatives **1** (0.5 mmol) and *i*PrOH (1 mL) were added in one portion. The pressure tube was placed in a preheated oil bath at 120 °C and stirred for 16 h. After cooling down the reaction mixture to room temperatures (23°C), then added the internal standard for tested the GC yield of the products. After removal of all volatiles in vacuo the crude mixture was purified by column chromatography on silica gel to afford the isolated yield of products.

**General Procedure 2:** Transfer hydrogenation of carbamates **4**

In a glovebox, a pressure tube equipped with a stir bar was charged with Mn-**IV** (6.2 mg, 0.01 mmol, 2 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 6 mol%). The tube was removed from the glovebox, then, toluene (1 mL) was added, and the mixture was stirred at room temperatures (23°C) for 5 min. Subsequently, carbamate **4** (0.50 mmol) and *i*PrOH (1 mL) were added in one portion. The pressure tube was placed in a preheated oil bath at 120 °C and stirred for 16 h. After cooling down the reaction mixture to room temperatures (23°C), then added the internal standard for tested the GC yield of the products. After removal of all volatiles in vacuo the crude mixture was purified by column chromatography on silica gel to afford the isolated yield of products.

**General Procedure 3:** Transfer hydrogenation of amides **4** to amines and alcohols (C–N bond cleavage)

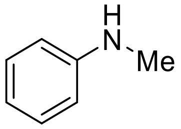
In a glovebox, a pressure tube equipped with a stir bar was charged with Mn-**IV** (6.2 mg, 0.01 mmol, 2 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 6 mol%). The tube was removed from the glovebox, then, toluene (1 mL) was added, and the mixture was stirred at room temperatures (23°C) for 5 min. Subsequently, amide **5** (0.50 mmol) and *i*PrOH (1 mL) were added in one portion. The pressure tube was placed in a preheated oil bath at 100 °C and stirred for 16 h. After cooling down the reaction mixture to room temperatures (23°C), then added the internal standard for tested the GC yield of the products. After removal of all volatiles in vacuo the crude mixture was purified by column chromatography on silica gel to afford the isolated yield of products.

**General Procedure 4:** Transfer hydrogenation of polyurethane **7**.

In a glovebox, a pressure tube equipped with a stir bar was charged with Mn-**IV** (6.20 mg, 0.01 mmol, 2.0 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 6.0 mol%). The tube was removed from the glovebox, then, THF (1 mL) was added, and the mixture was stirred at room temperatures (23°C) for 5 min. Subsequently, 0.5 mmol of substrate **7** was used (according to the repeating unit of polyurethanes) and *i*PrOH (1 mL) were added in one portion. The pressure tube was placed in a preheated oil bath at 150 °C and stirred for 24 h. After cooling to room temperatures (23°C) mesitylene was added as internal standard and the yields for diamine **8**, diol **9** and methanol **3a** were determined by GC. After removal of all volatiles in vacuo the crude mixture was purified by column chromatography on silica gel to afford the isolated yield of products.

## 6.2 Characterization data of products

*N*-Methylaniline (**2g**)[15]



**According to the GP-1 (Table 2)**: Mn-**IV** (6.4 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.3 mg, 0.03 mmol, 6 mol%), **1h** (113 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of amine **2a** and methanol. The compound **2g** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 50:1 and 3% of $Et_3N$) as colorless solid (39.0 mg, 0.365 mmol, 73 %)

**According to the GP-2 (Table 3)**: Mn-**IV** (6.2 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.5 mg, 0.03 mmol, 6 mol%), **4i** (82.5 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2g** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 50:1 and 3% of $Et_3N$) as colorless solid (44.2 mg, 0.414 mmol, 83 %)

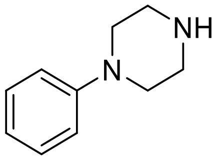
**According to the GP-3 (Table 5)**: Mn-**IV** (6.3 mg, 0.01 mmol, 2.0 mol%), KO*t*Bu (3.2 mg, 0.03 mmol, 6.0 mol%), **5f** (67.5 mg, 0.500 mmol), toluene (1.0 mL) and *i*PrOH (1.0 mL) was converted. The mixture was put in preheated oil bath (100 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2g** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 50:1 and 3% of $Et_3N$) as colorless solid (43.3 mg, 0.405 mmol, 81%)

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.36 – 7.18 (m, 2H), 6.79 (m 1H), 6.73 – 6.65 (m, 2H), 3.63 (s, 1H), 2.89 (s, 3H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 149.38, 129.27, 117.31, 112.49, 30.79 ppm.

The spectroscopic data correspond to those reported in the literature.[15]

4-Phenyl-1-piperazine (**2h**)[16]



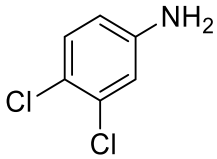
**According to the GP-1 (Table 2)**: Mn-**IV** (6.5 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.2 mg, 0.03 mmol, 6 mol%), **1i** (140 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol and amine **2a**. The compound **2h** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 20:1 and 3% of $Et_3N$) as yellow oil (58.3 mg, 0.359 mmol, 72%)

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.29 (m, 2H), 7.00 – 6.84 (m, 3H), 3.21 – 3.12 (m, 4H), 3.10 – 3.01 (m, 4H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 151.86, 129.11, 119.75, 116.13, 50.46, 46.20 ppm.

The spectroscopic data correspond to those reported in the literature.[16]

3,4-Dichloroaniline (**2j**)[17]



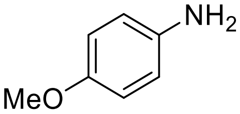
**According to the GP-1 (Table 1)**: Mn-**IV** (6.5 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.2 mg, 0.03 mmol, 6 mol%), **1j** (116 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2j** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 50:1 and 3% of $Et_3N$) as colorless solid (60.7 mg, 0.374 mmol, 75%)

**$^1$H-NMR** (400 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.20 (d, $J$ = 8.6 Hz, 1H), 6.79 (s, 1H), 6.53 (d, $J$ = 8.6 Hz, 1H), 3.74 (s, 2H) ppm.

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 25 °C) $\delta$ = 146.00, 132.70, 130.73, 121.13, 116.42, 114.61 ppm.

The spectroscopic data correspond to those reported in the literature.[17]

4-Methoxyaniline (**2w**)[18]



**According to the GP-2 (Table 4)**: Mn-**IV** (6.2 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.4 mg, 0.03 mmol, 6 mol%), **4s** (90.5 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (140 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The yield of *tert*-butanol **3e** was determined by $^1$H-NMR by using mesitylene as the internal standard. The compound **2w** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 20:1 and 3% of $Et_3N$) as yellow solid (49.7 mg, 0.406 mmol, 81%).

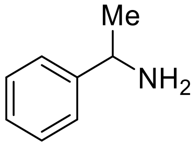
**According to the GP-3 (Table 5):** Mn-**IV** (6.4 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.5 mg, 0.03 mmol, 6 mol%), **5b** (75.5 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (100 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2w** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 20:1 and 3% of $Et_3N$) as yellow solid (52.6 mg, 0.411 mmol, 86%)

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 6.82 – 6.74 (m, 2H), 6.71 – 6.64 (m, 2H), 3.77 (s, 3H), 3.39 (s, 2H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 152.82, 139.97, 116.44, 114.83, 55.76 ppm.

The spectroscopic data correspond to those reported in the literature.[18]

1-Phenylethylamine (**2o**)[19]



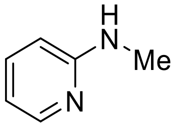
**According to the GP-2 (Table 3)**: Mn-**IV** (6.6 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.2 mg, 0.03 mmol, 6 mol%), **4e** (89.5 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2o** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 20:1 and 3% of $Et_3N$) as colorless oil (48.5 mg, 0.401 mmol, 80 %)

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.42 – 7.32 (m, 4H), 7.26 (m, 1H), 4.13 (q, *J* = 6.6 Hz, 1H), 1.61 (s, 2H), 1.41 (d, *J* = 6.6 Hz, 3H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 147.84, 128.50, 126.81, 125.71, 51.35, 25.73 ppm.

The spectroscopic data correspond to those reported in the literature.[19]

2-(*N*-Methylamino)pyridine (**2j**)[15]



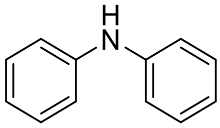
**According to the GP-2 (Table 3):** Mn-**IV** (6.6 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.2 mg, 0.03 mmol, 6 mol%), **4j** (83 mg, 0.50 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2j** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 50:1 and 3% of $Et_3N$) as colorless solid (33.9 mg, 0.314 mmol, 63%)

**$^1$H-NMR** (400 MHz, $CDCl_3$, 25 °C) $\delta$ = 8.05 (s, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 6.51 (d, *J* = 5.6, 1H), 6.38 – 6.19 (m, 1H), 5.05 (s, 1H), 2.84 (s, 3H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 159.73, 148.04, 137.33, 112.46, 106.20, 28.95 ppm.

The spectroscopic data correspond to those reported in the literature.[15]

Diphenylamine (**2s**)[20]



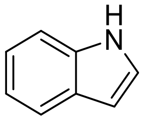
**According to the GP-2 (Table 3)**: Mn-**IV** (6.4 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.5 mg, 0.03 mmol, 6 mol%), **4k** (113 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2s** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 40:1 and 3% of $Et_3N$) as yellow solid (48.2 mg, 0.284 mmol, 57%)

**$^1$H-NMR** (400 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.39 – 7.26 (m, 4H), 7.19 – 7.07 (m, 4H), 7.05 – 6.93 (m, 2H), 5.78 (s, 1H) ppm.

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 25 °C) $\delta$ = 143.14, 129.40, 121.07, 117.88 ppm.

The spectroscopic data correspond to those reported in the literature.[20]

Indole (**2t**)[21]



**According to the GP-2 (Table 3)**: Mn-**IV** (6.6 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.4 mg, 0.03 mmol, 6 mol%), **4l** (87.5 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath

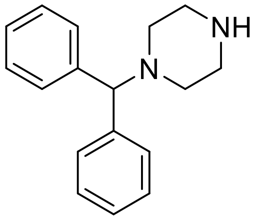
(120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2t** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 30:1 and 3% of $Et_3N$) as colorless solid (36.8 mg, 0.316 mmol, 63%)

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 8.08 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.09 (m, 3H), 6.63 (d, *J* = 3.1 Hz, 1H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 135.82, 127.90, 124.19, 122.03, 120.78, 119.87, 111.08, 102.65 ppm.

The spectroscopic data correspond to those reported in the literature.[21]

Diphenylmethylpiperazine (**2u**)[22]



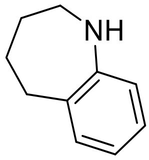
**According to the GP-2 (Table 3)**: Mn-**IV** (6.4 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.3 mg, 0.03 mmol, 6 mol%), **4m** (155 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2u** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 10:1 and 3% of $Et_3N$) as colorless solid (75.5 mg, 0.301 mmol, 60%)

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.48 – 7.39 (m, 4H), 7.33 – 7.24 (m, 4H), 7.23 – 7.16 (m, 2H), 4.24 (s, 1H), 2.99 – 2.78 (m, 4H), 2.39 (d, J = 4.9 Hz, 4H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 142.82, 128.57, 128.13, 127.01, 76.87, 53.48, 46.46 ppm.

The spectroscopic data correspond to those reported in the literature.[22]

2,3,4,5-Tetrahydro-1Hbenzo[b]azepine (**2v**)[23]



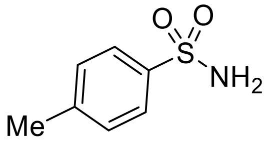
**According to the GP-2 (Table 3)**: Mn-**IV** (6.2 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.5 mg, 0.03 mmol, 6 mol%), **4n** (103 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (120 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The compound **2v** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 40:1 and 3% of $Et_3N$) as colorless solid (50.1 mg, 0.339 mmol, 68%)

**$^1$H-NMR** (400 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.14 (d, J = 7.4 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.86 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 3.17 – 3.01 (m, 2H), 2.90 – 2.74 (m, 2H), 1.94 – 1.78 (m, 2H), 1.72 – 1.67 (m, 2H) ppm.

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 25 °C) $\delta$ = 150.36, 133.78, 130.78, 126.59, 120.89, 119.39, 48.92, 36.08, 32.00, 26.93 ppm.

The spectroscopic data correspond to those reported in the literature.[23]

Toluene-4-sulfonamide (**2y**)[24]



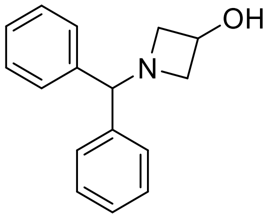
**According to the GP-2 (Table 4)**: Mn-**IV** (6.3 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.4 mg, 0.03 mmol, 6 mol%), **4v** (135 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (140 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol. The yield of *tert*-butanol **3e** was determined by $^1$H-NMR by using mesitylene as the internal standard. The compound **2y** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 20:1 and 3% of $Et_3N$) as colorless solid (49.6 mg, 0.29 mmol, 58%)

**$^1$H-NMR** (400 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.90 – 7.58 (m, 2H), 7.40 – 7.06 (m, 2H), 4.78 (s, 2H), 2.37 (s, 3H) ppm.

**$^{13}$C-NMR** (101 MHz, DMSO-$d_6$, 25 °C) $\delta$ = 142.34, 141.90, 129.78, 126.09, 21.38 ppm.

The spectroscopic data correspond to those reported in the literature.[24]

1-(Diphenylmethyl)-3-hydroxyazetidine (**3c**)[25]



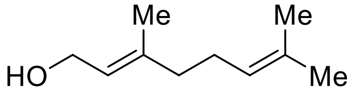
**According to the GP-2 (Table 3)**: Mn-**IV** (6.2 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.4 mg, 0.03 mmol, 6 mol%), **4p** (179 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (140 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol **3a** and amine **2a**. The compound **3c** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 3:1) as colorless solid (75.5 mg, 0.315 mmol, 63%)

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.48 – 7.38 (m, 4H), 7.36 – 7.27 (m, 4H), 7.26 – 7.17 (m, 2H), 4.49 (p, $J$ = 5.8 Hz, 1H), 4.40 (s, 1H), 3.69 – 3.48 (m, 2H), 3.04 – 2.86 (m, 2H), 2.67 (s, 1H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 141.78, 128.51, 127.46, 127.25, 78.42, 63.42, 62.09 ppm.

The spectroscopic data correspond to those reported in the literature.[25]

Geraniol (**3d**)[26]



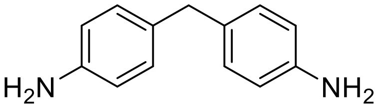
**According to the GP-2 (Table 3)**: Mn-**IV** (6.3 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.4 mg, 0.03 mmol, 6 mol%), **4q** (137 mg, 0.500 mmol), toluene (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (140 °C) and stirred for 16 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol **3a** and amine **2a**. The compound **3d** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 5:1) as colorless oil (42.3 mg, 0.276 mmol, 55%)

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 5.41 (d, $J$ = 6.9 Hz, 1H), 5.09 (t, $J$ = 6.7Hz, 1H), 4.14 (d, $J$ = 6.9 Hz, 2H), 2.14 – 1.98 (m, 4H), 1.90 – 1.73 (m, 1H), 1.69 – 1.66 (m, 6H), 1.63 (s, 3H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 139.52, 131.69, 123.91, 123.40, 59.27, 39.53, 26.38, 25.65, 17.65, 16.22 ppm.

The spectroscopic data correspond to those reported in the literature.[26]

4,4'-Diamino diphenyl methane (**8b**)[27]



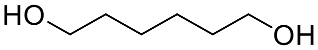
**According to the GP-4 (Figure 5)**: Mn-**IV** (6.4 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.4 mg, 0.03 mmol, 6 mol%), **7b** (207 mg, 0.500 mmol), THF (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (150 °C) and stirred for 24 h. The compound **8b** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 4:1 to 1:1) as colorless solid (40.6 mg, 0.206 mmol, 41%). In a second fraction **9b** (20.1 mg, 0.170 mmol, 34%) was isolated.

**$^1$H-NMR** (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 7.01 – 6.92 (m, 4H), 6.66 – 6.57 (m, 4H), 3.78 (s, 2H), 3.53 (brs, 4H) ppm.

**$^{13}$C-NMR** (75 MHz, $CDCl_3$, 25 °C) $\delta$ = 144.42, 132.14, 129.74, 115.39, 40.29 ppm.

The spectroscopic data correspond to those reported in the literature.[27]

1,6-hexanediol (**9b**)[27]



**According to the GP-4 (Figure 5)**: Mn-**IV** (6.4 mg, 0.01 mmol, 2 mol%), KO*t*Bu (3.4 mg, 0.03 mmol, 6 mol%), **7b** (207 mg, 0.500 mmol), THF (1 mL) and *i*PrOH (1 mL) was converted. The mixture was put in preheated oil bath (150 °C) and stirred for 24 h. Then, added the mesitylene as the internal standard and determined the GC yield of methanol **3a** and diamine **8b**. The compound **9b** was obtained by column chromatography ($SiO_2$, pentane:ethyl acetate = 1:4) as colorless solid (20.1 mg, 0.170 mmol, 34%). In a second fraction **8b** (40.6 mg, 0.206 mmol, 41%) was isolated.

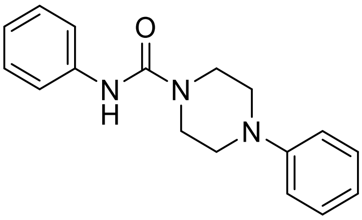
**$^1$H-NMR** (400 MHz, $CDCl_3$, 25 °C) $\delta$ = 3.61 (t, $J$ = 6.6 Hz, 4H), 2.22 (s, 2H), 1.62 – 1.48 (m, 4H), 1.45 – 1.29 (m, 4H) ppm.

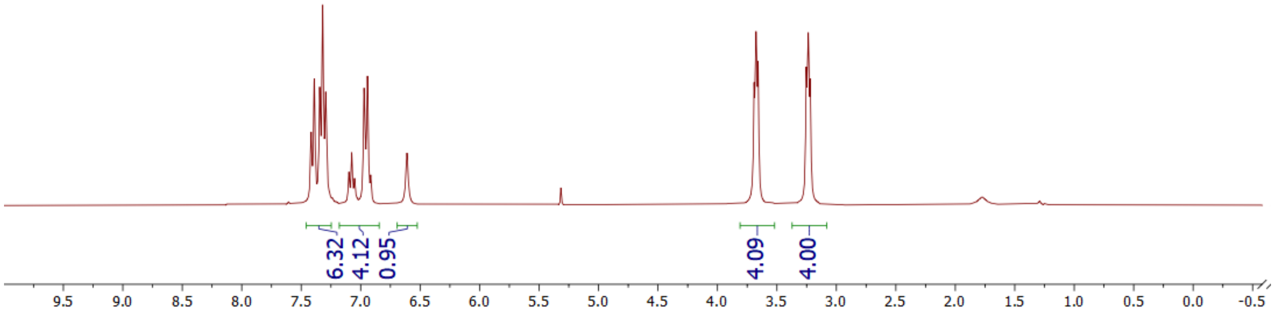
**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 25 °C) $\delta$ = 62.75, 32.69, 25.59 ppm.

The spectroscopic data correspond to those reported in the literature.[27]

