Supplementary Material (ESI) for Chemical Communications

Enantioselective synthesis of tertiary thiols by N→C aryl migration in lithiated thiocarbamates

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SUPPORTING INFORMATION

GENERAL PROCEDURES

General Procedure A – *Preparation of* N-*methyl*-N-*aryl-1*H-*imidazole-1-carboxamides*
Grzyb, J. A.; Shen, M.; Yoshina-Ishii, C.; Chi, W.; Brown, R. S.; Batey, R. A. *Tetrahedron* **2005**, *61*, 7153

Substituted *N*-methyl aniline (1 eq) was added to a solution of carbonyldiimidazole (CDI) (2 eq) in THF. The mixture was heated to reflux with stirring until completion. The mixture was cooled to rt and the solvent removed under reduced pressure. The resulting residue was redissolved in dichloromethane and washed with water. The organic fraction was dried over magnesium sulfate, filtered and the solvent removed under reduced pressure to afford the *N*-methyl-*N*-aryl-1*H*-imidazole-1-carboxamide.

General Procedure B – *Preparation of 3-methyl-1-(methyl(aryl)carbamoyl)-1*H-*imidazol-3-ium iodides*
Grzyb, J. A.; Shen, M.; Yoshina-Ishii, C.; Chi, W.; Brown, R. S.; Batey, R. A. *Tetrahedron* **2005**, *61*, 7153

Iodomethane (4 eq) was added to a solution of *N*-methyl-*N*-aryl-1*H*-imidazole-1-carboxamide (1 eq) in acetonitrile. The mixture was heated to reflux with stirring until consummation of starting material was observed by TLC. The mixture was cooled to rt and the solvent was removed under reduced pressure to afford the 3-methyl-1-(methyl(aryl)carbamoyl)-1*H*-imidazol-3-ium iodide.

General Procedure C – *Preparation of thiocarbamates from thioesters*

Lithium aluminium hydride (1 eq, 1M in THF) was added dropwise to a solution of 1-arylethyl ethanethioate (1 eq) in diethyl ether. The mixture was heated to reflux with stirring for 1.5 h then cooled to rt. Aqueous HCl (1 M) was added with care. The phases were separated and the aqueous layer extracted with diethyl ether. The combined ethereal fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude thiol was then dissolved in dichloromethane. 3-Methyl-1-(methyl(aryl)carbamoyl)-1*H*-imidazol-3-ium iodide (1.1 eq) and triethylamine (1.2 eq) were added. The mixture was stirred until completion was observed by TLC. The mixture was extracted with aqueous HCl, dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was then purified by flash column chromatography as required.

General Procedure D – *Preparation of thiocarbamates from thiols*

Benzylic thiol was dissolved in dichloromethane. 3-Methyl-1-(methyl(aryl)carbamoyl)-1*H*-imidazol-3-ium iodide (1.1 eq) and triethylamine (1.2 eq) were added. The mixture was stirred until completion was observed by TLC. The mixture was extracted twice with aqueous HCl (1M), dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was then purified by flash column chromatography as required.

General Procedure E – *Lithiation of benzylic thiocarbamates with LDA in THF*

n-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of diisopropylamine (3 eq) in THF (1 cm^3) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannular to a cooled (-78 °C) solution of benzylic thiocarbamate (0.05 g, 1 eq) in THF (1.5 cm^3). The mixture was allowed to stir for 1 or 2 hours. Propionic acid (3 eq) was added and the mixture allowed to warm to room temperature. Water (10 cm^3) and diethyl ether (10 cm^3) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm^3) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

General Procedure F – *Lithiation of benzylic thiocarbamates with LDA in THF/DMPU*

n-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of diisopropylamine (3 eq) in THF (1 cm^3) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannular to a cooled (-78 °C) solution of benzylic thiocarbamate (0.05 g, 1 eq) in THF (1 cm^3) and DMPU (0.5 cm^3). The mixture was allowed to stir for 1 or 2 hours. Propionic acid (3 eq) was added and the mixture allowed to warm to room temperature. Water (10 cm^3) and diethyl ether (10 cm^3) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm^3) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

General Procedure G – *Lithiation of benzylic thiocarbamates with LiTMP in THF*

n-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of *N*,*N*,*N'*,*N'*-tetramethylpiperidine (3 eq) in THF (1 cm^3) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannular to a cooled (-78 °C) solution of benzylic thiocarbamate (0.05 g, 1 eq) in THF (1.5 cm^3). The mixture was allowed to stir for 15 hours. Propionic acid (3 eq) was added and the mixture allowed to warm to room temperature. Water (10 cm^3) and diethyl ether (10 cm^3) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm^3) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

General Procedure H – *One-pot lithiation/deprotection of benzylic thiocarbamates with LiTMP in THF*

n-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of *N*,*N*,*N'*,*N'*-tetramethylpiperidine (3 eq) in THF (1 cm^3) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannular to a cooled (-78 °C) solution of benzylic thiocarbamate (0.05 g, 1 eq) in THF (1.5 cm^3). The mixture was allowed to stir for 15 hours. Propionic acid (3 eq) was added and the mixture allowed to warm to room temperature. Sodium ethoxide solution (21 % w/w in ethanol, 5 eq) was added and the mixture stirred for a further 20 min. Water (10 cm^3) and diethyl ether (10 cm^3) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm^3) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

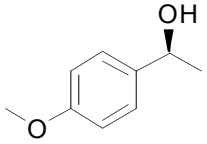
General Procedure I – *Benzylic thiols by deprotection of benzylic thiocarbamates*

Sodium ethoxide solution (21 % w/w in ethanol, 2 eq) was added to a solution of benzylic thiocarbamate (1 eq) in ethanol (1 cm^3) at 0 °C. This was stirred for 30 minutes and saturated ammonium chloride solution (1 cm^3) added. The mixture was allowed to warm to room temperature. Water (10 cm^3) and diethyl ether (10 cm^3) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm^3) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

SYNTHESIS OF PRECURSORS

s1: (*S*)-1-(4-Methoxyphenyl)ethanol

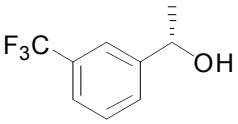
Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521



Triethylamine (2.02 cm^3, 12.0 mmol) and formic acid (1.13 cm^3, 30 mmol) were stirred together at 0 °C and allowed to warm to room temperature. 4-Methoxyacetophenone (0.751 g, 5 mmol) and [(p-cymene)RuCl((*S*,*S*)-N-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine(1-))] (0.156 g, 0.025 mmol) were added and the mixture was stirred for 72 hours. Water and EtOAc were added, the phases separated and the aqueous fraction extracted with EtOAc (3 x 10 cm^3). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 4:1) and the title compound was isolated as a colourless oil (0.728 g, 96%). $\boldsymbol{R_F}$: 0.38 (petrol/EtOAc, 1:1); $\boldsymbol{[\alpha]_D^{22}}$: -40.3º (*c*. 1.2, $CHCl_3$); **MS** m/z (EI) 151 (100%, M-H^+); **HRMS**: found 137.0597, M-CH_3 requires 137.0597; **IR** ν_{max} (film)/cm^{-1} 3373 (OH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.31 (d, *J* 8.8 Hz, 2H), 6.89 (d, *J* 8.8 Hz, 2H), 4.86 (q, *J* 4.8 Hz, 1H), 3.81 (s, 3H), 1.48 (d, *J* 4.8 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 159.0, 138.0, 126.7, 113.8, 70.0, 55.3, 25.1.

s2: (*S*)-1-(3-Trifluoromethylphenyl)ethanol

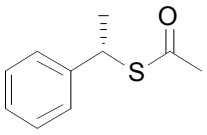
Biswas, K.; Prieto, O.; Goldsmith, P. J.; Woodward, S. *Angew. Chemie Int. Ed.; Eng.* **2005**, *44* (15), 2232



Triethylamine (2.02 cm^3, 12.0 mmol) and formic acid (1.13 cm^3, 30 mmol) were stirred together at 0 °C and allowed to warm to room temperature. 3-Trifluoromethylacetophenone (0.68 cm^3, 5 mmol) and [(p-cymene)RuCl((S,S)-N-(*p*-tolyenesulfonyl)-1,2-diphenylethylenediamine(1-))] (0.114 g, 0.018 mmol) were added and the mixture was stirred for 72 h. Water and EtOAc were added, the phases separated and the aqueous fraction extracted with EtOAc (3 x 10 cm^3). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 4:1) and the title compound isolated as a colourless oil (0.764 g, 79%). $\boldsymbol{R_F}$: 0.17 (petrol/EtOAc, 4:1); $\boldsymbol{[\alpha]_D^{22}}$: -14.4º (*c*. 1.1, $CHCl_3$); **MS** m/z (ES-) 189 (100%, M-H^+); **HRMS**: found 189.0525, M-H^+ requires 189.0527; **IR** ν_{max} (film)/cm^{-1} 3349 (OH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.58 - 7.45 (m, 3H), 4.97 (q, *J* 6.4 Hz, 1H), 2.01 (s, 1H), 1.52 (d, *J* 6.4 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 146.7, 131.0, 130.6, 129.0, 128.8, 125.5, 124.3, 124.3, 122.8, 122.2, 122.2, 69.9, 25.4.

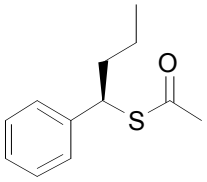
s3: Thioacetic acid S-((*S*)-1-phenylethyl) ester

Kawano, Y.; Kaneko, N.; Mukaiyama, T. *Chem. Lett.* **2005**, *34*, 1612



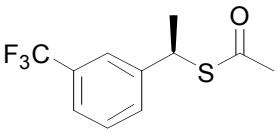
Oxalyl chloride (0.85 cm^3, 10 mmol) was added to a stirred solution of DMF (0.85 cm^3, 11 mmol) in DCM (30 cm^3) at 0 °C. The mixture was stirred for 5 minutes. (*R*)-1-phenylethanol (1.2 cm^3, 10 mmol), triethylamine (2.8 cm^3, 20 mmol) and ethanethioic S-acid (0.5 cm^3, 7 mmol) were added sequentially. The mixture was warmed to room temperature and stirred for 17 h. Water (5 cm^3) was added and the aqueous layer extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was subjected to flash column chromatography (40:1 petrol/diethyl ether) and the title compound isolated as a yellow oil (0.781 g, 62 %). $\boldsymbol{R_F}$: 0.58 (9:1 Petrol/diethyl ether); $\boldsymbol{[\alpha]_D^{22}}$: -226.9º (*c*. 1.3, $CHCl_3$); **MS** m/z (EI) 180 (20%, M^+); **HRMS**: found 180.0602, M^+ requires 180.0603; **IR** ν_{max}(film)/cm^{-1} 1690 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.24-7.35 (m, 5H), 4.75 (q, *J* 7.2 Hz, 1H), 2.30 (s, 3H), 1.66 (d, *J* 7.2 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 195.1, 142.6, 128.6, 127.3, 127.2, 43.0, 30.5, 22.2.

s4: Thioacetic acid S-((*R*)-1-phenylbutyl) ester



Oxalyl chloride (0.29 cm^3, 3.3 mmol) was added to a stirred solution of DMF (0.28 cm^3, 3.7 mmol) in DCM (20 cm^3) at 0 °C. The mixture was stirred for 5 min. (*S*)-1-phenylbutan-1-ol (0.51 g, 3.3 mmol), triethylamine (0.93 cm^3, 6.67 mmol) and ethanethioic S-acid (0.21 cm^3, 3.00 mmol) were added sequentially. The mixture was warmed to room temperature and stirred for 18 h. Water (5 cm^3) was added, the phases separated and the aqueous layer extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/diethyl ether, 40:1) and the title compound isolated as a yellow oil (0.110 g, 18%). $\boldsymbol{R_F}$: 0.46 (9:1, Petrol:Et_2O); $\boldsymbol{[\alpha]_D^{20}}$: 46.2º (c. 0.4, $CHCl_3$); **MS** m/z (ES+) 132 (100%, $M+Na^+$); **HRMS**: found 231.0829, $M+Na^+$ requires 231.0814; **IR** ν_{max}(film)/cm^{-1} 1690 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.33-7.19 (m, 5H), 4.56 (t, *J* 7.4 Hz, 1H), 2.27 (s, 3H), 1.88 (ap q, *J* 7.7 Hz, 2H), 1.40-1.21 (m, 2H), 0.88 (t, *J* 7.4 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 194.9, 142.0, 128.5, 127.6, 127.2, 47.8, 38.3, 30.5, 20.7, 13.6.

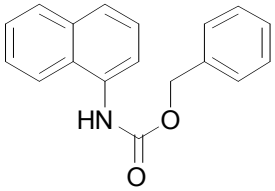
s5: Thioacetic acid S-[(*R*)-1-(3-trifluoromethylphenyl)ethyl] ester



Oxalyl chloride (0.27 cm^3, 3.1 mmol) was added to a stirred solution of DMF (0.26 cm^3, 3.4 mmol) in DCM (20 cm^3) at 0 °C. The mixture was stirred for 5 min. **s2** (0.6 g, 3.1 mmol), triethylamine (0.87 cm^3, 6.2 mmol) and ethanethioic S-acid (0.20 cm^3, 2.8 mmol) were added sequentially. The mixture was warmed to room temperature and stirred for 18 h. Water (5 cm^3) was added, the phases separated and the aqueous layer extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/diethyl ether, 40:1) and the title compound isolated as a yellow oil (0.315 g, 45%). $\boldsymbol{R_F}$ 0.33 (petrol/diethyl ether, 9:1); $\boldsymbol{[\alpha]_D^{22}}$: +125.9º (*c*. 1.0, $CHCl_3$); **MS** m/z (EI) 248 (20%, M^+); **HRMS**: found 248.0480, M^+ requires 248.0477; **IR** ν_{max} (film)/cm^{-1} 1693 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.59-7.42 (m, 4H), 4.78 (q, *J* 7.3 Hz, 1H), 2.32 (s, 3H), 1.67 (d, *J* 7.1 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 194.6, 143.9, 130.8, 129.0, 124.2, 124.1, 124.0, 123.9, 42.4, 30.4, 21.9.

s6: Naphthalen-1-ylcarbamic acid benzyl ester

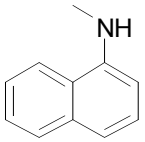
Azzena, U.; Dettori, G.; Pisano, L.; Pittalis, M. *Syn. Comm.* **2007**, *37*, 3623



Benzyl chloroformate (1.90 cm^3, 13 mmol) was added dropwise to a stirred mixture of naphthalen-1-amine (1.557 g, 11 mmol) and pyridine (1.10 cm^3, 14 mmol) at room temperature. The mixture was stirred for 20 h. The mixture was partitioned between saturated aqueous sodium bicarbonate solution and DCM and separated. The aqueous fraction was extracted with DCM (3 x 20 cm^3), the combined organic fractions dried over sodium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 9:1) and the title compound isolated as an amorphous pink solid (2.857 g, 98 %). $\boldsymbol{R_F}$: 0.31 (9:1, Petrol:EtOAc); **Mpt**: 136-138 ºC (DCM); **MS** m/z (ES+) 278 (45%, $M+H^+$), 300 (30%, $M+Na^+$); **HRMS**: found 278.1180, $M+H^+$ requires 278.1179; **IR** ν_{max}(film)/cm^{-1} 3277 (NH), 1690 (C=O); **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 7.89-7.86 (m, 3H), 7.69 (d, *J* 8.0 Hz, 1 H), 7.55-7.35 (m, 8H), 7.01 (br s, 1H), 5.27 (s, 2H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 136.1, 134.1, 132.4, 128.8, 128.7, 128.4, 128.4, 126.3, 126.0, 125.8, 125.1, 120.4, 120.4, 119.1, 67.3.

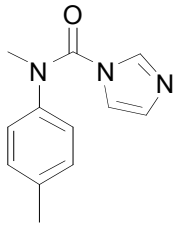
s7: N-Methylnaphthalen-1-amine

Iagarashi, T.; Shimokawa, M.; Iwasaki, M.; Nagata, K.; Fujii, M.; Sakurai, T. *Synlett* **2007**, *9*, 1436



Lithium aluminium hydride (6.8 cm^3, 2 M in THF, 14 mmol) was added dropwise at 0 °C to a solution of **s6** (2.481 g, 9 mmol) in THF (50 cm^3). The mixture was heated to reflux and stirred for 4 hours then allowed to cool to room temperature. Water (0.5 cm^3) was added dropwise followed by stirring for 10 minutes. Aqueous sodium hydroxide solution (15 % w/w) was added followed by stirring for 30 min. Water (1.5 cm^3) was added and the mixture stirred for 1 hour. The resulting suspension was filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 9:1) to afford the title compound as a brown oil (1.167 g, 82%). $\boldsymbol{R_F}$: 0.25 (9:1, Petrol:EtOAc); **MS** m/z (ES+) 158 (100%, $M+H^+$); **HRMS**: found 158.0973, $M+H^+$ requires 158.0964; **IR** ν_{max}(film)/cm^{-1} 3440 (NH); **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 7.78-7.83 (m, 2H), 7.36-7.45 (m, 3H), 7.24-7.27 (m, 1H), 6.62 (d, *J* 7.5 Hz, 1H), 4.45 (br s, 1H), 3.03 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ 144.6, 134.3, 128.7, 126.7, 125.7, 124.7, 123.5, 119.8, 117.3, 103.8, 31.1.

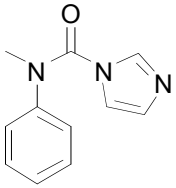
s8: N-Methyl-N-*p*-tolyl-1*H*-imidazole-1-carboxamide



General procedure A was followed using N,4-dimethylbenzeneamine (1.3 cm^3, 10 mmol), CDI (3.244 g, 20 mmol) in THF (20 cm^3) with stirring for 18 hours. The title compound was isolated as colourless prisms (1.7821 g, 83 %). $\boldsymbol{R_F}$: 0.45 (EtOAc); **Mpt**: 118-121 ºC (DCM); **MS** m/z (ES+) 216 (100%, $M+H^+$); **HRMS**: found 216.1133, $M+H^+$ requires 216.1131; **IR** ν_{max}(film)/cm^{-1} 1687 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.53 (s, 1H), 7.16 (d, *J* 8.1 Hz), 6.99 (d, *J* 8.1 Hz), 6.87 (m, 1H), 6.80, (m, 1H), 3.45 (s, 3H), 2.34 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 150.3, 140.3, 138.2, 137.7, 130.9, 128.9, 125.7, 118.5, 40.2, 21.1.

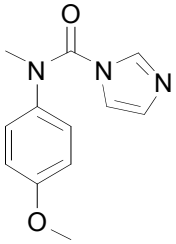
s9: Imidazole-1-carboxylic acid methylphenylamide

Batey, R. A.; Santhakumar, V.; Yoshina-Ishii, C.; Taylor, S. D. *Tetrahedron Lett.* **1998**, *39*, 6267



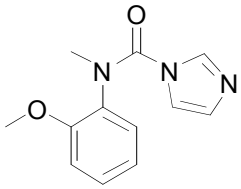
General procedure A was followed using methylphenylamine (1.09 cm^3, 10.0 mmol), CDI (3.240 g, 20.0 mmol) in THF (20 cm^3) with stirring for 20 hours. The title compound was isolated as colourless prisms (2.005 g, 99 %). $\boldsymbol{R_F}$: 0.4 (EtOAc); **Mpt**: 55-57 ºC (DCM); **MS** m/z (ES+) 202 (35%, $M+H^+$); **HRMS**: found 202.0984, $M+H^+$ requires 202.0975; **IR** ν_{max}(film)/cm^{-1} 1700 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.58 (br s, 1H), 7.42 - 7.31 (m, 3H), 7.15 - 7.12 (m, 2H), 6.86 (m, 1H), 6.82 (m, 1H), 3.50 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 150.3, 143.0, 137.7, 130.3, 129.0, 128.1, 126.0, 118.4, 40.2.

s10: N-(4-Methoxyphenyl)-N-methyl-1*H*-imidazole-1-carboxamide



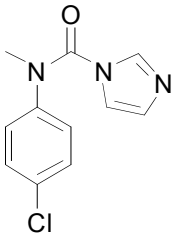
General procedure A was followed using 4-methoxy-N-methylbenzenamine (0.503 g, 3.67 mmol), CDI (1.130 g, 7.00 mmol) in THF (10 cm^3) with stirring for 6 hours. The title compound was isolated as a pink amorphous solid (0.810 g, 95 %). $\boldsymbol{R_F}$: 0.1 (1:1, Petrol:EtOAc); **Mpt**: 47-49 ºC (DCM); **MS** m/z (ES+) 232 (20%, $M+H^+$); **HRMS**: found 232.1074, $M+H^+$ requires 232.1081; **IR** ν_{max}(film)/cm^{-1} 1698 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.54 (s, 1H), 7.04 (d, *J* 9.0 Hz, 2H), 6.88 (m, 3H), 6.81 (s, 1H), 3.80 (s, 3H), 3.44 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 159.1, 150.3, 137.8, 135.5, 128.9, 127.2, 118.6, 115.4, 55.5, 40.4.

s11: N-(2-Methoxyphenyl)-N-methyl-1*H*-imidazole-1-carboxamide



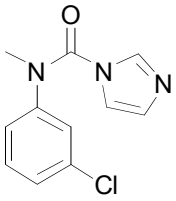
General procedure A was followed using 2-methoxy-N-methyl aniline (1.375 g, 10 mmol), CDI (3.244 g, 20 mmol) in THF (20 cm^3) with stirring for 48 h. The title compound was isolated as off-white prisms (2.180 g, 94 %). $\boldsymbol{R_F}$: 0.58 (EtOAc); **Mpt**: 60-62 ºC (DCM); **MS** m/z (ES+) 232 (100%, $M+H^+$); **HRMS**: found 232.1085, $M+H^+$ requires 232.1081; **IR** ν_{max}(film)/cm^{-1} 1702 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.59 (s, 1H), 7.29 (ddd, *J* 1.7, 7.6 and 8.3 Hz, 1H), 7.17 (dd, *J* 1.6 and 7.7 Hz, 1H), 6.97 (ddd, *J* 1.2, 7.6 and 7.6 Hz, 1H), 6.90, (m, 2H), 6.78 (s, 1H), 3.71 (s, 3H), 3.37 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 154.2, 151.3, 137.4, 131.6, 129.8, 128.6, 127.8, 121.7, 118.1, 112.4, 55.6, 39.1.

s12: N-(4-Chlorophenyl)-N-methyl-1*H*-imidazole-1-carboxamide



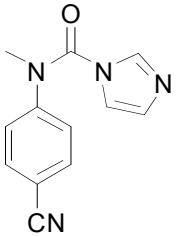
General procedure A was followed using 4-chloro-N-methylbenzenamine (1.20 cm^3, 10 mmol) and CDI (3.246 g, 20 mmol) in THF (20 cm^3) with stirring for 23 h. The title compound was isolated as an amorphous white solid (2.3104 g, 99 %). $\boldsymbol{R_F}$: 0.37 (EtOAc); **Mpt**: 110-112 ºC (DCM); **MS** m/z (ES+) 236 (100%, $M+H^+$); **HRMS**: found 236.0596, $M+H^+$ requires 236.0585; **IR** ν_{max}(film)/cm^{-1} 1700 (C=O); **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 7.59 (s, 1H), 7.35 (m, 2H), 7.05 (m, 2H), 6.86 (m, 2H), 3.47 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 150.1, 141.5, 137.6, 133.9, 130.5, 129.3, 127.1, 118.3, 40.1.

s13: Imidazole-1-carboxylic acid (3-chlorophenyl)methylamide



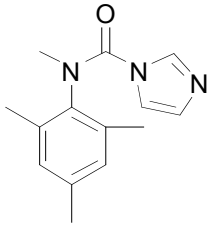
General procedure A was followed using (3-chlorophenyl)methylamine (1.73 cm^3, 14.12 mmol), CDI (4.580 g, 28.24 mmol) in THF (30 cm^3) with stirring for 2 days. The title compound was isolated as colourless prisms (3.30 g, 99 %). $\boldsymbol{R_F}$: 0.35 (EtOAc); **Mpt**: 73-75 ºC (DCM); **MS** m/z (ES+) 236 (40%, $M+H^+$); **HRMS**: found 236.0595, $M+H^+$ requires 236.0585; **IR** ν_{max}(film)/cm^{-1} 1700 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.63 (ap t, J 1.0 Hz, 1H), 7.32 - 7.30 (m, 2H), 7.19 (m, 1H), 7.00 - 6.97 (m, 1H), 6.89 - 6.88 (m, 1H), 6.86 (m, 1H), 3.42 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 150.1, 144.2, 137.6, 135.8, 131.2, 129.4, 128.3, 126.1, 124.1, 118.3, 40.1.

s14: Imidazole-1-carboxylic acid (4-cyanophenyl)methylamide



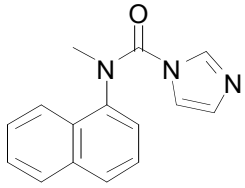
General procedure A was followed using 4-methylaminobenzonitrile (1.518 g, 11.50 mmol), CDI (3.680 g, 22.72 mmol) in THF (20 cm^3) with stirring for 10 days. The title compound was isolated as colourless prisms (2.43 g, 95 %). $\boldsymbol{R_F}$: 0.35 (EtOAc); **Mpt**: 136-138 ºC (DCM); **MS** m/z (ES+) 249 (35%, $M+Na^+$); **HRMS**: found 249.0747, $M+Na^+$ requires 249.0747; **IR** ν_{max}(film)/cm^{-1} 1700 (C=O), 2229 (nitrile); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.68 (d, J 8.8 Hz, 2H), 7.64 (br s, 1H), 7.22 (d, J 8.8 Hz, 2H), 6.89 (m, 1H), 6.86 (m, 1H), 3.54 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 147.0, 137.4, 134.1, 129.9, 126.0, 118.1, 117.6, 111.4, 39.7.

s15: Imidazole-1-carboxylic acid methyl(2,4,6-trimethylphenyl)amide



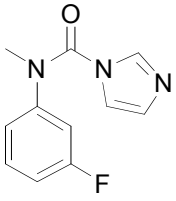
General procedure A was followed using methyl(2,4,6-trimethylphenyl)amine (0.92 cm^3, 5.77 mmol), CDI (1.957 g, 12.10 mmol) in THF (20 cm^3) with stirring for 4 days. The title compound was isolated as a white amorphous solid (1.00 g, 71 %). $\boldsymbol{R_F}$: 0.53 (EtOAc); **Mpt**: 92-94 ºC (DCM); **MS** m/z (ES+) 266 (70%, $M+Na^+$); **HRMS**: found 266.1250, $M+Na^+$ requires 266.1264; **IR** ν_{max}(film)/cm^{-1} 1698 (C=O); **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 7.44 (br s, 1H), 6.94 (s, 2H), 6.85 (s, 1H), 6.81 (s, 1H), 3.33 (s, 3H), 2.30 (s, 3H), 2.15 (s, 6H);**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 150.3, 139.2, 137.5, 137.4, 135.1, 130.3, 129.0, 118.3, 38.0, 21.0, 17.5.

s16: Imidazole-1-carboxylic acid methylnaphthalen-1-ylamide



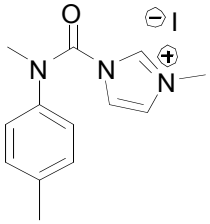
General procedure A was followed using **s7** (0.990 g, 6.37 mmol), CDI (2.064 g, 12.74 mmol) in THF (20 cm^3) with stirring for 2 days. The title compound was isolated as colourless prisms (1.21 g, 75 %). $\boldsymbol{R_F}$: 0.52 (EtOAc); **Mpt**: 107-109 ºC (DCM); **MS** m/z (ES+) 274 (100%, $M+Na^+$), 252 (15%, $M+H^+$); **HRMS**: found 252.1138, $M+H^+$ requires 252.1131; **IR** ν_{max}(film)/cm^{-1} 1682 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.97-7.89 (m, 3H), 7.67-7.60 (m, 2H), 7.52 (br s, 1H), 7.43 (t, *J* 7.8 Hz, 1H), 7.28-7.26 (m, 1H), 6.76 (br s, 1H), 6.69 (br s, 1H), 3.56 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 151.1, 138.9, 137.3, 134.8, 129.5, 129.2, 129.2, 128.7, 128.3, 127.3, 126.0, 125.1, 121.6, 118.2, 40.3.

s17: Imidazole-1-carboxylic acid (3-fluorophenyl)methylamide



General procedure A was followed using (3-fluorophenyl)methylamine (0.63 cm^3, 5.60 mmol), CDI (1.810 g, 11.20 mmol) in THF (10 cm^3) with stirring for 4 days. The title compound was isolated as white cubes (1.22 g, 99 %). $\boldsymbol{R_F}$: 0.39 (EtOAc); **Mpt**: 56-58 ºC (DCM); **MS** m/z (ES+) 220 (30%, $M+H^+$); **HRMS**: found 220.0887, $M+H^+$ requires 220.0881; **IR** ν_{max}(film)/cm^{-1} 1703 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.62 (s, 1H), 7.32 - 7.38 (m, 1H), 7.01 - 7.07 (m, 1H), 6.86 - 6.91 (m, 4H), 3.49 (s, 3H);**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 164.5, 162.0, 150.1, 144.4, 144.3, 137.6, 131.6, 131.5, 129.4, 121.7, 118.3, 115.3, 115.1, 113.5, 113.3, 40.1.