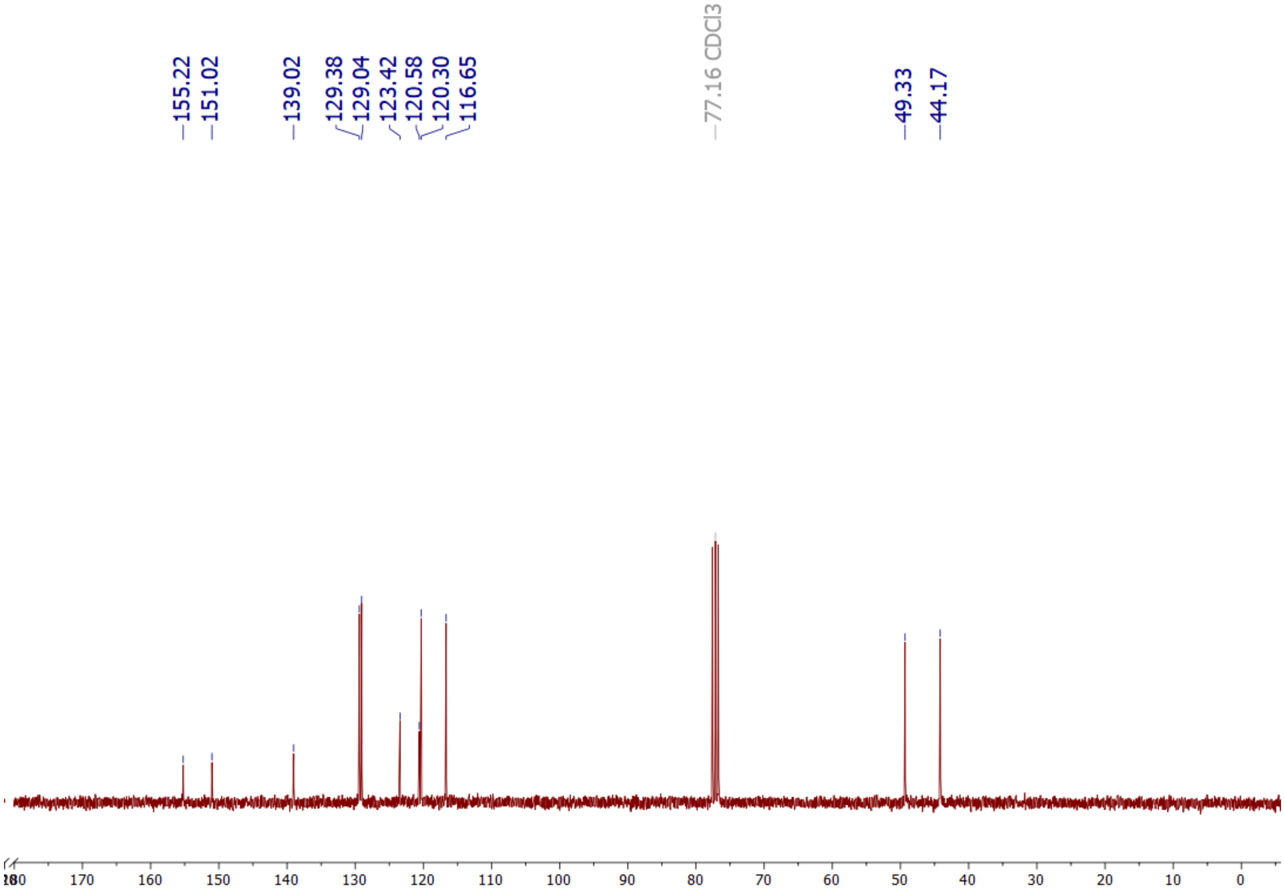
## 7. NMR spectra

*N*-4-Diphenylpiperazine-1-carboxamide (**1i**) $^{1}$H-NMR spectrum in $CDCl_3$

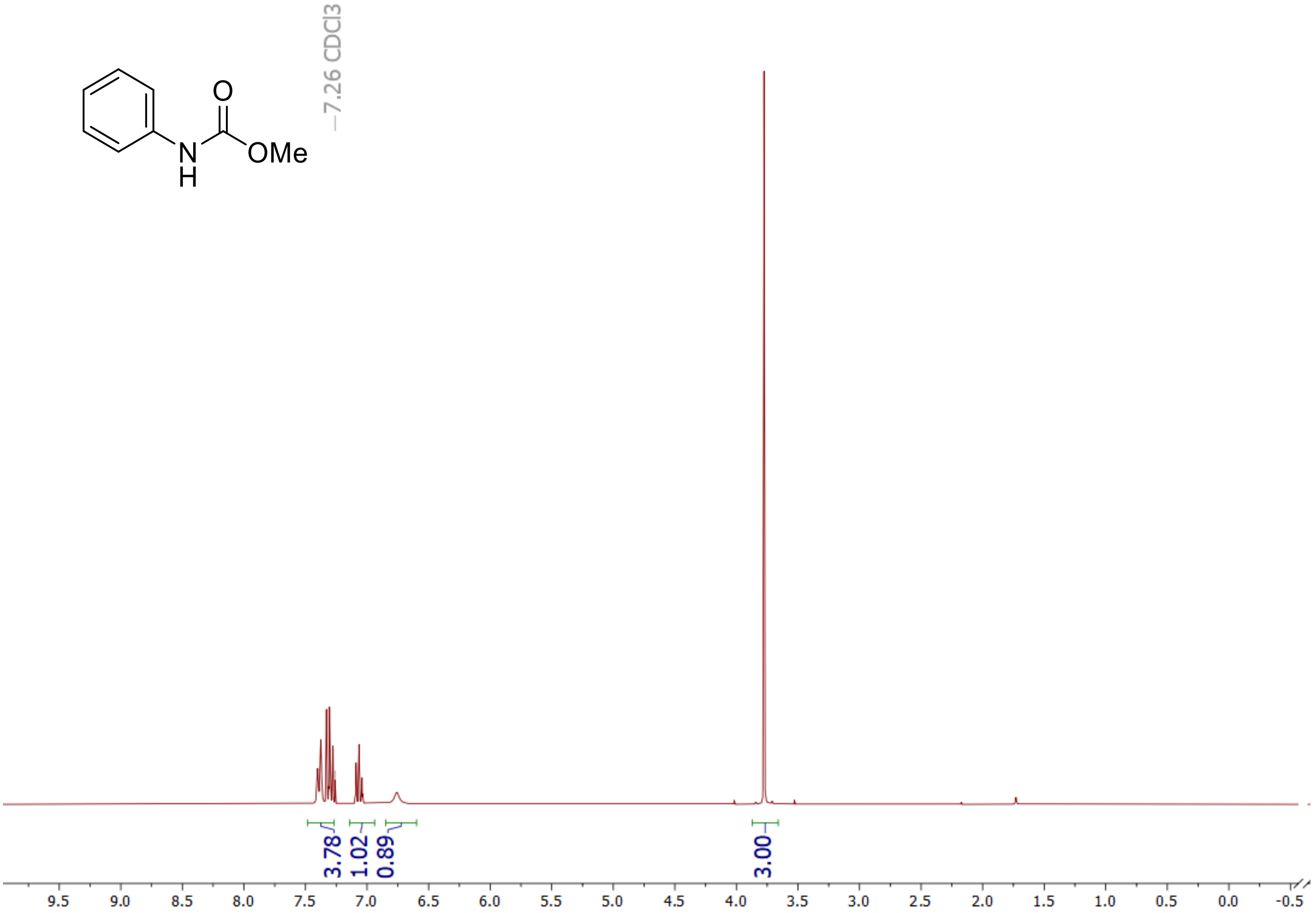




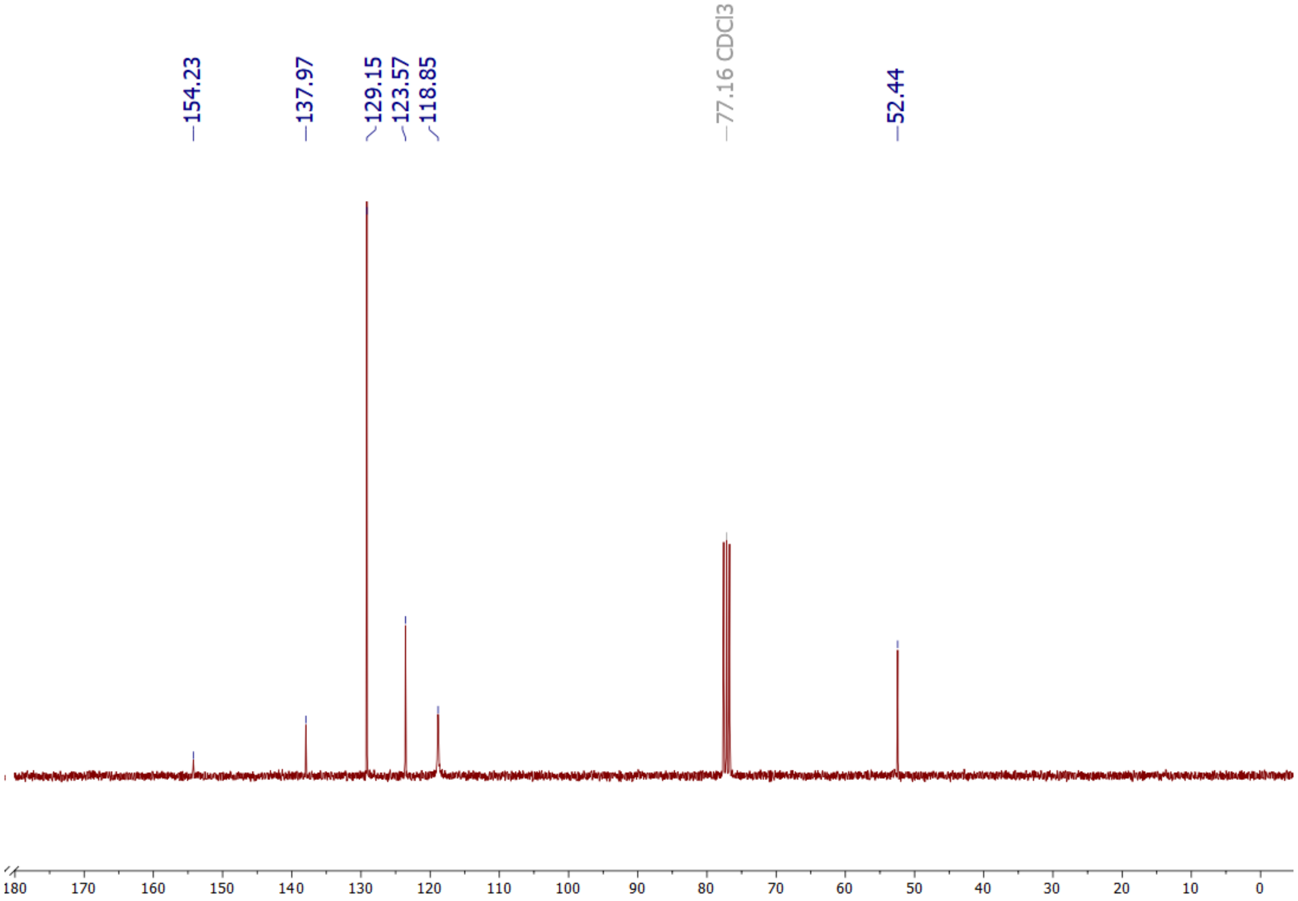
N,4-Diphenylpiperazine-1-carboxamide (**1i**) $^{13}$C-NMR spectrum in $CDCl_3$



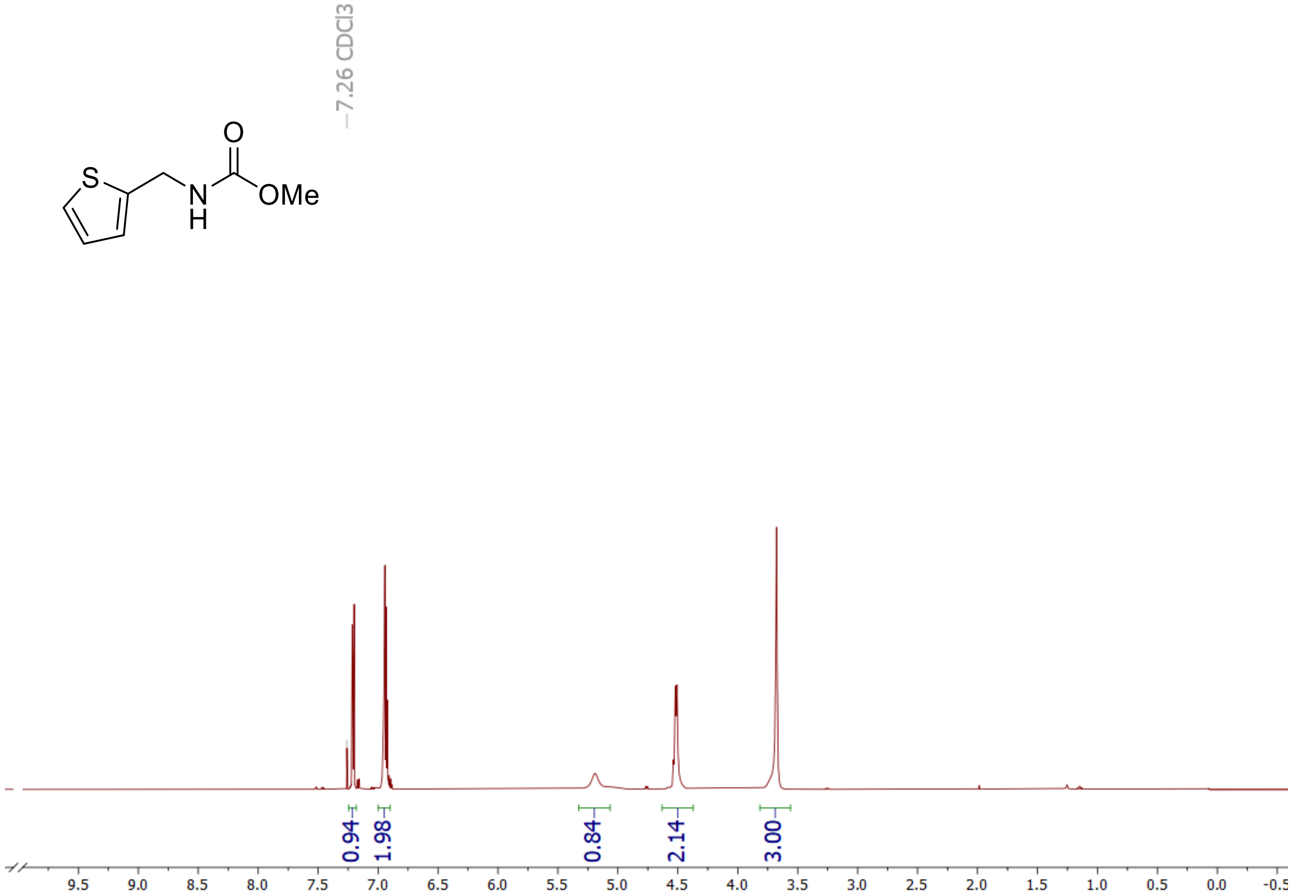
*N*-Phenyl methyl carbamate (**4b**) $^1$H-NMR spectrum in $CDCl_3$



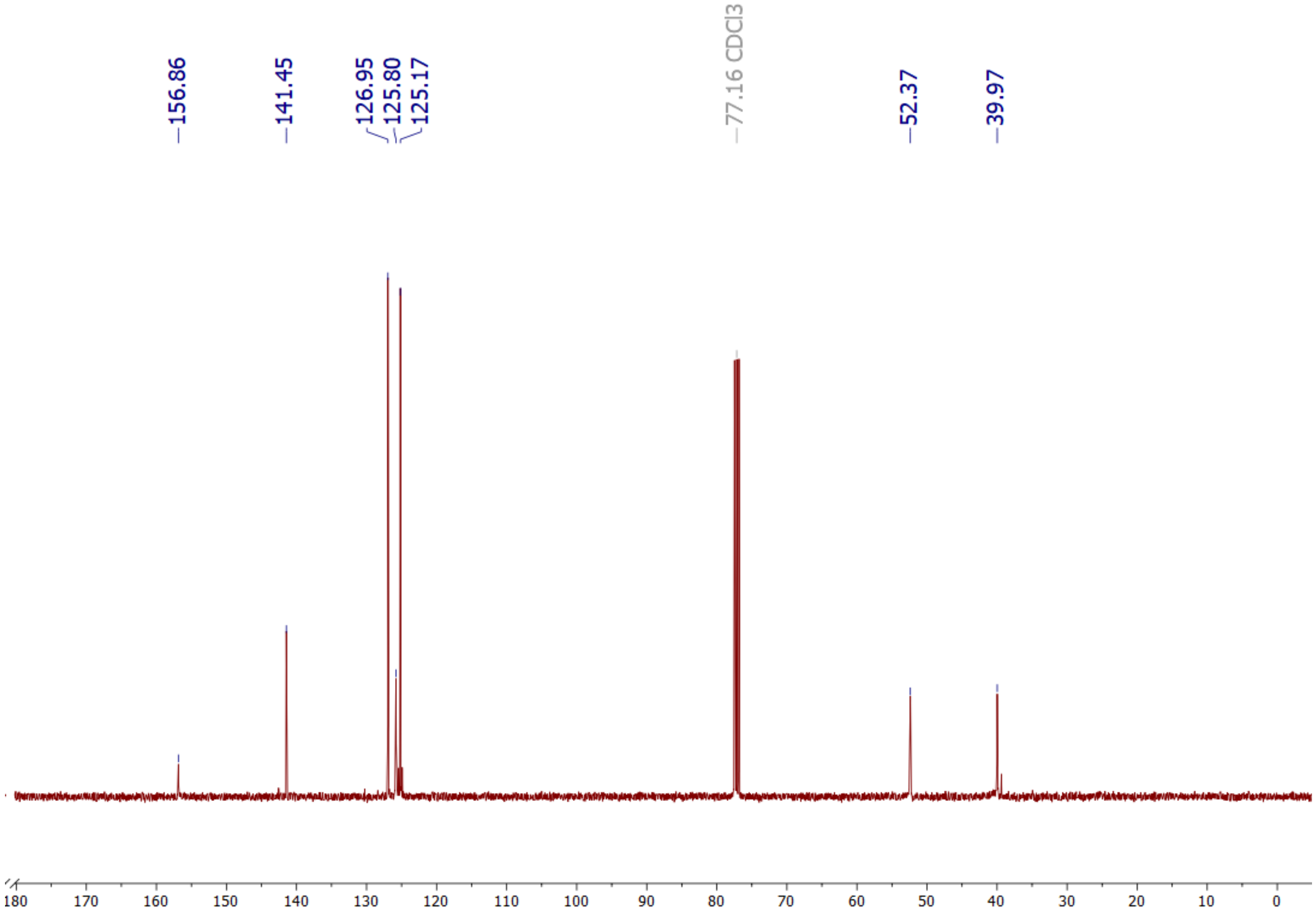
*N*-Phenyl methyl carbamate (**4b**) $^{13}$C-NMR spectrum in $CDCl_3$



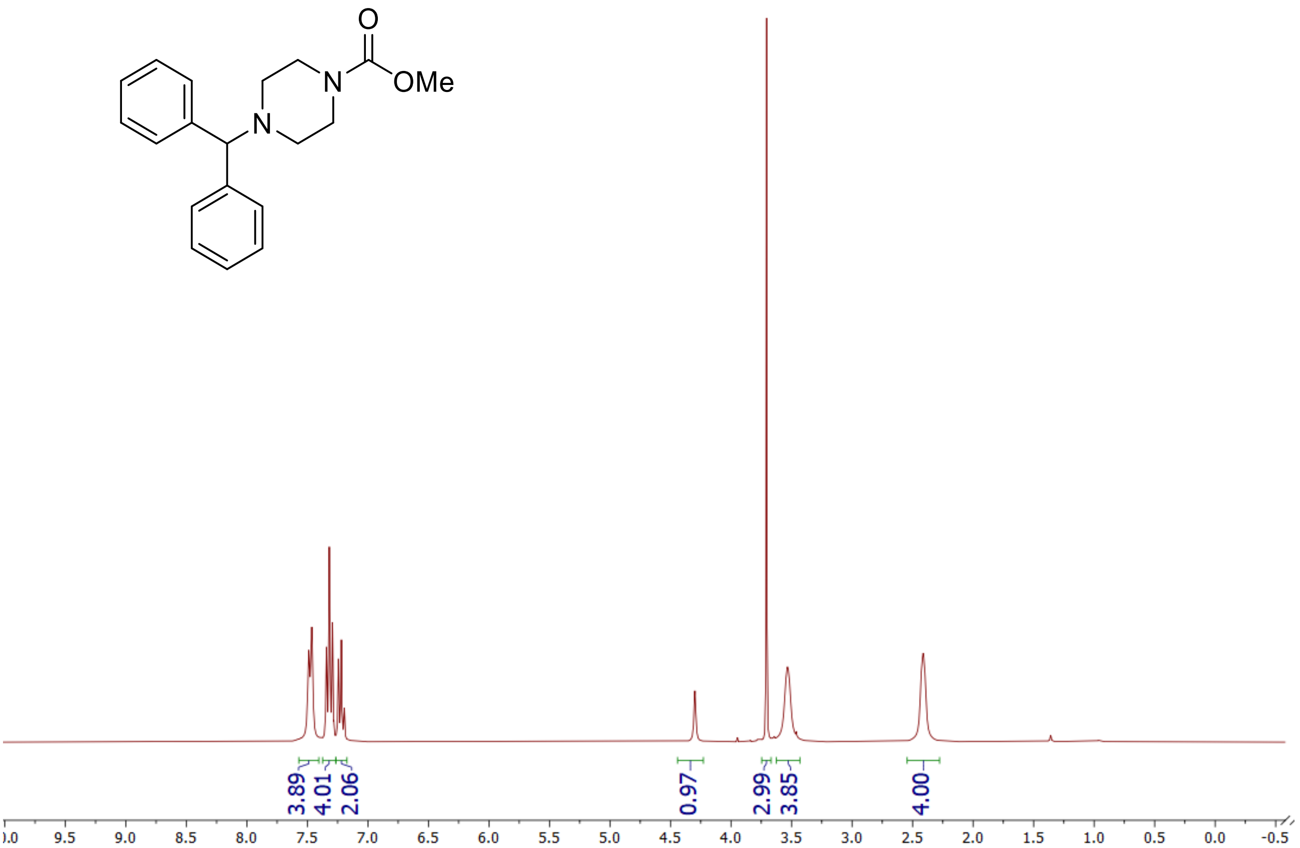
Thiophene-2-methylamine methyl carbamate (**4f**) $^{1}$H-NMR spectrum in CDCl$_3$



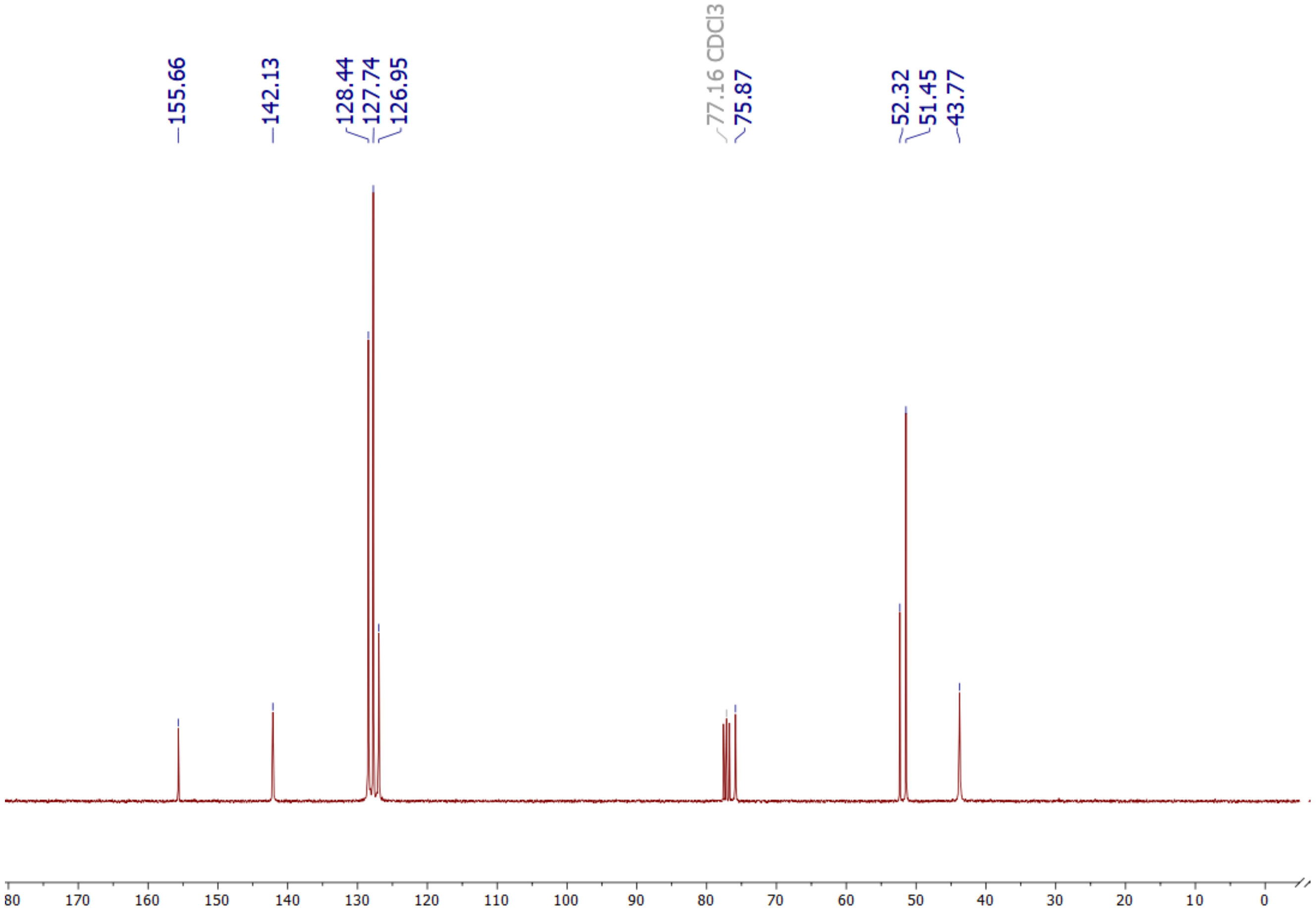
Thiophene-2-methylamine methyl carbamate (**4f**) $^{13}$C-NMR spectrum in CDCl$_3$