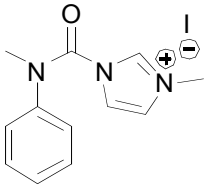
s18: 3-Methyl-1-(methyl(*p*-tolyl)carbamoyl)-1*H*-imidazol-3-ium iodide



General procedure B was followed using **s8** (2.137 g, 10 mmol) and iodomethane (2.49 cm^3, 40 mmol) in acetonitrile (20 cm^3) with stirring for 4.5 hours. The title compound was isolated as a yellow amorphous solid (3.343 g, 94 %). $\boldsymbol{R_F}$: 0.04 (EtOAc); **Mpt**: 144-146 ºC (MeCN); **MS** m/z (ES+) 230 (100%, $M-I^-$); **HRMS**: found 230.1295, $M-I^-$ requires 230.1288; **IR** ν_{max}(film)/cm^{-1} 1731 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.73 (br s, 1H), 7.51 (br s, 1H), 7.31 (d, *J* 8.3 Hz), 7.23 (d, *J* 8.3 Hz), 7.00 (br s, 1H), 4.10 (s, 3H), 3.50 (s, 3H), 2.34 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 145.9, 139.7, 138.4, 137.9, 131.5, 126.4, 123.5, 121.0, 41.2, 38.1, 21.2.

s19: 1-Methyl -3-(methylphenylcarbamoyl)-3*H*-imidazol-1-ium iodide

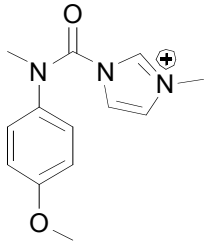
Batey, R. A.; Santhakumar, V.; Yoshina-Ishii, C.; Taylor, S. D. *Tetrahedron Lett.* **1998**, *39*, 6267



General procedure B was followed using **s9** (2.012 g, 10.00 mmol) and iodomethane (2.49 cm^3, 40.00 mmol) in acetonitrile (20 cm^3) with stirring for 4 hours. The title compound was isolated as yellow prisms (3.204 g, 93 %). $\boldsymbol{R_F}$: 0.03 (EtOAc); **Mpt**: 104-106 ºC (DCM); **MS** m/z (ES+) 216 (100%, $M-I^-$); **HRMS**: found 216.1121, $M-I^-$

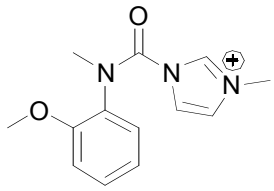
requires 216.1131; **IR** ν_{max}(film)/cm^{-1} 1729 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.77 (br s, 1H), 7.50-7.38 (m, 6H), 7.07 (br s, 1H), 4.10 (s, 3H), 3.56 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 145.8, 140.5, 138.4, 130.9, 129.4, 126.7, 123.3, 121.0, 41.1, 38.1.

s20: 1-((4-Methoxyphenyl)(methyl)carbamoyl)-3-methyl-1*H*-imidazol-3-ium iodide



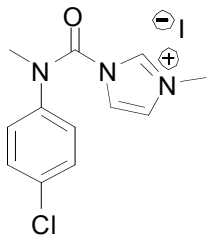
General procedure B was followed using **s10** (0.520 g, 2.20 mmol) and iodomethane (0.54 cm^3, 8.70 mmol) in acetonitrile (10 cm^3) with stirring for 2 hours. The title compound was isolated as a dull green amorphous solid (0.7678 g, 95 %). $\boldsymbol{R_F}$: 0.03 (EtOAc); **Mpt**: 139-141 ºC (MeCN); **MS** m/z (ES+) 246 (100%, M-I$^-$); **HRMS**: found 246.1240, M-I$^-$ requires 246.1237; **IR** ν_{max}(film)/cm^{-1} 1731 (C=O); **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 9.69 (br s, 1H), 7.39 (d, *J* 8.5 Hz), 7.35 (br s, 1H), 7.02 (br s, 1H), 6.95 (d, *J* 8.5 Hz), 4.10 (s, 3H), 3.82 (s, 3H), 3.51 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 159.9, 145.9, 138.4, 133.0, 128.0, 123.3, 121.1, 116.0, 55.7, 41.3, 38.1.

s21: 1-((2-Methoxyphenyl)(methyl)carbamoyl)-3-methyl-1*H*-imidazol-3-ium iodide



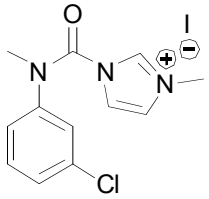
General procedure B was followed using **s11** (1.161 g, 5 mmol) and iodomethane (1.25 cm^3, 20 mmol) in acetonitrile (20 cm^3) with stirring for 16 hours. The title compound was isolated as an orange amorphous solid (1.860 g, 99 %). $\boldsymbol{R_F}$: 0.03 (EtOAc); **Mpt**: 158-160 ºC (MeCN); **MS** m/z (ES+) 246 (100%, M-I$^-$); **HRMS**: found 246.1232, M-I$^-$ requires 246.1237; **IR** ν_{max}(film)/cm^{-1} 1739 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.71 (br s, 1H), 7.64 (br s, 1H), 7.59 (dd, *J* 1.6, 7.8 Hz, 1H), 7.34 (dt, *J* 1.6, 8.3 Hz, 1H), 7.16 (br s, 1H), 7.05 (dt, *J* 1.1, 7.7 Hz, 1H), 6.91 (dd, *J* 0.9, 8.3 Hz, 1H), 4.11 (s, 3H), 3.81 (s, 3H), 3.39 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 153.3, 147.1, 137.3, 131.1, 129.1, 128.5, 123.7, 122.5, 120.6, 112.6, 56.5, 40.0, 38.1.

s22: 1-((4-Chlorophenyl)(methyl)carbamoyl)-3-methyl-1*H*-imidazol-3-ium iodide
Ebdrup, S.; Refsgaard, H. H. F.; Fledelius, C.; Jocobsen, P. *J. Med. Chem.* **2007**, *50*, 5449



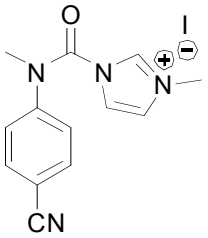
General procedure B was followed using **s12** (1.184 g, 5 mmol) and iodomethane (1.25 cm^3, 20 mmol) in acetonitrile (20 cm^3) with stirring for 8 hours. The title compound was isolated as an orange amorphous solid (1.744 g, 92 %). $\boldsymbol{R_F}$: 0.03 (EtOAc); **Mpt**: 120-122 ºC (MeCN); **MS** m/z (ES+) 250 (100%, M-I$^-$); **HRMS**: found 250.0736, M-I$^-$ requires 250.0742; **IR** ν_{max}(film)/cm^{-1} 1731 (C=O); **^{1}H-NMR** (CD_3OD, 400 MHz) δ 9.29 (br s, 1H), 7.48-7.45 (m, 3H), 7.38 (d, *J* 8.7 Hz), 7.31 (br s, 1H), 3.91 (s, 3H), 3.53 (s, 3H); **^{13}C-NMR** (CD_3OD, 100 MHz) δ 147.6, 141.3, 135.7, 131.6, 129.3, 124.6, 122.8, 41.0, 37.3.

s23: 3-[(3-Chlorophenyl)methylcarbamoyl]-1-methyl-3*H*-imidazol-1-ium iodide



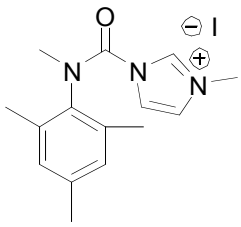
General procedure B was followed using **s13** (3.009 g, 12.74 mmol) and iodomethane (3.17 cm^3, 50.95 mmol) in acetonitrile (60 cm^3) with stirring for 4 hours. The title compound was isolated as yellow prisms (4.786 g, 99 %). $\boldsymbol{R_F}$: 0.03 (EtOAc); **Mpt**: 112-114 ºC (DCM); **MS** m/z (ES+) 250 (100%, M-I$^-$); **HRMS**: found 250.0757, M-I$^-$ requires 250.0742; **IR** ν_{max}(film)/cm^{-1} 1731 (C=O); **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 9.99 (br s, 1H), 7.59 - 7.36 (m, 5H), 7.18 (br s, 1H), 4.14 (s, 3H), 3.57 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75.5 MHz) δ 141.7, 138.7, 135.9, 132.1, 129.7, 126.3, 125.8, 123.4, 121.0, 41.3, 38.1.

s24: 3-[(4-Cyanophenyl)methylcarbamoyl]-1-methyl-3*H*-imidazol-1-ium iodide



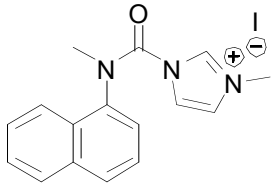
General procedure B was followed using **s14** (2.209 g, 9.73 mmol) and iodomethane (2.43 cm^3, 38.94 mmol) in acetonitrile (40 cm^3) with stirring for 4 hours. The title compound was isolated as yellow prisms (3.532 g, 98 %). $\boldsymbol{R_F}$: 0.03 (EtOAc); **Mpt**: 178-180 ºC (DCM); **MS** m/z (ES+) 241 (100%, M-I^-); **HRMS**: found 241.1077, M-I^- requires 241.1084; **IR** ν_{max}(film)/cm^{-1} 1729 (C=O), 2229 (nitrile); **^{1}H-NMR** (CD_3OD, 400 MHz) δ 9.36 (br s, 1H, exchanges with MeOD), 7.83 (d, *J* 8.4 Hz, 2H), 7.60 (d, *J* 8.4 Hz, 2H), 7.50 (br s, 1H), 7.38 (br s, 1H), 3.94 (s, 3H), 3.59 (s, 3H);**^{13}C-NMR** (CD_3OD, 100 MHz) δ 147.6, 146.5, 139.9, 135.4, 128.4, 124.8, 122.8, 118.7, 113.4, 40.7, 37.3.

s25: 1-Methyl-3-[methyl(2,4,6-trimethylphenyl)carbamoyl]-3*H*-imidazol-1-ium iodide



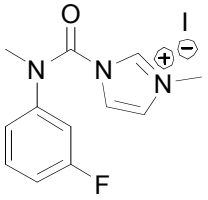
General procedure B was followed using **s15** (0.989 g, 4.10 mmol) and iodomethane (1.02 cm^3, 16.45 mmol) in acetonitrile (20 cm^3) with stirring for 4 hours. The title compound was isolated as yellow prisms (0.512 g, 96 %). $\boldsymbol{R_F}$: 0.05 (EtOAc); **Mpt**: 160 ºC (decomposition); **MS** m/z (ES+) 258 (100%, M-I^-); **HRMS**: found 258.1598, M-I^- requires 258.1601; **IR** ν_{max}(film)/cm^{-1} 1724 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.38 (br s, 1H), 7.78 (m, 1H), 7.00 (s, 2H), 6.61 (m, 1H), 4.18 (s, 3H), 3.38 (s, 3H), 2.32 (s, 3H), 2.24 (s, 6H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 145.9, 140.7, 138.3, 135.2, 134.9, 131.0, 124.8, 120.2, 39.0, 38.7, 21.1, 18.1).

s26: 1-Methyl-3-(methylnaphthalen-1-ylcarbamoyl)-3*H*-imidazol-1-ium iodide



General procedure B was followed using **s16** (1.005 g, 3.98 mmol) and iodomethane (0.99 cm^3, 15.94 mmol) in acetonitrile (20 cm^3) with stirring for 4 hours. The title compound was isolated as yellow prisms (1.498 g, 96 %). $\boldsymbol{R_F}$: 0.02 (EtOAc); **Mpt**: 83-85 ºC (DCM); **MS** m/z (ES+) 266 (100%, M-I^-); **HRMS**: found found 266.1288, M-I^- requires 266.1288; **IR** ν_{max}(film)/cm^{-1} 1721 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.86 (br s, 1H), 7.98-7.87 (m, 4H), 7.73-7.69 (m, 1H), 7.65-7.59 (m, 2H), 7.19 (br s, 1H), 6.73 (br s, 1H), 4.04 (s, 3H), 3.64 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 146.9, 138.4, 136.2, 134.6, 130.5, 129.4, 129.1, 128.4, 127.6, 127.0, 126.7, 123.6, 120.9, 120.2, 41.0, 38.0.

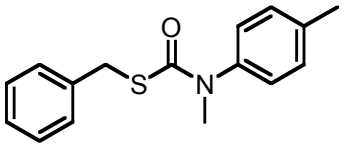
s27: 3-[(3-Fluorophenyl)methylcarbamoyl]-1-methyl-3*H*-imidazol-1-ium iodide



General procedure B was followed using **s17** (1.098 g, 5.00 mmol) and iodomethane (1.25 cm^3, 20.00 mmol) in acetonitrile (20 cm^3) with stirring for 4 hours. The title compound was isolated as yellow prisms (1.598 g, 88 %). $\boldsymbol{R_F}$: 0.03 (EtOAc); **Mpt**: 115-117 ºC (DCM); **MS** m/z (ES+) 234 (100%, M-I^-); **HRMS**: found 234.1035, M-I^- requires 234.1043; **IR** ν_{max}(film)/cm^{-1} 1731 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.92 (br s, 1H), 7.52 (m, 1H), 7.45 (td, *J* 8.0, 6.4 Hz, 1H), 7.37 - 7.35 (m, 1H), 7.31 (dt, *J* 8.8, 2.0 Hz, 1H), 7.23 (br s, 1H), 7.12 - 7.08 (m, 1H), 4.07 (s, 3H), 3.50 (s, 3H);**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 164.3, 161.8, 145.8, 142.0, 141.9, 141.9, 138.5, 132.3, 132.2, 123.6, 123.0, 121.2, 116.7, 116.5, 114.3, 114.0, 41.3, 38.1.

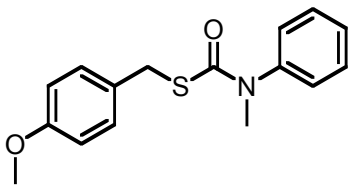
EXPERIMENTAL DATA FOR COMPOUNDS REPORTED

5a: Methylphenylthiocarbamic acid S-(4-methylbenzyl) ester



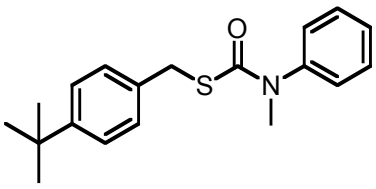
General procedure D was followed using benzyl thiol (0.24 cm^3, 2.0 mmol), **s18** (0.81 g, 2.2 mmol) and triethylamine (0.34 cm^3, 2.4 mmol) in DCM (10 cm^3) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as a colourless oil (0.523 g, 95 %). $\boldsymbol{R_F}$: 0.31 (8:1, Petrol:EtOAc); **MS** m/z (ES+) 294 (100%, $M+Na^+$); **HRMS**: found 294.0928, $M+Na^+$ requires 294.0923; **IR** ν_{max}(film)/cm^{-1} 1656 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.31-7.14 (m, 9H), 4.09 (s, 2H), 3.32 (s, 3H), 2.37 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.6, 138.1, 130.2, 129.0, 128.5, 128.2, 128.1, 127.0, 38.4, 35.5, 21.2.

5b: Methylphenylthiocarbamic acid 4-methoxybenzyl ester



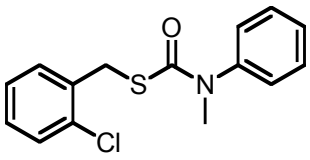
General procedure D was followed using (4-methoxyphenyl)methanethiol (0.61 cm^3, 4.4 mmol), **s19** (1.507 g, 4.4 mmol) and triethylamine (0.73 cm^3, 5.3 mmol) in DCM (20 cm^3) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (1.192 g, 95 %). $\boldsymbol{R_F}$: 0.11 (8:1, Petrol:EtOAc); **Mpt**: 74-76 ºC (DCM); **MS** m/z (ES+) 310 (100%, $M+Na^+$); **HRMS**: found 310.0881, $M+Na^+$ requires 310.0872; **IR** ν_{max}(film)/cm^{-1} 1650 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.41-7.32 (m, 3H), 7.27-7.25 (m, 2H), 7.22 (d, *J* 8.0 Hz, 2H), 6.79 (d, *J* 8.0 Hz, 2H), 4.05 (s, 2H), 3.76 (s, 3H), 3.33 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.7, 158.7, 142.0, 130.1, 130.0, 129.5, 128.4, 128.3, 113.9, 55.3, 38.3, 35.0.

5c: Methylphenylthiocarbamic acid 4-*tert*-butylbenzyl ester



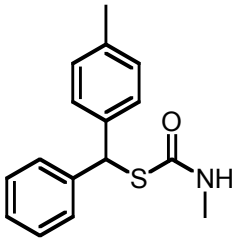
General procedure D was followed using (4-*tert*-butylphenyl)methanethiol (0.52 cm^3, 2.8 mmol), **s19** (1.078 g, 3.1 mmol) and triethylamine (0.58 cm^3, 4.1 mmol) in DCM (20 cm^3) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 15:1) to afford the title compound as an amorphous colourless solid (0.845 g, 97 %). $\boldsymbol{R_F}$: 0.28 (8:1, Petrol:EtOAc); **Mpt**: 67-69 ºC (DCM); **MS** m/z (ES+) 336 (100%, $M+Na^+$); **HRMS**: found 336.1397, $M+Na^+$ requires 336.1393; **IR** ν_{max}(film)/cm^{-1} 1654 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.42-7.22 (m, 9H), 4.09 (s, 2H), 3.35 (s, 3H), 1.29 (s, 9H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.7, 150.0, 134.8, 129.5, 128.7, 128.4, 128.4, 128.3, 125.4, 38.4, 35.2, 34.5, 31.3.

5d: Methylphenylthiocarbamic acid 2-chlorobenzyl ester



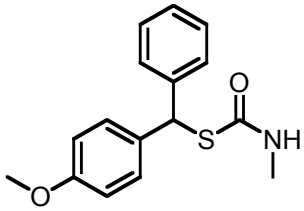
General procedure D was followed using (2-chlorophenyl)methanethiol (0.41 cm^3, 3.2 mmol), **s19** (1.197 g, 3.5 mmol) and triethylamine (0.66 cm^3, 4.7 mmol) in DCM (20 cm^3) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 10:1) to afford the title compound as an amorphous colourless solid (0.787 g, 86 %). $\boldsymbol{R_F}$: 0.24 (8:1, Petrol:EtOAc); **Mpt**: 67-78 ºC (DCM); **MS** m/z (ES+) 314 (100%, $M+Na^+$), 292 (20%, $M+H^+$); **HRMS**: found 292.0547, $M+H^+$ requires 292.0557; **IR** ν_{max}(film)/cm^{-1} 1651 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.50-7.47 (m, 1H), 7.41-7.25 (m, 6H), 7.20-7.13 (m, 2H), 4.22 (s, 2H), 3.33 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.4, 141.8, 136.0, 134.2, 131.3, 129.5, 129.4, 128.6, 128.3, 126.9, 38.5, 33.3.

6a: Methylthiocarbamic acid phenyl-*p*-tolylmethyl ester



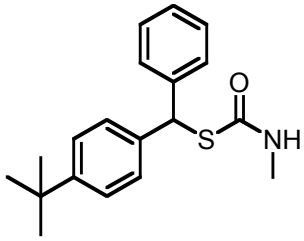
General procedure F was followed using **5a** (0.045 g, 0.17 mmol), diisopropylamine (0.08 cm^3, 0.55 mmol), *n*-butyllithium (0.29 cm^3, 1.6 M, 0.46 mmol) and propionic acid (0.04 cm^3, 0.50 mmol) with stirring for 2 hours. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous colourless solid (0.032 g, 73 %). $\boldsymbol{R_F}$: 0.09 (8:1, Petrol:EtOAc); **Mpt**: 113-115 ºC (DCM); **MS** m/z (ES+) 294 (100%, $M+Na^+$); **HRMS**: found 294.0924, $M+Na^+$ requires 294.0923; **IR** ν_{max}(film)/cm^{-1} 1648 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.39 (d, *J* 8.0 Hz, 2H), 7.32-7.21 (m, 5H), 7.12 (d, *J* 8.0 Hz, 2H), 5.94 (s, 1H), 5.24 (br s, 1H), 2.85 (d, *J* 4.0 Hz, 3H), 2.32 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 166.6, 141.6, 138.4, 136.9, 129.2, 128.5, 128.3, 128.2, 127.1, 52.8, 28.0, 21.1.

6b: Methylthiocarbamic acid (4-methoxyphenyl)phenylmethyl ester



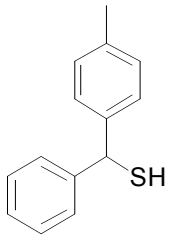
General procedure F was followed using **5b** (0.057 g, 0.18 mmol), diisopropylamine (0.07 cm^3, 0.52 mmol), *n*-butyllithium (0.29 cm^3, 1.5 M, 0.43 mmol) and propionic acid (0.04 cm^3, 0.50 mmol) with stirring for 2 hours. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous colourless solid (0.055 g, 96 %). $\boldsymbol{R_F}$: 0.06 (8:1, Petrol:EtOAc); **Mpt**: 84-86 ºC (DCM); **MS** m/z (ES+) 310 (100%, $M+Na^+$); **HRMS**: found 310.0870, $M+Na^+$ requires 310.0872; **IR** ν_{max}(film)/cm^{-1} 1644 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.40-7.38 (m, 2H), 7.33-7.21 (m, 5H), 6.84 (d, *J* 8.0 Hz, 2H), 5.94 (s, 1H), 5.29 (br s, 1H), 3.79 (s, 3H), 2.85 (d, *J* 4.0 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 166.6, 158.6, 141.7, 133.5, 129.5, 128.5, 128.3, 127.1, 113.9, 55.3, 52.5, 28.0.

6c: Methylthiocarbamic acid (4-*tert*-butylphenyl)phenylmethyl ester



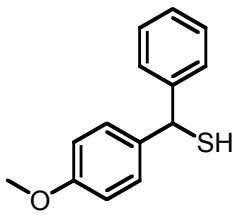
General procedure F was followed using **5c** (0.050 g, 0.16 mmol), diisopropylamine (0.07 cm^3, 0.48 mmol), *n*-butyllithium (0.27 cm^3, 1.5 M, 0.40 mmol) and propionic acid (0.04 cm^3, 0.50 mmol) with stirring for 2 hours. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as a colourless oil (0.042 g, 83 %). $\boldsymbol{R_F}$: 0.09 (8:1, Petrol:EtOAc); **MS** m/z (ES+) 336 (100%, $M+Na^+$); **HRMS**: found 336.1380, $M+Na^+$ requires 336.1393; **IR** ν_{max}(film)/cm^{-1} 1653 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.42 (d, *J* 7.6 Hz, 2H), 7.33-7.21 (m, 7H), 5.96 (s, 1H), 5.32 (br s, 1H), 2.83 (d, *J* 4.8 Hz, 3H), 1.30 (s, 9H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 165.6, 148.9, 140.7, 137.2, 127.4, 127.3, 126.9, 126.0, 124.4, 51.6, 33.4, 30.3, 26.9.

7a: Phenyl-*p*-tolylmethanethiol



General procedure I was followed using sodium ethoxide solution (0.04 cm^3, 0.10 mmol) and **6a** (0.015 g, 0.06 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.007 g, 57 %). $\boldsymbol{R_F}$: 0.55 (8:1, Petrol:EtOAc); **MS** m/z (ES-) 213 (55%, M-H^+), 181 (50%, M-SH^-); **HRMS**: found 214.0816, M requires 214.0811; **IR** ν_{max}(film)/cm^{-1} 2560 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.42 (d, *J* 7.6 Hz, 2H), 7.34-7.22 (m, 5H), 7.14 (d, *J* 8.0 Hz, 2H), 5.44 (d, *J* 4.8 Hz, 1H), 2.34 (s, 3H), 2.27 (d, *J* 5.0 Hz, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 143.6, 140.5, 136.9, 129.2, 128.5, 127.8, 127.1, 47.5, 21.0.

7b: (4-Methoxyphenyl)phenylmethanethiol

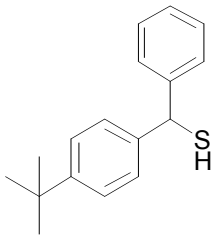


General procedure I was followed using sodium ethoxide solution (0.09 cm^3, 0.23 mmol) and **6b** (0.033 g, 0.12 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.031 g, 99 %).

The title compound was also isolated from the following procedure:

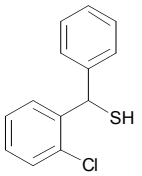
n-Butyllithium (0.29 cm^3, 1.5 M in hexanes, 0.44 mmol) was added to a solution of diisopropylamine (0.07 cm^3, 0.52 mmol) in THF (1 cm^3) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannular to a cooled (-78 °C) solution of **5b** (0.055 g, 0.19 mmol) in THF (1 cm^3) and DMPU (0.5 cm^3). The mixture was allowed to stir for 2 hours. Methanol (1 cm^3) was added and the mixture allowed to warm to room temperature. Water (10 cm^3) and diethyl ether (10 cm^3) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm^3) and the combined organic fractions dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was then purified by flash column chromatography (petrol/EtOAc, 15:1) to afford the title compound as a colourless oil (0.027 g, 62 %). $\boldsymbol{R_F}$: 0.40 (8:1, Petrol:EtOAc); **MS** m/z (EI) 229 (20%, M-H^+); **HRMS**: found 229.0685, M-H^+ requires 229.0682; **IR** ν_{max}(film)/cm^{-1} 2559 (w, S-H); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.42 (d, *J* 4.0 Hz, 2H), 7.35-7.32 (m, 4H), 7.26-7.23 (m, 1H), 6.86 (d, *J* 4.0 Hz, 2H), 5.44 (d, *J* 4.0 Hz, 1H), 3.80 (s, 3H), 2.27 (d, *J* 4.0 Hz, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 157.6, 142.7, 134.5, 127.9, 127.5, 126.7, 126.1, 112.8, 54.3, 46.2.

7c: (4-*tert*-Butylphenyl)phenylmethanethiol



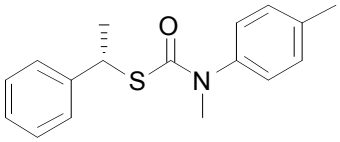
General procedure I was followed using sodium ethoxide solution (0.07 cm^3, 0.18 mmol) and **6c** (0.028 g, 0.09 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.018 g, 78 %). $\boldsymbol{R_F}$: 0.54 (8:1, Petrol:EtOAc); **MS** m/z (EI) 223 (100%, M-SH^-); **HRMS**: found 223.1472, M-SH^- requires 223.1481; **IR** ν_{max}(film)/cm^{-1} 2558 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.37 (d, *J* 7.3 Hz, 2H), 7.32-7.11 (m, 7H), 5.37 (d, *J* 5.0 Hz, 1H), 2.22 (d, *J* 5.0 Hz, 1H), 1.24 (s, 9H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 149.0, 142.5, 139.2, 127.5, 126.8, 126.3, 126.1, 124.4, 46.4, 33.4, 30.3.

7d: (2-Chlorophenyl)phenylmethanethiol



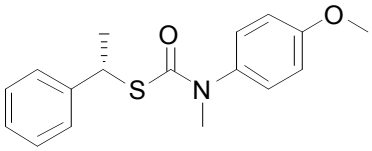
n-Butyllithium (0.17 cm^3, 0.43 mmol, 2.5 M in hexanes) was added to a solution of diisopropylamine (0.07 cm^3, 0.51 mmol) in THF (1 cm^3) at 0 °C. This was stirred for 15 minutes and then cooled to -60 °C. This solution was added by cannular to a cooled (-60 °C) solution of **5d** (0.053 g, 0.17 mmol) in THF (1 cm^3) and DMPU (0.5 cm^3). The mixture was allowed to stir for 15 hours. Propionic acid (0.04 cm^3, 0.51 mmol) was added and the mixture allowed to warm to room temperature. Water (10 cm^3) and diethyl ether (10 cm^3) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm^3) and the combined organic fractions dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was then purified by flash column chromatography (petrol) to afford the title compound as a colourless oil (0.017 g, 41 %). $\boldsymbol{R_F}$: 0.57 (8:1, Petrol:EtOAc); **MS** m/z (EI) 201 (75%, M-SH^-); **HRMS**: found 201.0460, M-SH^- requires 201.0466; **IR** ν_{max}(film)/cm^{-1} 2559 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.64-7.61 (dd, *J* 7.8 1.5 Hz, 1H), 7.44-7.42 (d, *J* 7.6 Hz, 2H), 7.38-7.18 (m, 6H), 5.92 (d, *J* 5.6 Hz, 1H), 2.35 (d, *J* 5.6 Hz, 1H);**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 141.9, 141.0, 132.9, 129.7, 129.7, 128.6, 128.4, 128.0, 127.3, 127.2, 43.8.

8a: Methyl-*p*-tolylthiocarbamic acid (*S*)-1-phenylethyl ester



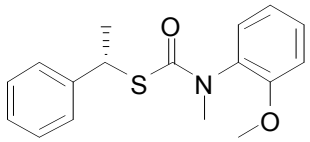
General procedure C was followed using **s3** (0.302 g, 1.67 mmol) and lithium aluminium hydride (1.67 cm^3, 1.67 mmol, 1 M in THF) in diethyl ether (7 cm^3) followed by **s18** (0.585 g, 1.64 mmol) and triethylamine (0.23 cm^3, 1.64 mmol) in DCM (10 cm^3) with stirring for 24 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.376 g, 79 %). $\boldsymbol{R_F}$: 0.30 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: -8.4º (*c*. 1.1, $CHCl_3$); **Mpt**: 76-78 ºC (DCM); **MS** m/z (ES+) 286 (20%, $M+H^+$), 308 (100%, $M+Na^+$); **HRMS**: found 286.1268, $M+Na^+$ requires 286.1260; **IR** ν_{max}(film)/cm^{-1} 1656 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.33-7.11 (m, 9H), 4.67 (q, *J* 7.1 Hz, 1H), 3.28 (s, 3H), 2.36 (s, 3H), 1.63 (d, *J* 7.1 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.3, 143.4, 139.3, 130.1, 128.4, 128.1, 127.4, 127.0, 44.9, 38.3, 22.9, 21.2; **HPLC**: er 98:2, General conditions I: t_r 5.2 (maj), 6.0 (min).

8b: (4-Methoxyphenyl)methylthiocarbamic acid S-((*S*)-1-phenylethyl) ester



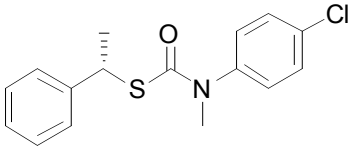
General procedure C was followed using **s3** (0.246 g, 1.34 mmol) and lithium aluminium hydride (1.34 cm^3, 1.34 mmol, 1 M in THF) in diethyl ether (9 cm^3) followed by **s20** (0.483 g, 1.3 mmol) and triethylamine (0.18 cm^3, 1.3 mmol) in DCM (10 cm^3) with stirring for 26 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 19:1) and the title compound isolated as a colourless oil (0.250 g, 62 %). $\boldsymbol{R_F}$: 0.35 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{21}}$: 4.9º (*c*. 1.1, $CHCl_3$); **MS** m/z (ES+) 302 (5%, $M+H^+$); **HRMS**: found 302.1201, $M+H^+$ requires 302.1209; **IR** ν_{max}(film)/cm^{-1} 1651 (C=O); **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 7.34-7.18 (m, 5H), 7.15 (d, *J* 8.8 Hz, 2H), 6.88 (d, *J* 8.8 Hz, 2H), 4.66 (q, *J* 7.1 Hz, 1H), 3.81 (s, 3H), 3.27 (s, 3H), 1.62 (d, *J* 7.1 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.6, 143.4, 129.8, 129.7, 128.4, 127.4, 127.0, 114.6, 55.4, 44.9, 38.4, 23.0; **HPLC**: er 96:4, General conditions I: t_r 7.7 (maj), 8.8 (min).