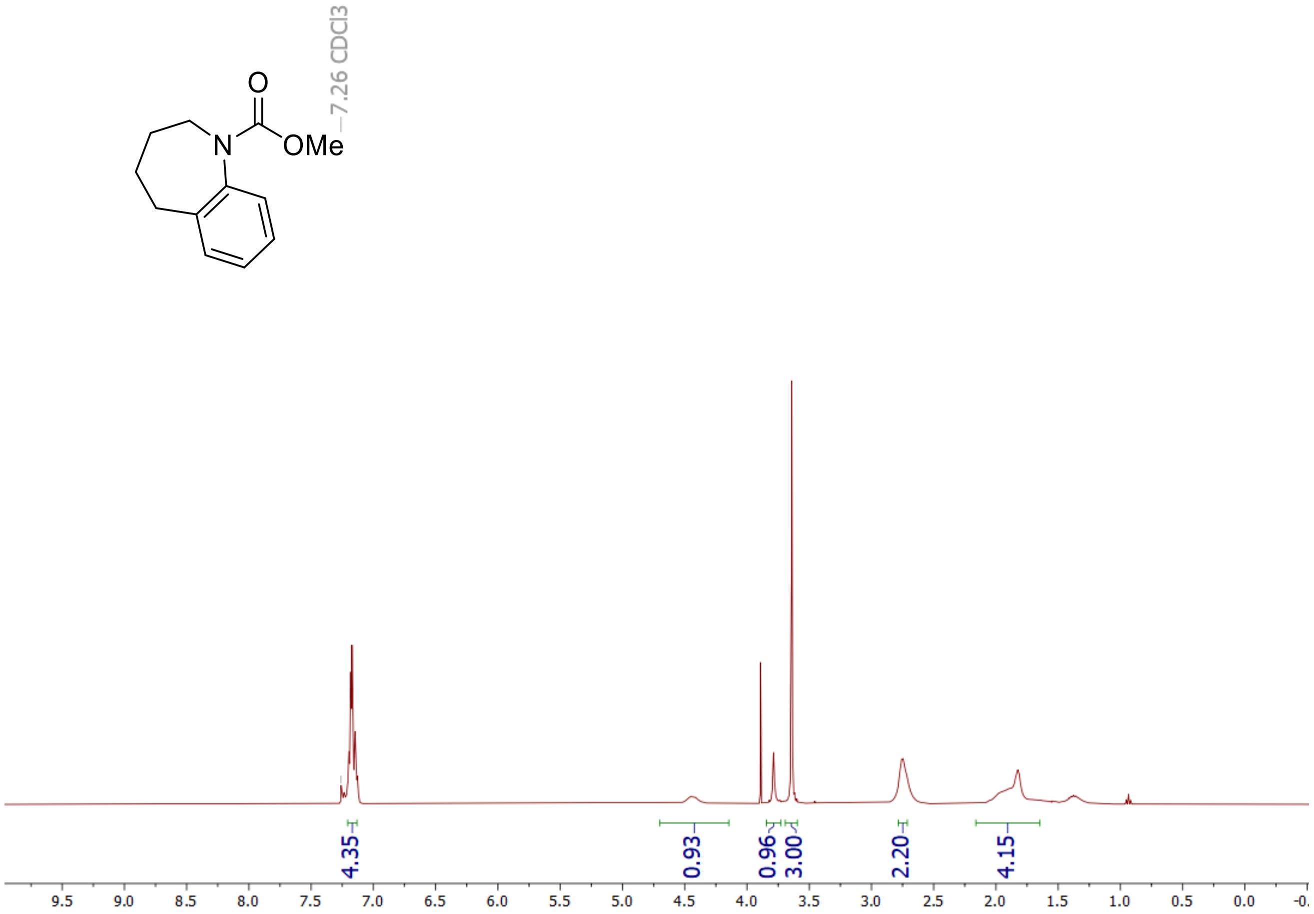
Methyl 4-benzhydrylpiperazine-1-carboxylate (**4m**) $^{1}$H-NMR spectrum in CDCl$_3$



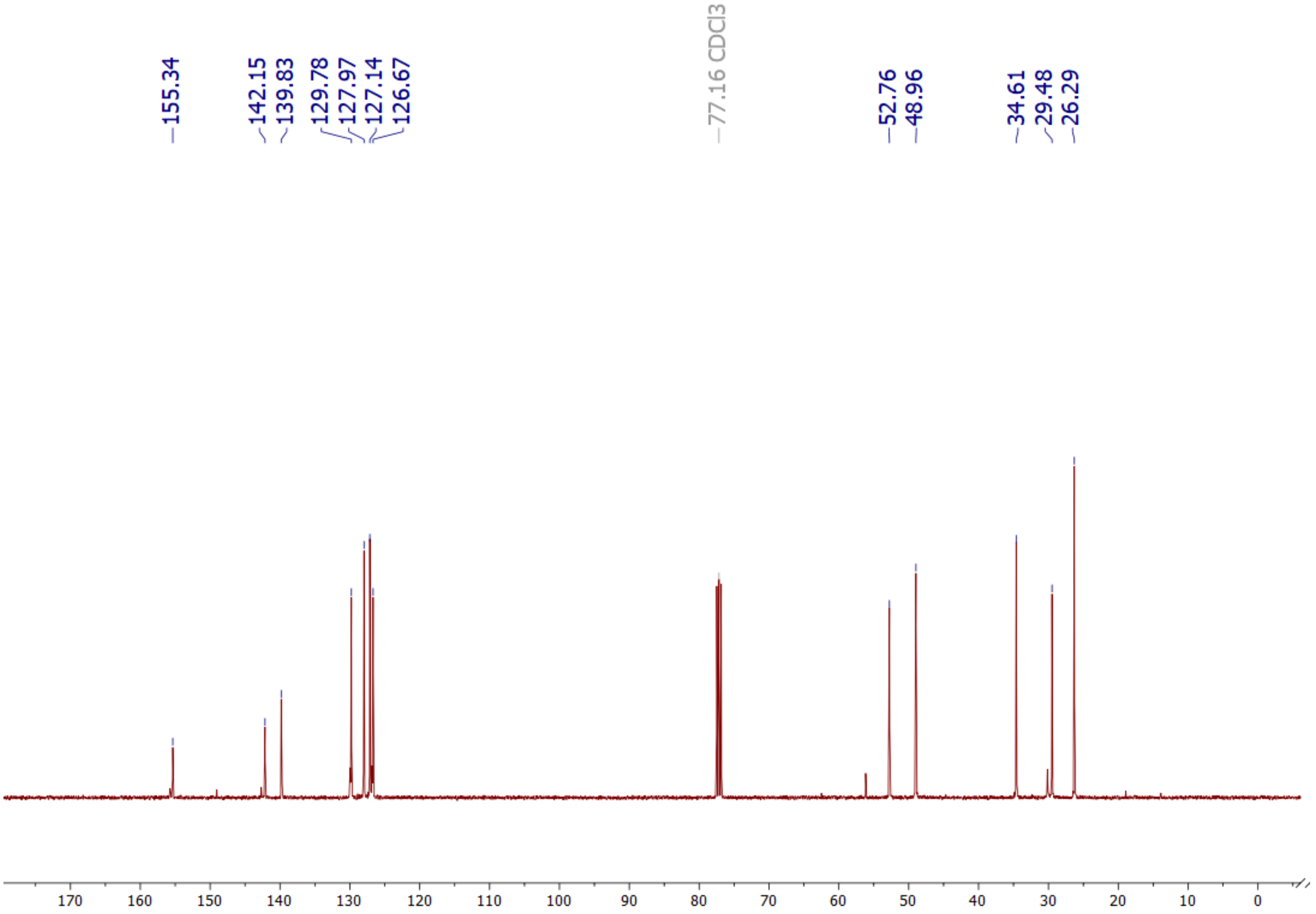
Methyl 4-benzhydrylpiperazine-1-carboxylate (**4m**) $^{13}$C-NMR spectrum in CDCl$_3$



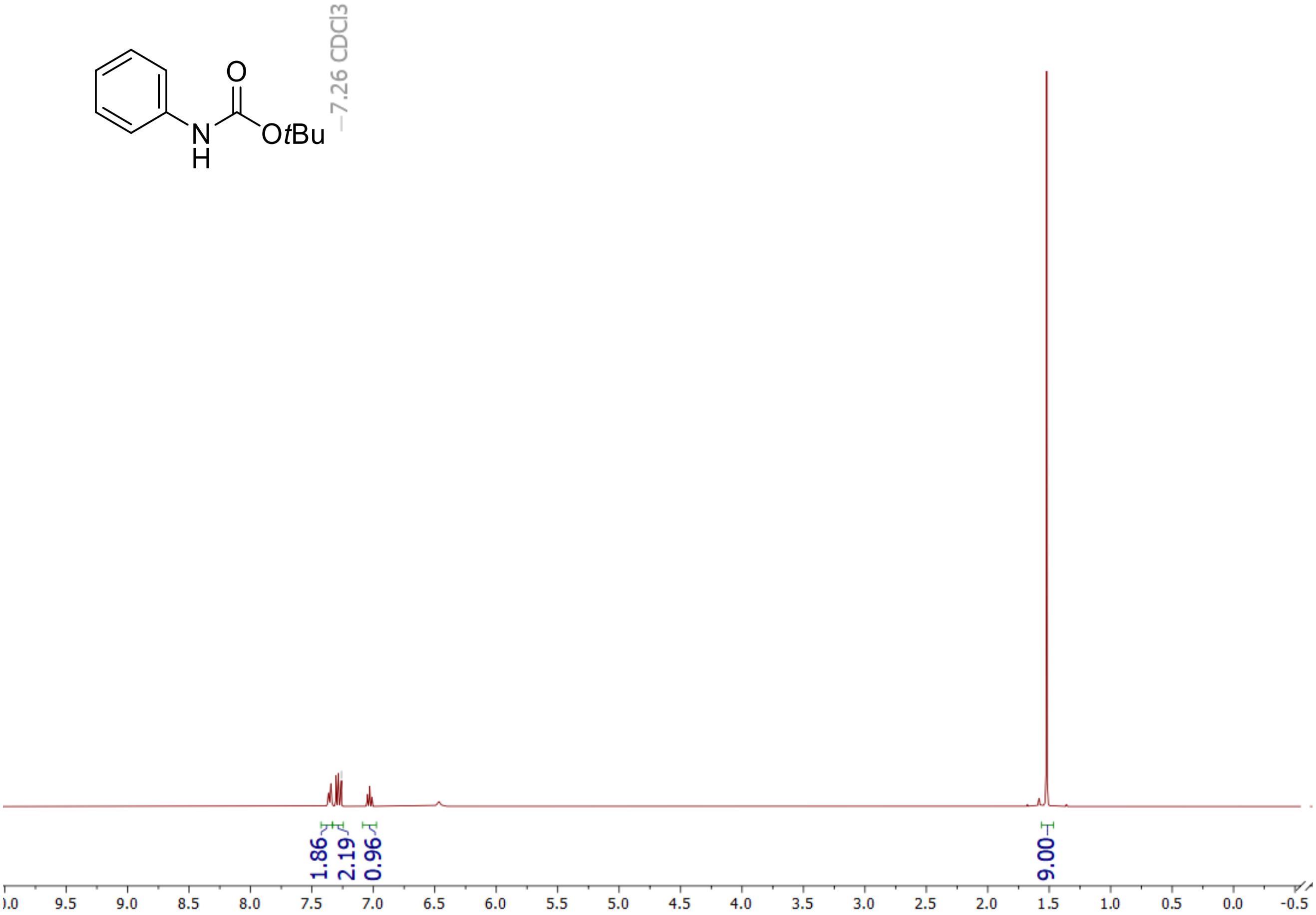
Methyl 2,3,4,5-tetrahydro-1H-benzo[b]azepine-1-carboxylate (**4n**) $^{1}$H-NMR spectrum in $CDCl_3$



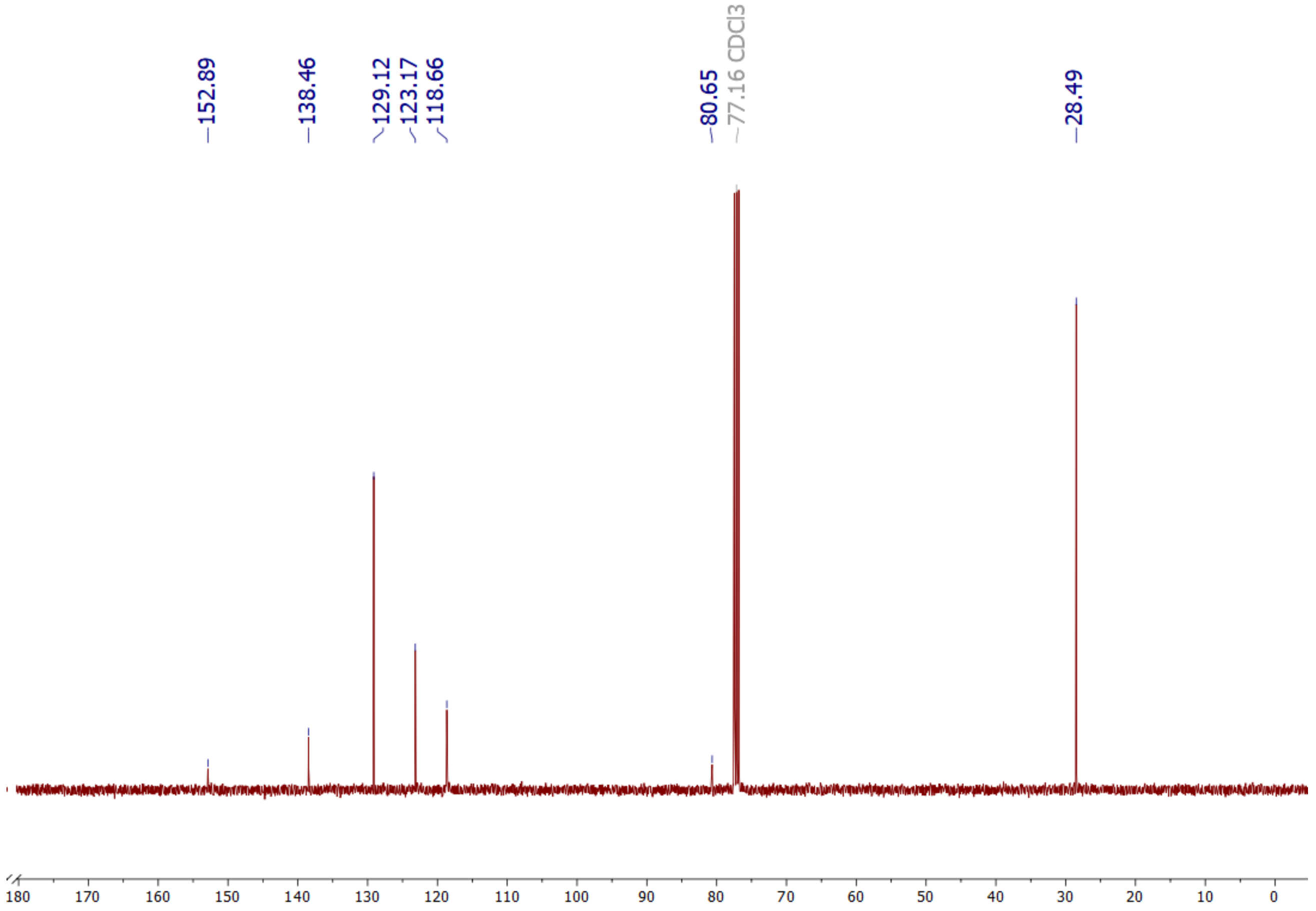
Methyl 2,3,4,5-tetrahydro-1H-benzo[b]azepine-1-carboxylate (**4n**) $^{13}$C-NMR spectrum in $CDCl_3$



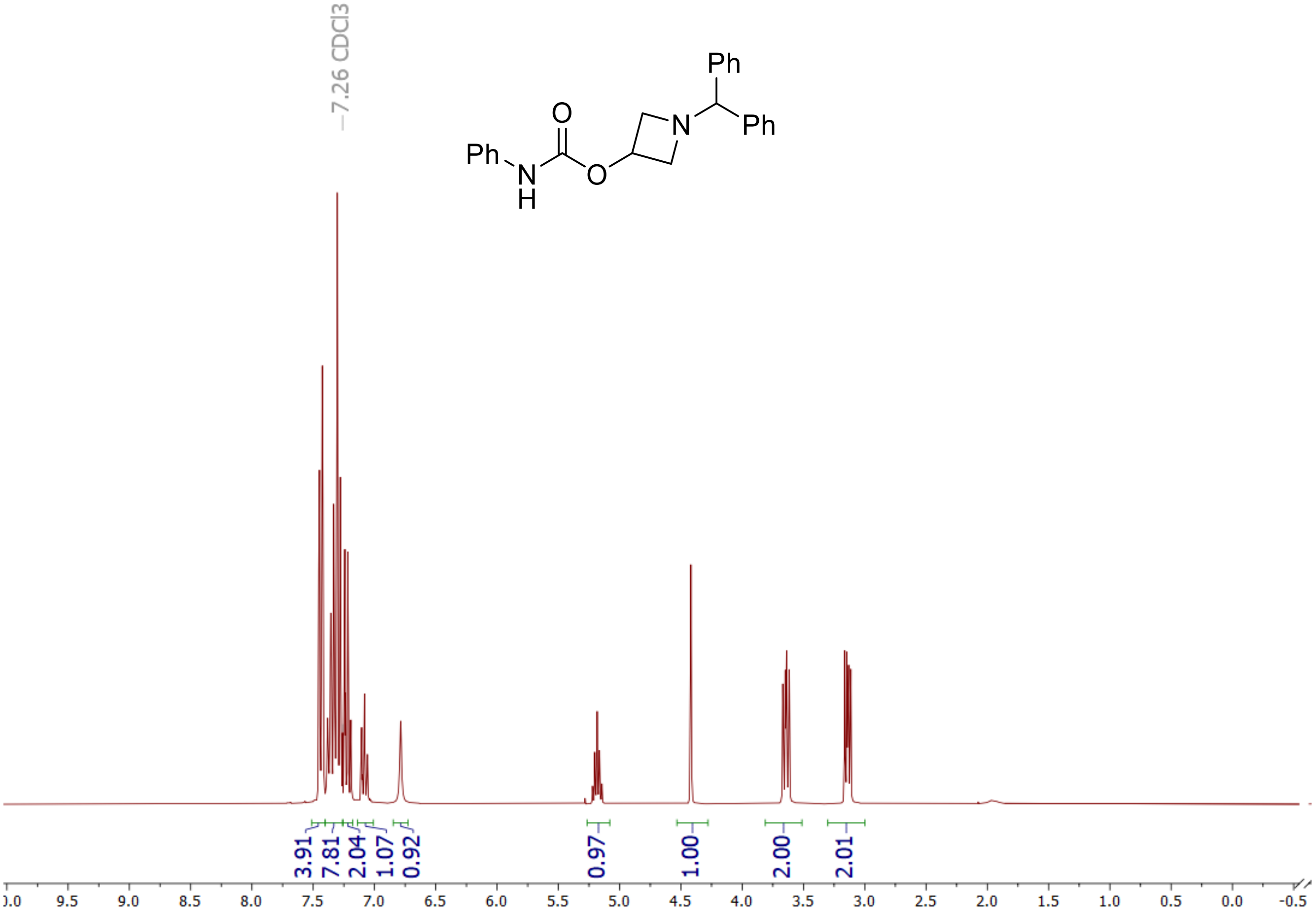
*tert*-Butyl phenylcarbamate (**4r**) $^1$H-NMR spectrum in $CDCl_3$



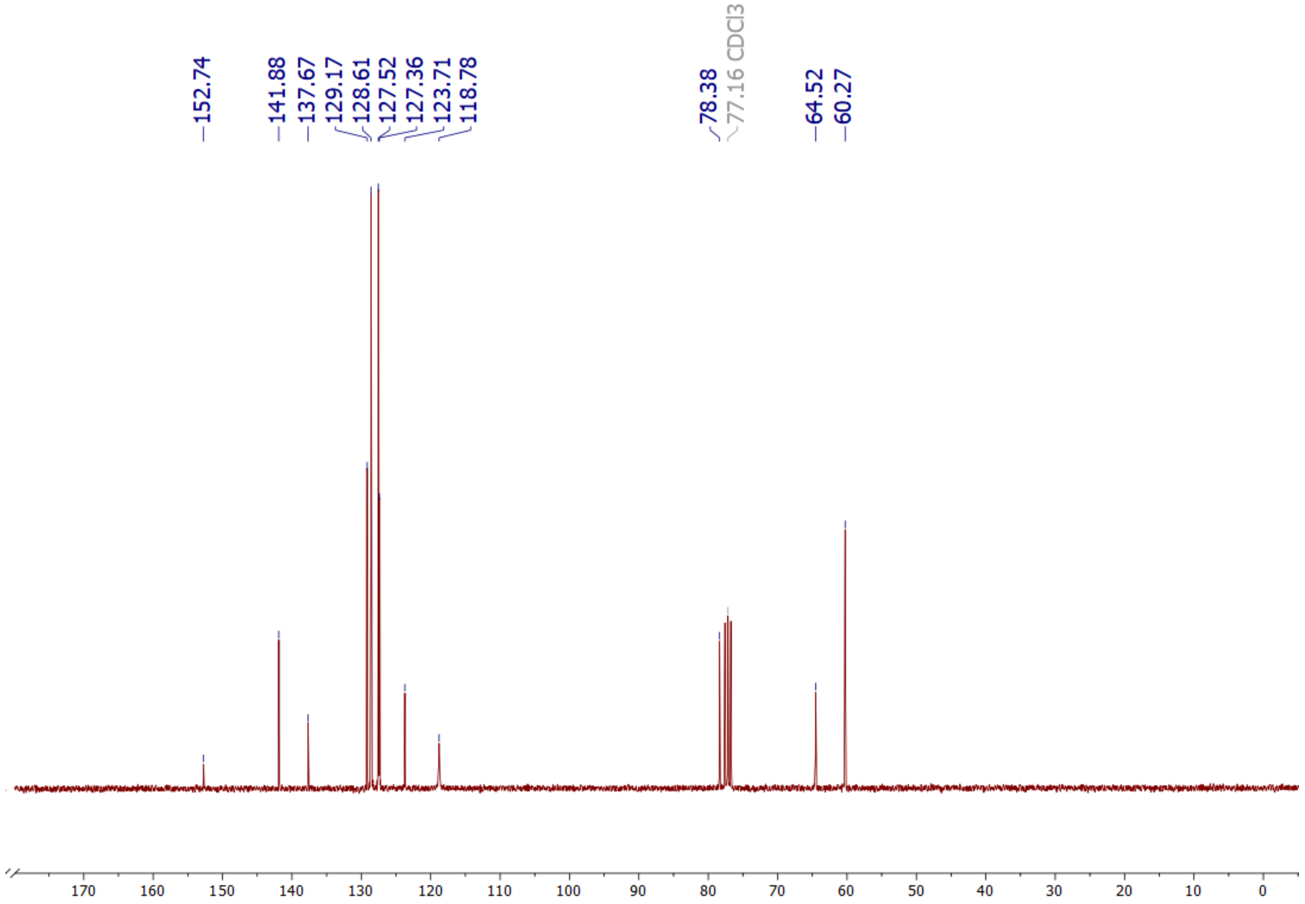
*tert*-Butyl phenylcarbamate (**4r**) $^{13}$C-NMR spectrum in $CDCl_3$



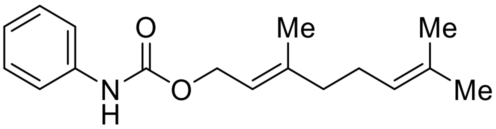
(1-Benzhydrylazetidin-3-yl) *N*-phenylcarbamate (**4p**) $^1$H-NMR spectrum in $CDCl_3$