8c: (2-Methoxyphenyl)methylthiocarbamic acid S-((*S*)-1-phenylethyl) ester



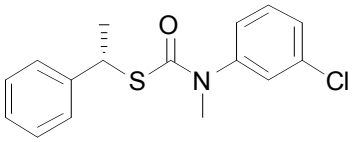
General procedure C was followed using **s3** (0.270 g, 1.50 mmol) and lithium aluminium hydride (1.50 cm^3, 1.50 mmol, 1 M in THF) in diethyl ether (7 cm^3) followed by **s21** (0.560 g, 1.50 mmol) and triethylamine (0.21 cm^3, 1.50 mmol) in DCM (10 cm^3) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.410 g, 91 %). $\boldsymbol{R_F}$: 0.17 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: -18º (*c*. 1.6, $CHCl_3$); **Mpt**: 97-99 ºC (petrol); **MS** m/z (ES+) 324 (100%, $M+Na^+$); **HRMS**: found 324.1022, $M+Na^+$ requires 324.1029; **IR** ν_{max}(film)/cm^{-1} 1656 (C=O); mixture of 2 rotamers **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.36-7.15 (m, 14H), 6.99-6.90 (m, 4H), 4.68 (q, *J* 7.0 Hz, 1H), 4.67 (q, *J* 7.0 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 3H), 3.22 (s, 6H), 1.63 (d, *J* 7.1 Hz, 3H), 1.61 (d, *J* 7.1 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 169.0, 168.9, 156.2, 156.1, 143.6, 143.5, 130.8, 130.7, 130.1, 130.0, 128.4, 128.3, 127.4, 126.9, 126.8, 120.8, 120.7, 112.2, 112.2, 55.7, 55.5, 44.6, 44.6, 36.8, 23.0, 22.9; **HPLC**: er 97:3, General conditions I: t_r 9.1 (min), 10.9 (maj).

8d: (4-Chlorophenyl)methylthiocarbamic acid S-((*S*)-1-phenylethyl) ester



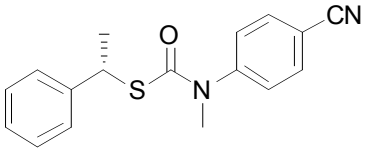
General procedure C was followed using **s3** (0.482 g, 2.68 mmol) and lithium aluminium hydride (2.68 cm^3, 2.68 mmol, 1 M in THF) in diethyl ether (10 cm^3) followed by **s22** (1.015 g, 2.70 mmol) and triethylamine (0.38 cm^3, 2.70 mmol) in DCM (10 cm^3) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.596 g, 73 %). $\boldsymbol{R_F}$: 0.29 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: -6.5º (*c*. 1.1, $CHCl_3$); **MS** m/z (ES+) 328 (100%, $M+Na^+$); **HRMS**: found 328.0533, $M+Na^+$ requires 328.0533; **IR** ν_{max}(film)/cm^{-1} 1656 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.28-7.18 (m, 6H), 7.15-7.10 (m, 3H), 4.60 (q, *J* 7.1 Hz, 1H), 3.20 (s, 3H), 1.56 (d, *J* 7.3 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 167.2, 142.1, 139.5, 133.1, 128.6, 128.5, 127.4, 126.3, 126.1, 44.0, 37.1, 21.9; **HPLC**: er 98:2, General conditions I: t_r 5.9 (maj), 7.9 (min).

8e: (3-Chlorophenyl)methylthiocarbamic acid (*S*)-1-phenylethyl ester



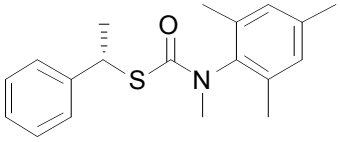
General procedure C was followed using **s3** (0.182 g, 1.00 mmol) and lithium aluminium hydride (1.00 cm^3, 1.00 mmol, 1 M in THF) in diethyl ether (7 cm^3) followed by **s23** (0.415 g, 1.10 mmol) and DCM (10 cm^3) with stirring for 16 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as a colourless oil (0.283 g, 92%). $\boldsymbol{R_F}$: 0.19 (petrol/EtOAc, 8:1); $\boldsymbol{[\alpha]_D^{22}}$: -17.9º (*c*. 0.9, $CHCl_3$); **MS** m/z (ES+) 306 (60%, $M+H^+$); **HRMS**: found 306.0722, $M+H^+$ requires 306.0714; **IR** ν_{max}(film)/cm^{-1} 1656 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.35 - 7.15 (m, 9H), 4.70 (q, *J* 7.2 Hz, 1H), 3.30 (s, 3H) and 1.66 (d, *J* 7.2 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.2, 143.2, 143.1, 134.8, 130.3, 128.5, 128.5, 128.4, 127.4, 127.2, 45.1, 38.1, 22.9; **HPLC**: er 98:2, General conditions I: t_r 6.3 (maj), 7.5 (min).

8f: (4-Cyanophenyl)methylthiocarbamic acid (*S*)-1-phenylethyl ester



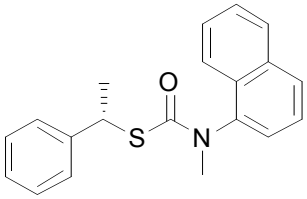
General procedure C was followed using **s3** (0.192 g, 1.00 mmol) and lithium aluminium hydride (1.00 cm^3, 1.00 mmol, 1 M in THF) in diethyl ether (7 cm^3) followed by **s24** (0.405 g, 1.10 mmol), triethylamine (0.17 cm^3, 1.20 mmol) and DCM (10 cm^3) with stirring for 18 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as colourless prisms (0.238 g, 77%). $\boldsymbol{R_F}$: 0.10 (petrol/EtOAc, 8:1); $\boldsymbol{[\alpha]_D^{22}}$: -12.0º (*c*. 1, $CHCl_3$); **Mpt**: 98-100 ºC (DCM); **MS** m/z (ES+) 319 (100%, $M+Na^+$); **HRMS**: found 319.0866, $M+Na^+$ requires 319.0876; **IR** ν_{max}(film)/cm^{-1} 1659 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.68 (d, *J* 8.4 Hz, 2H), 7.41 (d, *J* 8.4 Hz, 2H), 7.36 - 7.22 (m, 5H), 4.72 (q, *J* 7.2 Hz, 1H), 3.34 (s, 3H) and 1.68 (d, *J* 7.2 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.1, 146.3, 142.7, 133.3, 128.6, 128.1, 127.3, 127.3, 118.2, 45.3, 37.7, 22.8; **HPLC**: er 98:2, General conditions I: t_r 14.4 (maj), 18.9 (min).

8g: Methyl(2,4,6-trimethylphenyl)thiocarbamic acid (*S*)-1-phenyl-ethyl ester



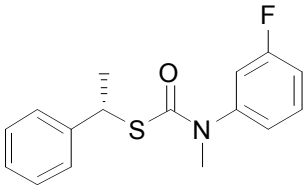
General procedure C was followed using **s3** (0.186 g, 1.03 mmol) and lithium aluminium hydride (1.03 cm^3, 1.03 mmol, 1 M in THF) in diethyl ether (7 cm^3) followed by **s25** (0.423 g, 1.10 mmol), triethylamine (0.17 cm^3, 1.20 mmol) and DCM (10 cm^3) with stirring for 20 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as colourless prisms (0.185 g, 55 %). $\boldsymbol{R_F}$: 0.10 (petrol/EtOAc, 8:1); $\boldsymbol{[\alpha]_D^{22}}$: -3.9º (*c*. 0.9, $CHCl_3$); **Mpt**: 45-47 ºC (DCM); **MS** m/z (ES+) 336 (100%, $M+Na^+$); **HRMS**: found 336.1394, $M+Na^+$ requires 336.1393; **IR** ν_{max}(film)/cm^{-1} 1656 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.33 - 7.16 (m, 5H), 6.93 (s, 1H), 6.88 (s, 1H), 4.67 (q, *J* 7.2 Hz, 1H), 3.16 (s, 3H), 2.29 (s, 3H), 2.23 (s, 3H), 2.07 (s, 3H) and 1.61 (d, *J* 7.2 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.5, 143.5, 138.8, 137.0, 136.8, 136.2, 129.6, 129.5, 128.3, 127.4, 126.9, 44.3, 35.3, 22.8, 21.1, 17.6, 17.5. Conditions for resolution on chrial HPLC were not found.

8h: Methylnaphthalen-1-ylthiocarbamic acid (*S*)-1-phenylethyl ester



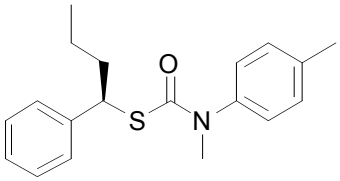
General procedure C was followed using **s3** (0.209 g, 1.16 mmol) and lithium aluminium hydride (1.16 cm^3, 1.16 mmol, 1 M in THF) in diethyl ether (7 cm^3) followed by **s26** (0.501 g, 1.27 mmol) and triethylamine (0.18 cm^3, 1.27 mmol) in DCM (10 cm^3) with stirring for 15 hours. The crude mixture was purified by flash column chromatography (petrol/DCM, 9:1) to afford the title compound as an amorphous white solid (0.274 g, 73 %). $\boldsymbol{R_F}$: 0.06 (9:1, Petrol:DCM); $\boldsymbol{[\alpha]_D^{21}}$: +1º (*c*. 1.2, $CHCl_3$); **Mpt**: 87-89 ºC (DCM); **MS** m/z (ES+) 344 (100%, $M+Na^+$); **HRMS**: found 344.1068, $M+Na^+$ requires 344.1080; **IR** ν_{max}(film)/cm^{-1} 1654 (C=O); mixture of 2 rotamers **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 7.96-7.84 (m, 4H), 7.68-7.35 (m, 10H), 7.29-7.17 (m, 10H), 4.72-7.65 (m, 2H), 3.42 (s, 3H), 3.40 (s, 3H), 1.60-1.52 (m, 6H); **^{13}C-NMR** ($CDCl_3$, 75.5 MHz) δ 169.2, 143.4,143.3, 134.7, 134.7, 128.4, 127.4, 126.9, 125.4, 122.6, 122.5, 44.9, 44.8, 38.1, 22.9, 22.8; **HPLC**: er 97:3, General conditions III: t_r 7.8 (min), 9.7 (maj).

8i: Methyl(2,4,6-trimethylphenyl)thiocarbamic acid (*S*)-1-phenylethyl ester



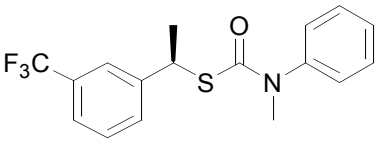
General procedure C was followed using **s3** (0.191 g, 1.05 mmol) and lithium aluminium hydride (1.05 cm^3, 1.05 mmol, 1 M in THF) in diethyl ether (7 cm^3) followed by **s27** (0.397 g, 1.10 mmol), triethylamine (0.17 cm^3, 1.20 mmol) and DCM (10 cm^3) with stirring for 20 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as a slightly yellow oil (0.275 g, 90%). $\boldsymbol{R_F}$: 0.19 (petrol/EtOAc, 8:1); $\boldsymbol{[\alpha]_D^{22}}$: -38.5º (*c*. 1.3, $CHCl_3$); **MS** m/z (ES+) 312 (100%, $M+Na^+$); **HRMS**: found 312.0815, $M+Na^+$ requires 312.0829; **IR** ν_{max}(film)/cm^{-1} 1659 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.38 - 7.21 (m, 6H), 7.08 - 6.98 (m, 3H), 4.70 (q, *J* 7.2 Hz, 1H), 3.31 (s, 3H) and 1.66 (d, *J* 7.2 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 168.2, 164.0, 161.5, 143.5, 143.4, 143.1, 130.5, 130.5, 128.5, 127.4, 127.2, 123.8, 115.4, 115.2, 45.0, 38.1, 22.9; **HPLC**: er 98:2, General conditions I: t_r 6.0 (maj), 7.0 (min).

8j: Methyl-*p*-tolylthiocarbamic acid S-((*R*)-1-phenylbutyl) ester



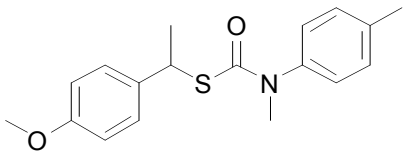
General procedure C was followed using **s4** (0.075 g, 0.36 mmol) and lithium aluminium hydride (0.36 cm^3, 0.36 mmol, 1 M in THF) in diethyl ether (5 cm^3) followed by **s18** (0.144 g, 0.40 mmol), triethylamine (0.06 cm^3, 0.43 mmol) and DCM (10 cm^3) with stirring for 18 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as colourless prisms (0.078 g, 69%). $\boldsymbol{R_F}$: 0.33 (petrol/EtOAc, 8:1); $\boldsymbol{[\alpha]_D^{20}}$: 29.4º (c. 2.2, $CHCl_3$); **Mpt**: 37-39 ºC (DCM); **MS** m/z (ES+) 336 (100%, $M+Na^+$), 314 (15%, $M+H^+$); **HRMS**: found 336.1393, $M+Na^+$ requires 336.1393; **IR** ν_{max}(film)/cm^{-1} 1649 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.28-7.25 (m, 4H), 7.23-7.18 (m, 3H), 7.11 (d, *J* 8.3 Hz, 2H), 4.52 (dd, *J* 6.6, 8.8 Hz, 1H), 3.27 (s, 3H), 2.37 (s, 3H), 1.97-1.79 (m, 2H), 1.38-1.15 (m, 3H), 0.87 (t, *J* 7.3 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 167.4, 141.6, 129.0, 127.4, 127.3, 127.1, 126.8, 125.8, 48.8, 38.0, 37.3, 20.2, 19.8, 12.7; **HPLC**: er 99:1, General conditions III: t_r 5.2 (maj), 6.1 (min).

8k: Methyl(3-triflouromethylphenyl)thiocarbamic acid (*R*)-1-phenylethyl ester



General procedure C was followed using **s5** (0.399 g, 1.59 mmol) and lithium aluminium hydride (1.60 cm^3, 1.60 mmol, 1 M in THF) in diethyl ether (8 cm^3) followed by **s19** (0.600 g, 1.75 mmol) and triethylamine (0.27 cm^3, 1.91 mmol) in DCM (10 cm^3) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.436 g, 80 %). $\boldsymbol{R_F}$: 0.17 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: -18º (*c*. 1.6, $CHCl_3$); **Mpt**: 97-99 ºC (petrol); **MS** m/z (ES+) 324 (100%, $M+Na^+$); **HRMS**: found 324.1022, $M+Na^+$ requires 324.1029; **IR** ν_{max}(film)/cm^{-1} 1656 (C=O); **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ δ 7.59 (br s, 1H), 7.53 (d, *J* 7.6 Hz, 1H), 7.47 (d, *J* 7.9 Hz, 1H), 7.43-7.36 (m, 4H), 7.26-7.25 (m, 2H), 4.74 (q, *J* 7.3 Hz, 1H), 3.31 (s, 3H), 1.63 (d, *J* 7.3 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 75.5 MHz) δ 167.7, 144.8, 141.9, 131.0, 131.0, 130.5, 129.5, 128.8, 128.5, 128.3, 124.1-123.8 (m), 44.3, 38.3, 22.6; **HPLC**: er 96:4, General conditions I: t_r 5.9 (min), 6.5 (maj).

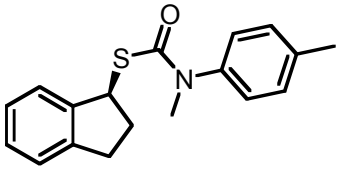
8l: Methyl-*p*-tolylthiocarbamic acid 1-(4-methoxyphenyl)ethyl ester



Oxalyl chloride (0.34 cm^3, 4.00 mmol, 1 eq) was added to a stirred solution of DMF (0.33 cm^3, 4.30 mmol, 1.1 eq) in DCM (10 cm^3) at 0 °C. The mixture was stirred for 5 min. (*S*)-1-(4-methoxyphenyl)ethanol (0.54 g, 3.60 mmol, 1 eq), triethylamine (1.10 cm^3, 7.90 mmol, 2 eq) and ethanethioic S-acid (0.25 cm^3, 3.60 mmol, 1 eq) were added sequentially. The mixture was warmed to room temperature and stirred for 18 h. Water (5 cm^3) was added, the phases separated and the aqueous layer extracted with EtOAc (3 x 10 cm^3). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude thioacetate was dissolved in diethyl ether (7 cm^3). Lithium aluminium hydride (1.2 cm^3, 1 M in THF, 1.20 mmol, 1 eq) was added dropwise. The mixture was heated to reflux with stirring for 1.5 h then cooled to room temperature. Aqueous HCl (3 cm^3, 1 M) was added with care. The phases were separated and the aqueous layer extracted with diethyl ether (3 x 10 cm^3). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude thiol was then dissolved in DCM (10 cm^3). **s18** (0.283 g, 0.79 mmol, 1.1 eq) and triethylamine (0.11 cm^3, 0.80 mmol, 1.2 eq) were added and the mixture was stirred for 72 h. The mixture was washed with aqueous HCl (2 x 7 cm^3,1M), dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as a waxy colourless oil (0.165 g, 15 %). $\boldsymbol{R_F}$: 0.19 (8:1, Petrol:EtOAc); **MS** m/z (ES+) 338 (100%, $M+Na^+$), 316 (20%, $M+H^+$); **HRMS**: found 338.1178, $M+Na^+$ requires 338.1186; **IR** ν_{max}(film)/cm^{-1} 1649 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.25 (d, *J* 8.8 Hz, 2H), 7.18 (d, *J* 8.1 Hz, 2H), 7.12 (d, *J* 8.6 Hz, 2H), 6.80 (d, *J* 8.8 Hz, 2H), 4.65 (q, *J* 7.3 Hz, 1H), 3.77 (s, 3H), 3.29 (s, 3H), 2.36 (s, 3H), 1.62 (d, *J* 7.3 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 75.5 MHz) δ 168.5, 125.5, 135.4, 130.1, 128.5, 113.7, 55.2, 44.4, 38.3, 23.0, 21.2.

Optically pure (S)-1-(4-methoxy-phenyl)-ethanol was used in this procedure. The product, however, was isolated as a racemic mixture. It is though that the electron rich nature of the benzylic ring promotes S_N1 nucleophilic addition of ethanethioic *S*-acid over the desired S_N2 mechanism.

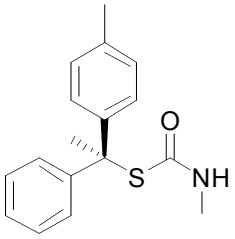
8m: Methyl-*p*-tolylthiocarbamic acid (*S*)-indan-1-yl ester



Oxalyl chloride (0.54 cm^3, 6.16 mmol, 1 eq) was added to a stirred solution of DMF (0.52 cm^3, 6.77 mmol, 1.1 eq) in DCM (50 cm^3) at 0 °C. The mixture was stirred for 5 min. (*R*)-indan-1-ol (0.83 g, 6.16 mmol, 1 eq), triethylamine (1.72 cm^3, 12.3 mmol, 2 eq) and ethanethioic S-acid (0.44 cm^3, 6.16 mmol, 1 eq) were added sequentially. The mixture was warmed to room temperature and stirred for 18 h. Water (20 cm^3) was added, the phases separated and the aqueous layer extracted with EtOAc (3 x 10 cm^3). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude thioacetate was dissolved in diethyl ether (20 cm^3). Lithium aluminium hydride (6.16 cm^3, 1 M in THF, 6.16 mmol, 1 eq) was added dropwise. The mixture was heated to reflux with stirring for 1.5 h then cooled to room temperature. Aqueous HCl (10 cm^3, 1 M) was added with care. The phases were separated and the aqueous layer extracted with diethyl ether (3 x 10 cm^3). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude thiol was then dissolved in DCM (20 cm^3). **s18** (2.42 g, 6.78 mmol, 1.1 eq) and triethylamine (1.03 cm^3, 7.39 mmol, 1.2 eq) were added and the mixture was stirred for 15 h. The mixture was washed with aqueous HCl (2 x 10 cm^3, 1M), dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 15:1) and the title compound isolated as a yellow oil (0.954 g, 52 %). $\boldsymbol{R_F}$: 0.33 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{21}}$: -38.7º (*c*. 1.0, $CHCl_3$); **MS** m/z (ES+) 320 (100%, $M+Na^+$); **HRMS**: found 320.1074, $M+Na^+$ requires 320.1080; **IR** ν_{max}(film)/cm^{-1} 1654

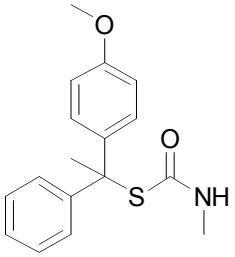
(C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.34-7.32 (m, 1H), 7.25-7.12 (m, 7H), 5.01 (dd, *J* 4.8, 7.6 Hz, 1H), 3.35 (s, 3H), 3.03-2.95 (m, 1H), 2.89-2.82 (m, 1H), 2.70-2.61 (m, 1H), 2.36 (s, 3H), 2.18-2.10 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 169.1, 143.9, 142.4, 139.5, 130.3, 130.1, 128.1, 127.6, 126.6, 125.1, 124.5, 49.6, 38.3, 34.7, 30.9, 21.2; **HPLC**: er 79:21, General conditions I: t_r 7.3 (maj), 8.7 (min).

9a: Methylthiocarbamic acid (*S*)-1-phenyl-1-*p*-tolylethyl ester



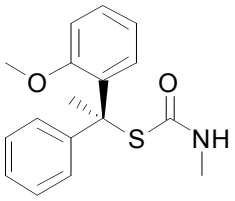
General procedure G was followed using *n*-BuLi (0.18 cm^3, 0.44 mmol, 2.5 M in hexanes), TMP (0.09 cm^3, 0.53 mmol), **8a** (0.050 g, 0.18 mmol) and propionic acid (0.04 cm^3, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.042 g, 83%). $\boldsymbol{R_F}$: 0.10 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: -4.9º (*c*. 1.2, $CHCl_3$); **Mpt**: 96-98 ºC (DCM); **MS** m/z (ES+) 308 (100%, $M+Na^+$); **HRMS**: found 308.1094, $M+Na^+$ requires 308.1080; **IR** ν_{max}(film)/cm^{-1} 1659 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.41 (d, *J* 8.0 Hz, 2H), 7.31 - 7.20 (m, 5H), 7.10 (d, *J* 8.0 Hz, 2H), 5.23 (s, 1H), 2.70 (d, *J* 4.4 Hz, 3H), 2.37 (s, 3H), 2.32 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75.5 MHz) δ 166.4, 145.6, 142.5, 136.6, 128.9, 128.1, 127.9, 127.8, 126.9, 59.6, 30.1, 27.5, 21.0; **HPLC**: er 96:4, General conditions II: t_r 11.6 (maj), 14.7 (min).

9b: (±)-Methylthiocarbamic acid 1-(4-methoxyphenyl)-1-phenylethyl ester



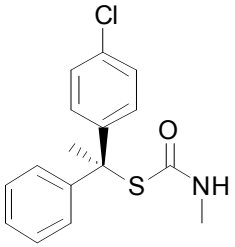
General procedure F was followed using **8b** (0.021 g, 0.07 mmol), diisopropylamine (0.03 cm^3, 0.21 mmol), *n*-BuLi (0.09 cm^3, 2.0 M, 0.18 mmol) and propionic acid (0.02 cm^3, 0.27 mmol) with stirring for 4 hours. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.020 g, 94 %). $\boldsymbol{R_F}$: 0.09 (8:1, Petrol:EtOAc); **Mpt**: 93-95 ºC (DCM); **MS** m/z (ES+) 324 (100%, $M+Na^+$); **HRMS**: found 324.1018, $M+Na^+$ requires 324.1029; **IR** ν_{max}(film)/cm^{-1} 1657 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.43-7.40 (m, 2H), 7.35-7.22 (m, 5H), 6.84 (d, *J* 9.0 Hz, 2H), 5.21 (d, *J* 4.1 Hz, 1H), 3.80 (s, 3H), 2.74 (d, *J* 4.5 Hz, 3H), 2.38 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 158.3, 145.6, 137.4, 129.1, 128.1, 127.8, 126.9, 113.4, 59.4, 55.2, 30.2, 27.5.

9c: Methylthiocarbamic acid (*S*)-1-(2-methoxyphenyl)-1-phenylethyl ester



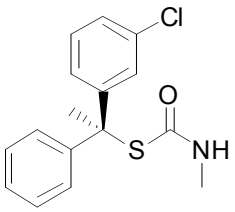
General procedure G was followed using *n*-BuLi (0.17 cm^3, 0.42 mmol, 2.5 M in hexanes), TMP (0.09 cm^3, 0.50 mmol), **8c** (0.049 g, 0.17 mmol) and propionic acid (0.04 cm^3, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.044 g, 89%). $\boldsymbol{R_F}$: 0.07 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{21}}$: -32.8º (*c*. 1.1, $CHCl_3$); **Mpt**: 125-127 ºC (diethyl ether); **MS** m/z (ES+) 302 (35%, $M+H^+$), 324 (45%, $M+Na^+$); **HRMS**: found 324.1019, $M+Na^+$ requires 324.1029; **IR** ν_{max}(film)/cm^{-1} 3324 (NH), 1652 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.73 (dd, *J* 7.8, 1.5 Hz, 1H), 7.33-7.16 (m, 6H), 7.02 (td, *J* 7.6, 1.3 Hz, 1H), 6.85 (dd, *J* 8.1, 1.0 Hz, 1H), 5.23 (br s, 1H), 3.43 (s, 3H), 2.75 (d, *J* 4.8 Hz, 3H), 2.40 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 157.2, 146.2, 133.0, 128.9, 127.8, 126.4, 126.3, 120.2, 113.0, 59.2, 55.5, 28.5, 27.5; **HPLC**: er 91:9, General conditions II: t_r 9.6 (maj), 12.4 (min).

9d: Methylthiocarbamic acid (*S*)-1-(4 chlorophenyl)-1-phenylethyl ester



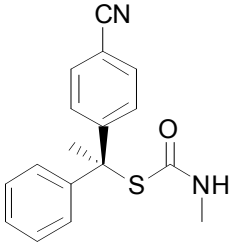
General procedure G was followed using *n*-BuLi (0.17 cm^3, 0.41 mmol, 2.5 M in hexanes), TMP (0.08 cm^3, 0.49 mmol), **8d** (0.046 g, 0.16 mmol) and propionic acid (0.04 cm^3, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.044 g, 94%). $\boldsymbol{R_F}$: 0.07 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{20}}$: -18.8º (*c*. 1.5, $CHCl_3$); **MS** m/z (ES+) 328 (100%, $M+Na^+$); **HRMS**: found 328.0527, $M+Na^+$ requires 328.0533; **IR** ν_{max}(film)/cm^{-1} 1660 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.40-7.23 (m, 9H), 5.20 (br s, 1H), 2.76 (d, *J* 4.5 Hz, 3H), 2.37 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 145.1, 144.1, 132.7, 129.5, 128.2, 128.1, 127.6, 127.1, 59.2, 30.1, 27.5; **HPLC**: er 96:4, General conditions II: t_r 8.9 (maj), 10.7 (min).

9e: Methylthiocarbamic acid (*S*)-1-(3-chlorophenyl)-1-phenylethyl ester



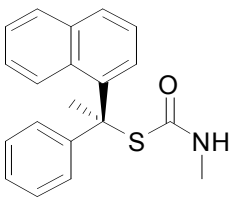
General procedure G was followed using *n*-BuLi (0.17 cm^3, 0.41 mmol, 2.5 M in hexanes), TMP (0.08 cm^3, 0.49 mmol), **8e** (0.049 g, 0.16 mmol) and propionic acid (0.04 cm^3, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as a colourless oil (0.038 g, 69%). $\boldsymbol{R_F}$: 0.10 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: -10.3º (c. 0.9, $CHCl_3$); **MS** m/z (ES+) 328 (100%, $M+Na^+$); **HRMS**: found 328.0531, $M+Na^+$ requires 328.0533; **IR** ν_{max}(film)/cm^{-1} 1651 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.43-7.45 (m, 1H), 7.37-7.21 (m, 8H), 5.21 (br s, 1H), 2.76 (d, *J* 4.8 Hz, 3H), 2.38 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75.5 MHz) δ 165.7, 147.6, 144.9, 134.0, 129.2, 128.3, 128.2, 127.7, 127.2, 127.1, 126.2, 59.2, 30.0, 27.6; **HPLC**: er 96:4, General conditions II: t_r 11.0 (min), 15.9 (maj).

9f: Methylthiocarbamic acid (*S*)-1-(4-cyanophenyl)-1-phenylethyl ester



General procedure G was followed using *n*-BuLi (0.17 cm^3, 0.42 mmol, 2.5 M in hexanes), TMP (0.09 cm^3, 0.51 mmol), **8f** (0.048 g, 0.17 mmol) and propionic acid (0.04 cm^3, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.037 g, 78%). $\boldsymbol{R_F}$: 0.04 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: -3.8º (*c*. 1.6, $CHCl_3$); **MS** m/z (ES+) 319 (80%, $M+Na^+$); **HRMS**: found 319.0875, $M+Na^+$ requires 319.0876; **IR** ν_{max}(film)/cm^{-1} 2227 (CN), 1674 (C=O); **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 7.61 (s, 4H), 7.34-7.24 (m, 5H), 5.25 (br s, 1H), 2.76 (d, *J* 4.5 Hz, 3H), 2.38 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 151.0, 144.5, 131.8, 129.0, 128.4, 127.5, 118.8, 110.6, 59.3, 29.8, 27.6; **HPLC**: er 97:3, General conditions II: t_r 12.3 (min), 13.8 (maj).