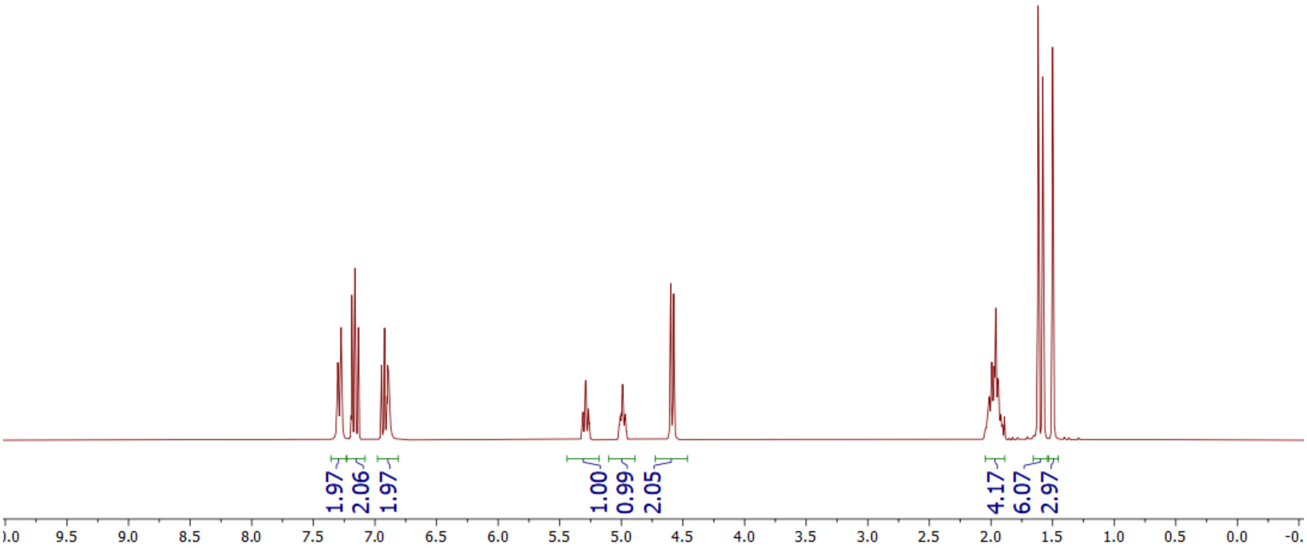


(1-Benzhydrylazetidin-3-yl) *N*-phenylcarbamate (**4p**) $^{13}$C-NMR spectrum in $CDCl_3$

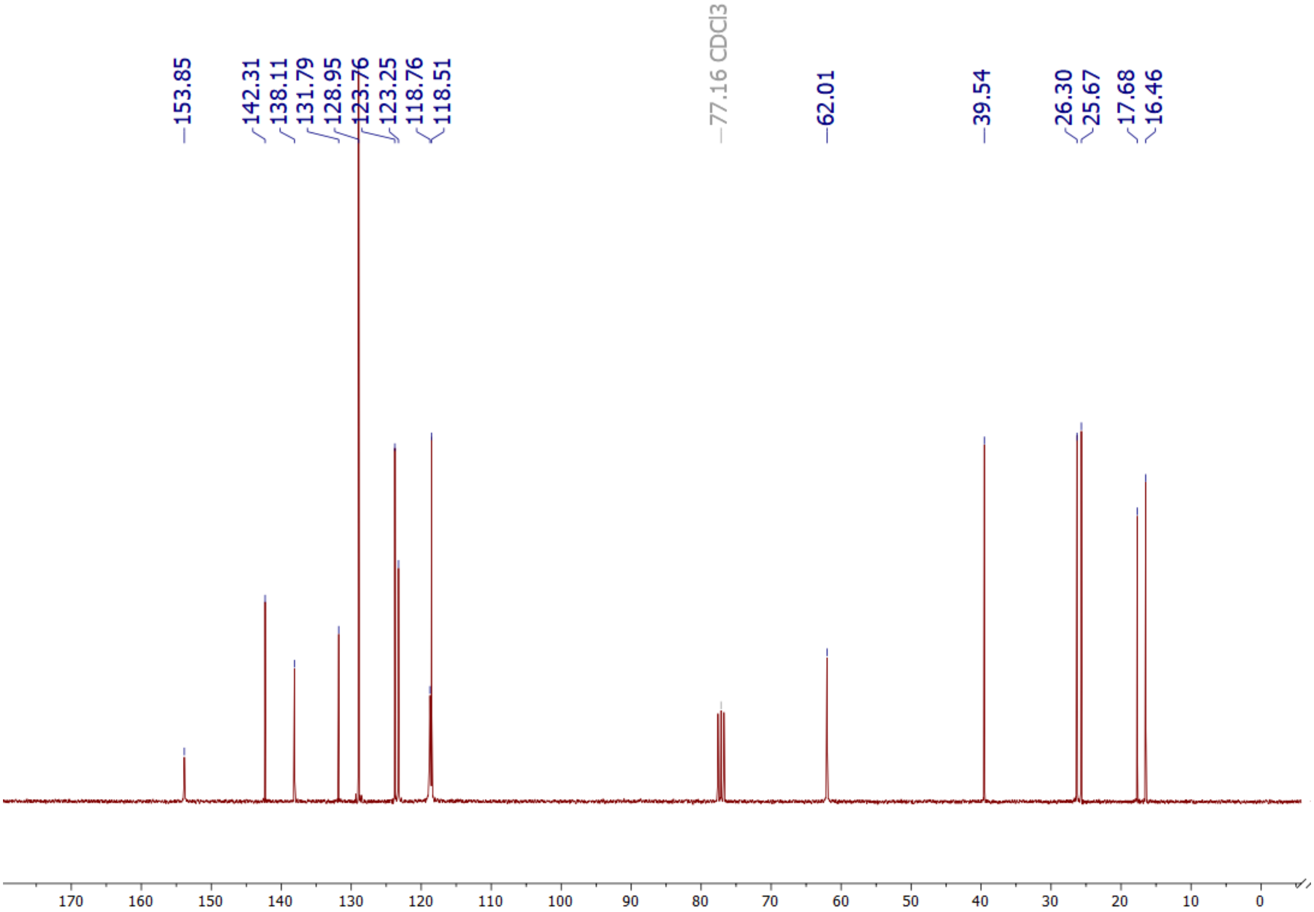


(*E*)-3,7-Dimethylocta-2,6-dien-1-yl phenylcarbamate (**4q**) $^1$H-NMR spectrum in CDCl$_3$

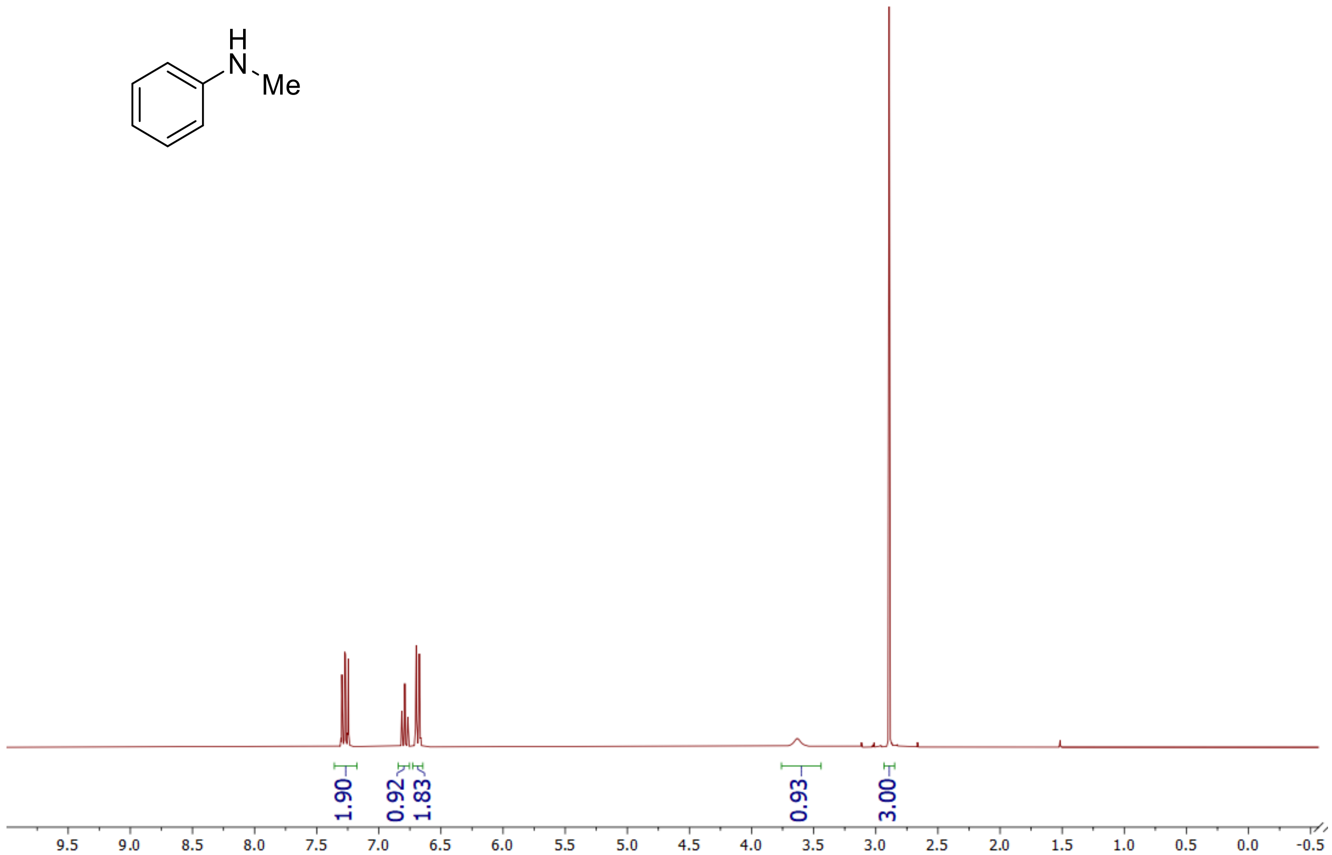




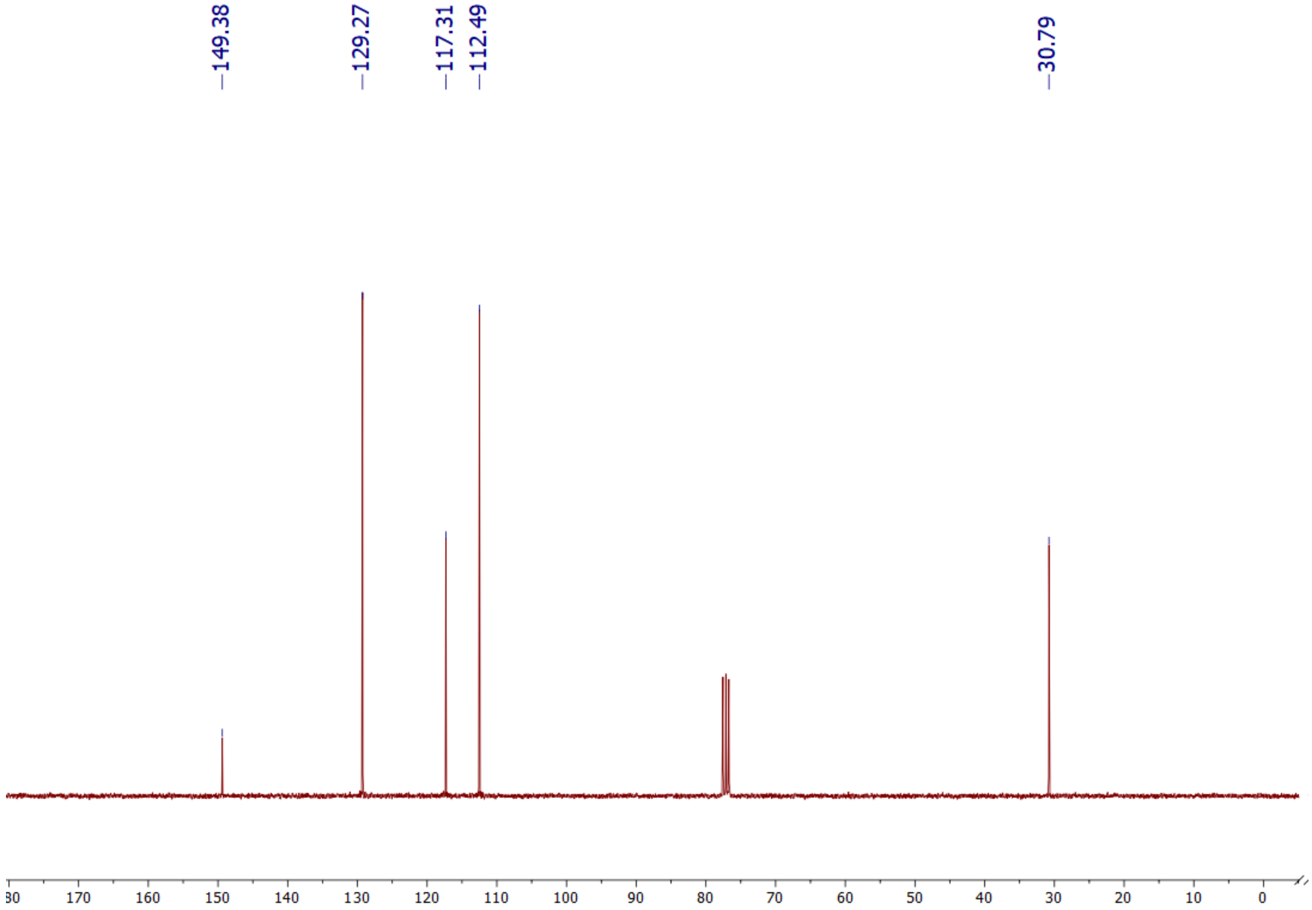
(*E*)-3,7-Dimethylocta-2,6-dien-1-yl phenylcarbamate (**4q**) $^{13}$C-NMR spectrum in CDCl$_3$



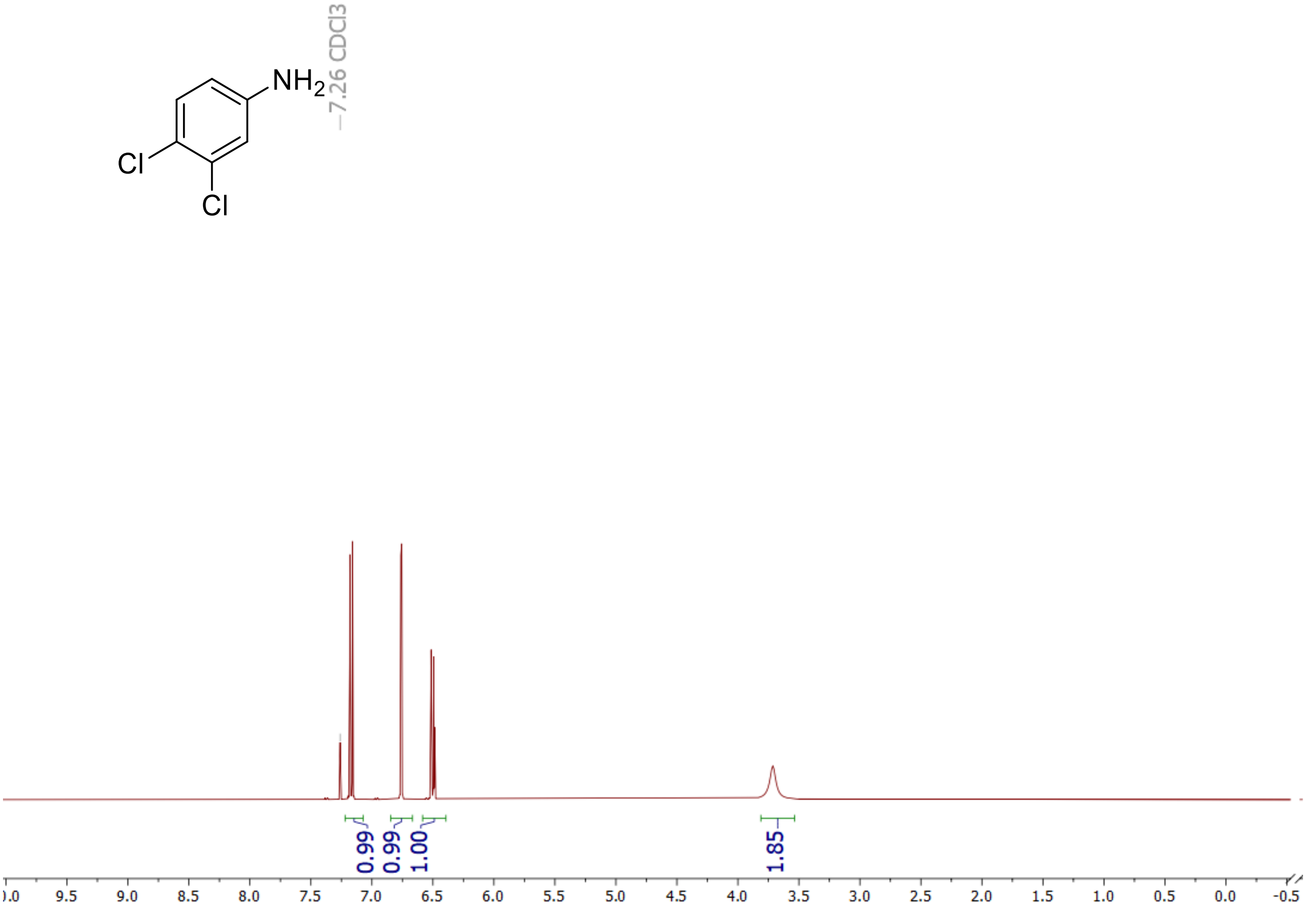
*N*-Methylaniline (**2g**) $^1$H-NMR spectrum in $CDCl_3$



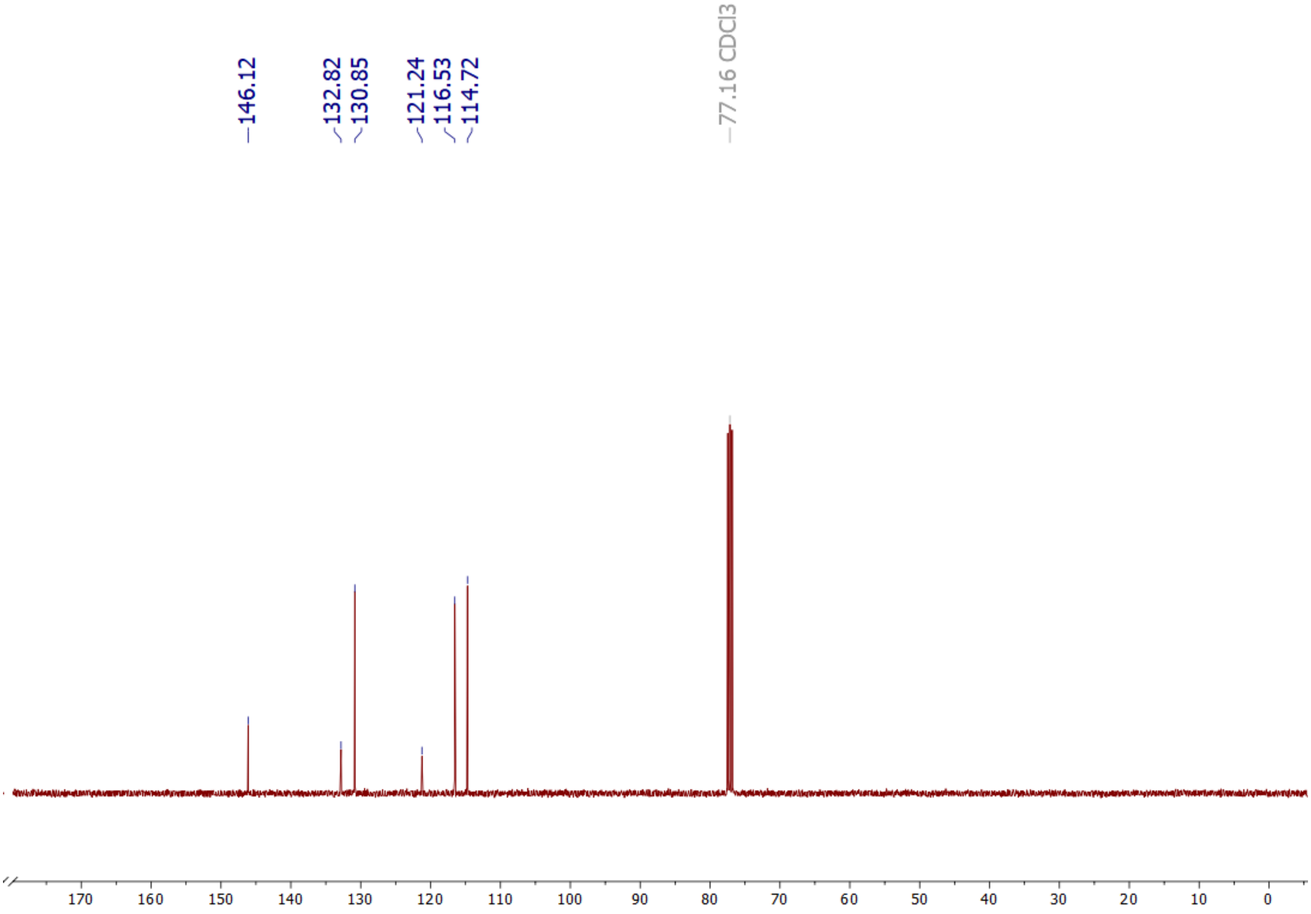
*N*-Methylaniline (**2g**) $^{13}$C-NMR spectrum in $CDCl_3$



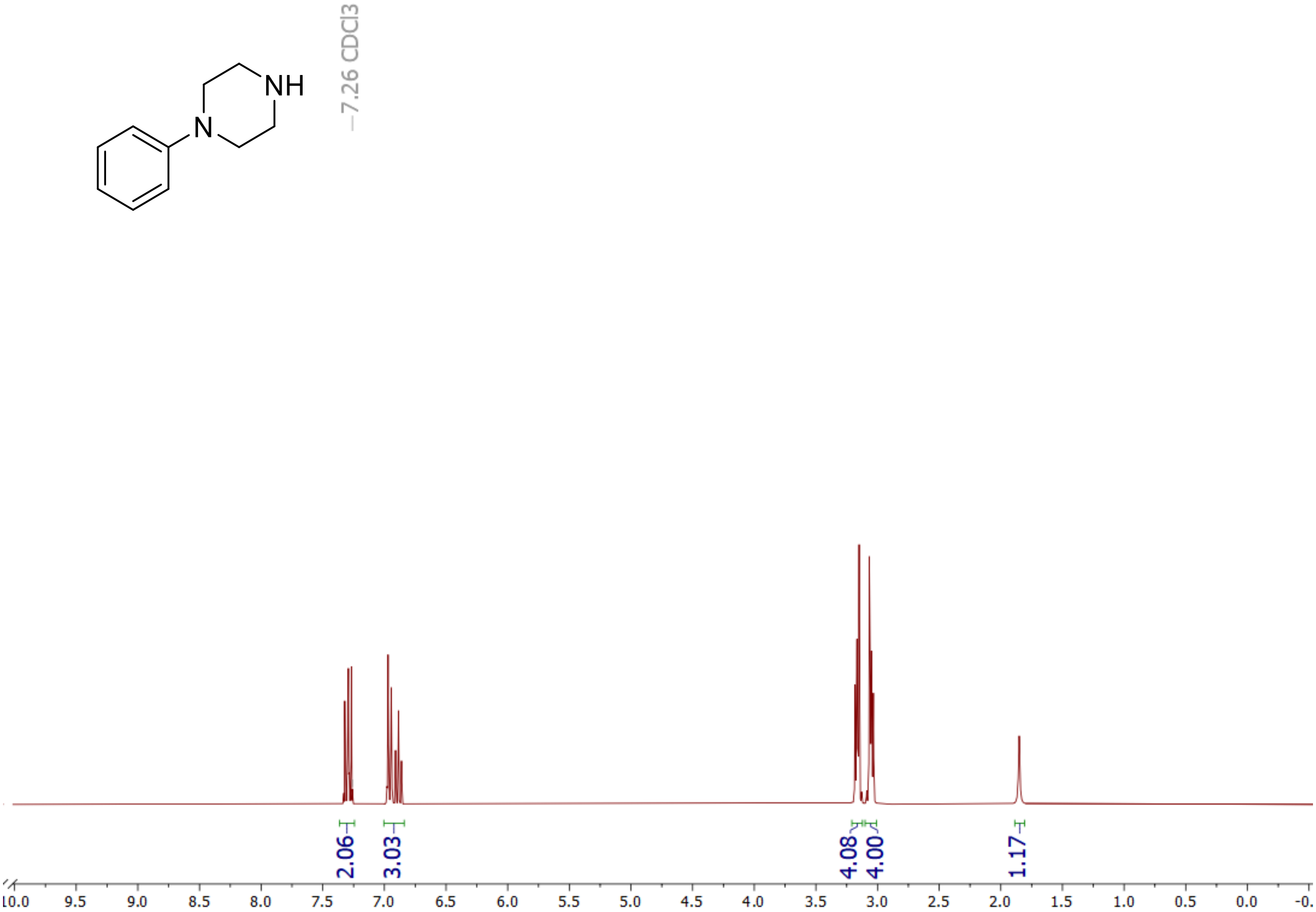
3,4-Dichloroaniline (**2j**) $^1$H-NMR spectrum in $CDCl_3$



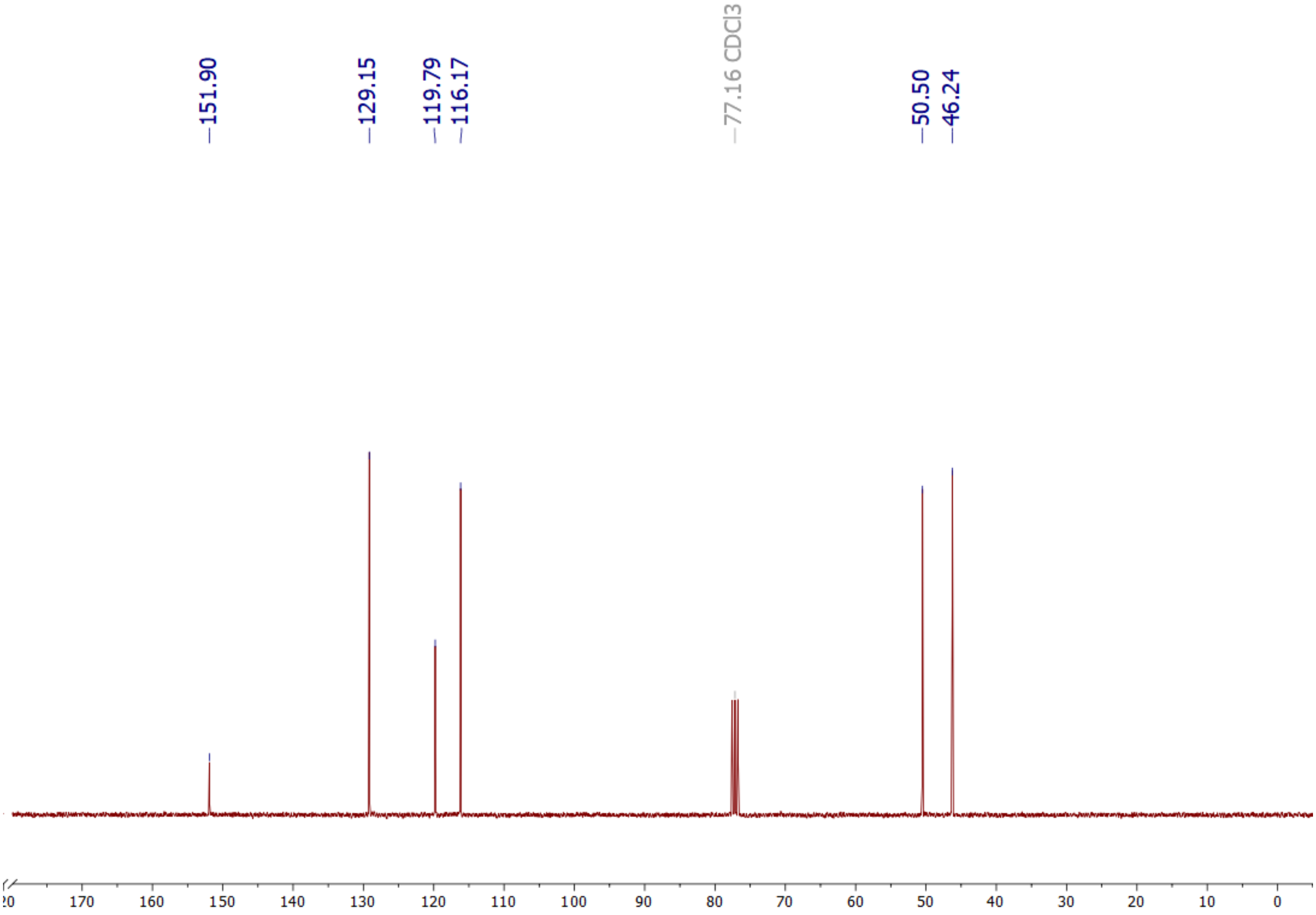
3,4-Dichloroaniline (**2j**) $^{13}$C-NMR spectrum in $CDCl_3$



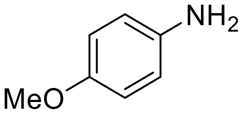
4-Phenyl-1-piperazine (**2h**) $^1$H-NMR spectrum in $CDCl_3$

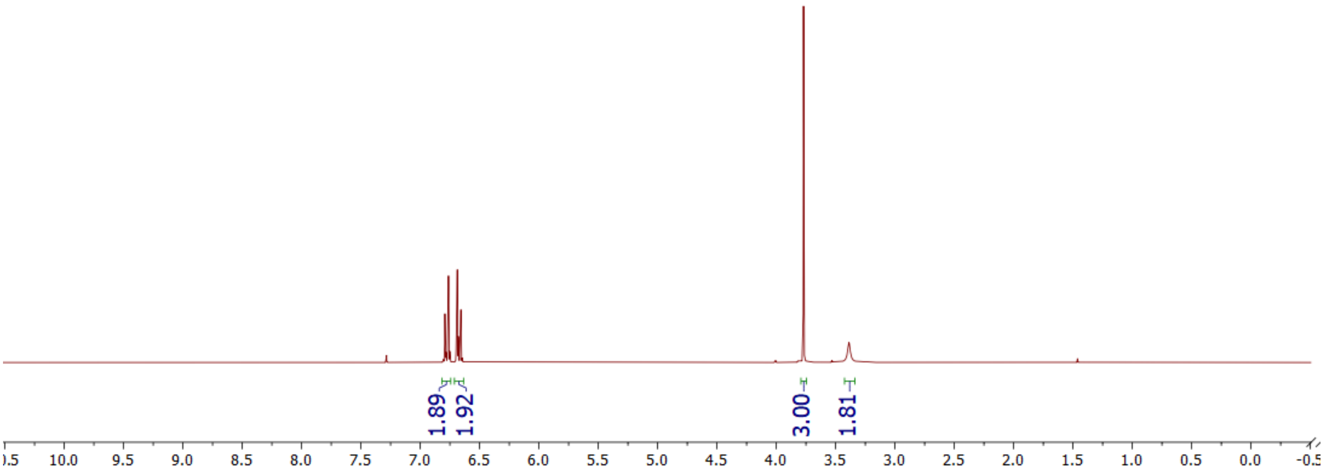


4-Phenyl-1-piperazine (**2h**) $^{13}$C-NMR spectrum in $CDCl_3$

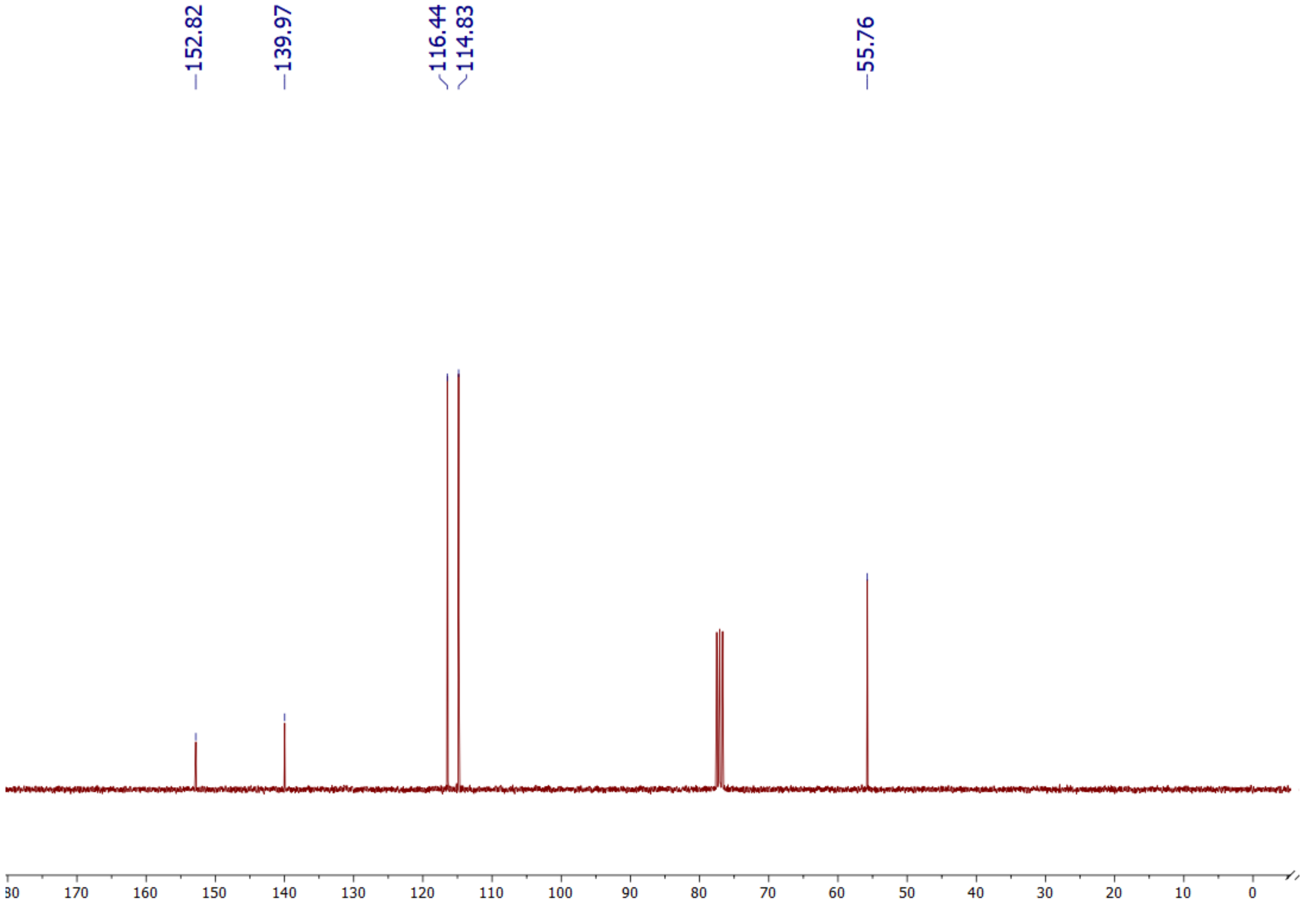


4-Methoxy-aniline (**2w**) $^1$H-NMR spectrum in $CDCl_3$

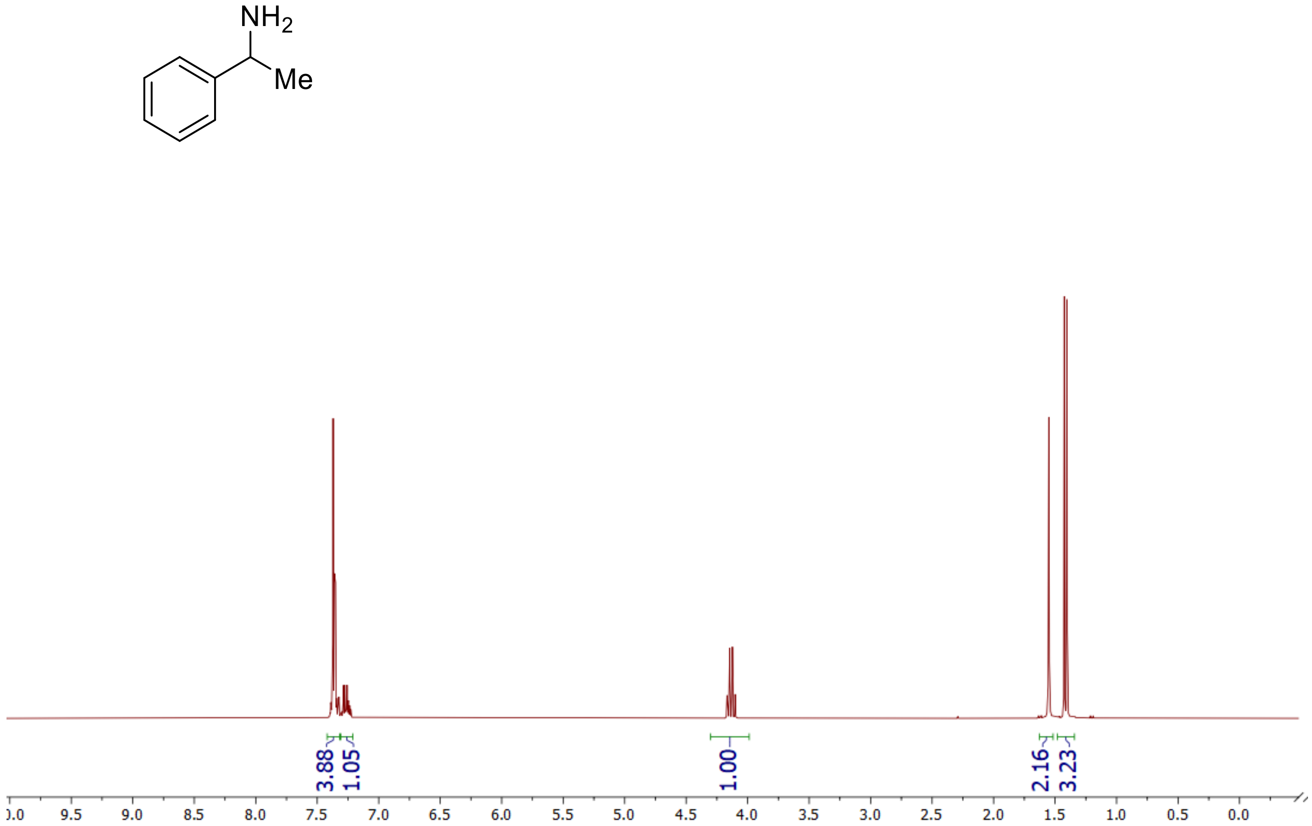




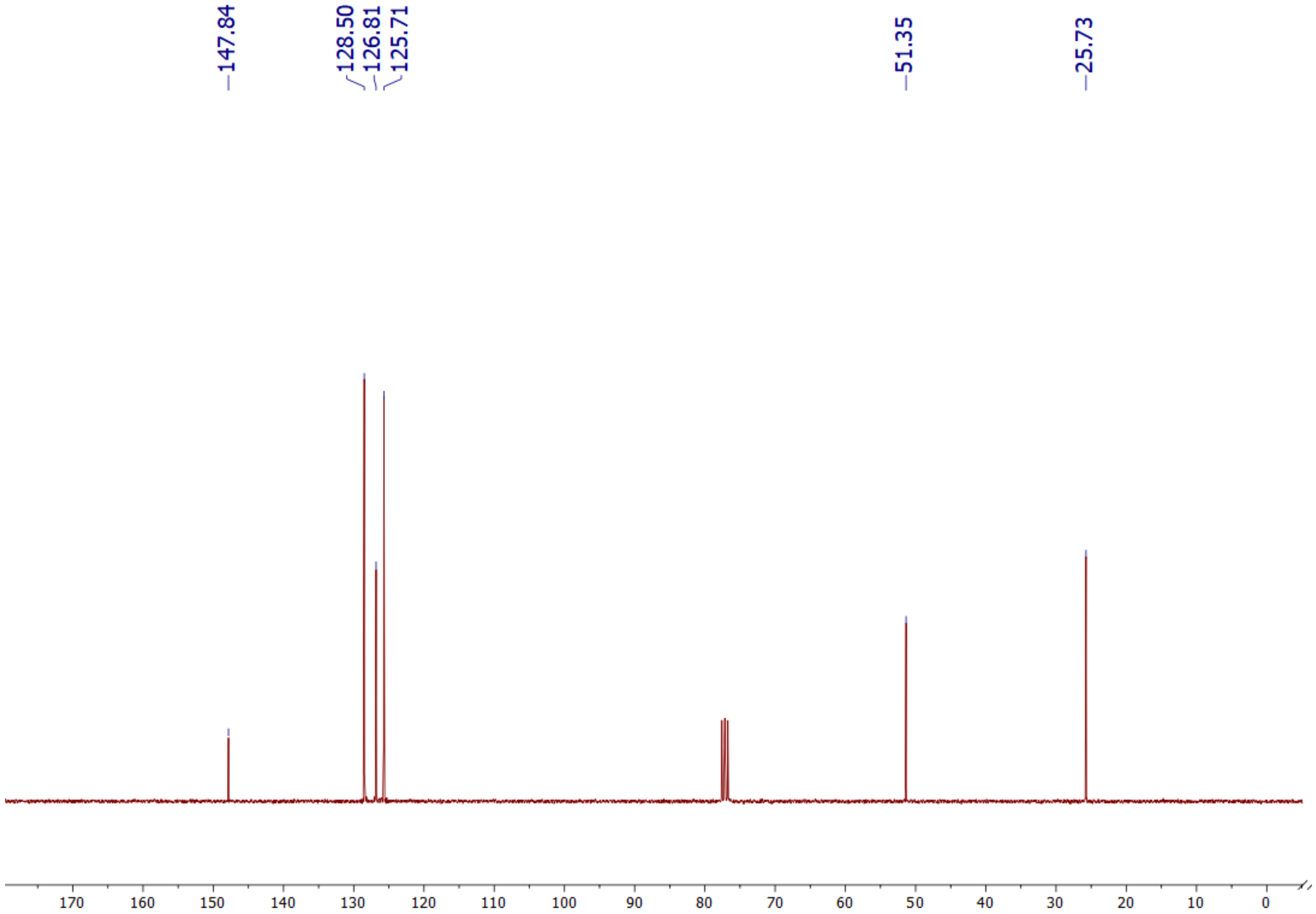
4-Methoxy-aniline (**2m**) $^{13}$C-NMR spectrum in $CDCl_3$



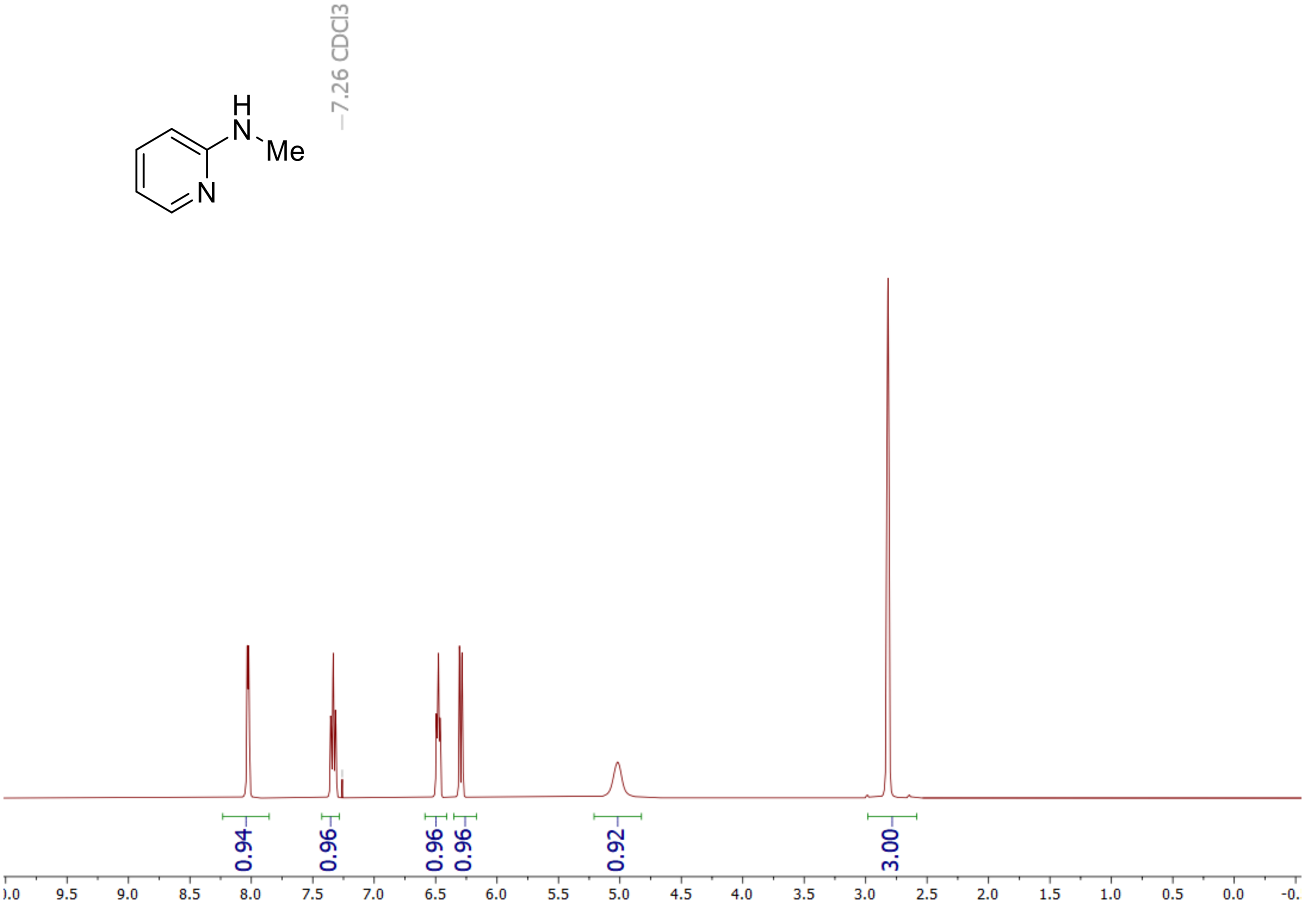
1-Phenylethylamine (**2o**) $^1$H-NMR spectrum in $CDCl_3$