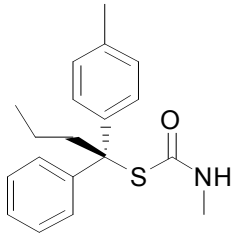
9h: Methylthiocarbamic acid (*S*)-1-naphthalen-1-yl-1-phenylethyl ester



General procedure G was followed using *n*-BuLi (0.19 cm^3, 0.40 mmol, 2.12 M in hexanes), TMP (0.08 cm^3, 0.48 mmol), **8h** (0.052 g, 0.16 mmol) and propionic acid (0.04 cm^3, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.051 g, 98%). $\boldsymbol{R_F}$: 0.07 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{21}}$: -218.6º (c. 0.3, $CHCl_3$); **Mpt**: 59-61 ºC (DCM); **MS** m/z (ES+) 344 (100%, $M+Na^+$); **HRMS**: found 322.1252, $M+H^+$ requires 322.1260; **IR** ν_{max}(film)/cm^{-1} 1667 (C=O); **^{1}H-NMR** ($CDCl_3$,

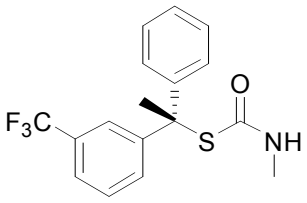
500 MHz) δ 7.96 (d, *J* 7.3 Hz, 1H), 7.84 (ap t, *J* 8.6 Hz, 2H), 7.71 (d, *J* 8.8 Hz, 1H), 7.54 (ap t, *J* 7.7 Hz, 1H), 7.36-7.30 (m, 3H), 7.27-7.15 (m, 4H), 5.11 (br s, 1H), 2.61 (d, *J* 4.1 Hz, 3H), 2.52 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 165.8, 147.0, 138.9, 135.0, 130.5, 129.3, 129.0, 128.5, 128.1, 126.8, 126.6, 124.9, 124.6, 124.5, 60.2, 33.0, 27.4; **HPLC**: er 96:4, General conditions II: t_r 9.1 (maj), 10.0 (min).

9j: Methylthiocarbamic acid (*R*)-1-phenyl-1-*p*-tolylbutyl ester



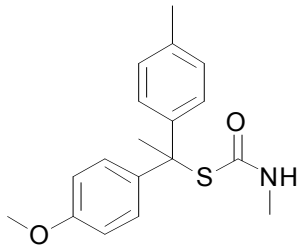
General procedure G was followed using *n*-BuLi (0.16 cm^3, 0.41 mmol, 2.5 M in hexanes), TMP (0.08 cm^3, 0.49 mmol), **8j** (0.051 g, 0.16 mmol) and propionic acid (0.04 cm^3, 0.49 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.038 g, 74%). $\boldsymbol{R_F}$: 0.12 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{20}}$: -2.0º (*c*. 1, $CHCl_3$); **Mpt**: 97-99 ºC (petrol); **MS** m/z (ES+) 336 (100%, $M+Na^+$); **HRMS**: found 336.1401, $M+Na^+$ requires 336.1393; **IR** ν_{max}(film)/cm^{-1} 1659 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.39 (d, *J* 8.1 Hz, 2H), 7.31-7.20 (m, 5H), 7.10 (d, *J* 8.1 Hz, 2H), 5.13 (br s, 1H), 2.65 (m, 5H), 2.33 (s, 3H), 1.29-1.19 (m, 2H), 0.89 (t, *J* 7.31 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 145.2, 142.0, 136.3, 128.4, 128.3, 127.7, 126.6, 63.6, 42.7, 21.0, 18.8, 14.3; **HPLC**: er 98:2, General conditions II: t_r 10.5 (min), 11.5 (maj).

9k: Methylthiocarbamic acid (*S*)-1-phenyl-1-(3-trifluoromethylphenyl)ethyl ester



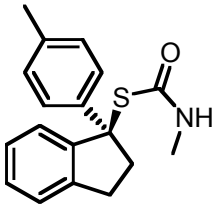
General procedure G was followed using *n*-BuLi (0.15 cm^3, 0.37 mmol, 2.5 M in hexanes), TMP (0.08 cm^3, 0.44 mmol), **8k** (0.053 g, 0.15 mmol) and propionic acid (0.04 cm^3, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.045 g, 85%). $\boldsymbol{R_F}$: 0.06 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{20}}$: -5.4º (*c*. 1.4, $CHCl_3$); **Mpt**: 82-84 ºC (DCM); **MS** m/z (ES+) 362 (100%, $M+Na^+$); **HRMS**: found 340.0976, $M+H^+$ requires 340.0977; **IR** ν_{max}(film)/cm^{-1} 1659 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ .74 (br s, 1H), 7.64 (d, *J* 7.8 Hz, 1H), 7.51 (d, *J* 7.8 Hz, 1H), 7.43 (ap t, *J* 7.8 Hz, 1H), 7.35-7.25 (m, 5H), 5.24 (br s, 1H), 2.75 (d, *J* 4.3 Hz, 3H), 2.42 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75.5 MHz) δ 165.6, 146.6, 144.8, 131.5, 130.5, 130.1, 128.5, 128.3, 127.6, 127.3, 124.7, 124.7, 123.8, 123.7, 59.3, 30.0, 27.6; **HPLC**: er 67:33, General conditions II: t_r 5.6 (min), 6.6 (maj).

9l: (±)-Methylthiocarbamic acid 1-(4-methoxyphenyl)-1-*p*-tolylethyl ester



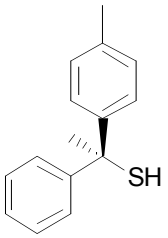
General procedure E was followed using *n*-BuLi (0.22 cm^3, 0.40 mmol, 1.8 M in hexanes), diisopropylamine (0.07 cm^3, 0.48 mmol), **8l** (0.040 g, 0.16 mmol) and propionic acid (0.04 cm^3, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as a slightly yellow amorphous solid (0.034 g, 86%). $\boldsymbol{R_F}$: 0.06 (8:1, Petrol:EtOAc); **Mpt**: 91-93 ºC (DCM); **MS** m/z (ES+) 225 (100%, M-($SCONHCH_3$)), 338 (45%, $M+Na^+$); **HRMS**: found 338.1190, $M+Na^+$ requires 338.1186; **IR** ν_{max}(film)/cm^{-1} 1656 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.35-7.29 (m, 4H), 7.12 (d, *J* 8.1 Hz, 2H), 6.84 (d, *J* 8.8 Hz, 2H), 5.20 (br d, *J* 3.5 Hz, 1H), 3.80 (s, 3H), 2.73 (d, *J* 4.5 Hz, 3H), 2.36 (s, 3H), 2.33 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75.5 MHz) δ 166.6, 158.3, 142.7, 137.6, 136.6, 129.1, 128.8, 127.7, 113.4, 59.2, 55.2, 30.3, 27.5, 21.0.

9m: Methylthiocarbamic acid (*R*)-1- *p*-tolylindan-1-yl ester



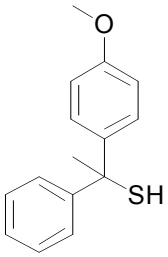
General procedure G was followed using *n*-BuLi (0.18 cm^3, 0.40 mmol, 2.3 M in hexanes), TMP (0.06 cm^3, 0.48 mmol), **8m** (0.056 g, 0.16 mmol) and propionic acid (0.04 cm^3, 0.50 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.049 g, 87%). $\boldsymbol{R_F}$: 0.05 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: -4.7º (*c*. 0.9, $CHCl_3$); **Mpt**: 96-98 ºC (DCM); **MS** m/z (ES+) 320 (100%, $M+Na^+$); **HRMS**: found 320.1086, $M+Na^+$ requires 320.1080; **IR** ν_{max}(film)/cm^{-1} 1654 (C=O); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.41-7.37 (m, 3H), 7.30-7.20 (m, 3H), 7.13 (d, *J* 8.0 Hz, 2H), 5.20 (br s, 1H), 3.14-2.89 (m, 3H), 2.82-2.73 (m, 4H), 2.33 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 145.7, 143.6, 140.8, 136.5, 128.9, 127.9, 127.3, 126.7, 125.7, 124.8, 66.1, 42.8, 30.5, 27.5, 21.0; **HPLC**: er 74:26, General conditions II: t_r 8.0 (min), 10.4 (maj).

10a: (*S*)-1-(4-Methylphenyl)-1-phenylethanethiol



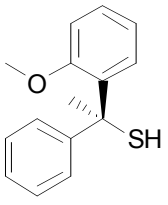
General procedure I was followed using sodium ethoxide solution (0.08 cm^3, 0.21 mmol) and **9a** (0.029 g, 0.10 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.015 g, 63 %). $\boldsymbol{R_F}$: 0.63 (9:1 Petrol/EtOAc); $\boldsymbol{[\alpha]_D^{21}}$: -3.6º (*c*. 1.3, $CHCl_3$); **MS** m/z (ES-) 227 (100%, $M-H^+$); **HRMS**: found 227.0915, $M-H^+$ requires 227.0900; **IR** ν_{max}(film)/cm^{-1} 2565 (w, SH); **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ 7.42-7.38 (m, 2H), 7.19-7.30 (m, 5H), 7.08 (d, *J* 8.0 Hz, 2H), 2.45 (s, 1H), 2.30 (s, 3H), 2.11 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 148.5, 145.4, 136.3, 128.8, 128.1, 127.1, 127.0, 126.6, 53.4, 34.8, 20.9.

10b: (±)-1-(4-Methoxyphenyl)-1-phenylethanethiol



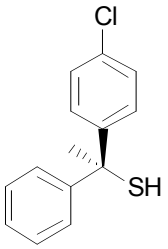
General procedure I was followed using sodium ethoxide solution (0.02 cm^3, 0.07 mmol) and **9b** (0.018 g, 0.06 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.013 g, 94 %). $\boldsymbol{R_F}$: 0.53 (8:1, Petrol:EtOAc); **MS** m/z (EI) 211 (100%, $M-SH^-$); **HRMS**: found 211.1123, $M-SH^-$ requires 211.1117; **IR** ν_{max}(film)/cm^{-1} 2558 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.46-7.43 (m, 2H), 7.37-7.21 (m, 5H), 6.84 (d, *J* 8.8 Hz, 2H), 3.81 (s, 3H), 2.50 (s, 1H), 2.15 (s, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 158.2, 148.6, 140.5, 128.3, 128.1, 127.1, 126.6, 113.3, 55.3, 53.2, 35.0.

10c: (*S*)-1-(2-Methoxyphenyl)-1-phenylethanethiol



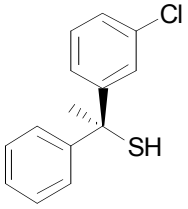
General procedure I was followed using sodium ethoxide solution (0.04 cm^3, 0.12 mmol) and **9c** (0.031 g, 0.10 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.024 g, 97 %). $\boldsymbol{R_F}$: 0.49 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{21}}$: -53.0º (c. 1.7, $CHCl_3$); **MS** m/z (ES-) 243 (100%, $M-H^+$); **HRMS**: found 244.0922, $M-H^+$ requires 244.0916; **IR** ν_{max}(film)/cm^{-1} 2589 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.63 (dd, *J* 7.8, 1.8 Hz, 1H), 7.43-7.40 (m, 2H), 7.31-7.15 (m, 4H), 7.03 (td, *J* 7.6, 1.3 Hz, 1H), 6.87 (dd, *J* 8.1, 1.0 Hz, 1H), 3.46 (s, 3H), 3.17 (q, *J* 1.3 Hz, 1H), 2.04 (d, *J* 1.3 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 157.0, 149.4, 136.5, 128.6, 127.7, 126.5, 125.8, 125.7, 120.5, 112.7, 55.3, 51.7, 32.9.

10d: (*S*)-1-(4-Chlorophenyl)-1-phenylethanethiol



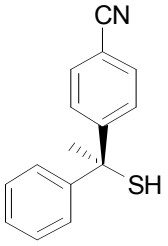
General procedure I was followed using sodium ethoxide solution (0.06 cm^3, 0.16 mmol) and **9d** (0.016 g, 0.05 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.012 g, 97 %). $\boldsymbol{R_F}$: 0.63 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: 5.1º (*c*. 0.8, $CHCl_3$); **MS** m/z (EI) 215 (100%, M-SH^-); **HRMS**: found 215.0622, M-SH^- requires 215.0622; **IR** ν_{max}(film)/cm^{-1} 2557 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.41-7.22 (m, 9H), 2.48 (s, 1H), 2.13 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 146.7, 145.9, 131.5, 127.6, 127.2, 127.1, 125.9, 52.1, 33.7.

10e: (*S*)-1-(3-Chlorophenyl)-1-phenylethanethiol



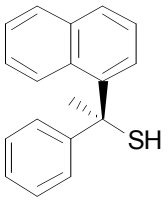
General procedure H was followed using **8e** (0.046 g, 0.16 mmol), *n*-butyllithium (0.26 cm^3, 0.41 mmol, 1.6 M in hexanes), TMP (0.08 cm^3, 0.49 mmol), propionic acid (0.03 cm^3, 0.47 mmol) and sodium ethoxide (0.25 cm^3, 0.82 mmol, 21 % w/w in ethanol). The crude product was purified by column chromatography (petrol/EtOAc, 20:1) and the title compound isolated as a colourless oil (0.016 g, 41 %). $\boldsymbol{R_F}$: 0.53 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: 7.3º (*c*. 0.2, $CHCl_3$); **MS** m/z (ES-) 247 (100%, M-H^+); **HRMS**: found 247.0361, M-H^+ requires 247.0353; **IR** ν_{max}(film)/cm^{-1} 2292 (CH); **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 7.47 (s, 1H), 7.41 (d, *J* 7.9 Hz, 2H), 7.34-7.21 (m, 6H), 2.50 (s, 1H), 2.14 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 150.6, 147.5, 134.0, 129.4, 128.3, 127.4, 127.0, 126.9, 125.6, 53.3, 34.5;

10f: 4-((*S*)-1-phenyl-1-sulfanylethyl)benzonitrile



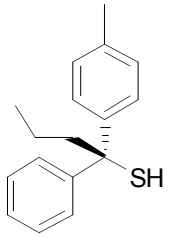
General procedure I was followed using sodium ethoxide solution (0.05 cm^3, 0.17 mmol) and **9f** (0.017 g, 0.06 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.013 g, 98 %). $\boldsymbol{R_F}$: 0.40 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{21}}$: 7.8º (*c*. 1.3, $CHCl_3$); **MS** m/z (EI) 206 (100%, M-SH^-); **HRMS**: found 206.0967, M-SH^- requires 206.0964; **IR** ν_{max}(film)/cm^{-1} 2228 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.61 (d, *J* 8.8 Hz, 2H), 7.56 (d, *J* 8.8 Hz, 2H), 7.40-7.25 (m, 5H), 2.51 (s, 1H), 2.15 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 153.9, 146.8, 132.0, 128.4, 128.0, 127.2, 126.9, 118.7, 110.6, 53.4, 34.3.

10h: (*S*)-1-Naphthalen-1-yl-1-phenylethanethiol



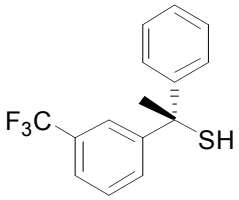
General procedure I was followed using sodium ethoxide solution (0.04 cm^3, 0.09 mmol) and **9h** (0.015 g, 0.05 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.006 g, 51 %). $\boldsymbol{R_F}$: 0.58 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{22}}$: -11.4º (*c*. 0.8, $CHCl_3$); **MS** m/z (EI) 231 (100%, M-SH^-); **HRMS**: found 231.1165, M-SH^- requires 231.1168; **IR** ν_{max}(film)/cm^{-1} 2568 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.92-7.90 (m, 1H), 7.84 (d, *J* 7.8 Hz, 2H), 7.62 (d, *J* 8.1 Hz, 1H), 7.54-7.50 (m, 1H), 7.44-7.42 (m, 2H), 7.38-7.34 (m, 1H), 7.27-7.17 (m, 4H), 2.78 (s, 1H), 2.26 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 148.9, 142.5, 135.1, 130.4, 128.9, 128.4, 127.8, 126.4, 126.1, 125.1, 124.8, 123.8, 53.8, 37.5.

10j: (*R*)-1-Phenyl-1-*p*-tolylbutane-1-thiol



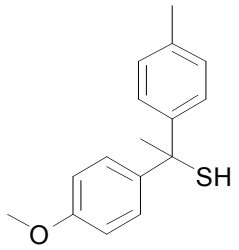
General procedure I was followed using sodium ethoxide solution (0.02 cm^3, 0.05 mmol) and **9j** (0.009 g, 0.03 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.007 g, 98 %). $\boldsymbol{R_F}$: 0.72 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{20}}$: -5.6º (*c*. 0.5, $CHCl_3$); **MS** m/z (EI) 223 (100%, M-SH^-), 256 (5 %, M); **HRMS**: found 256.1284, M requires 256.1280; **IR** ν_{max}(film)/cm^{-1} 2565 (w, SH); **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 7.40-7.37 (m, 2H), 7.31-7.28 (m, 2H), 7.25-7.19 (m, 3H), 7.10 (d, *J* 8.1 Hz, 2H), 2.43-2.39 (m, 2H), 2.33 (s, 3H), 2.29 (s, 1H), 1.26-1.19 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 146.7, 143.7, 135.1, 127.6, 126.9, 126.6, 126.5, 125.4, 45.6, 28.7, 19.9, 17.8, 13.3.

10k: (*S*)-1-Phenyl-1-(3-trifluoromethylphenyl)ethanethiol



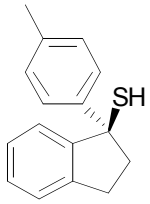
General procedure I was followed using sodium ethoxide solution (0.06 cm^3, 0.16 mmol) and **9k** (0.027 g, 0.08 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.018 g, 76 %). $\boldsymbol{R_F}$: 0.58 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{20}}$: 2.5º (c. 1.8, $CHCl_3$); **MS** m/z (ES-) 281 (100%, M-H^+); **HRMS**: found 281.0614, M-H^+ requires 281.0617; **IR** ν_{max}(film)/cm^{-1} 2557 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 77.79 (s, 1H), 7.58 (d, *J* 7.8 Hz, 1H), 7.51 (d, *J* 7.6 Hz, 1H), 7.44-7.40 (m, 3H), 7.33 (t, *J* 7.4 Hz, 2H), 7.28-7.25 (m, 1H), 2.54 (s, 1H), 2.18 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 149.5, 147.3, 130.9, 130.3, 128.6, 128.4, 127.1, 127.0, 123.7, 123.6, 122.8, 53.3, 34.6, 29.7.

10l: (±)-1-(4-Methoxyphenyl)-1-*p*-tolylethanethiol



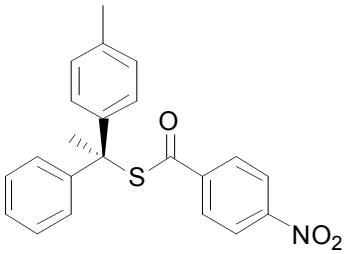
General procedure I was followed using sodium ethoxide solution (0.05 cm^3, 0.13 mmol) and **9l** 0.020 g, 0.06 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.012 g, 75 %). $\boldsymbol{R_F}$: 0.59 (8:1, Petrol:EtOAc); **MS** m/z (EI) 224 (90%, M-SH_2); **HRMS**: found 224.1199, M-SH_2 requires 224.1196; **IR** ν_{max}(film)/cm^{-1} 2553 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.36 (d, *J* 8.8 Hz, 2H), 7.33 (d, *J* 8.3 Hz, 2H), 7.12 (d, *J* 8.1 Hz, 2H), 6.83 (d, *J* 9.1 Hz, 2H), 3.81 (s, 3H), 2.48 (s, 1H), 2.34 (s, 3H), 2.14 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 157.1, 144.6, 139.6, 135.2, 127.7, 127.2, 125.9, 112.2, 54.2, 52.0, 34.0, 19.9.

10m: (*R*)-1-*p*-Tolylinadan-1-thiol



General procedure I was followed using sodium ethoxide solution (0.05 cm^3, 0.12 mmol) and **9m** (0.018 g, 0.06 mmol). The crude product was purified by flash column chromatography (*n*-pentane) and the title compound isolated as a colourless oil (0.013 g, 89 %). $\boldsymbol{R_F}$: 0.57 (8:1, Petrol:EtOAc); $\boldsymbol{[\alpha]_D^{20}}$: -10.0º (c. 1.3, $CHCl_3$); **MS** m/z (EI) 206 (100%, M-H_2S); **HRMS**: found 206.1090, M-H_2S requires 206.1090; **IR** ν_{max}(film)/cm^{-1} 2563 (w, SH); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 7.37-7.24 (m, 6H), 7.12 (d, *J* 8.1 Hz, 2H), 3.07 (ddd, *J* 15.6, 7.6, 6.8 Hz, 1H), 2.88 (ddd, *J* 15.6, 7.3, 6.3 Hz, 1H), 2.73 (ddd, *J* 13.1, 7.6, 6.3 Hz, 1H), 2.57 (ddd, *J* 13.6, 7.8, 6.1 Hz, 1H), 2.36 (s, 1H), 2.34 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 149.2, 143.1, 142.5, 136.5, 128.8, 127.5, 127.1, 127.0, 124.9, 124.7, 60.2, 48.0, 30.4, 20.9.

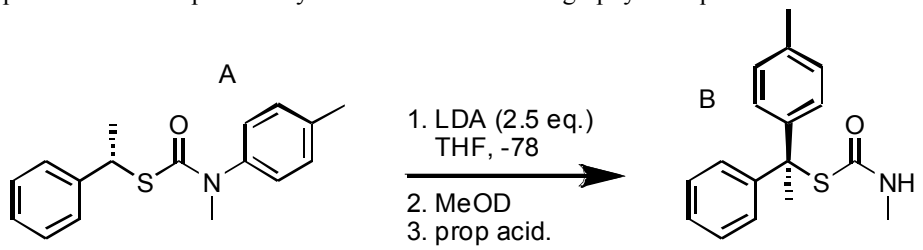
11: 4-Nitrothiobenzoic acid S-((*S*)-1-phenyl-1-*p*-tolylethyl) ester



Sodium hydride (0.004 g, 0.10 mmol, 60 % in mineral oil) was added to a solution of **10a** (0.015 g, 0.06 mmol) in THF (3 cm^3) at 0 °C. The mixture was stirred for 3 minutes and 4-nitro-benzoyl chloride (0.024 g, 0.13 mmol) was added. The mixture was warmed to room temperature and stirred for 18 hours. The mixture was cooled to 0 °C and water (2 cm^3) was added with care. The mixture was partitioned between saturated aqueous ammonium chloride and EtOAc and the phases separated. The aqueous fraction was extracted with EtOAc (3 x 10 cm^3). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 15:1) and the title compound isolated as colourless prisms (0.016 g, 66 %). $\boldsymbol{R_F}$: 0.43 (8:1, Petrol:EtOAc); **Mpt**: 85-87 ºC (DCM); $\boldsymbol{[\alpha]_D^{22}}$: -7.2º (*c*. 0.9, $CHCl_3$); **MS** m/z (ES+) 400 (60%, $M+Na^+$); **HRMS**: found 400.0964, $M+Na^+$ requires 400.0978; **IR** ν_{max}(film)/cm^{-1} 1664 (C=O), 1529 (NO_2 sy), 1350 (NO_2 as); **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 8.26 (d, J 8.8 Hz, 2H), 8.06 (d, J 8.8 Hz, 2H), 7.44 (d, J 8.6 Hz, 2H), 7.36-7.26 (m, 5H), 7.15 (d, J 8.3 Hz, 2H), 2.46 (s, 3H), 2.35 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75.5 MHz) δ 188.8, 150.3, 144.6, 142.2, 141.5, 137.1, 129.0, 128.3, 128.2, 127.7, 127.6, 127.3, 123.8, 61.3, 28.7, 21.0.

DEUTERATION EXPERIMENTS

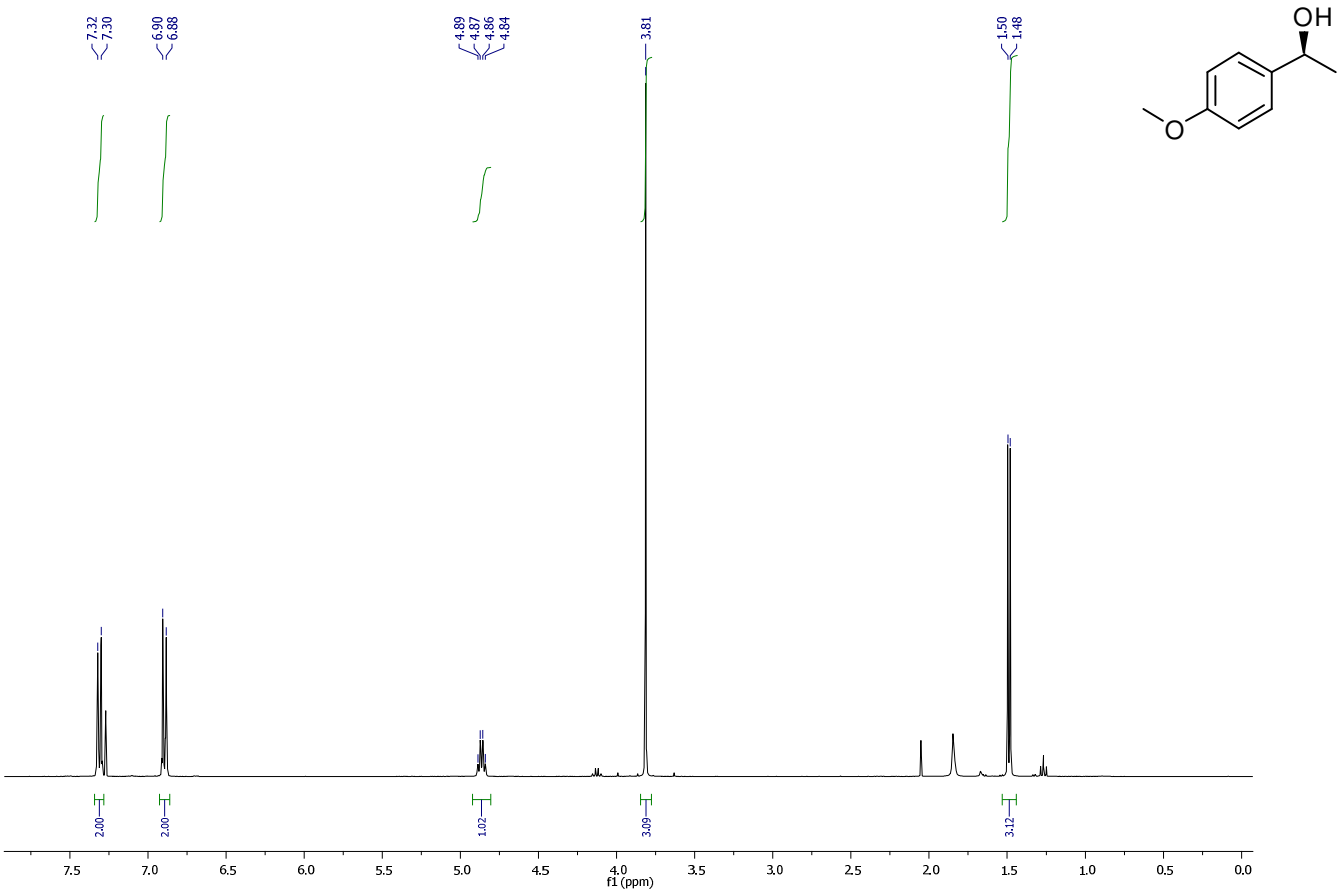
n-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of diisopropylamine (3 eq) in THF (1 cm^3) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannular to a cooled (-78 °C) solution of **8a** (0.05 g, 1 eq) in THF (1.5 cm^3). The mixture was allowed to stir for the time specified in the table (below). CD_3OD (3 eq) was added dropwise followed immediately by propionic acid (5 eq) and the mixture allowed to warm to room temperature. Water (10 cm^3) and diethyl ether (10 cm^3) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm^3) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

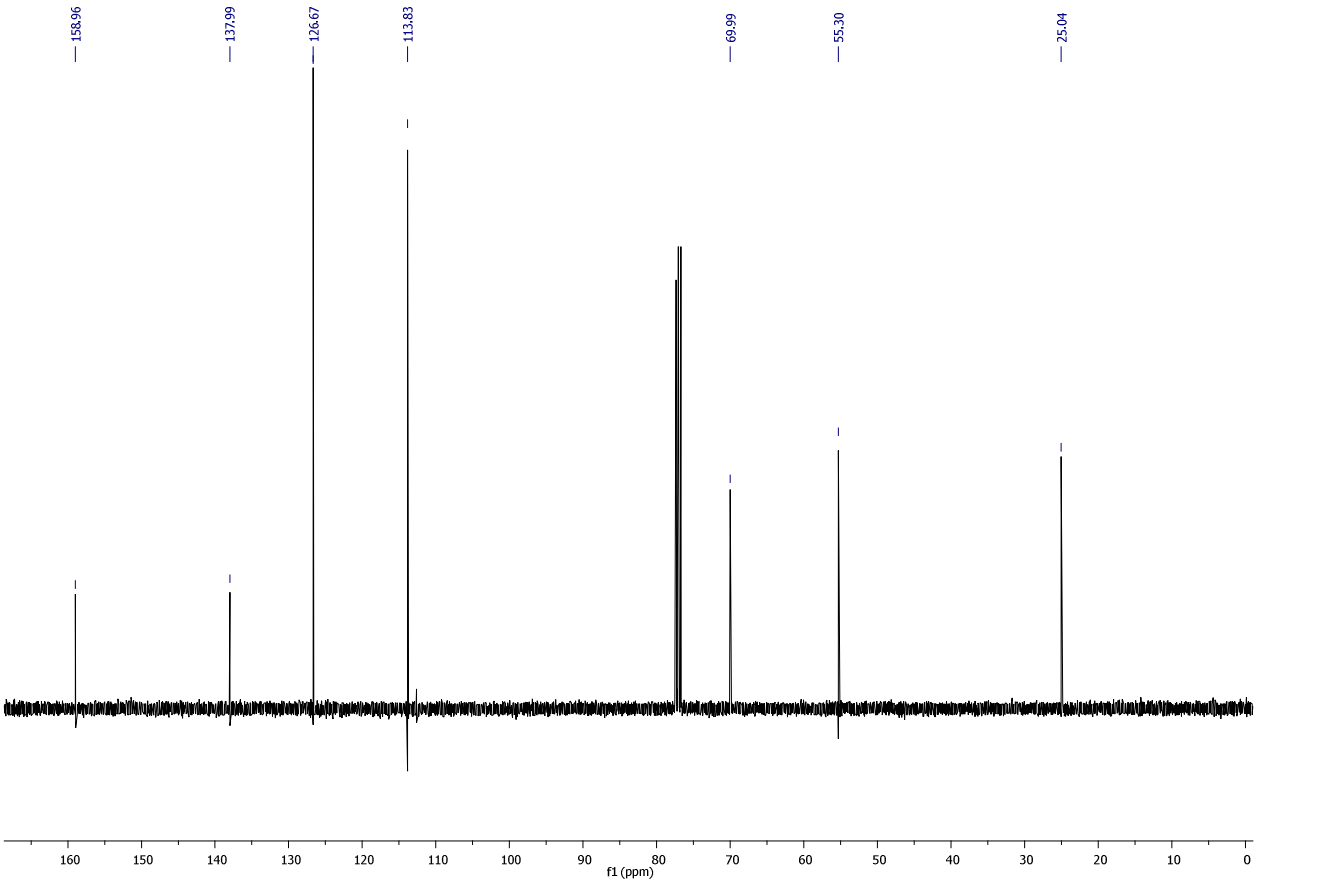


	A				B			
Reaction time (min)	**Yield**	**er**	**%D NMR[a]**	**%D MS[b]**	**Yield**	**er**	**%D NMR[a]**	**%D MS[b]**
2	nd	95:5	11	7	-	-	-	-
10	72	80:20	39	40	18	94:6	10	0
20	64	77:23	41	42	19	63:7	2	1
30	-	-	-	-	64	88:12	3	0
40	15	54:46	35	33	76	88:12	2	2

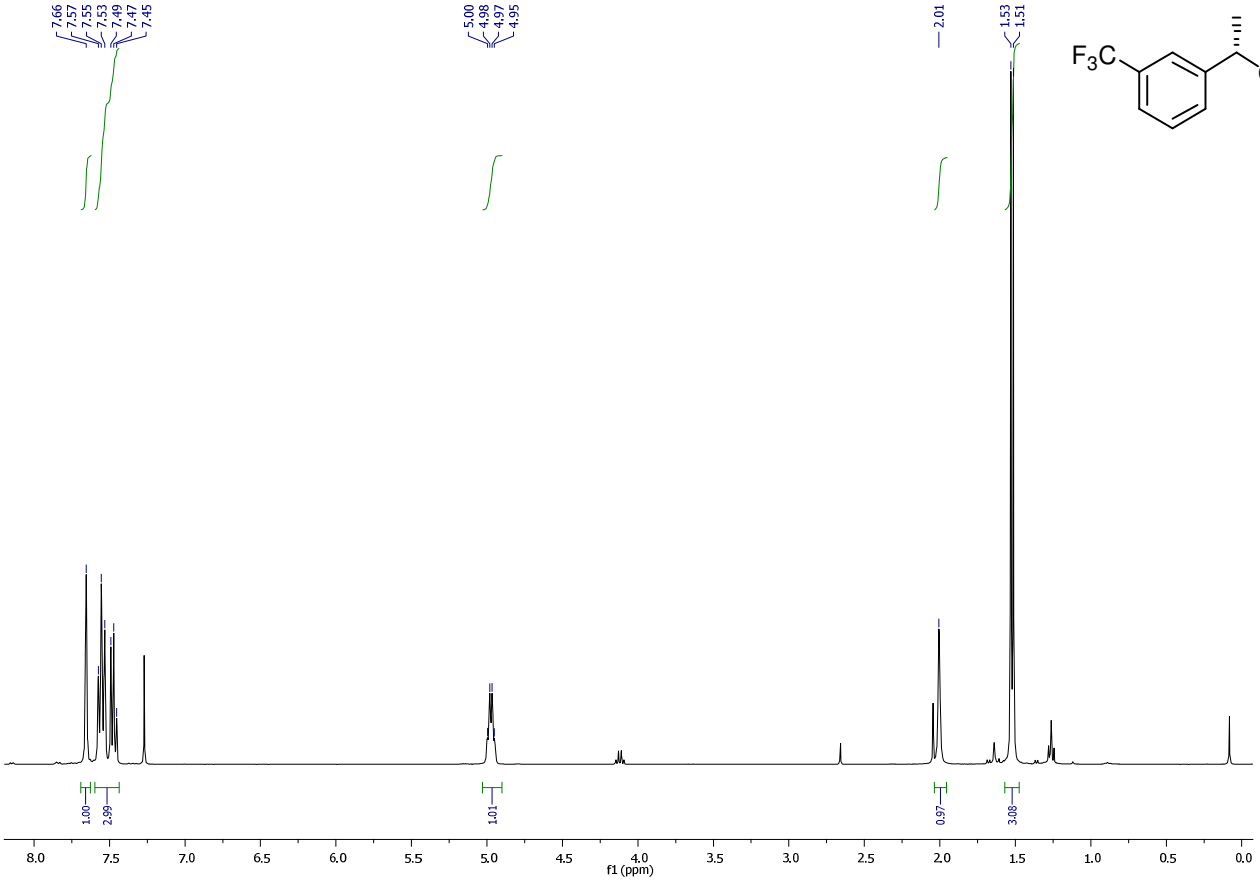
[a]% deuteration calculated by integration in ^1H NMR.
[b]% deuteration measured in mass spectrometry (ES+) with correction for ^{13}C.