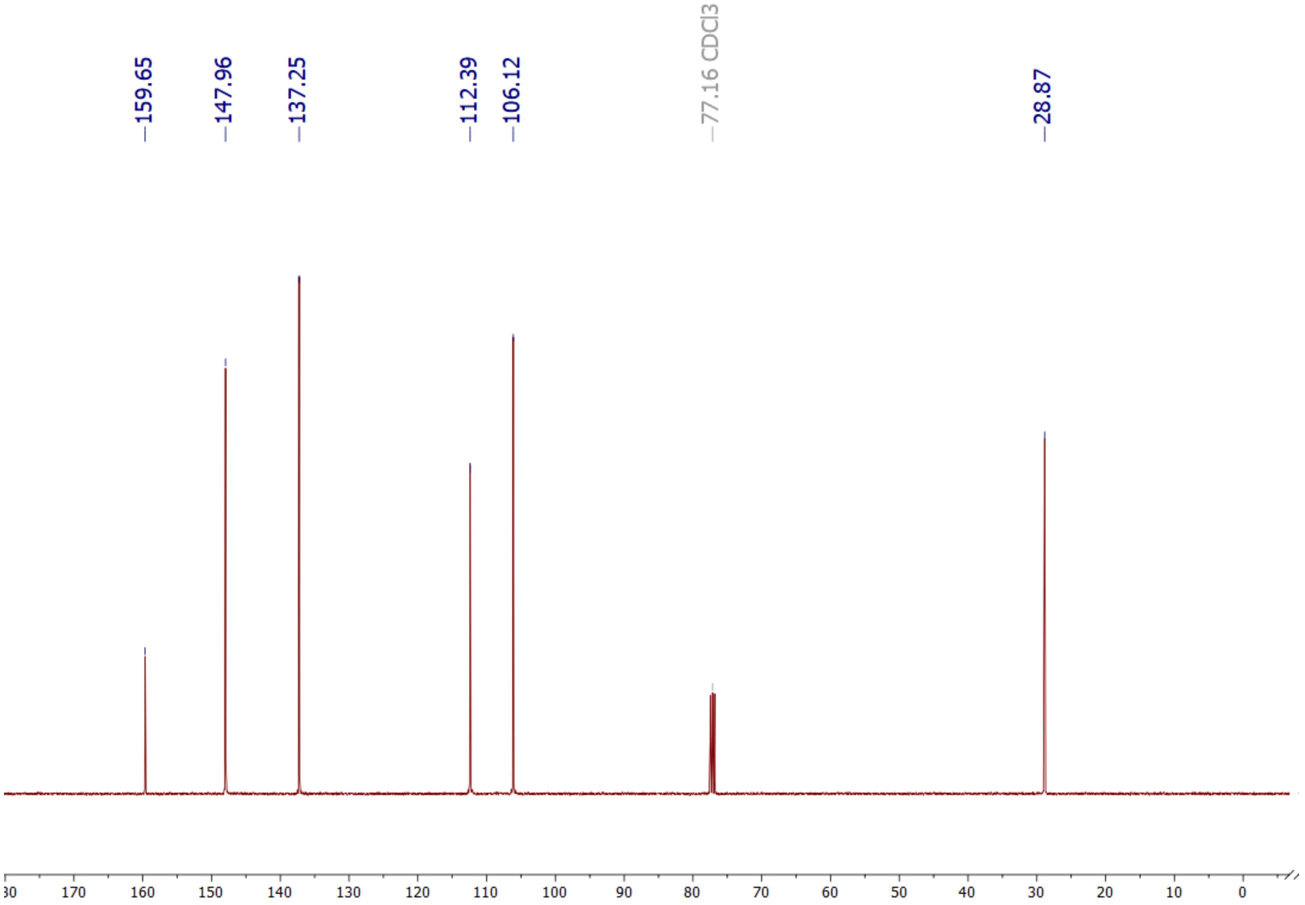
1-Phenylethylamine (**2o**) $^1$H-NMR spectrum in $CDCl_3$



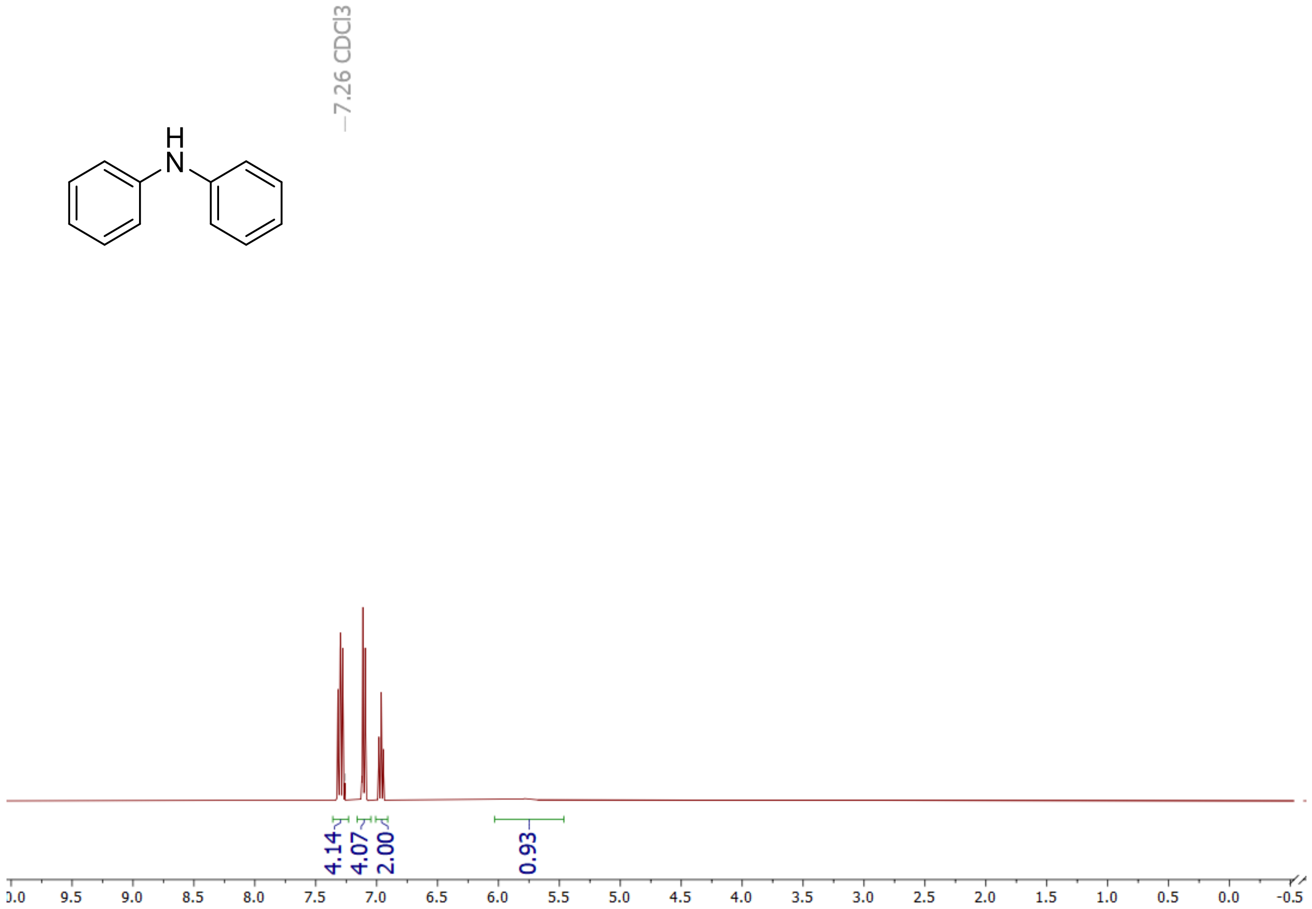
2-(*N*-Methylamino)pyridine (**2j**) $^1$H-NMR spectrum in CDCl$_3$



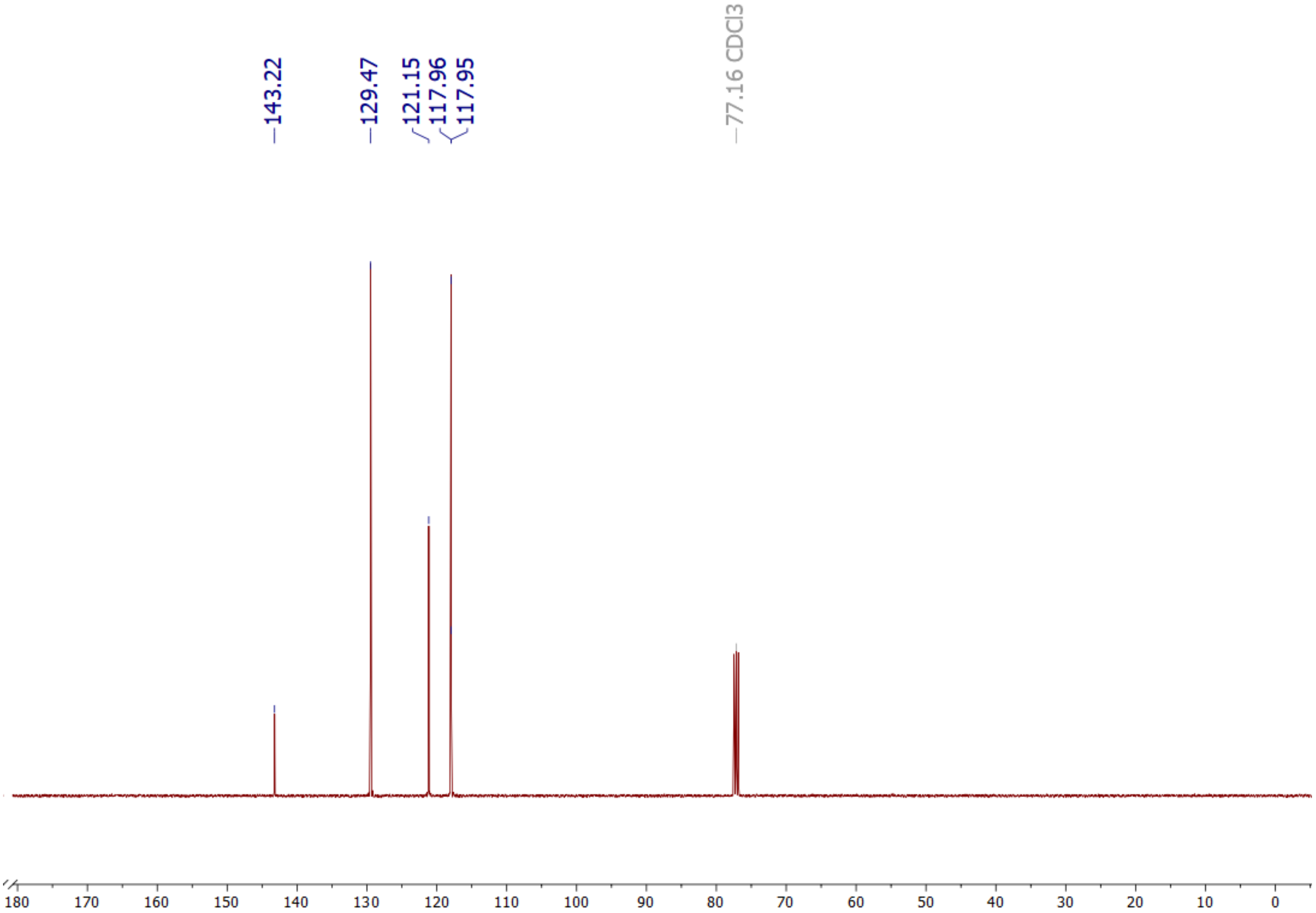
2-(*N*-Methylamino)pyridine (**2j**) $^{13}$C-NMR spectrum in CDCl$_3$



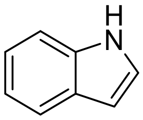
Diphenylamine (**2s**) $^1$H-NMR spectrum in $CDCl_3$

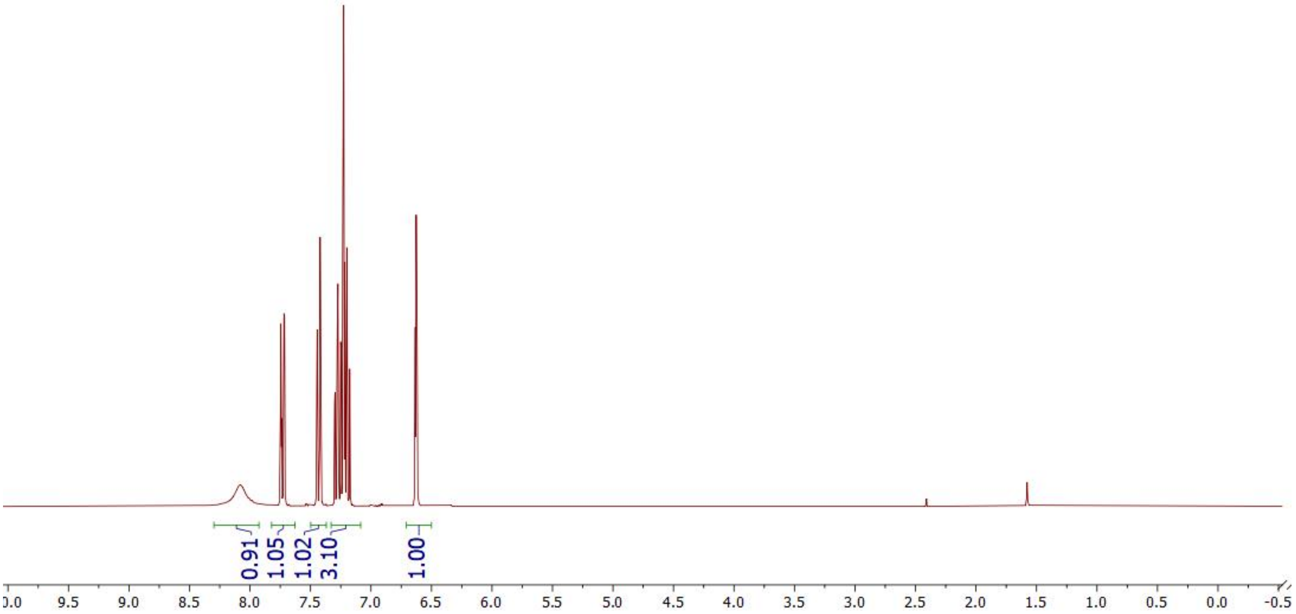


Diphenylamine (**2s**) $^{13}$C-NMR spectrum in $CDCl_3$

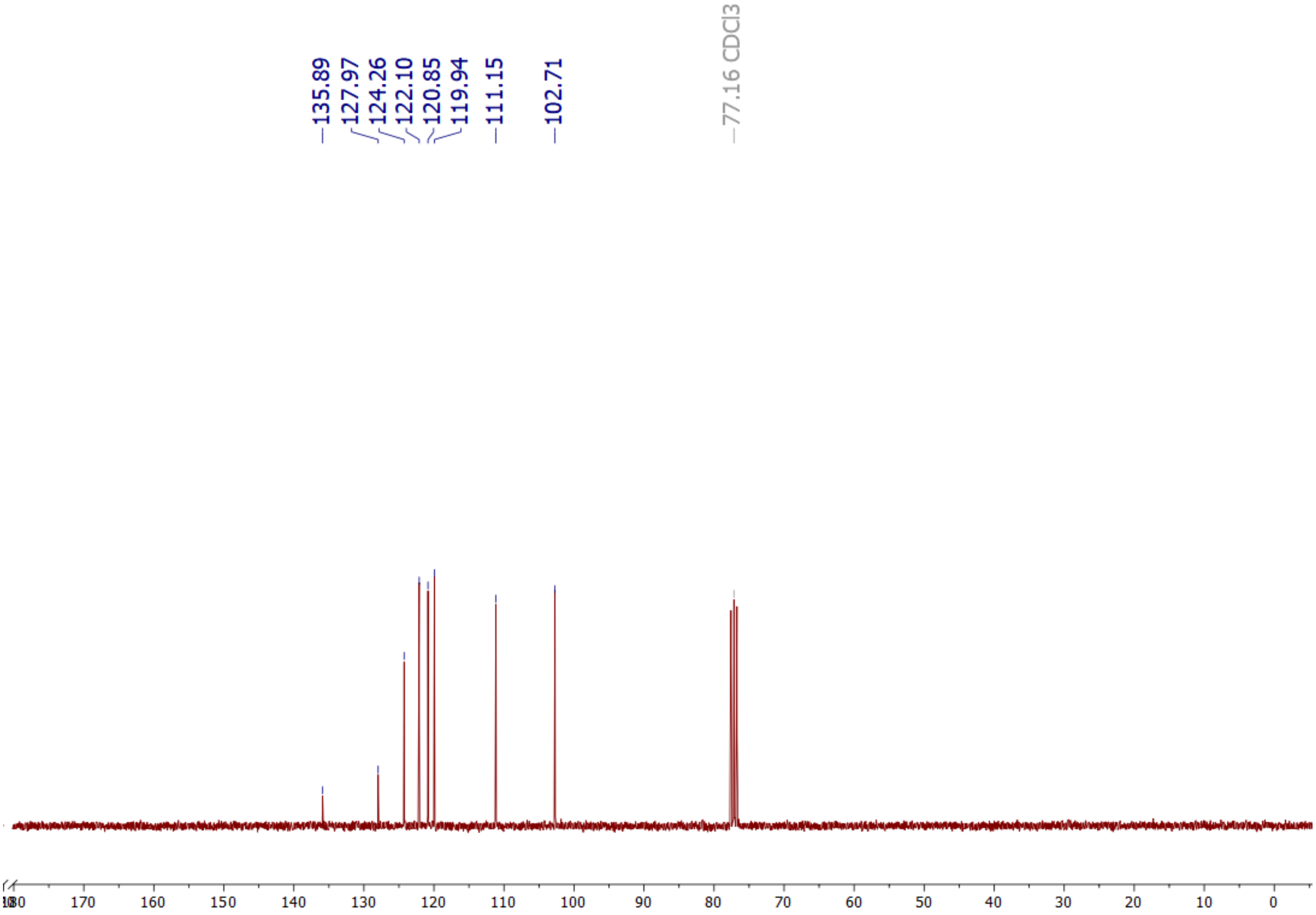


Indole (**2t**) $^{1}$H-NMR spectrum in $CDCl_3$

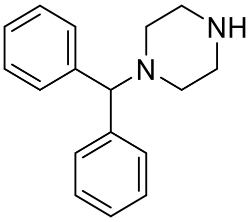


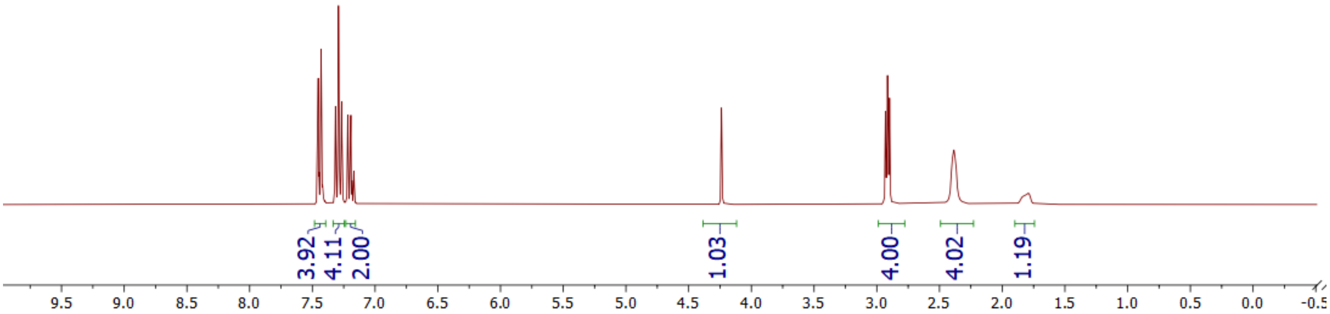


Indole (**2t**) $^{13}$C-NMR spectrum in $CDCl_3$

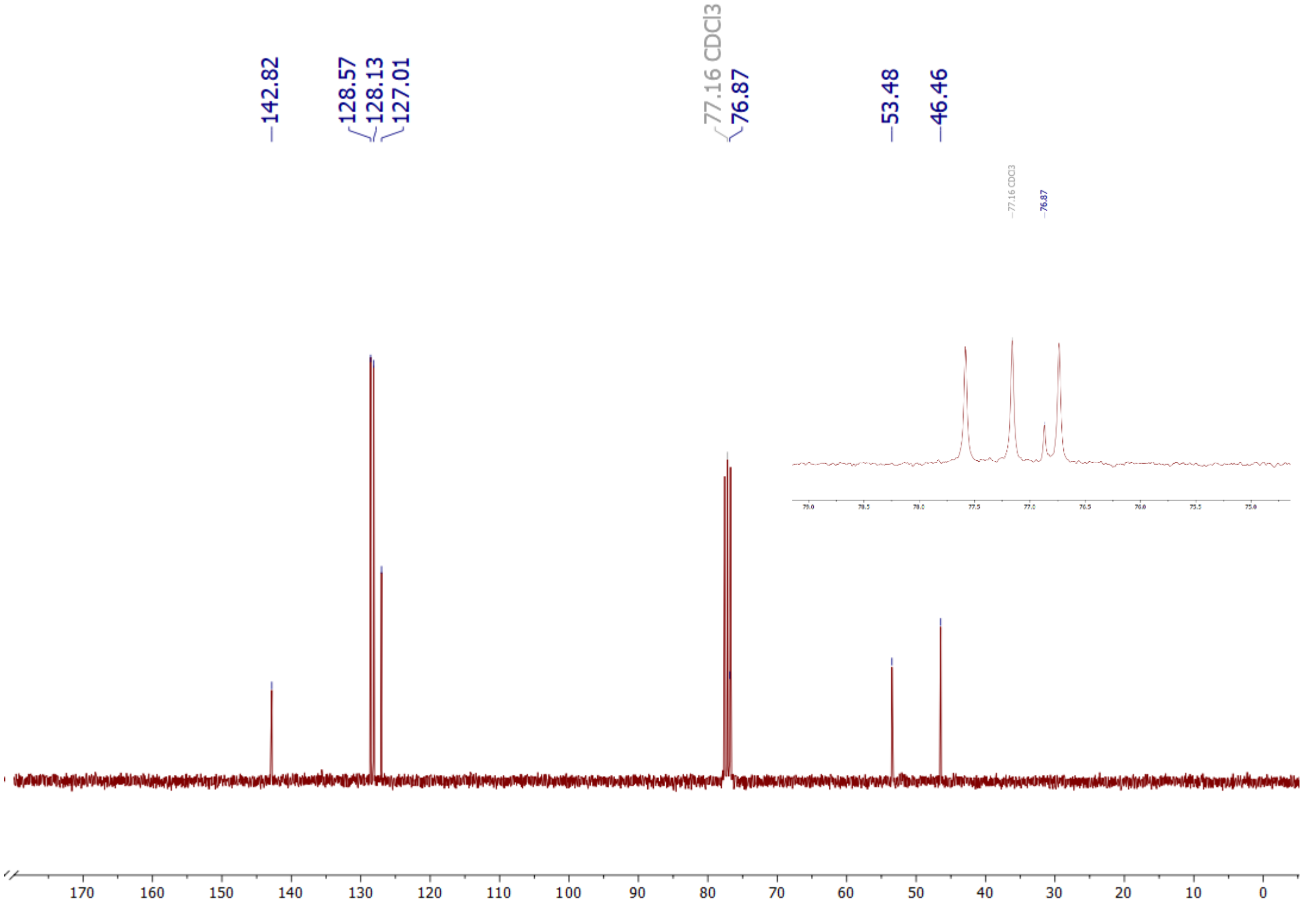


Diphenylmethylpiperazine (**2u**) $^1$H-NMR spectrum in $CDCl_3$

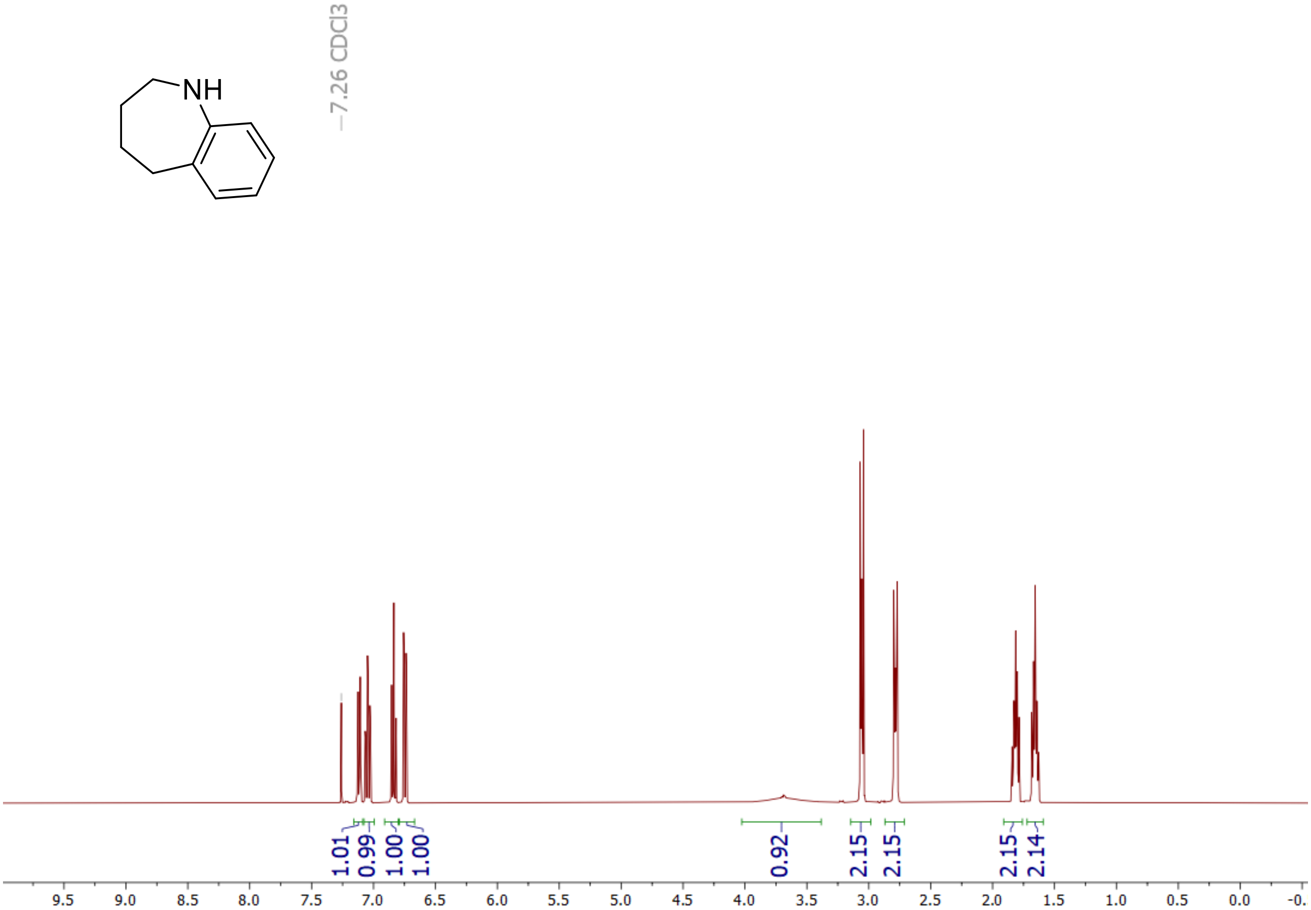




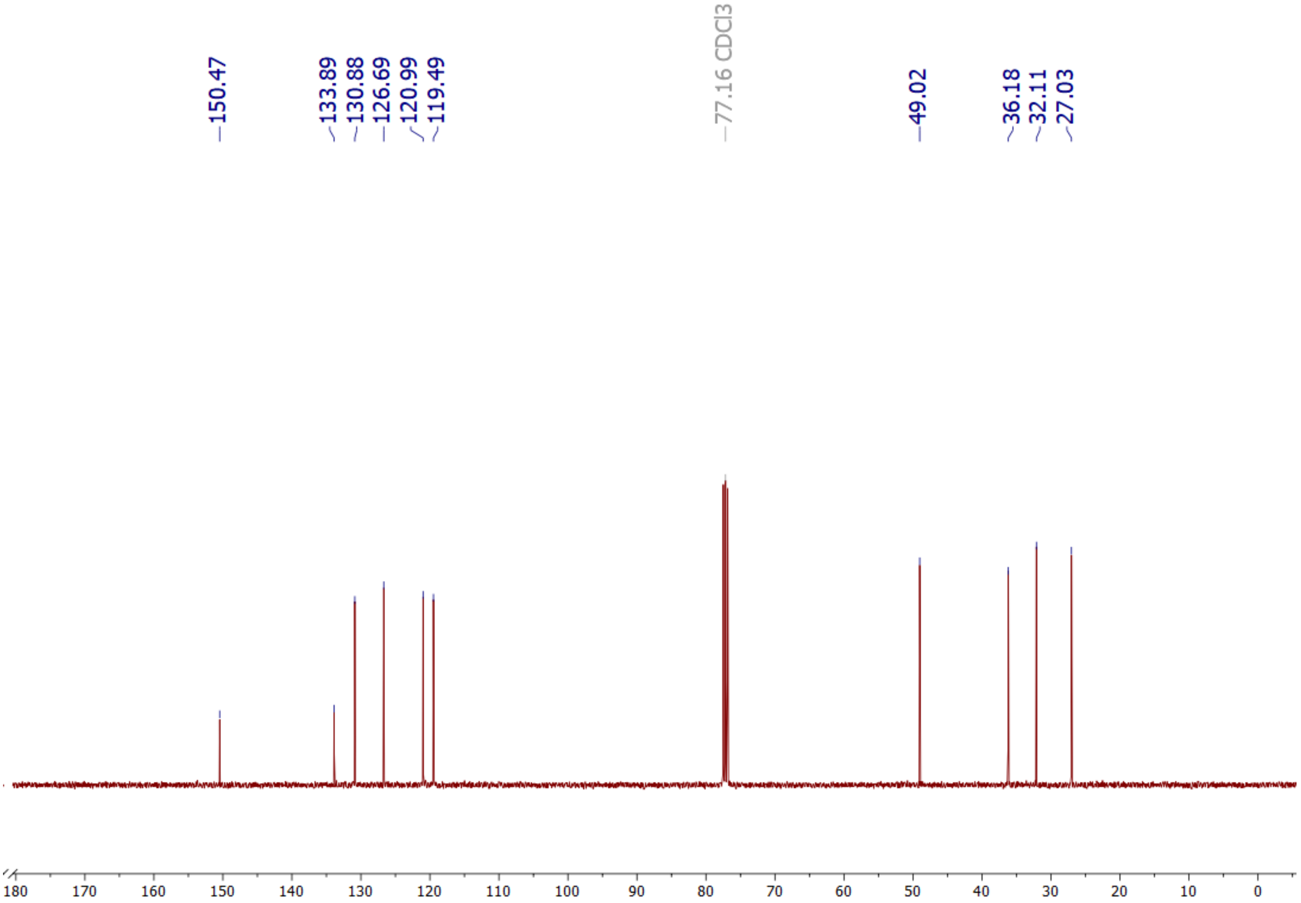
Diphenylmethylpiperazine (**2u**) $^{13}$C-NMR spectrum in $CDCl_3$



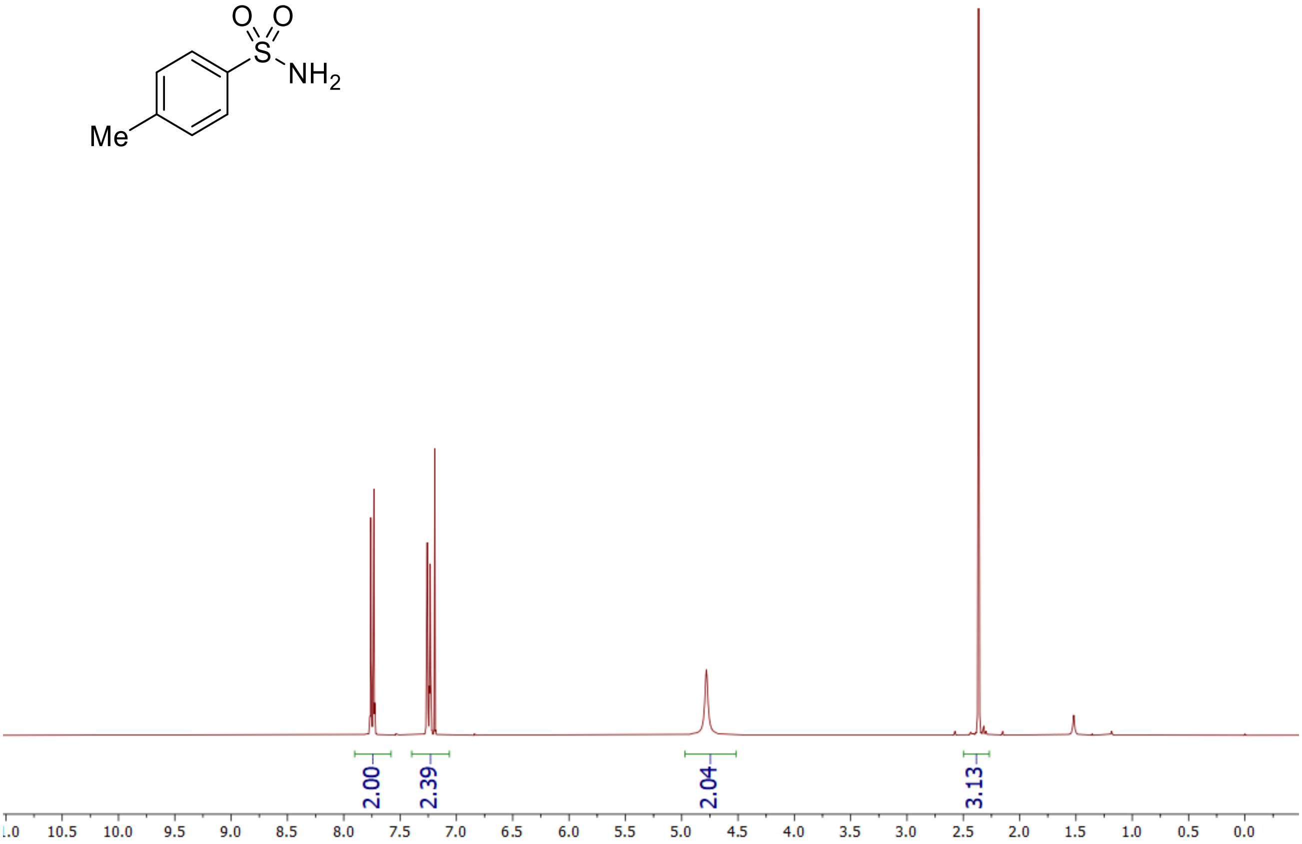
2,3,4,5-Tetrahydro-1Hbenzo[b]azepine (**2v**) $^{1}$H-NMR spectrum in $CDCl_3$



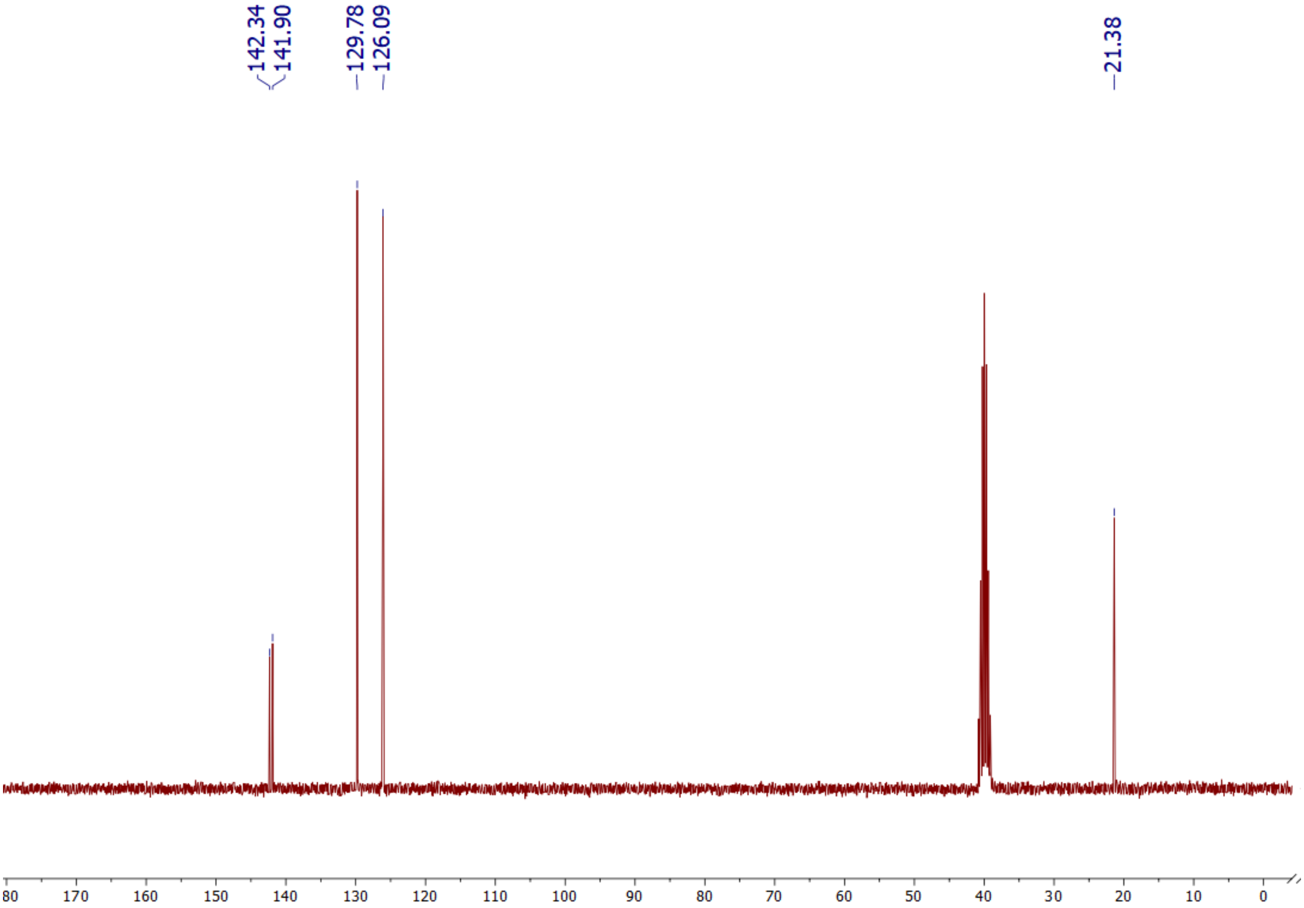
2,3,4,5-Tetrahydro-1Hbenzo[b]azepine (**2v**) $^{13}$C-NMR spectrum in $CDCl_3$



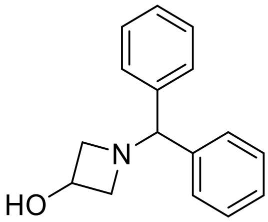
Toluene-4-sulfonamide (**2y**) $^1$H-NMR spectrum in $CDCl_3$