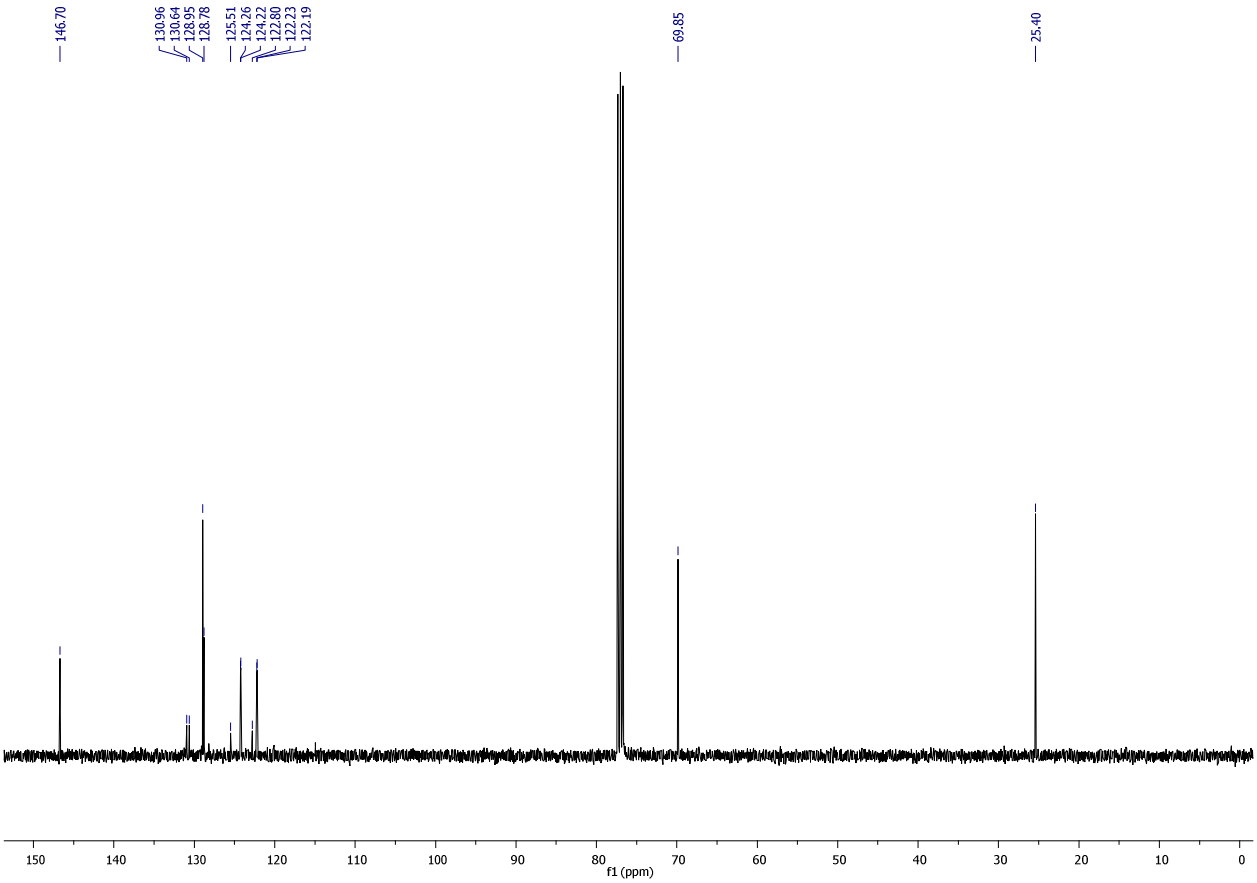
s1: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



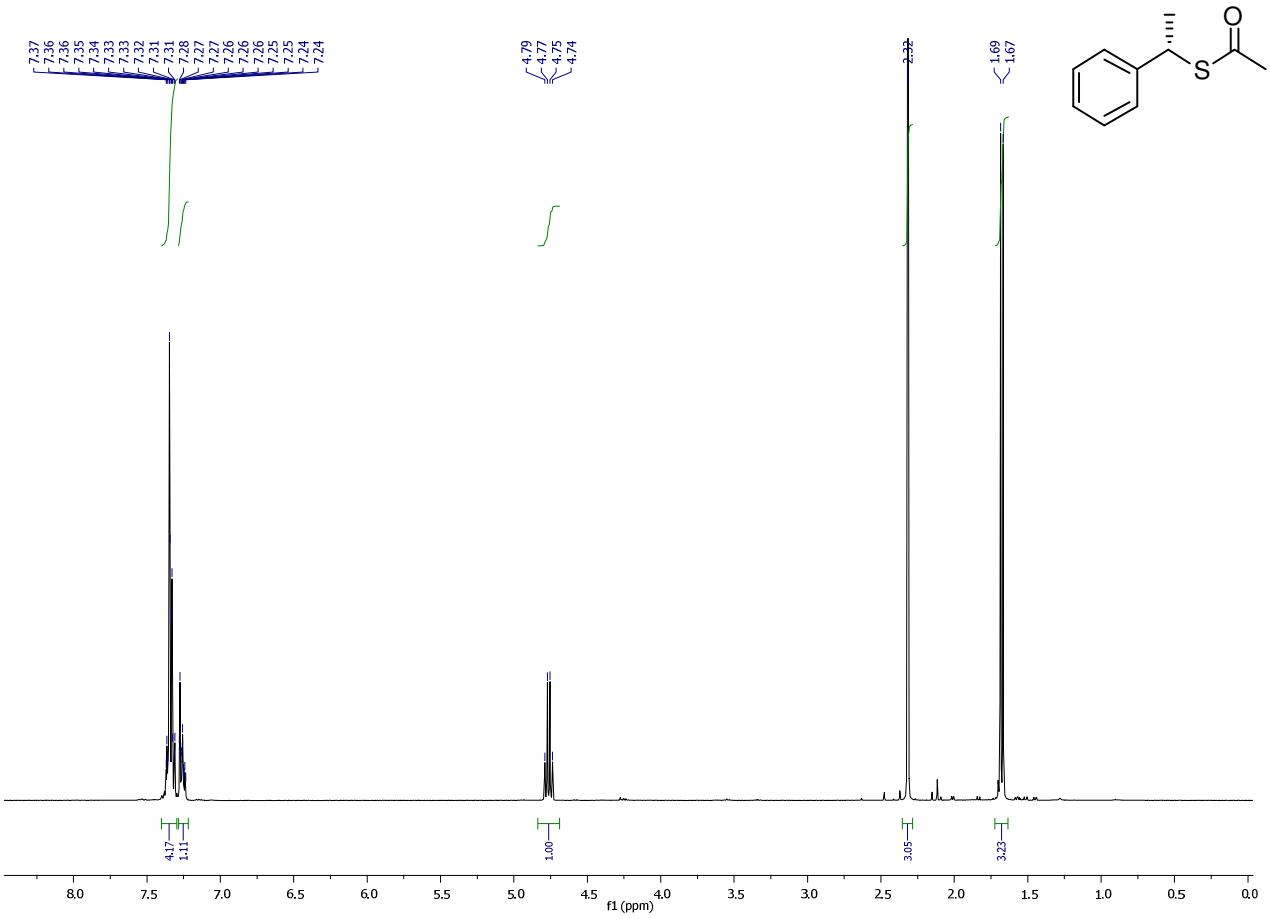


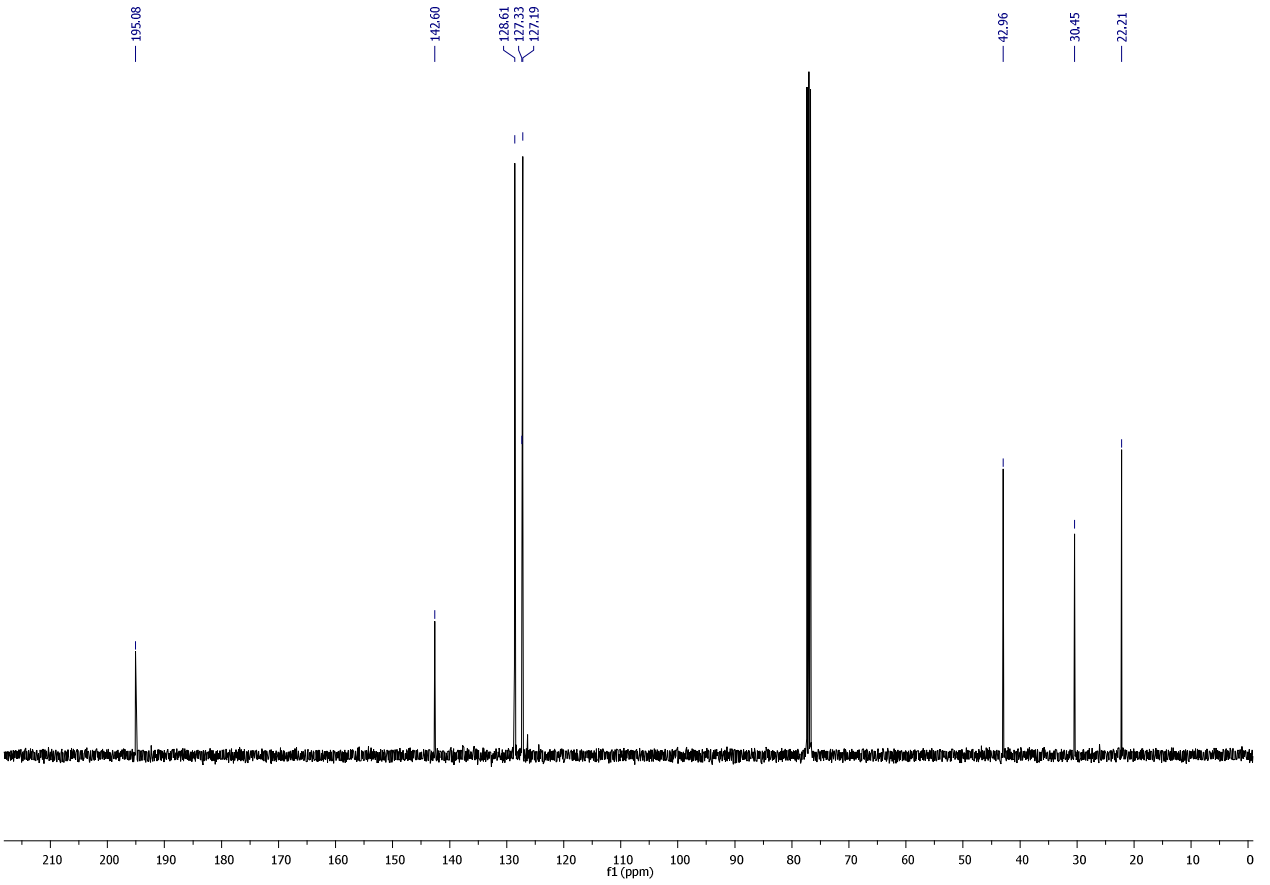
s2: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



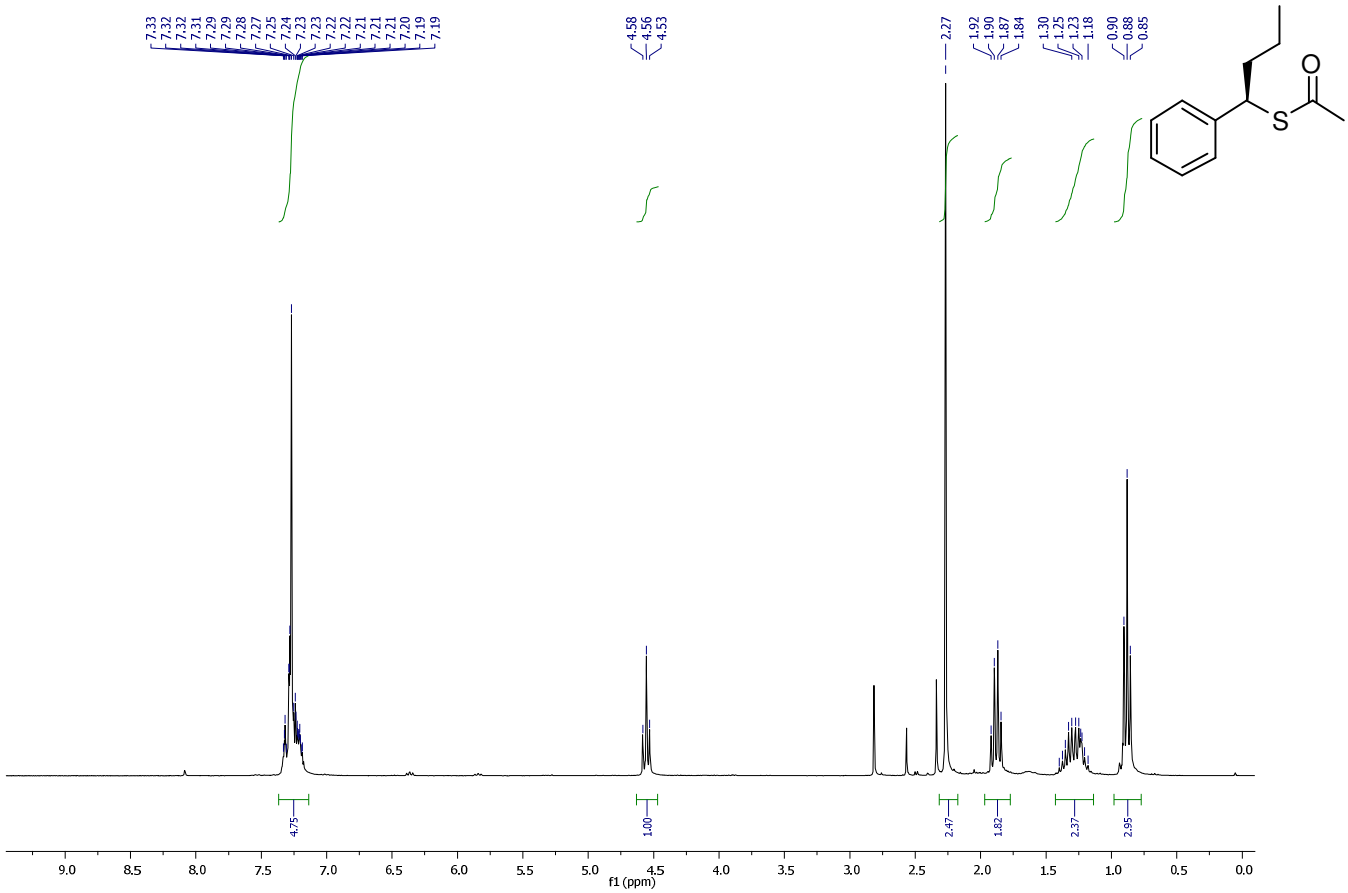


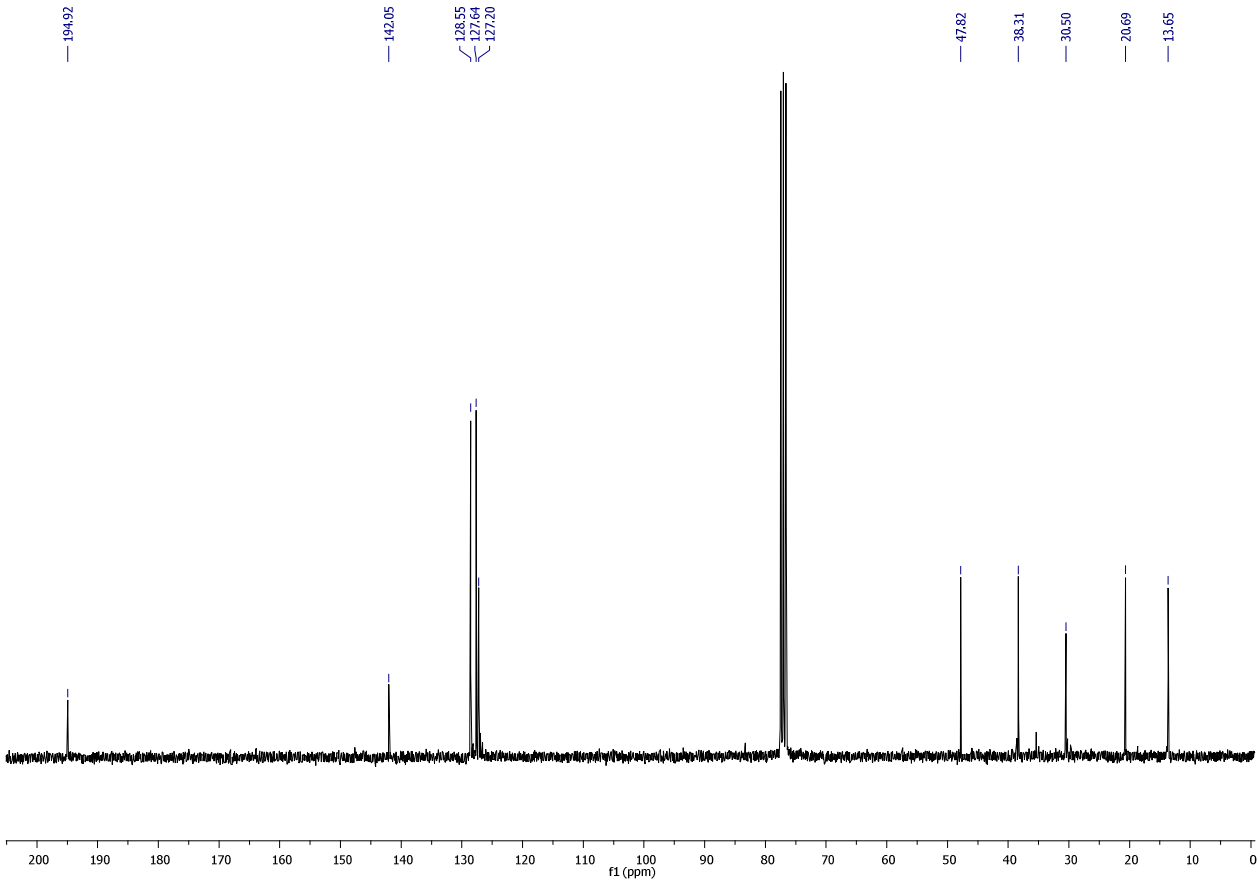
s3: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



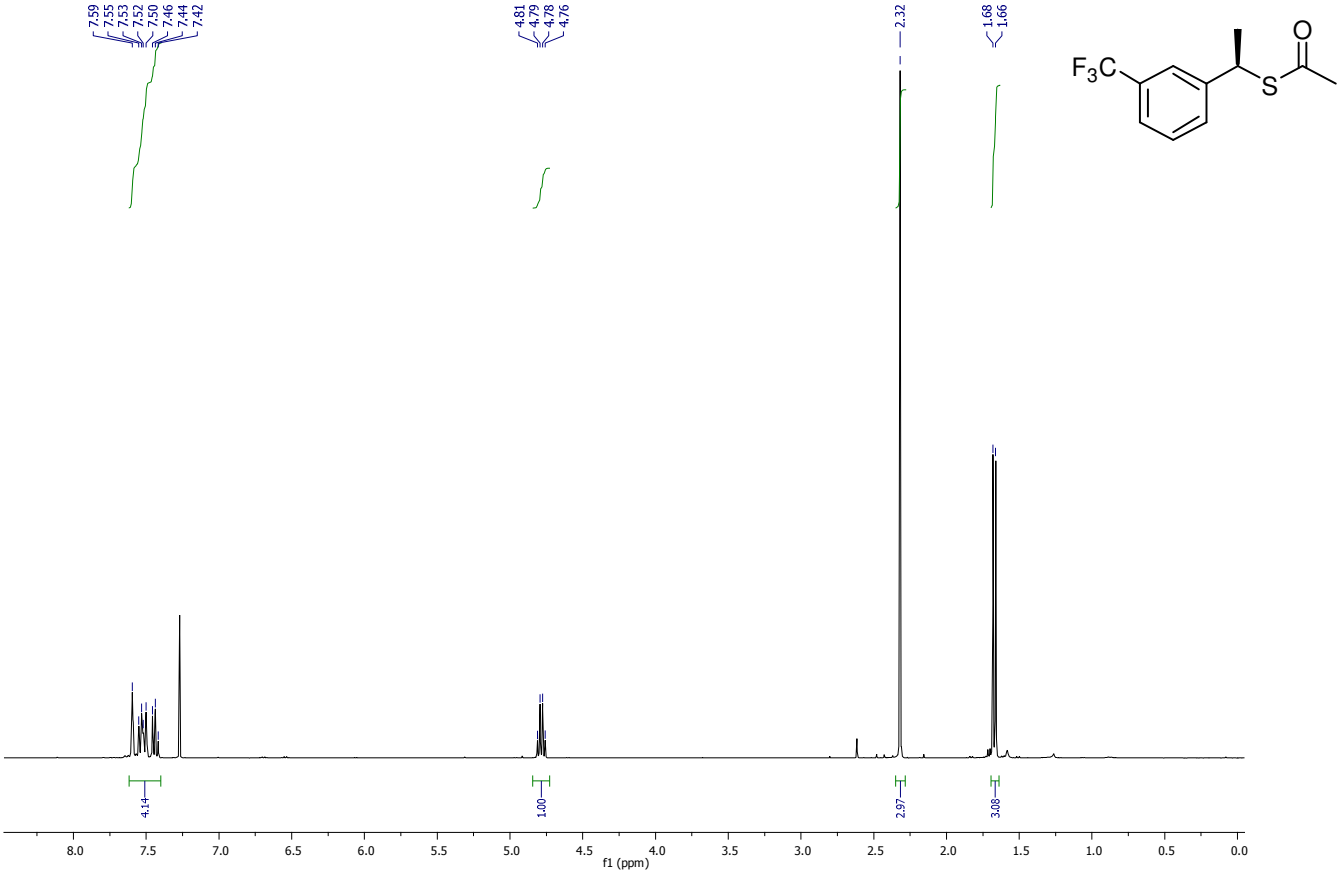


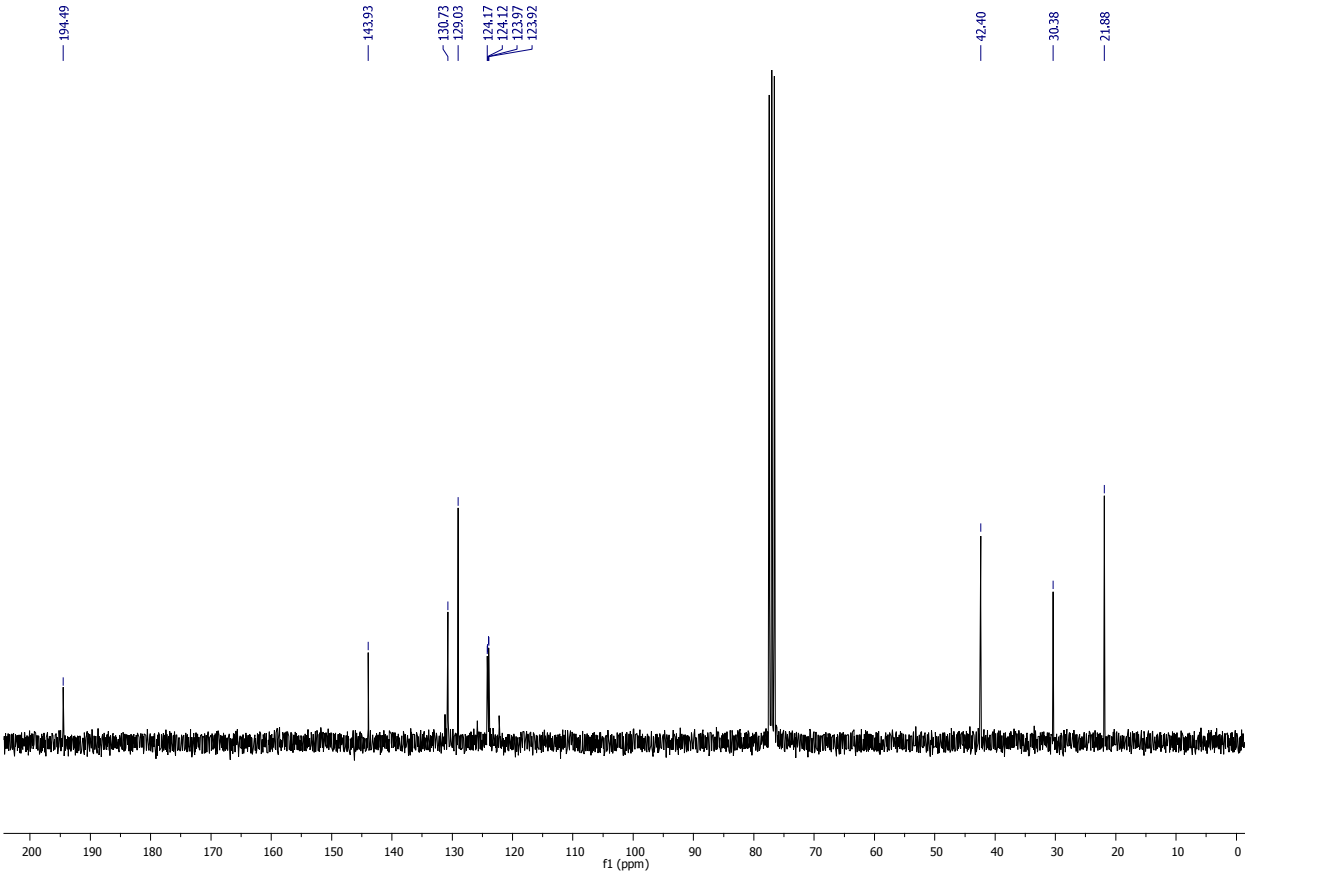
s4: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



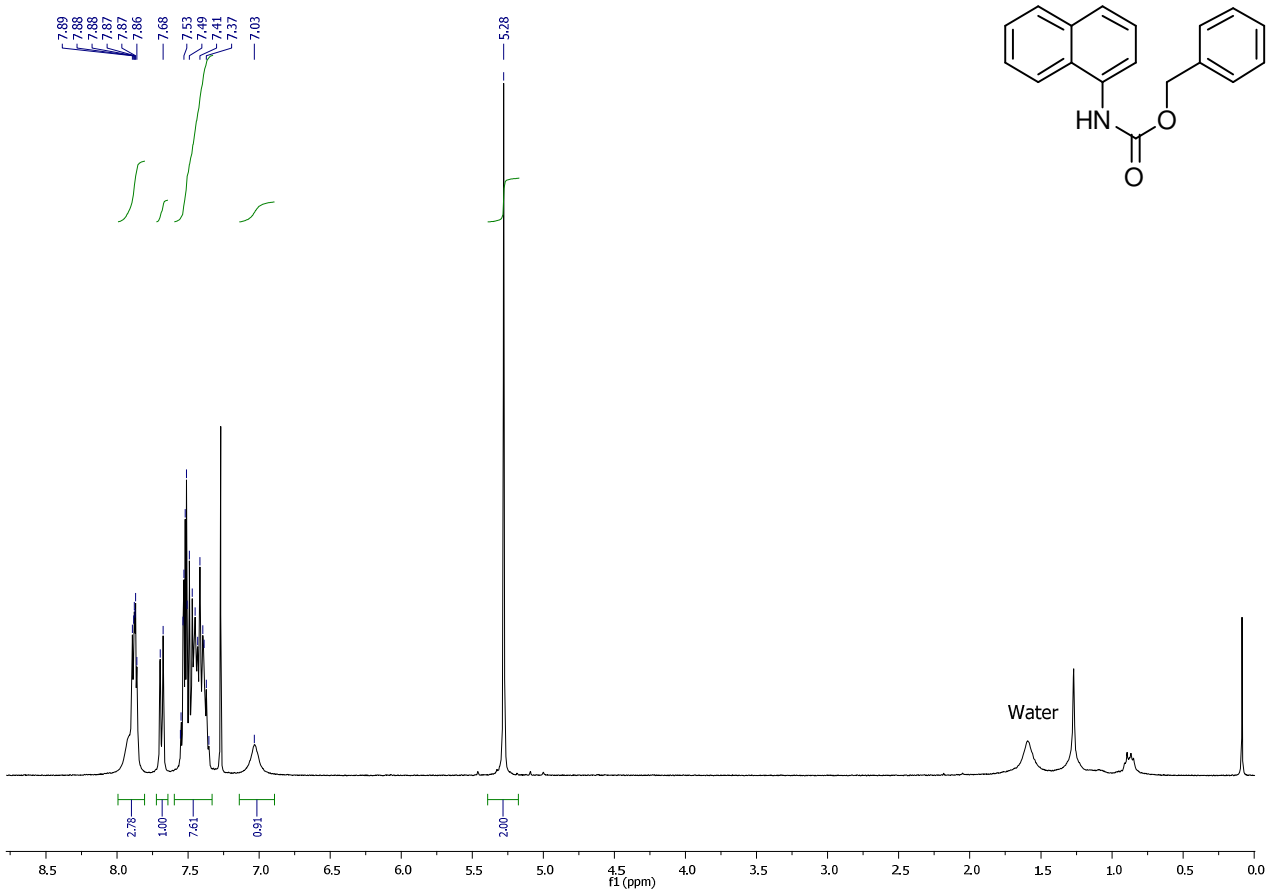


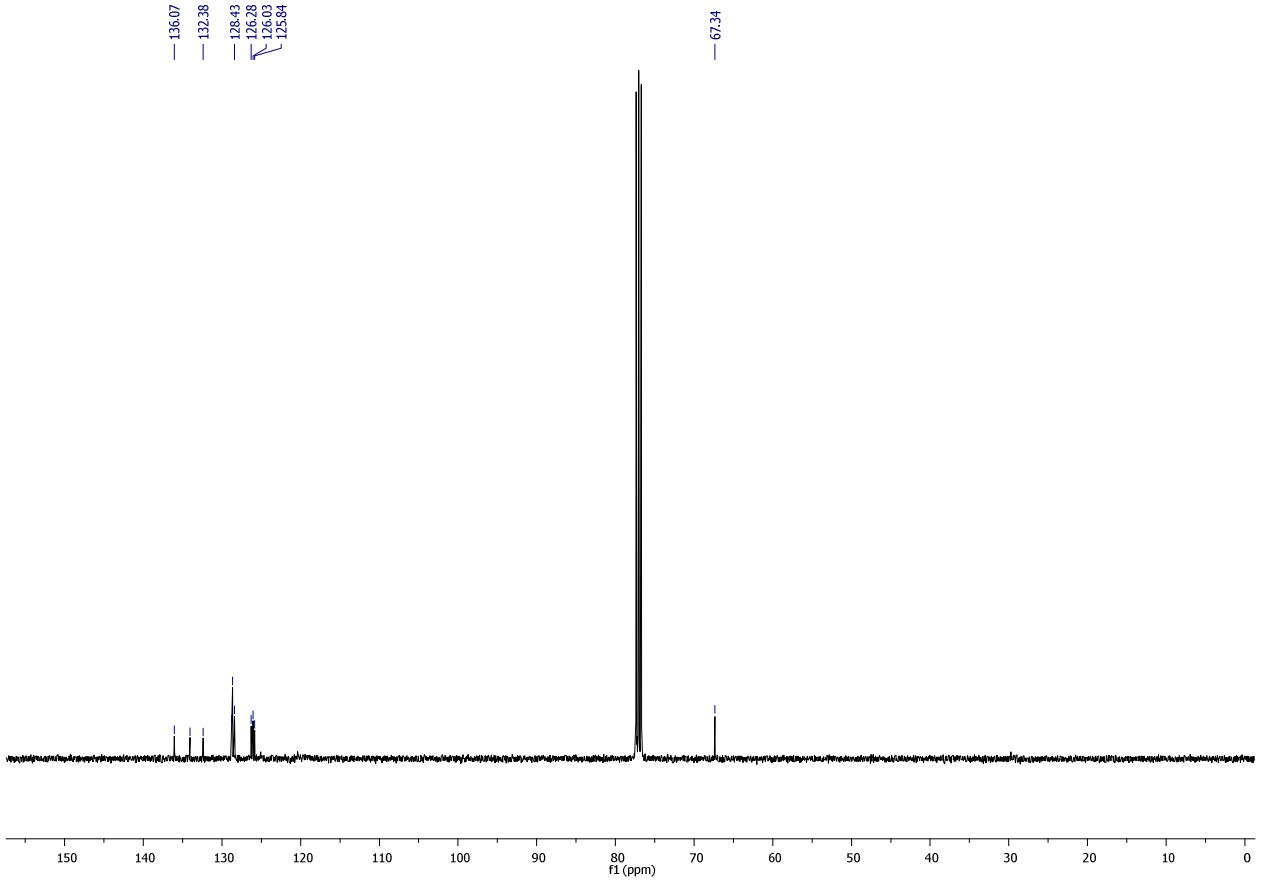
s5: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



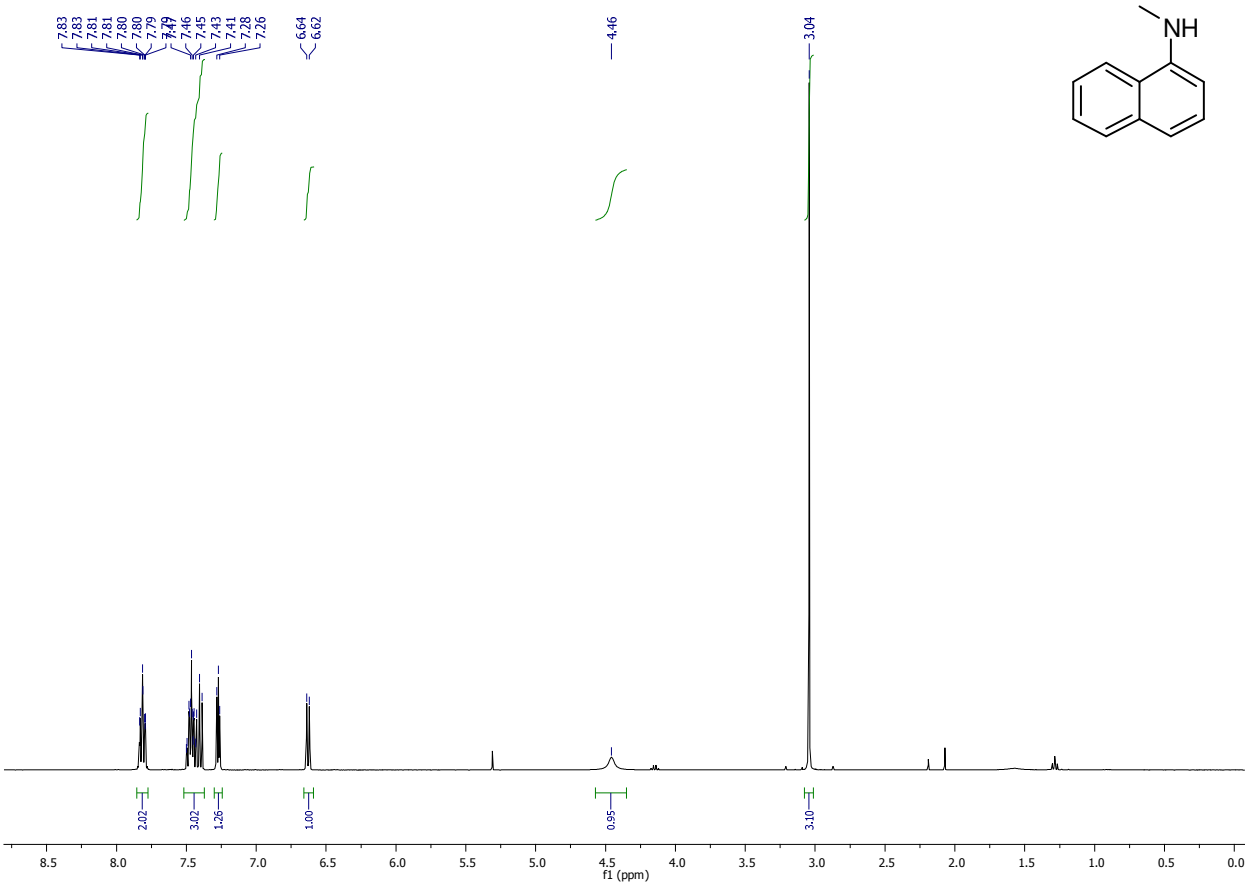


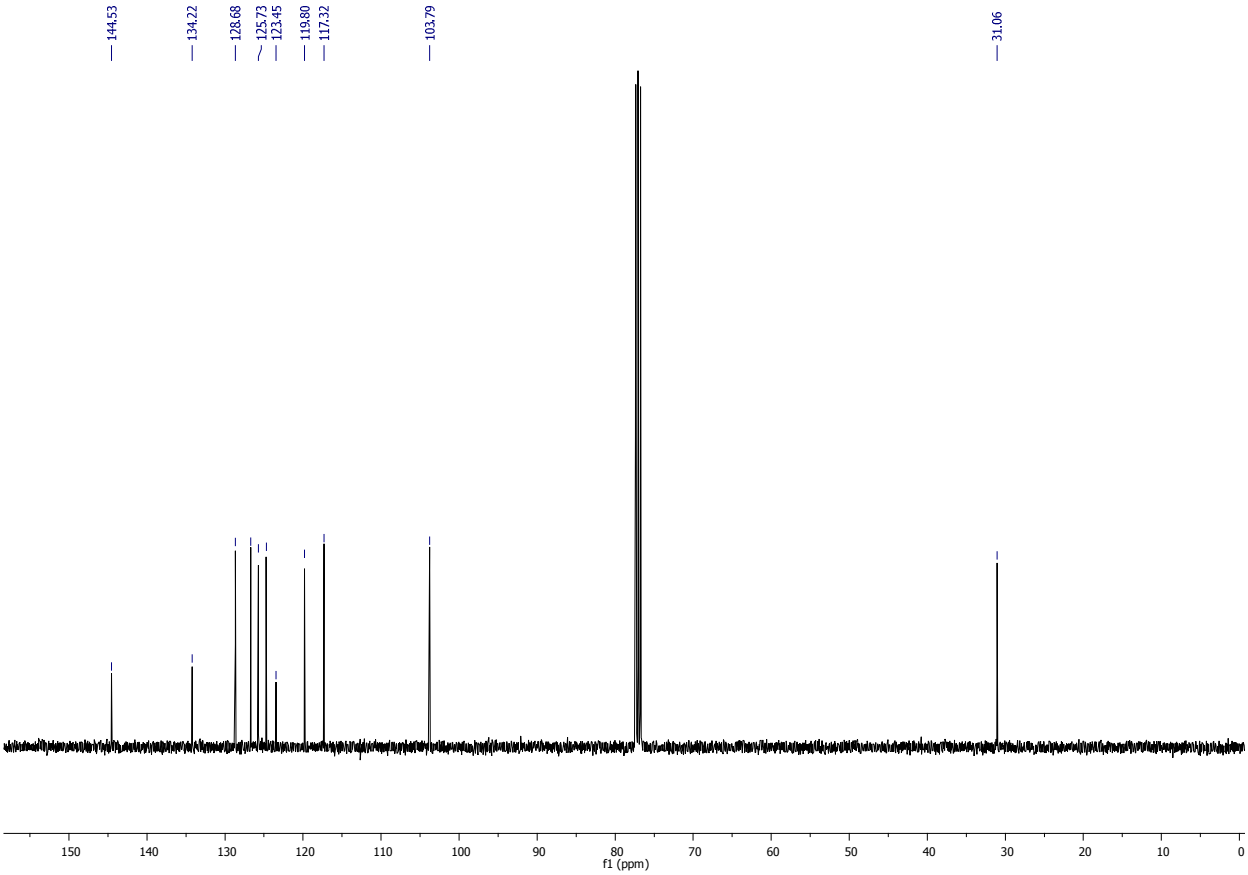
s6: ^{1}H-NMR: 300 MHz, **^{13}C-NMR**: 100 MHz



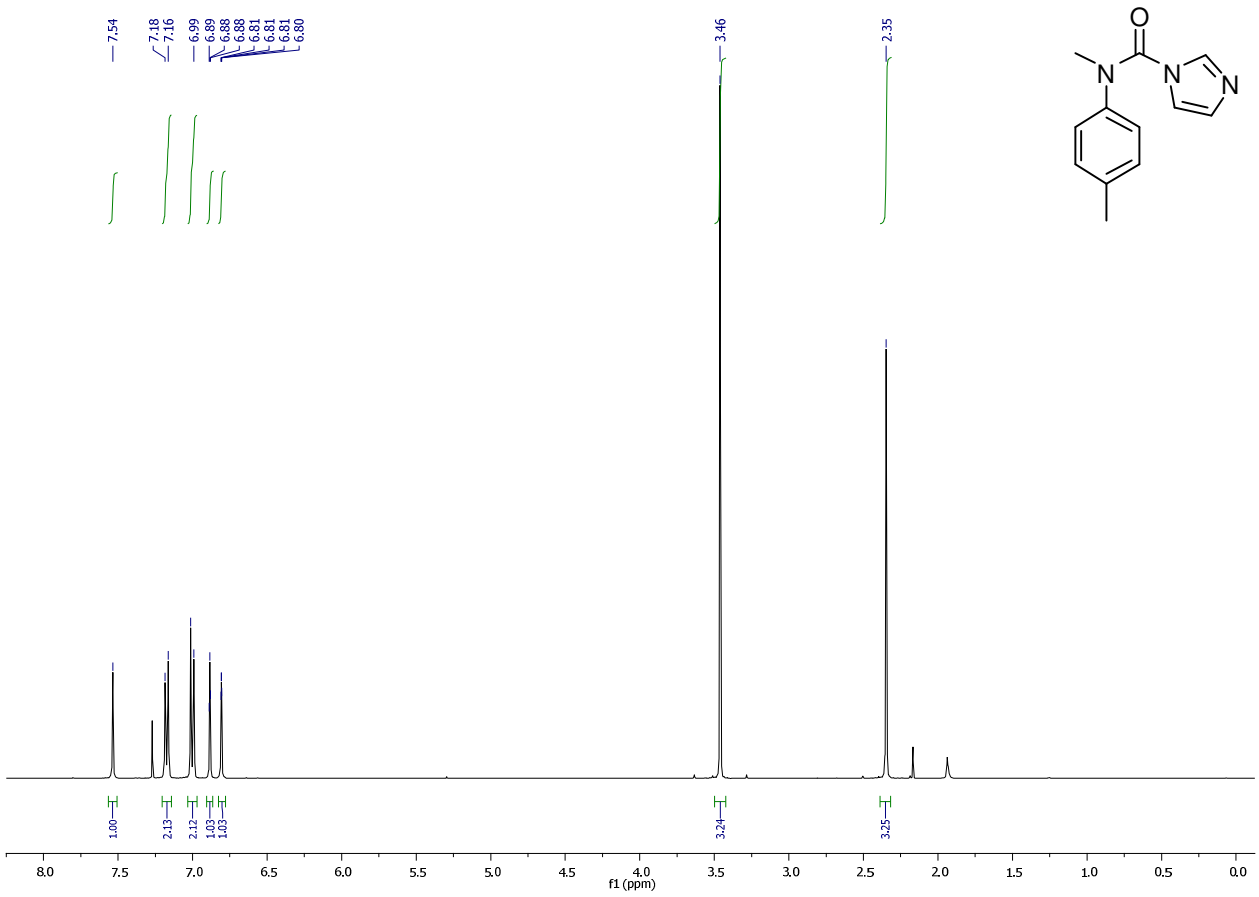


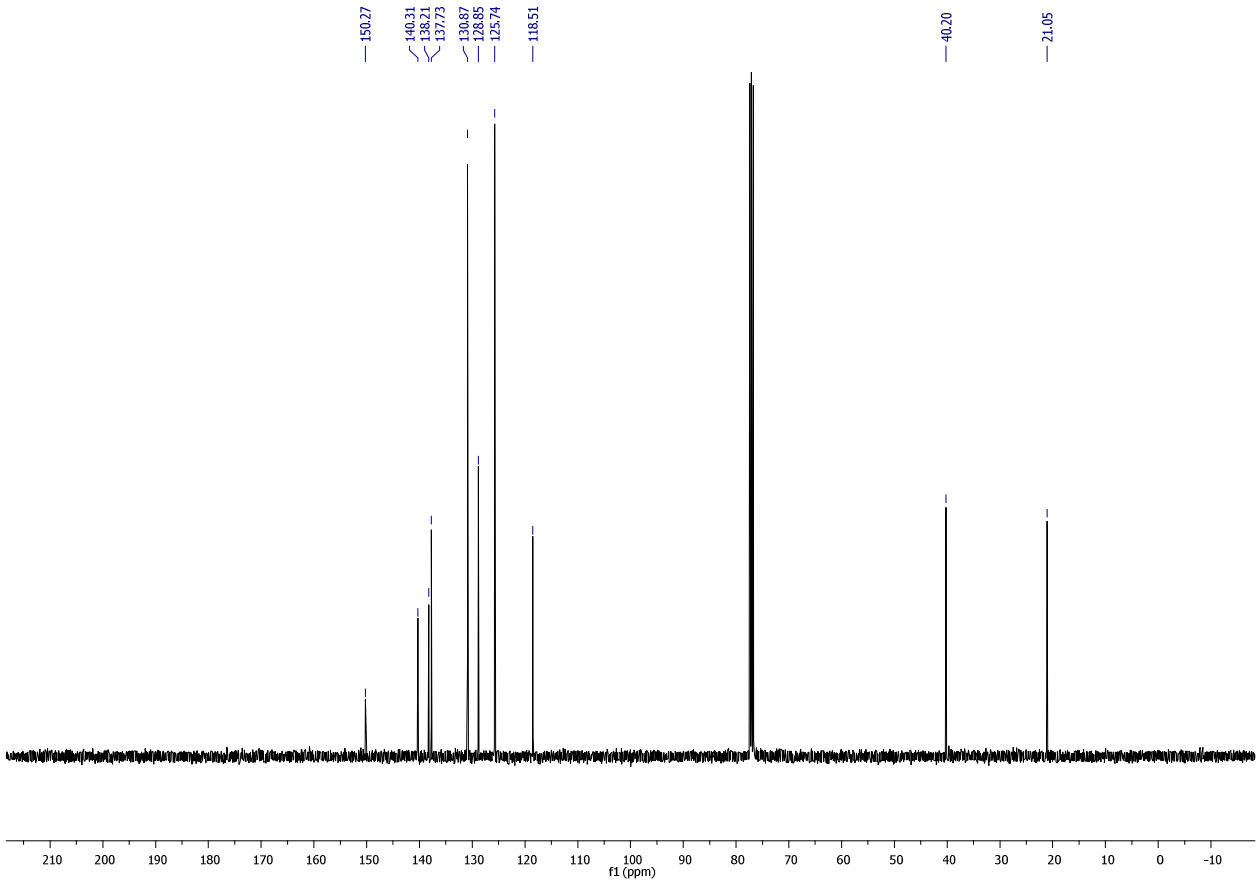
s7: ^{1}H-NMR: 300 MHz, **^{13}C-NMR**: 75 MHz



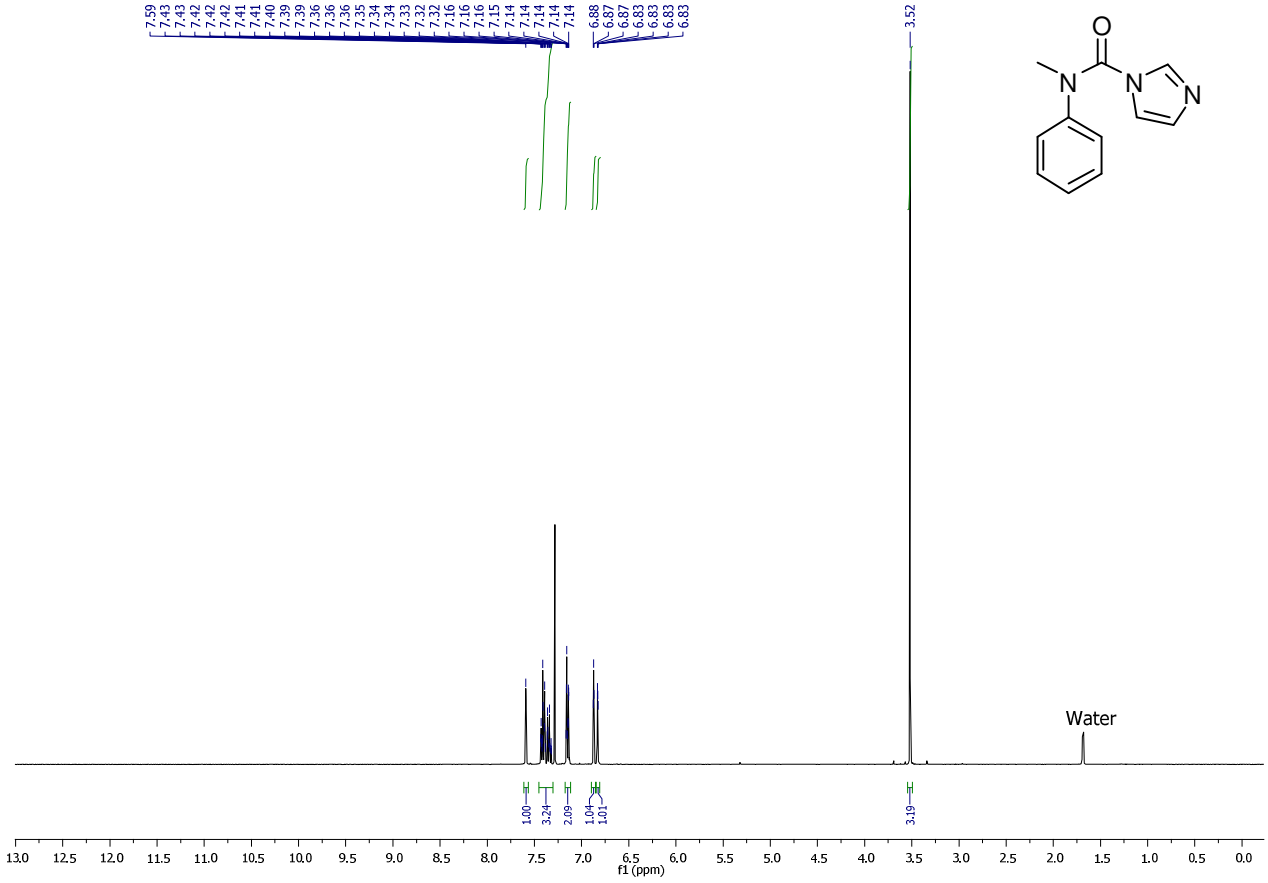


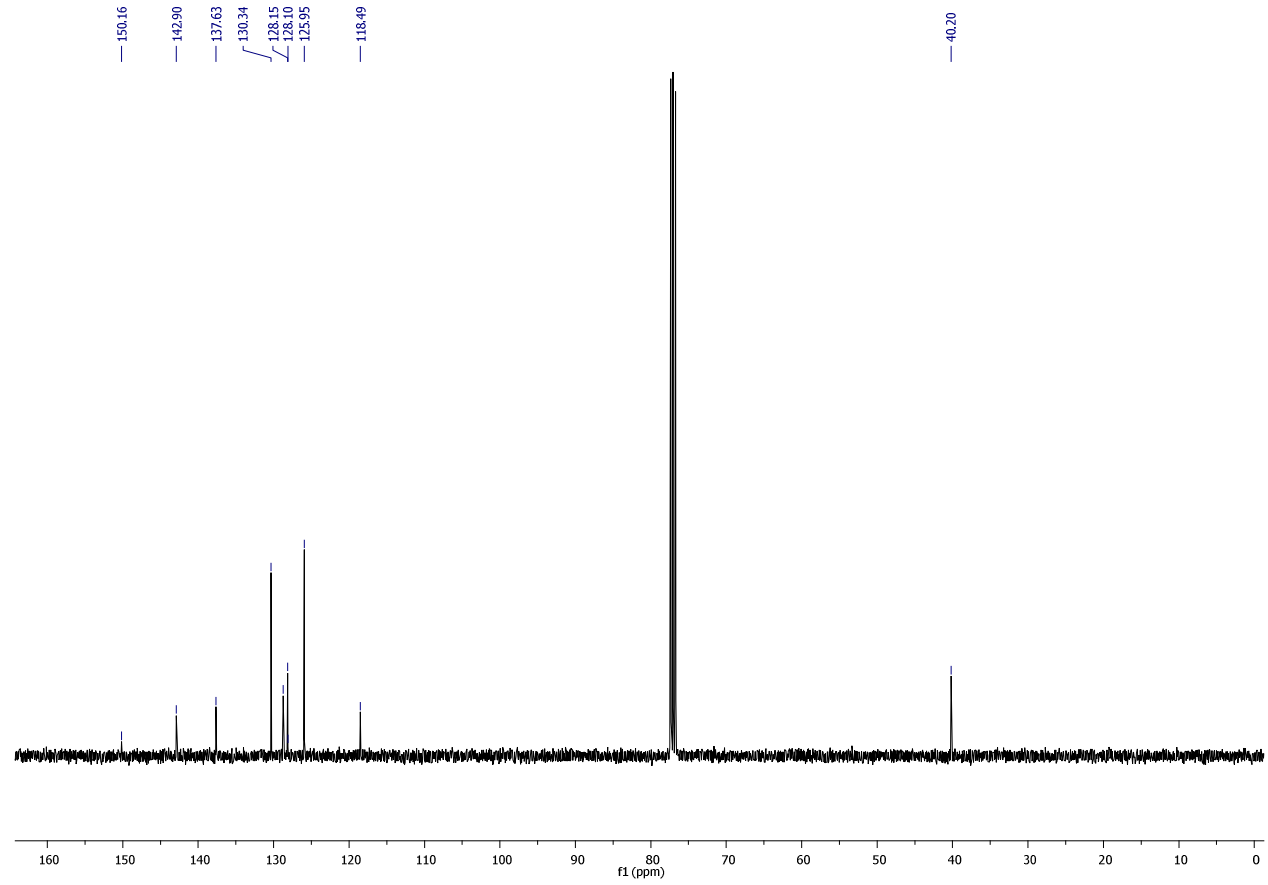
s8: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