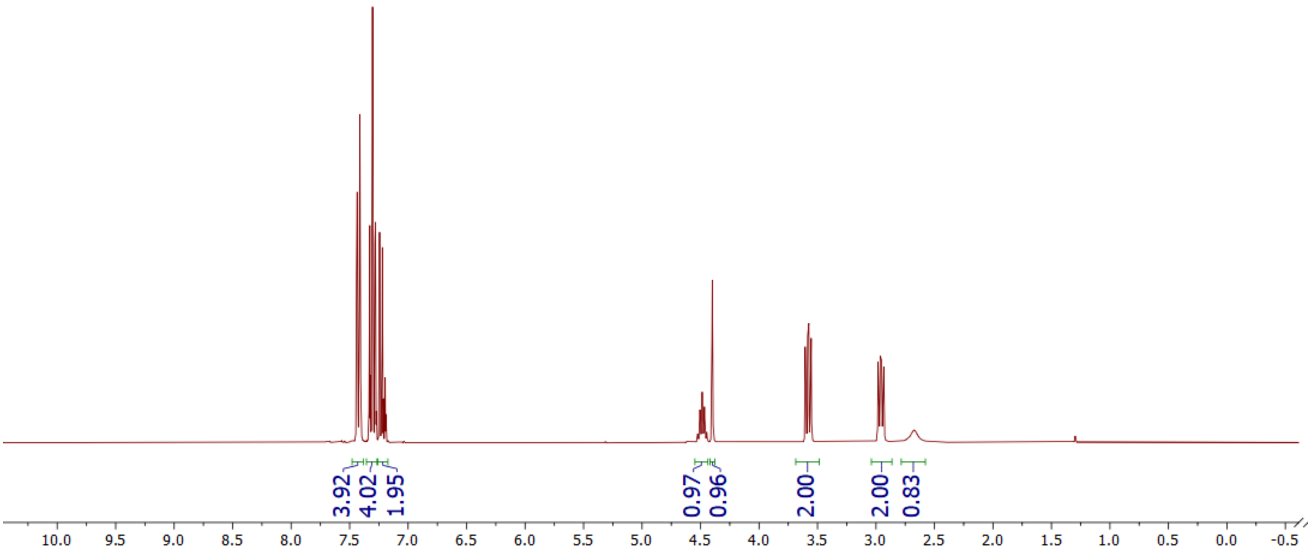


Toluene-4-sulfonamide (**2y**) $^{13}$C-NMR spectrum in DMSO-$d_6$

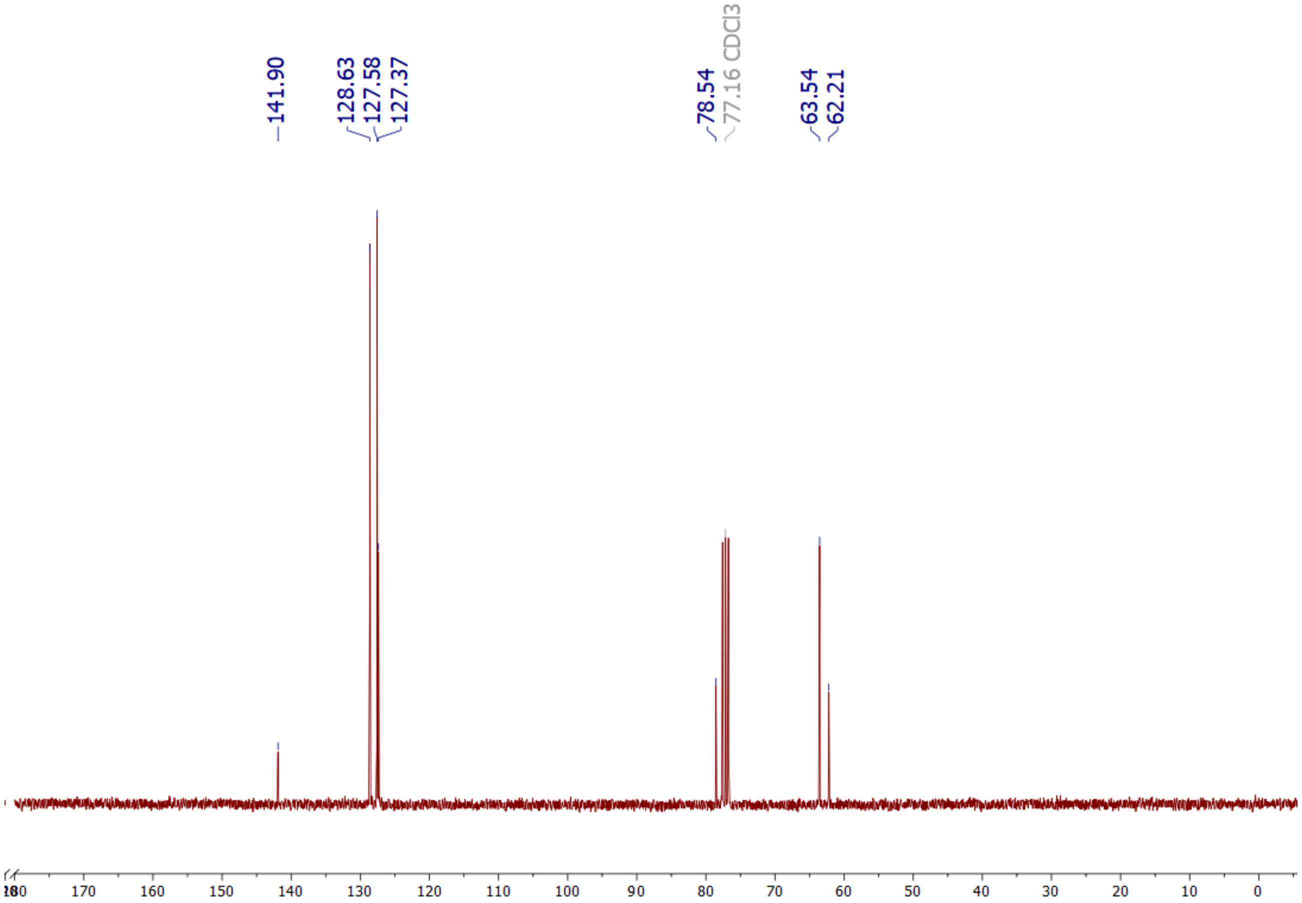


1-(Diphenylmethyl)-3-hydroxyazetidine (**3c**) $^1$H-NMR spectrum in $CDCl_3$

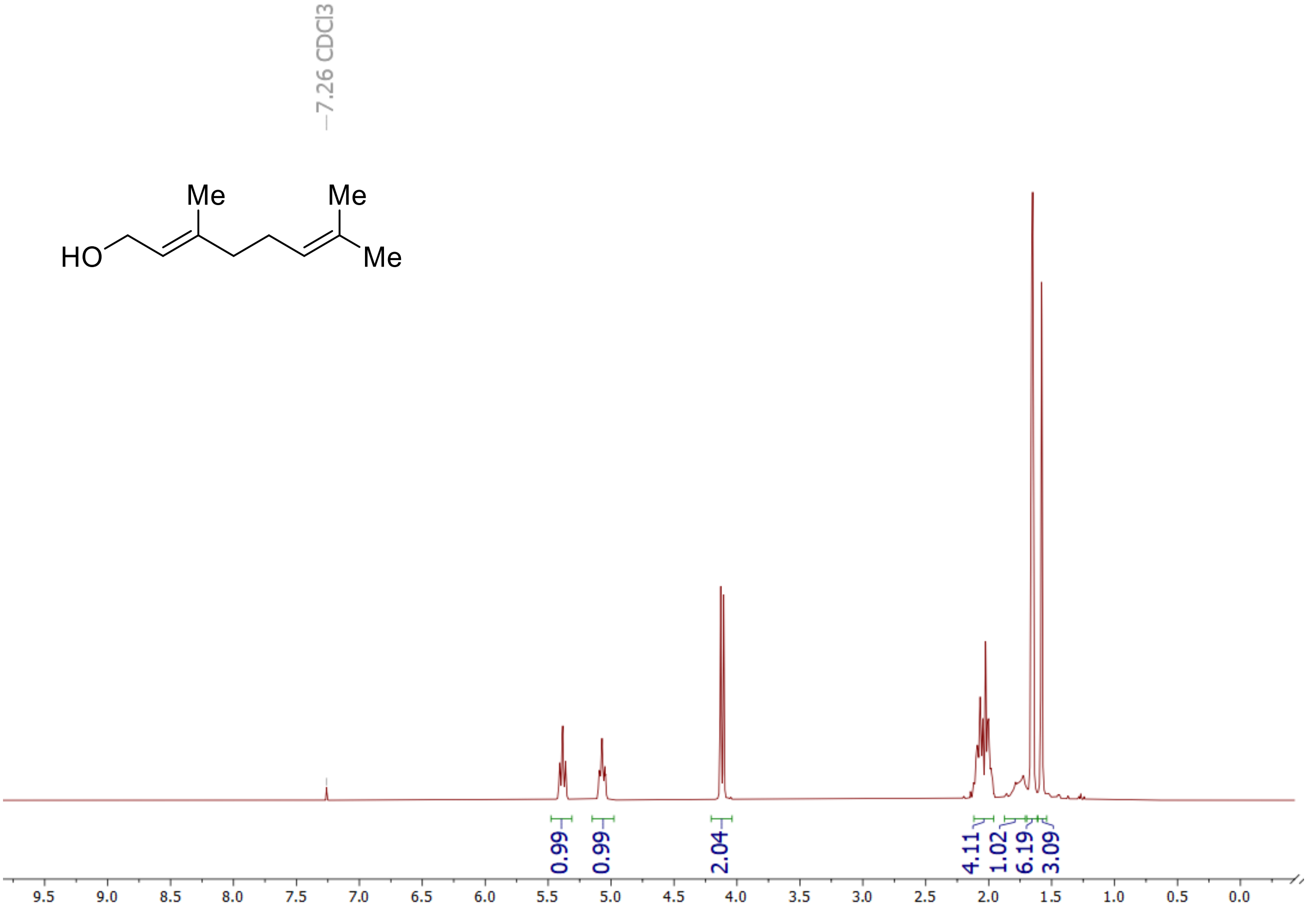




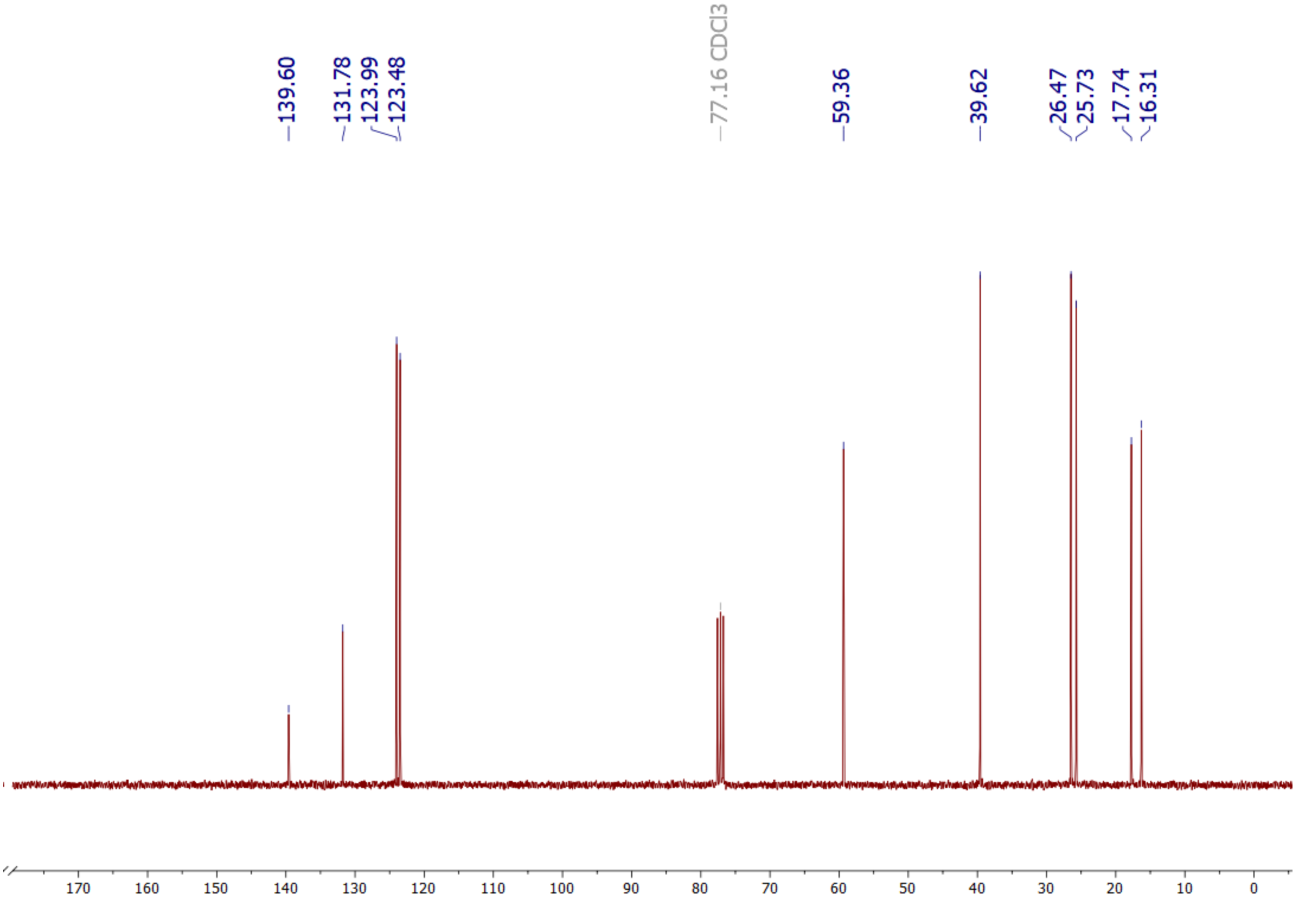
1-(Diphenylmethyl)-3-hydroxyazetidine (**3c**) $^{13}$C-NMR spectrum in $CDCl_3$



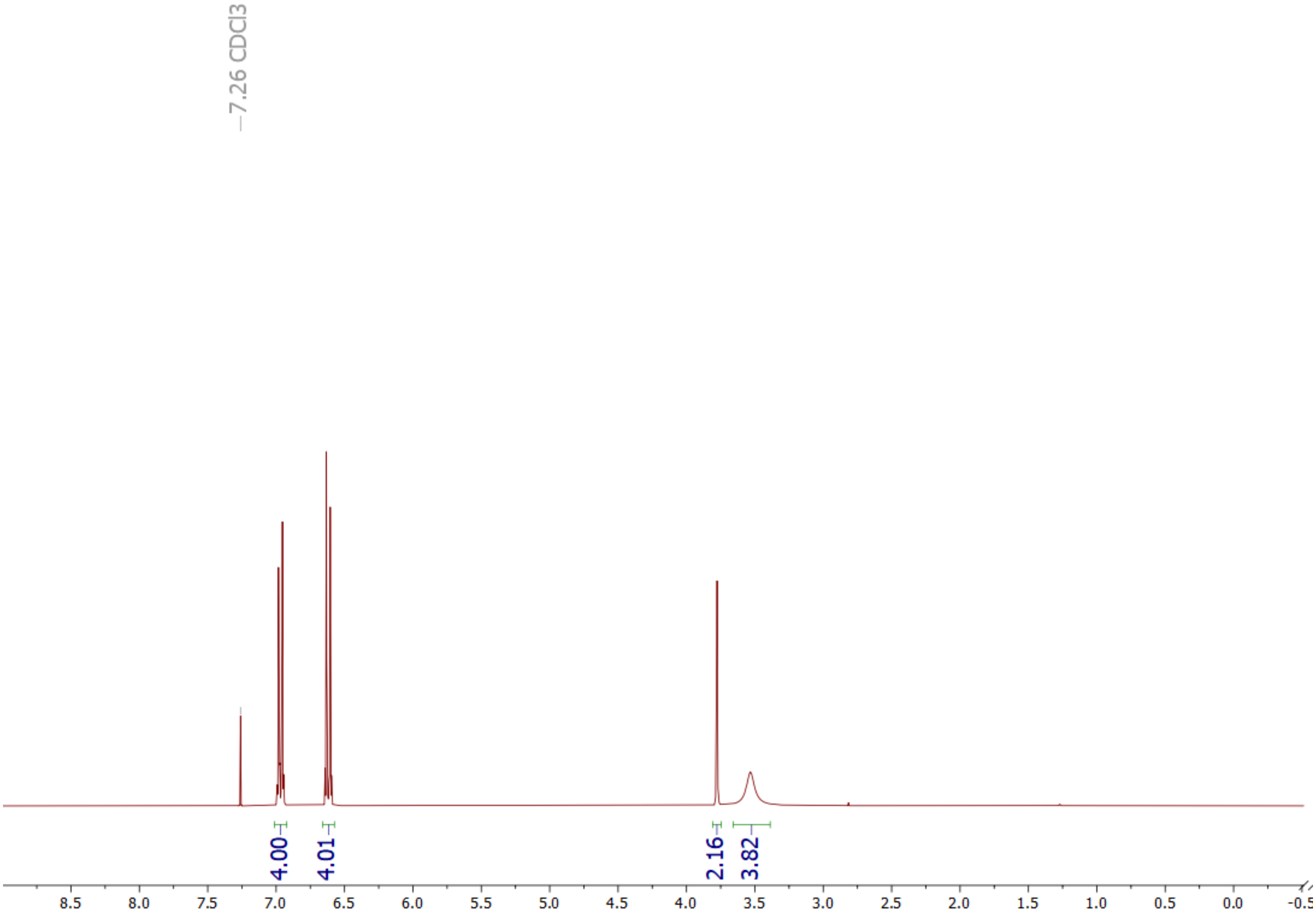
Geraniol (**3d**) $^1$H-NMR spectrum in $CDCl_3$



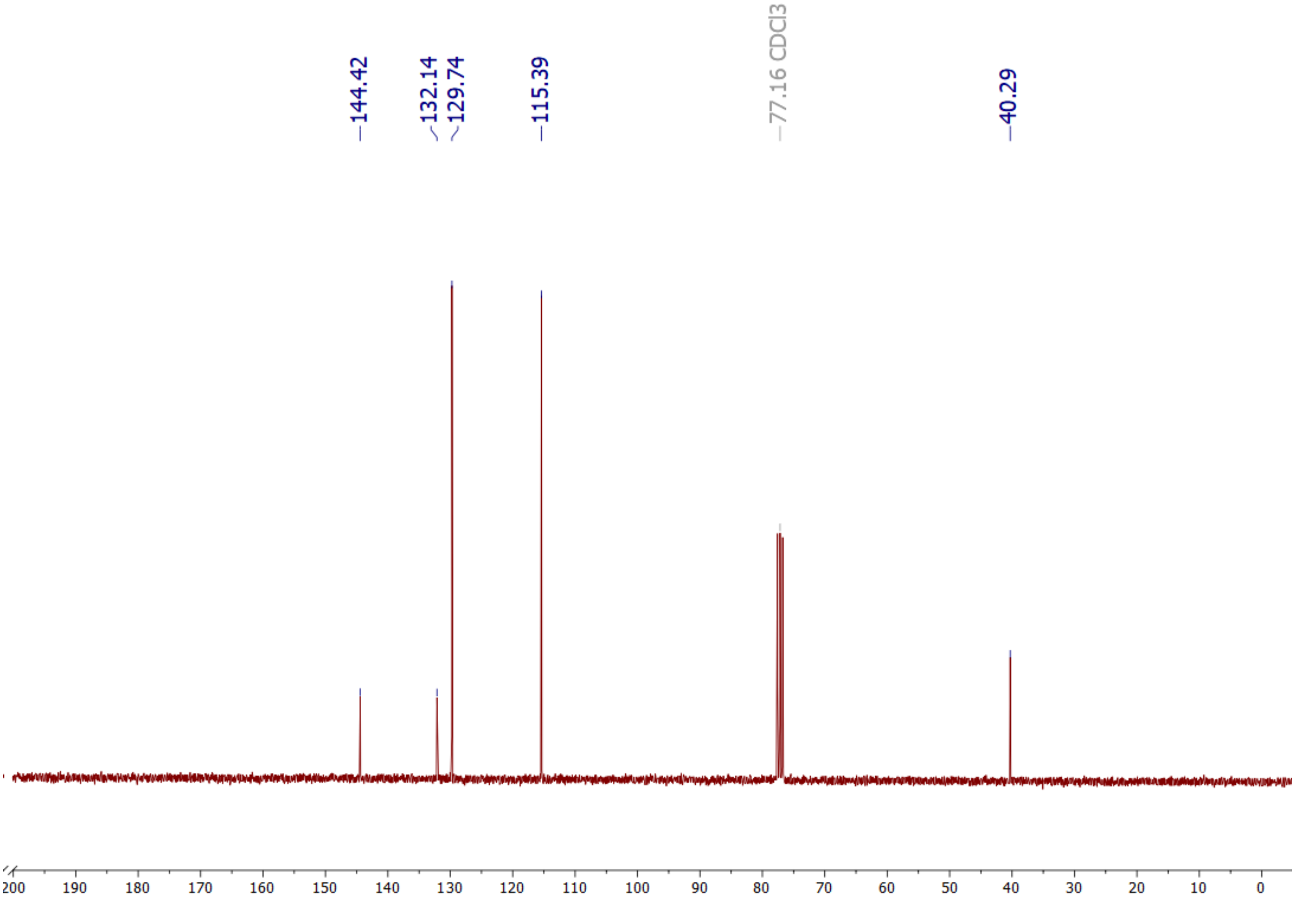
Geraniol (**3d**) $^{13}$C-NMR spectrum in $CDCl_3$



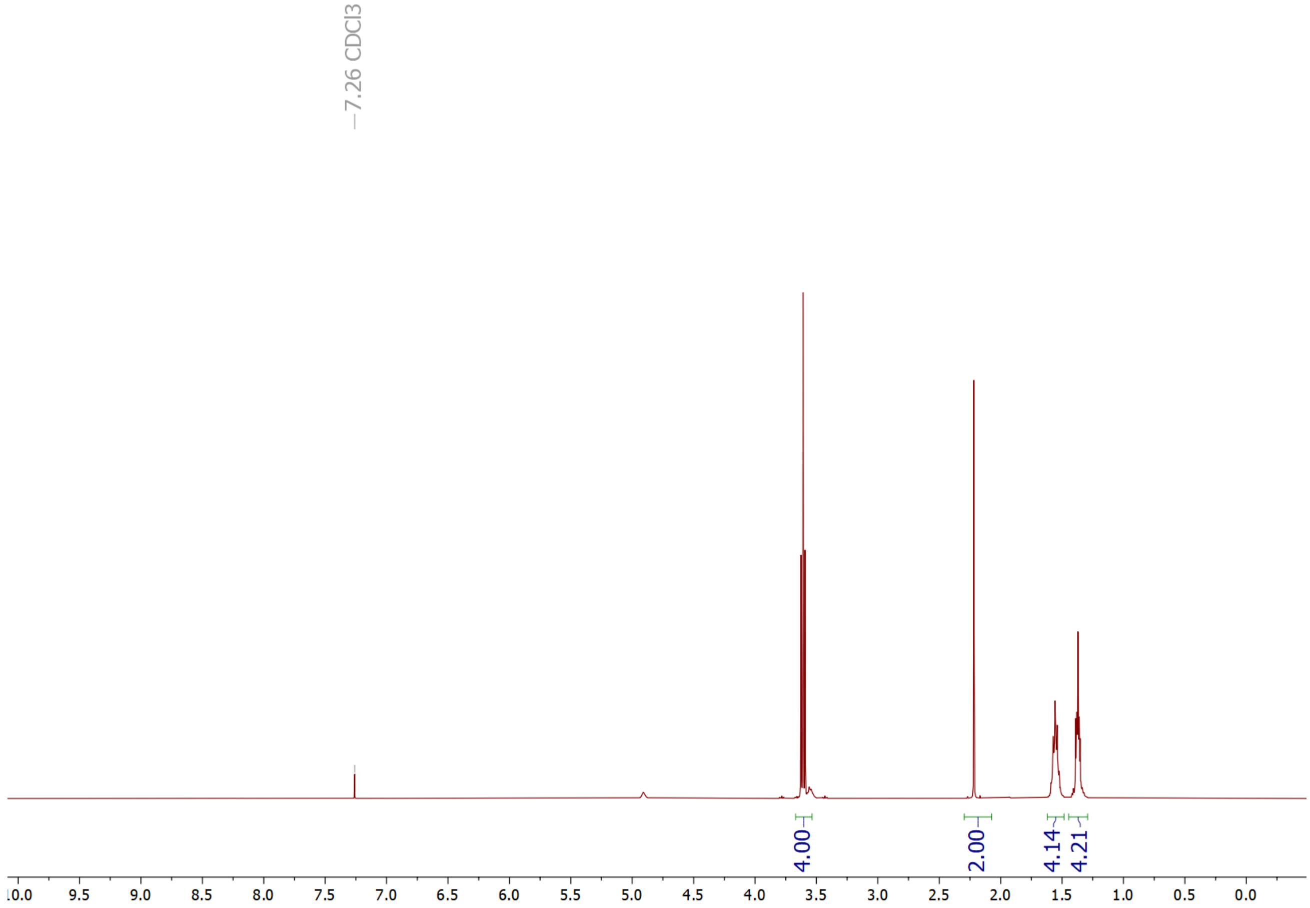
4,4'-Diamino diphenyl methane (**8b**) $^1$H-NMR spectrum in CDCl$_3$



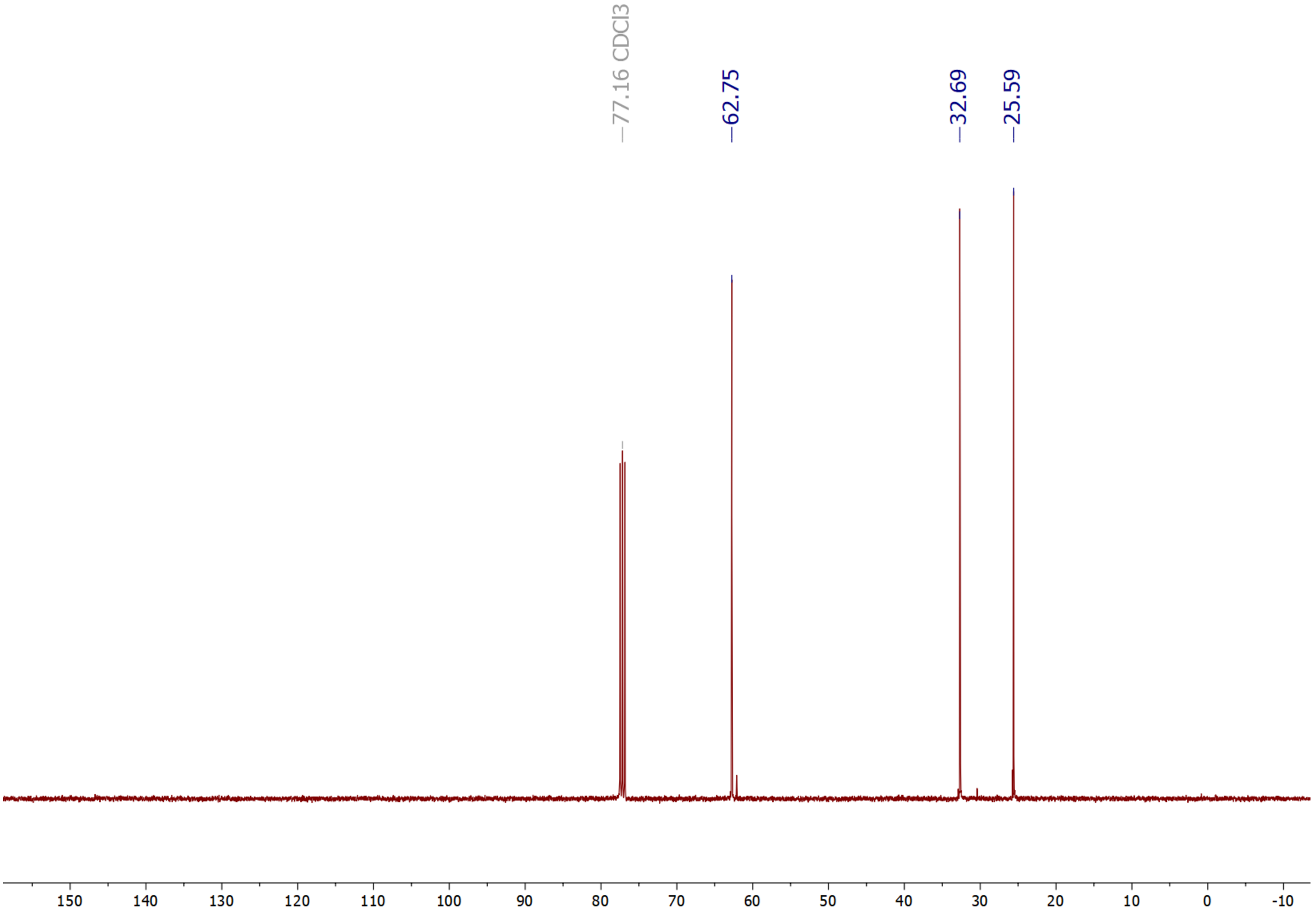
4,4'-Diamino diphenyl methane (**8b**) $^{13}$C-NMR spectrum in CDCl$_3$



1,6-hexanediol (**9b**) $^{1}$H-NMR spectrum in CDCl$^{3}$



1,6-hexanediol (**9b**) $^{13}$C-NMR spectrum in CDCl$^{3}$



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