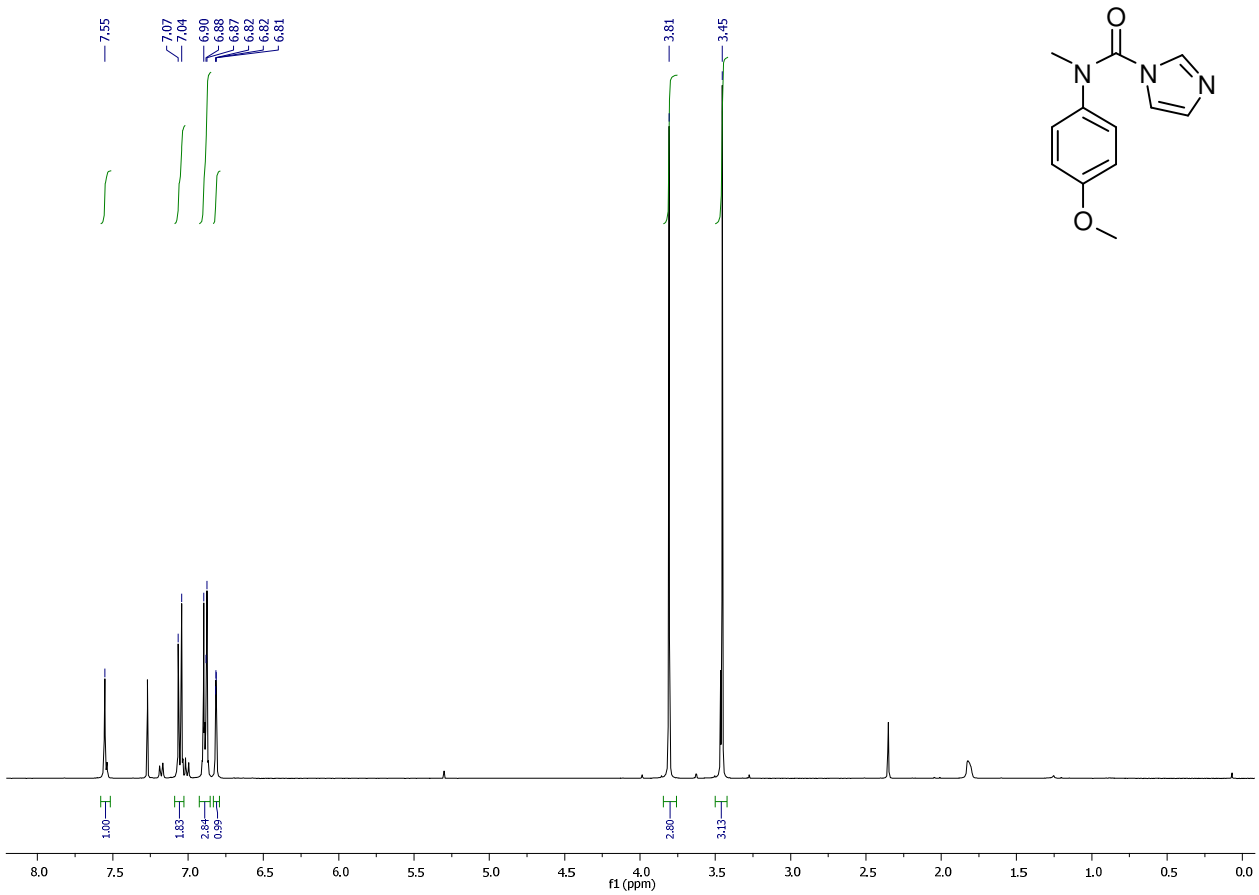


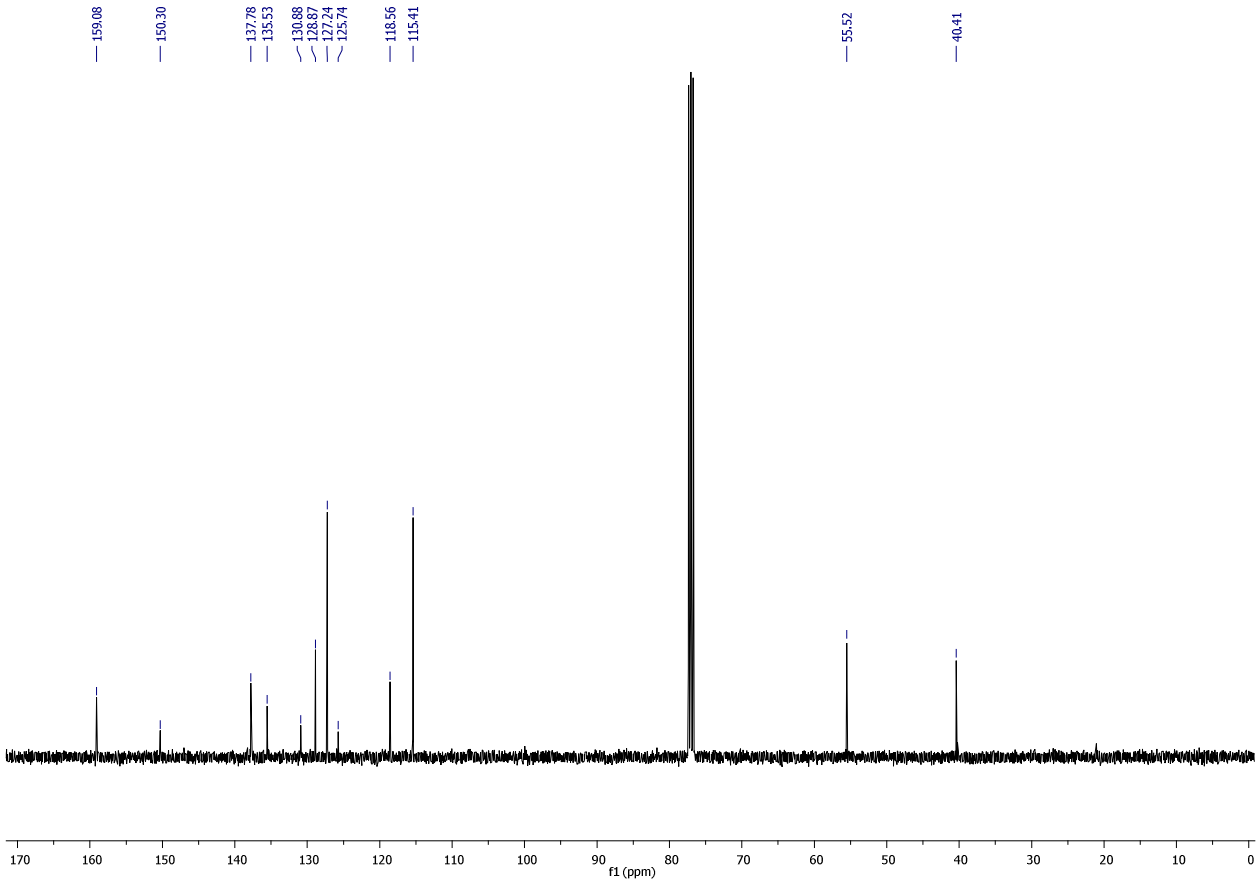
s9: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



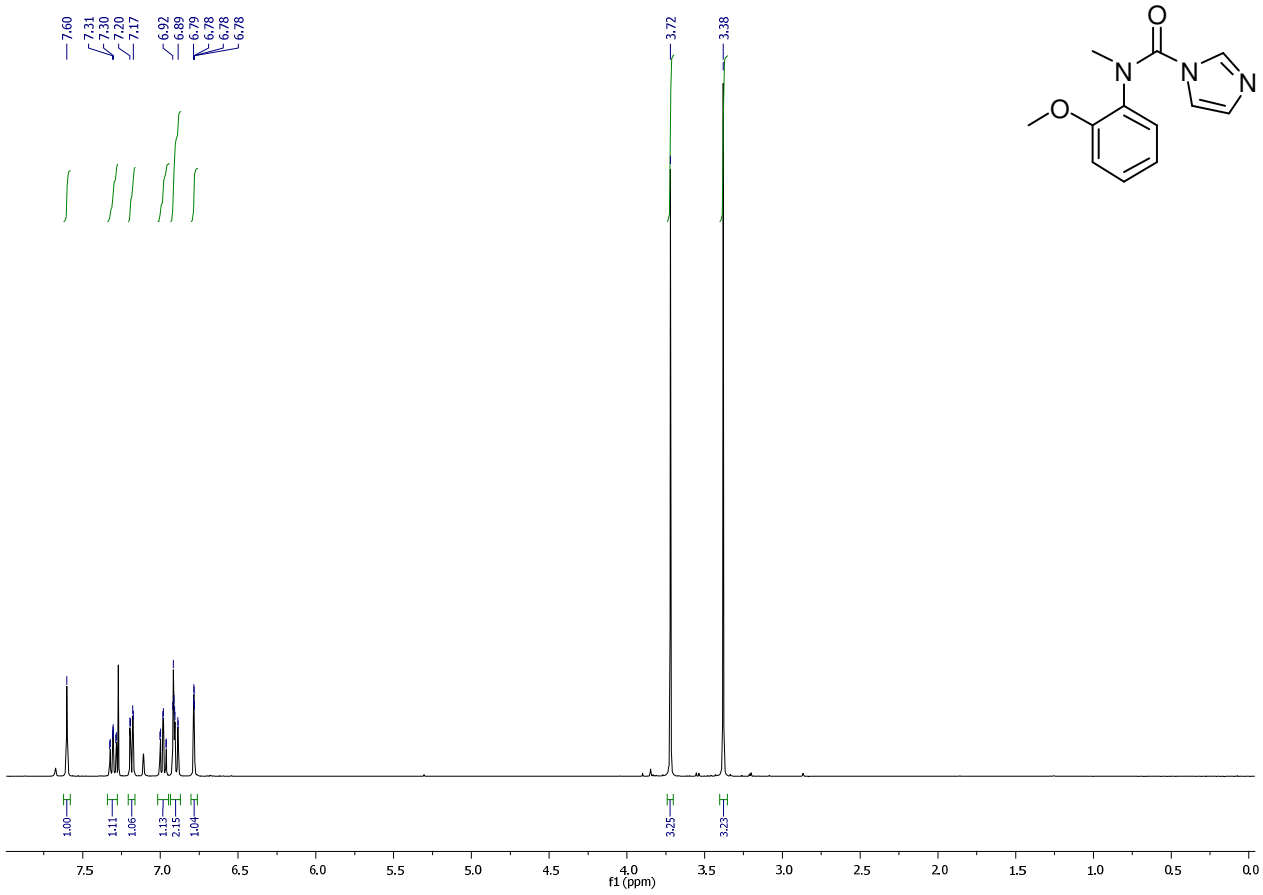


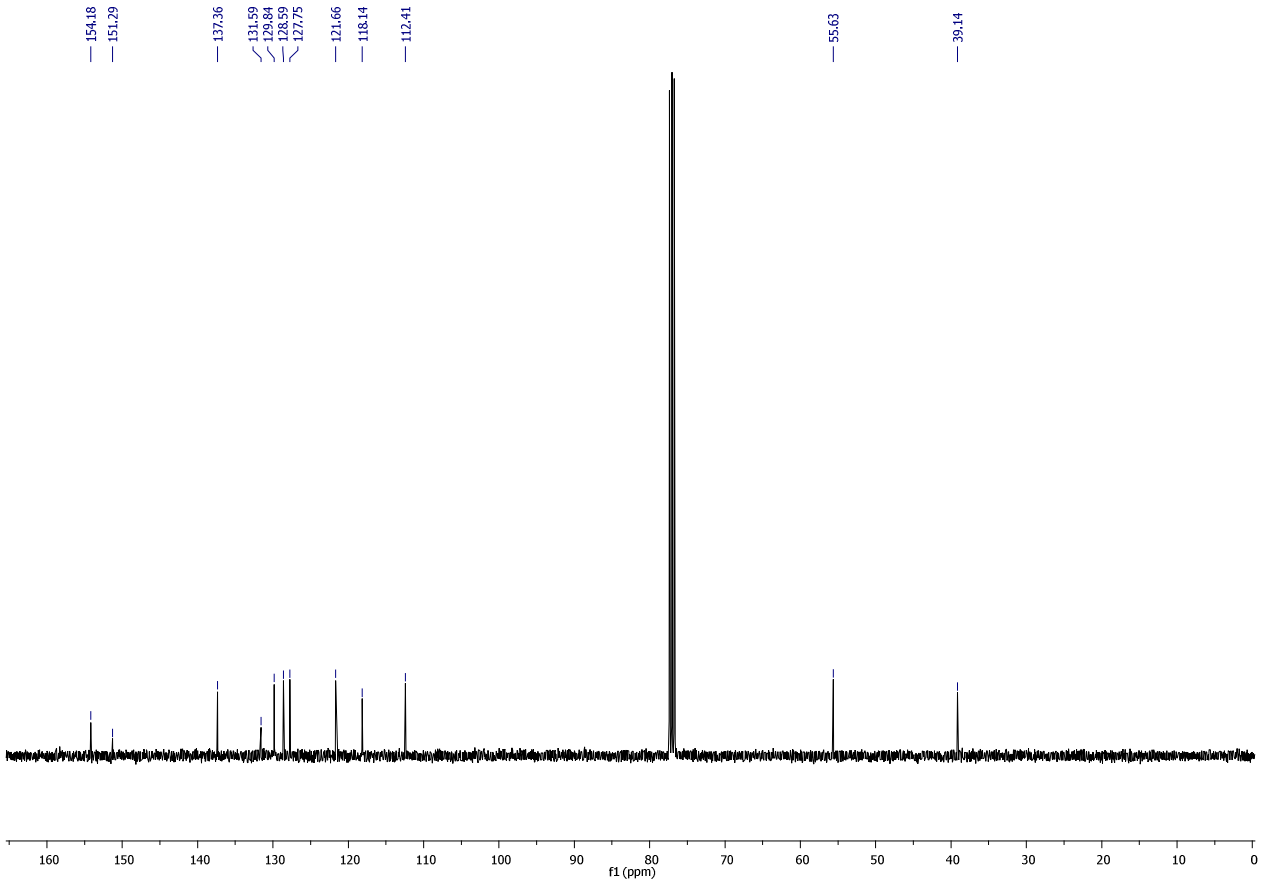
s10: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



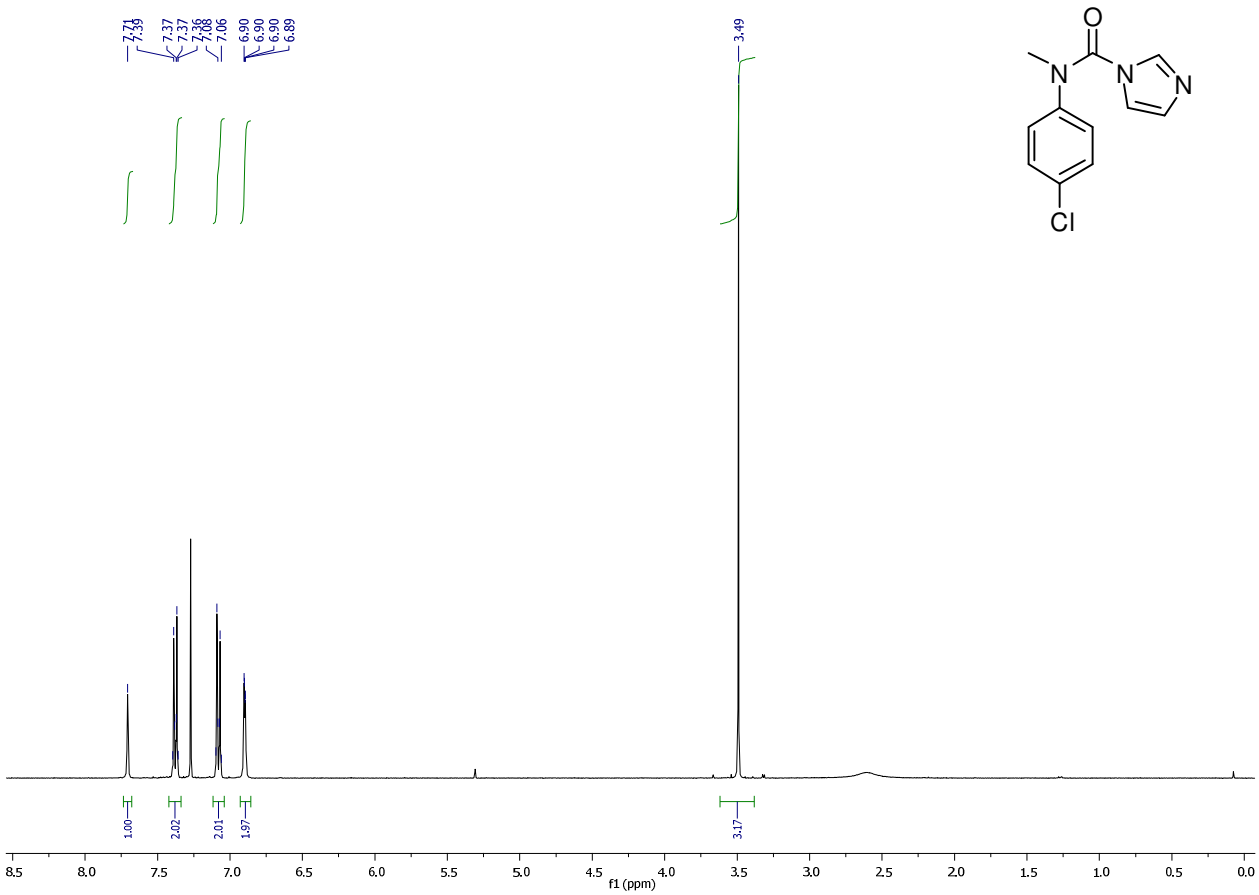


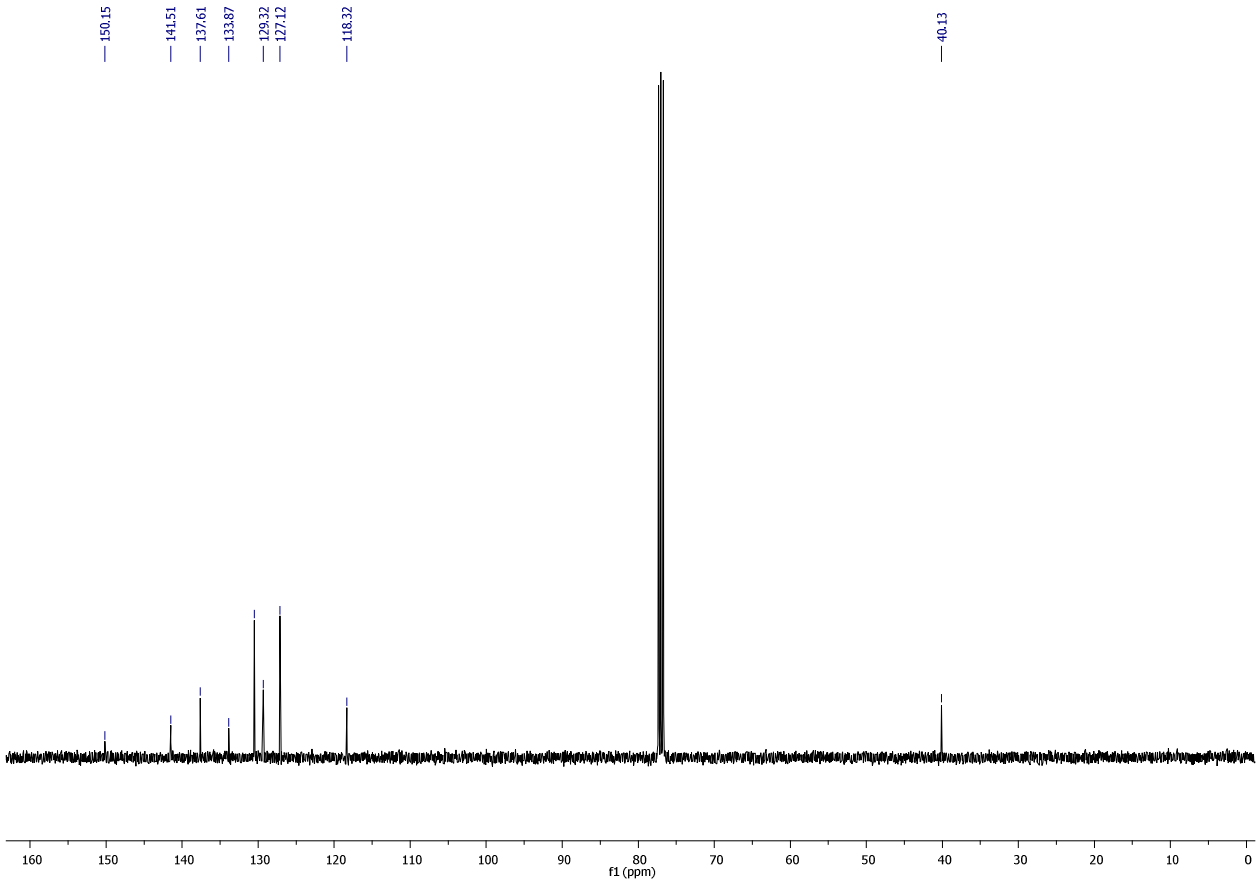
s11: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



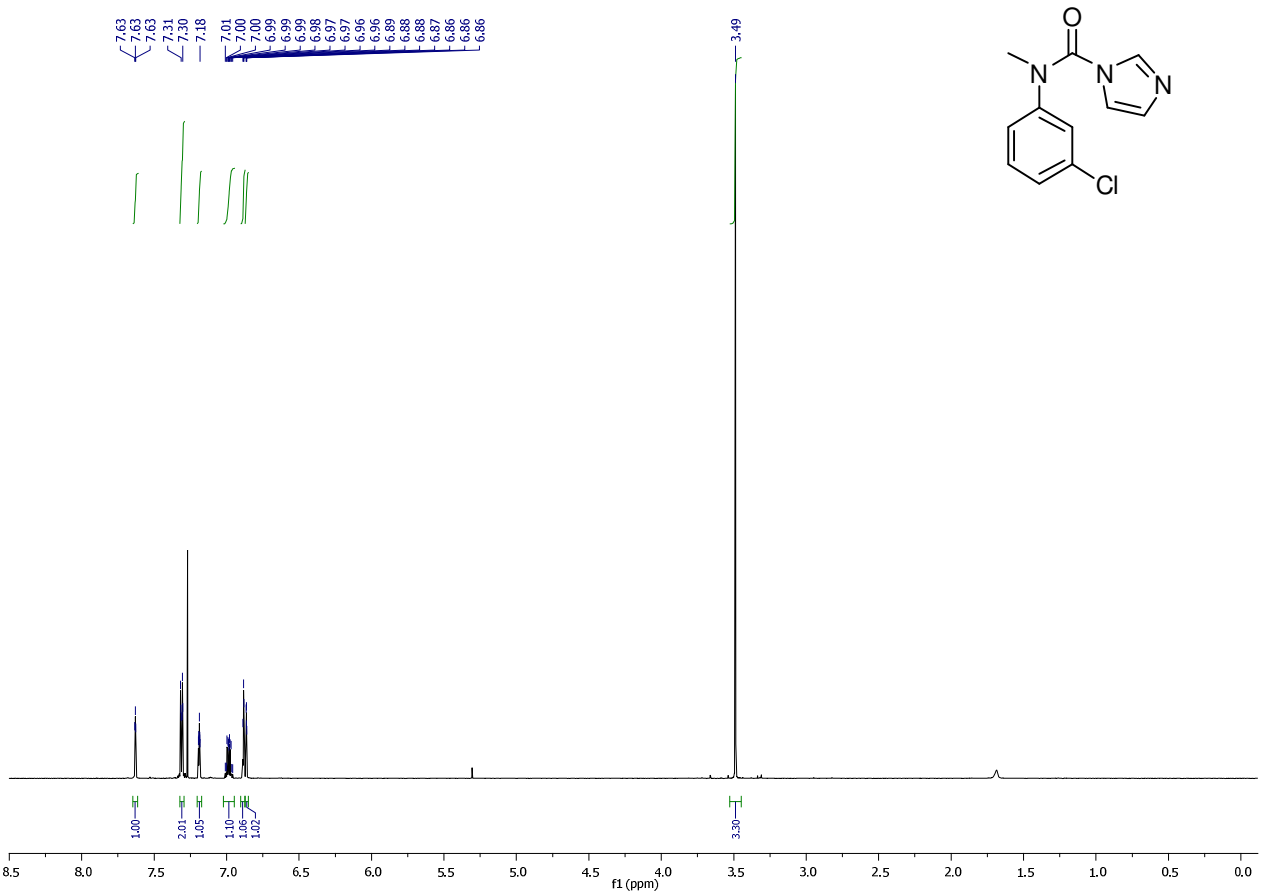


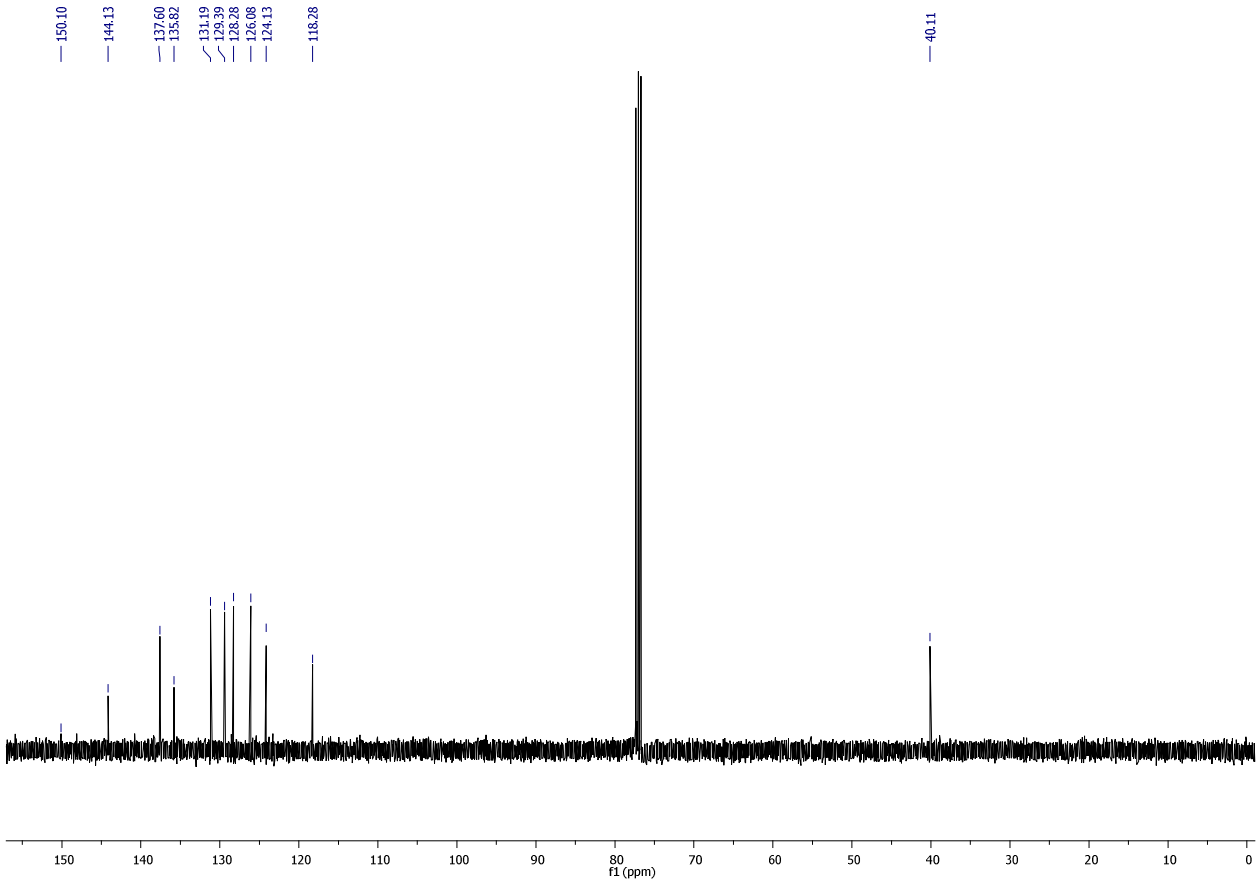
s12: ^{1}H-NMR: 300 MHz, **^{13}C-NMR**: 100 MHz



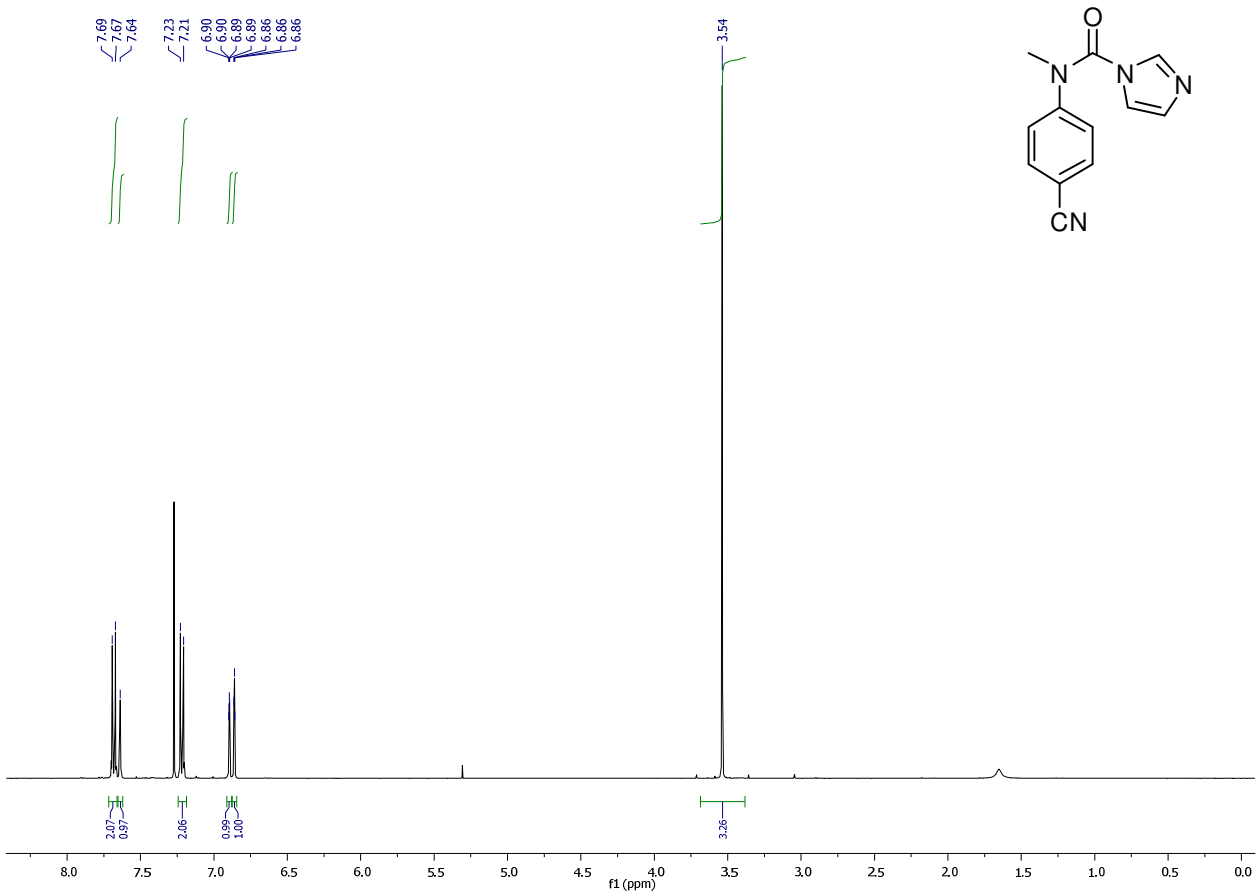


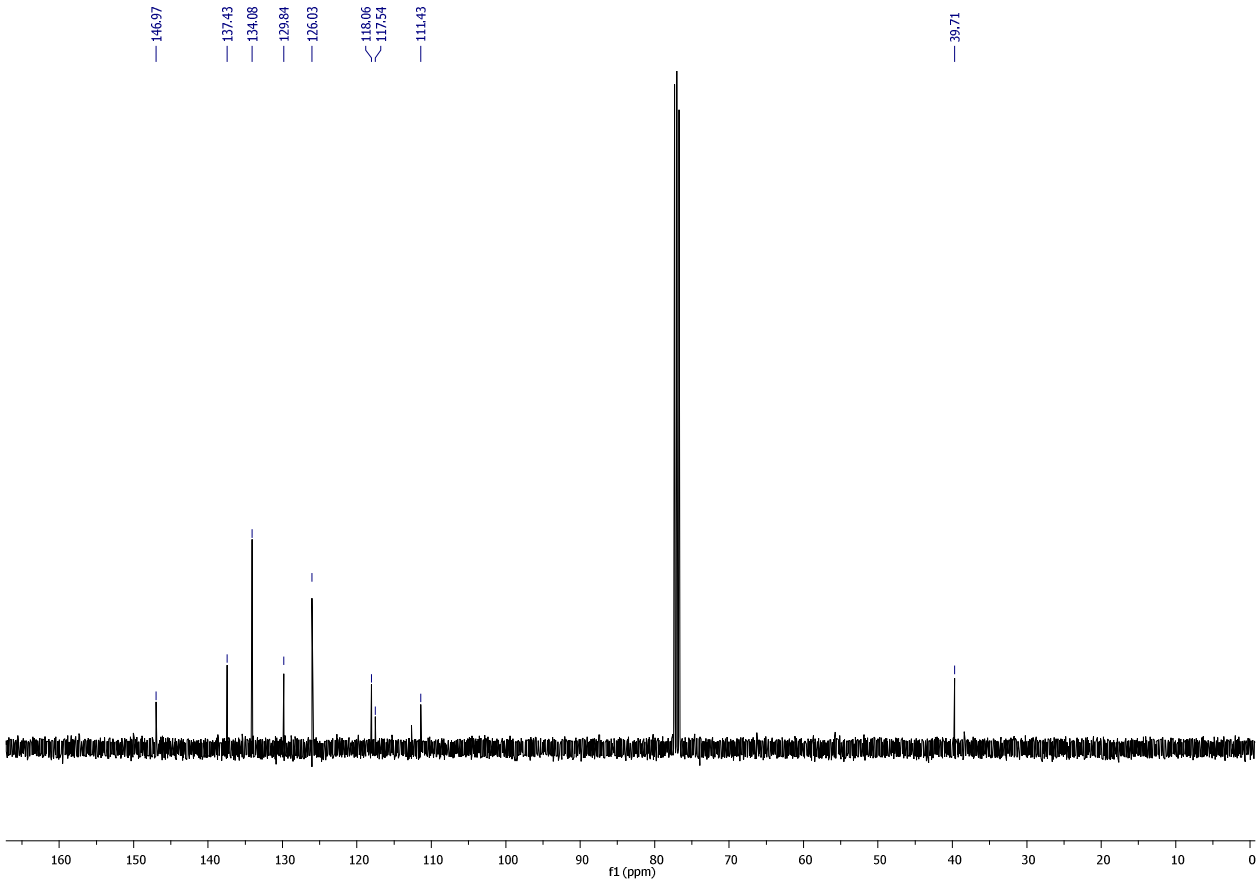
s13: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



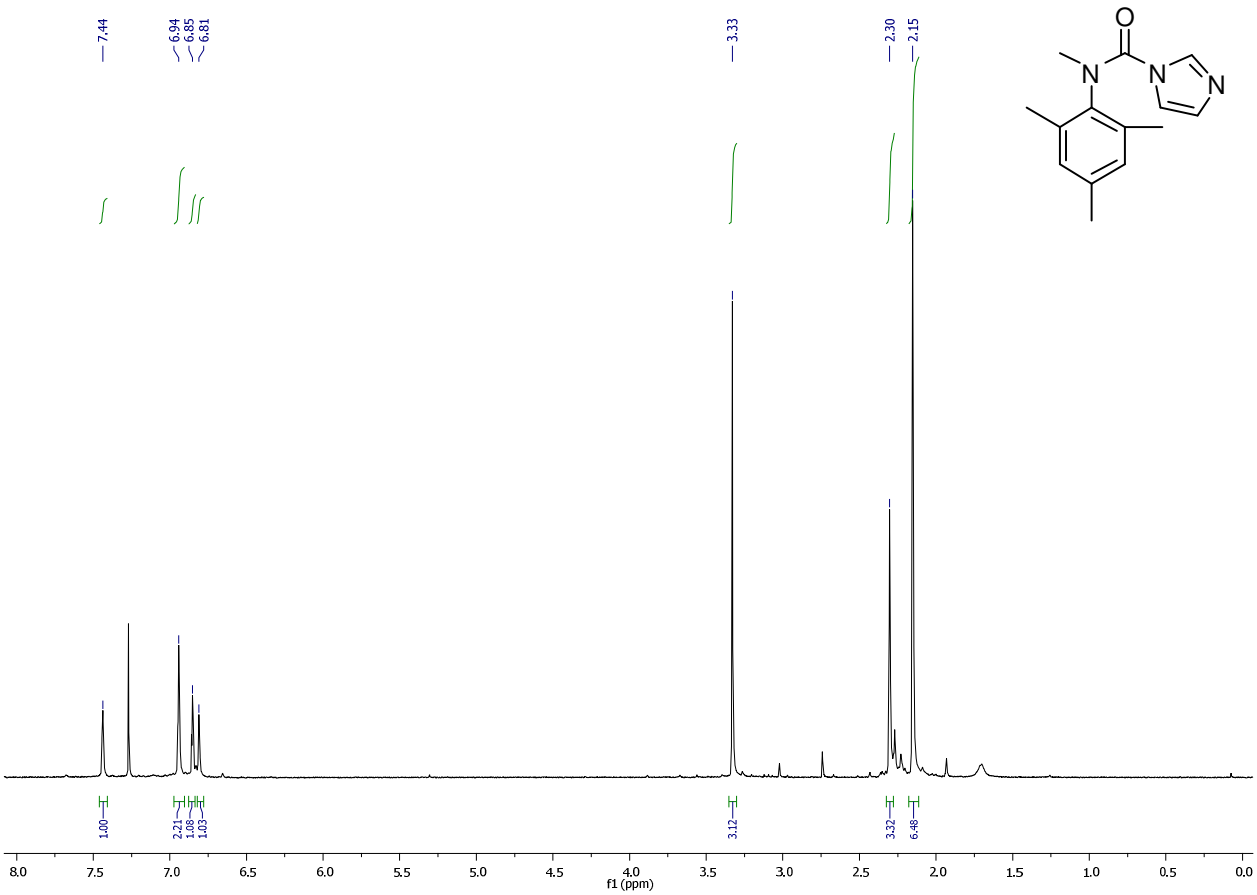


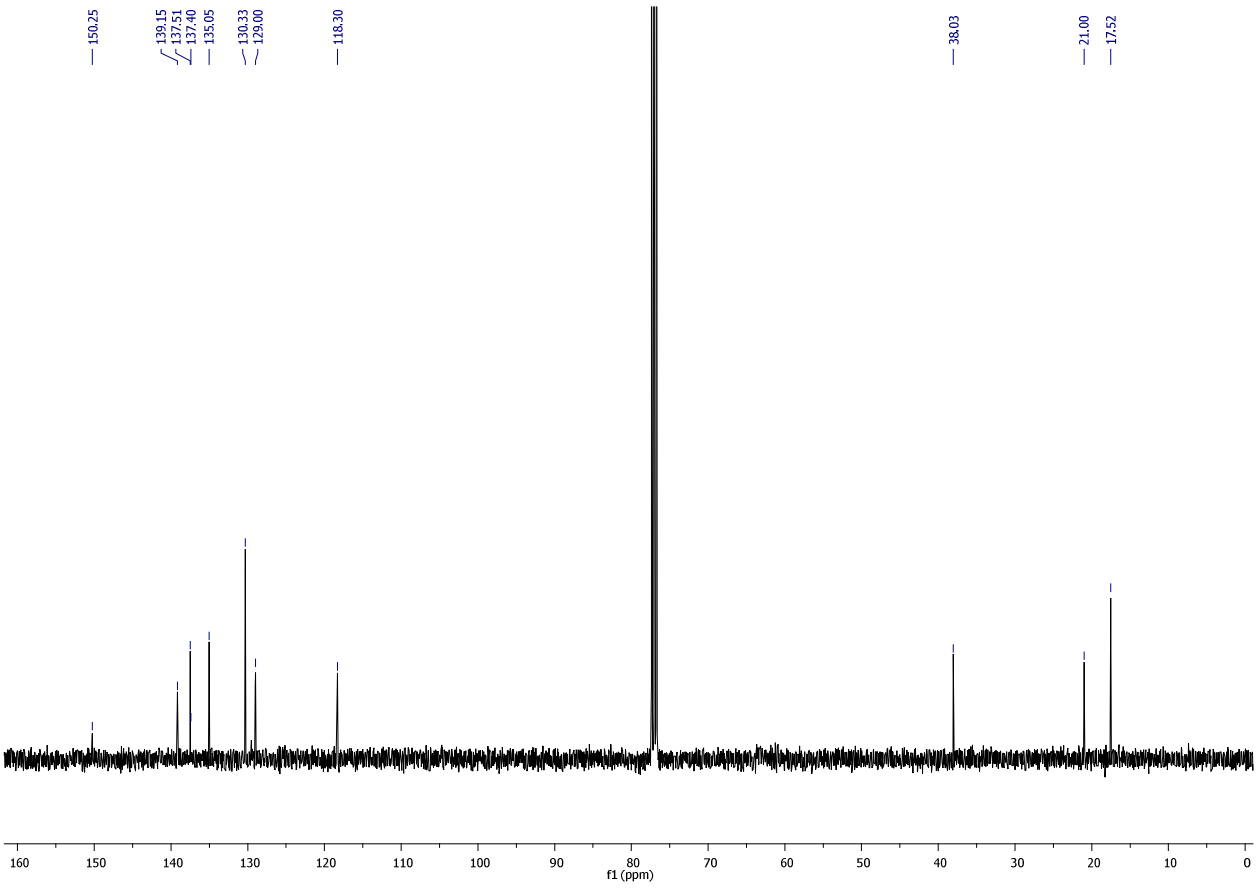
s14: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



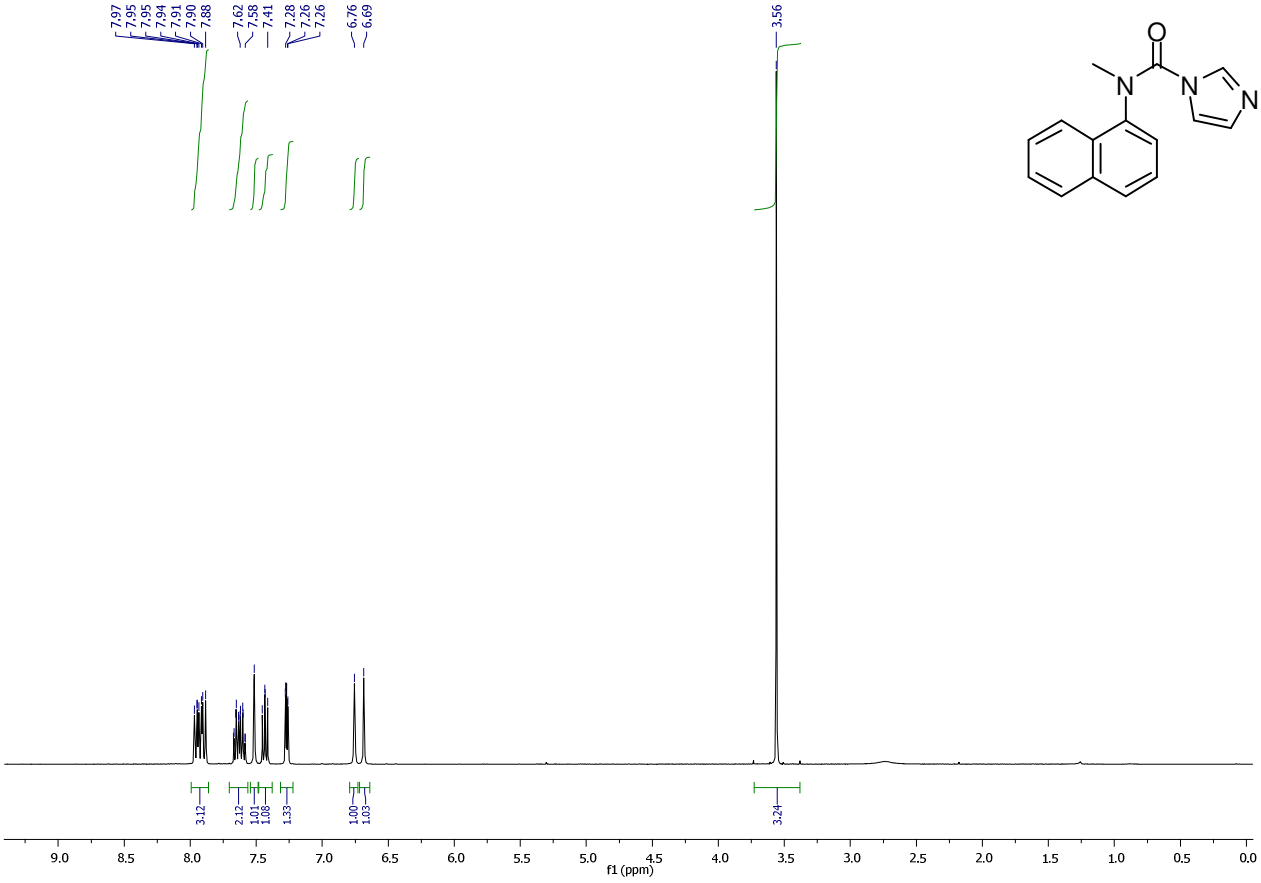


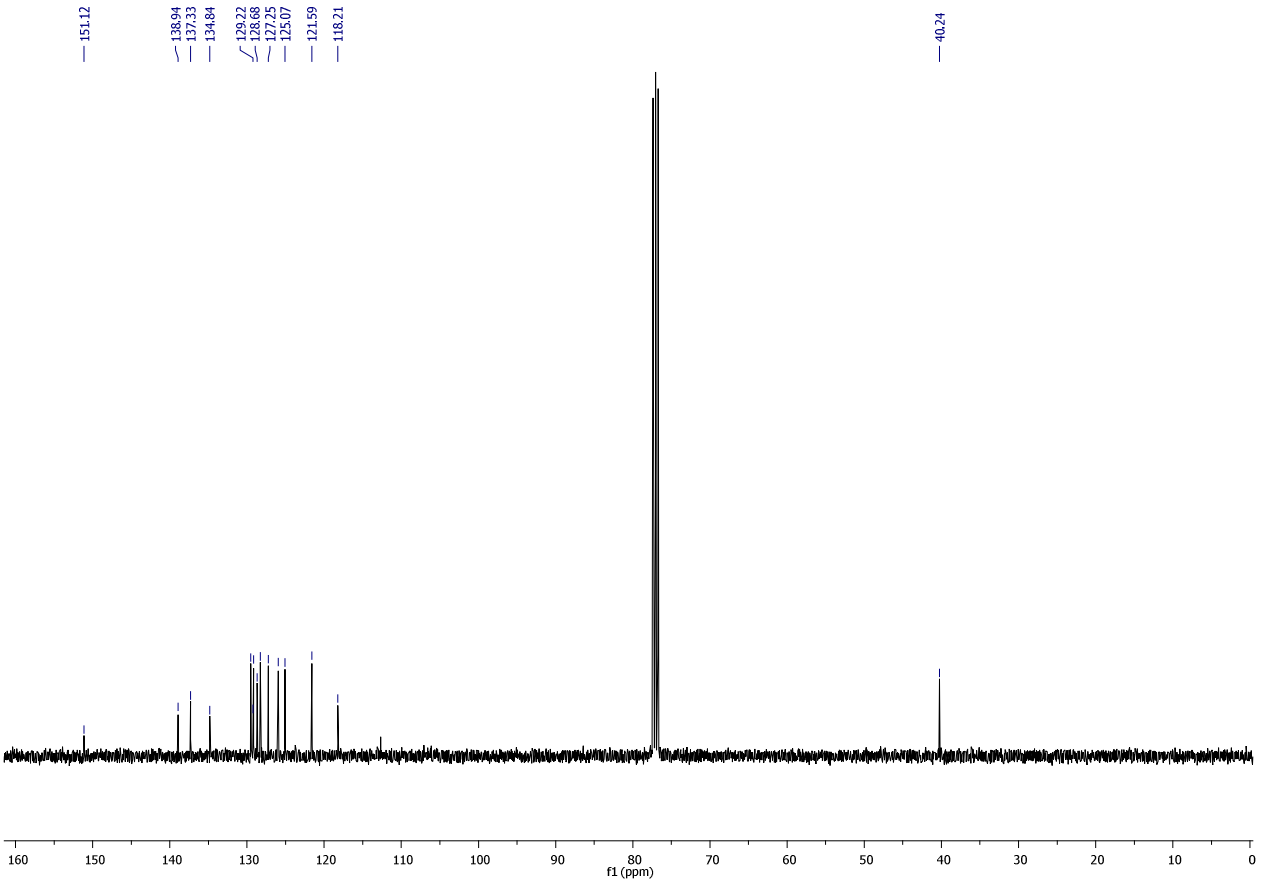
s15: ^{1}H-NMR: 300 MHz, **^{13}C-NMR**: 100 MHz



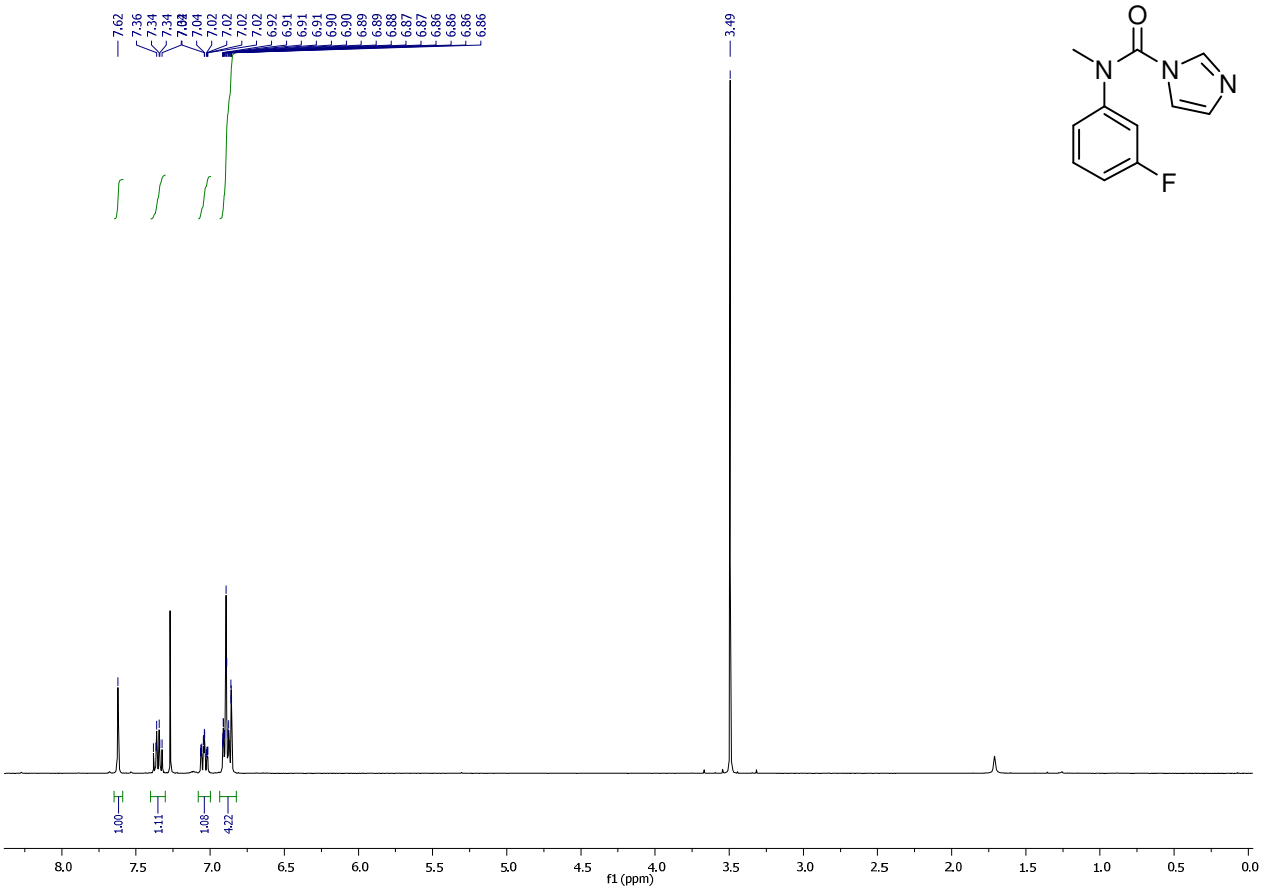


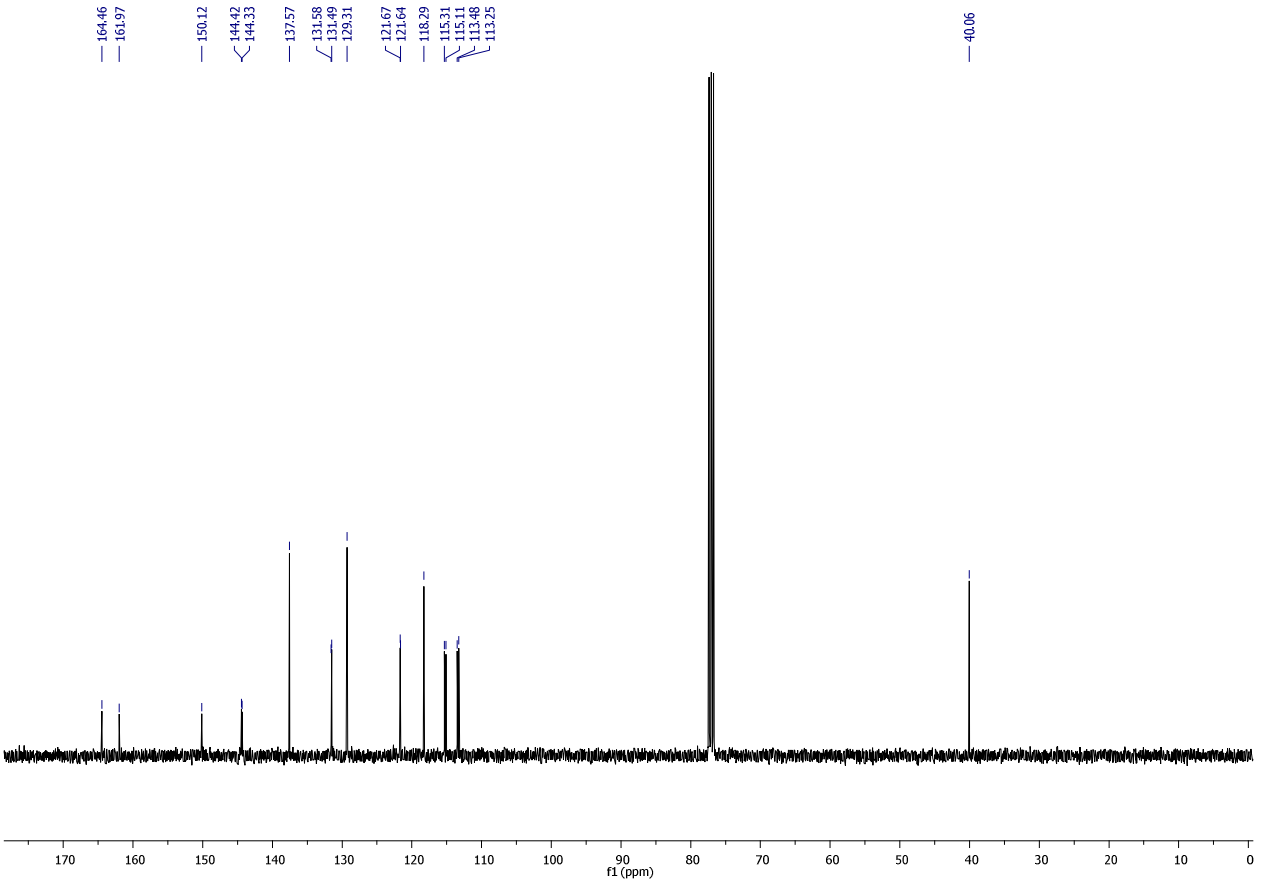
s16: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



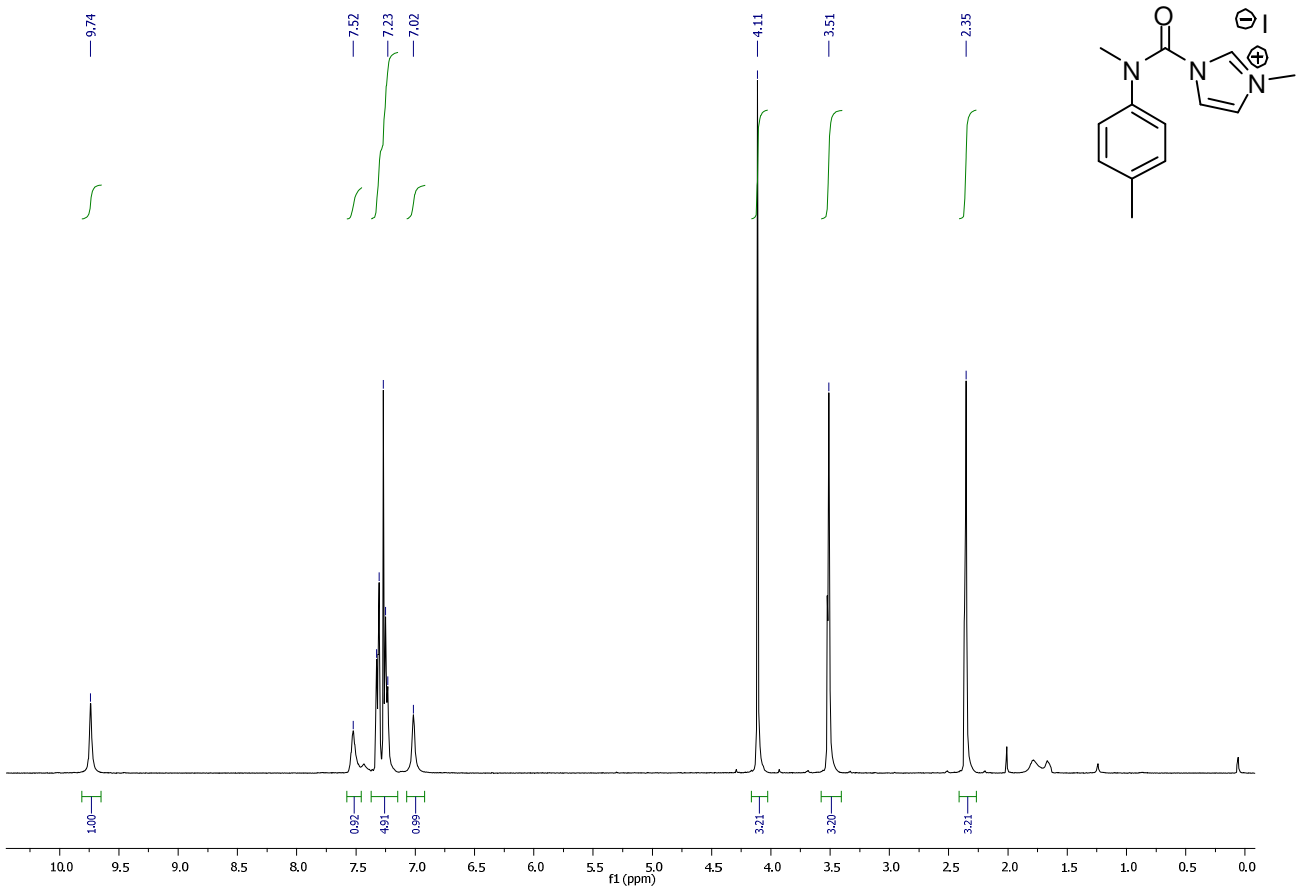


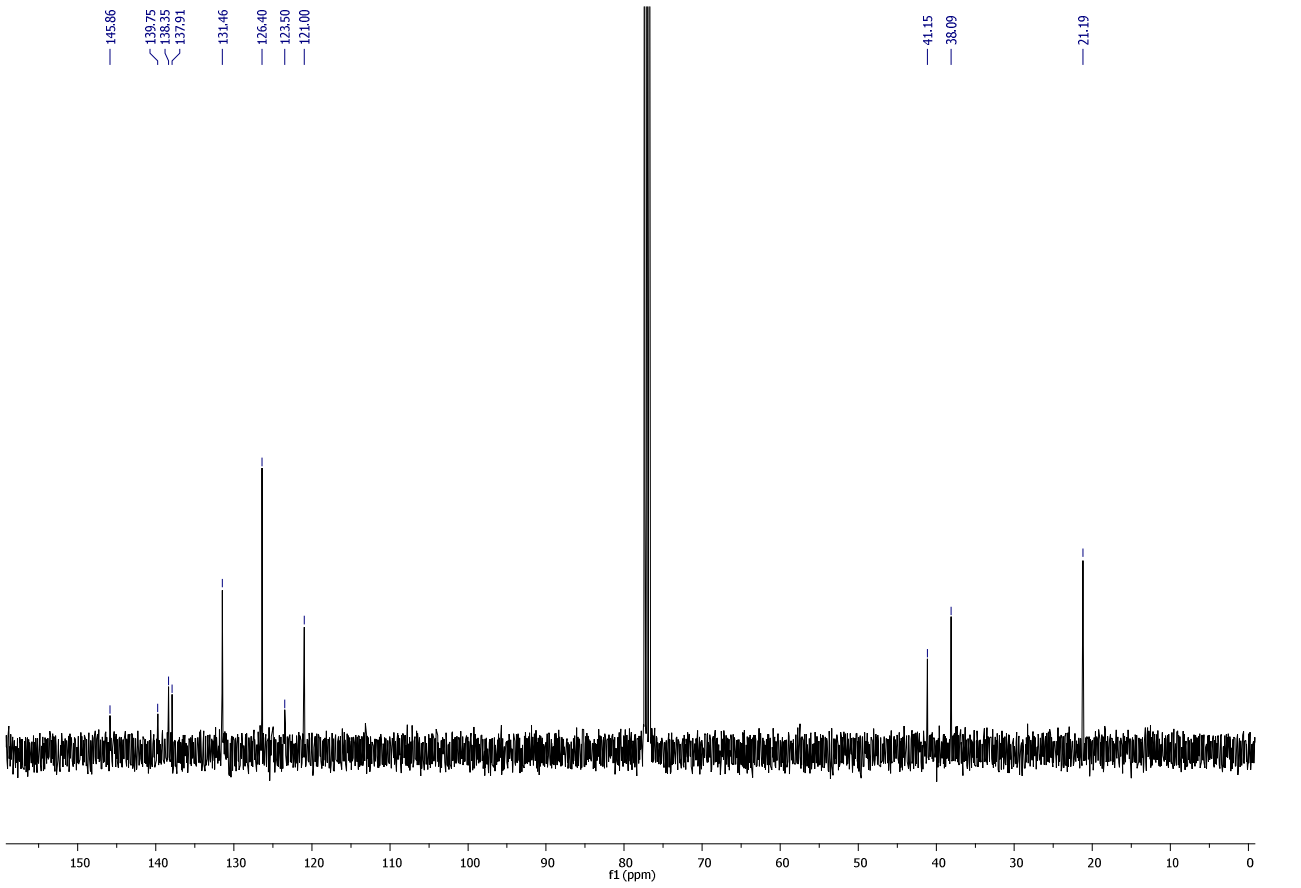
s17: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



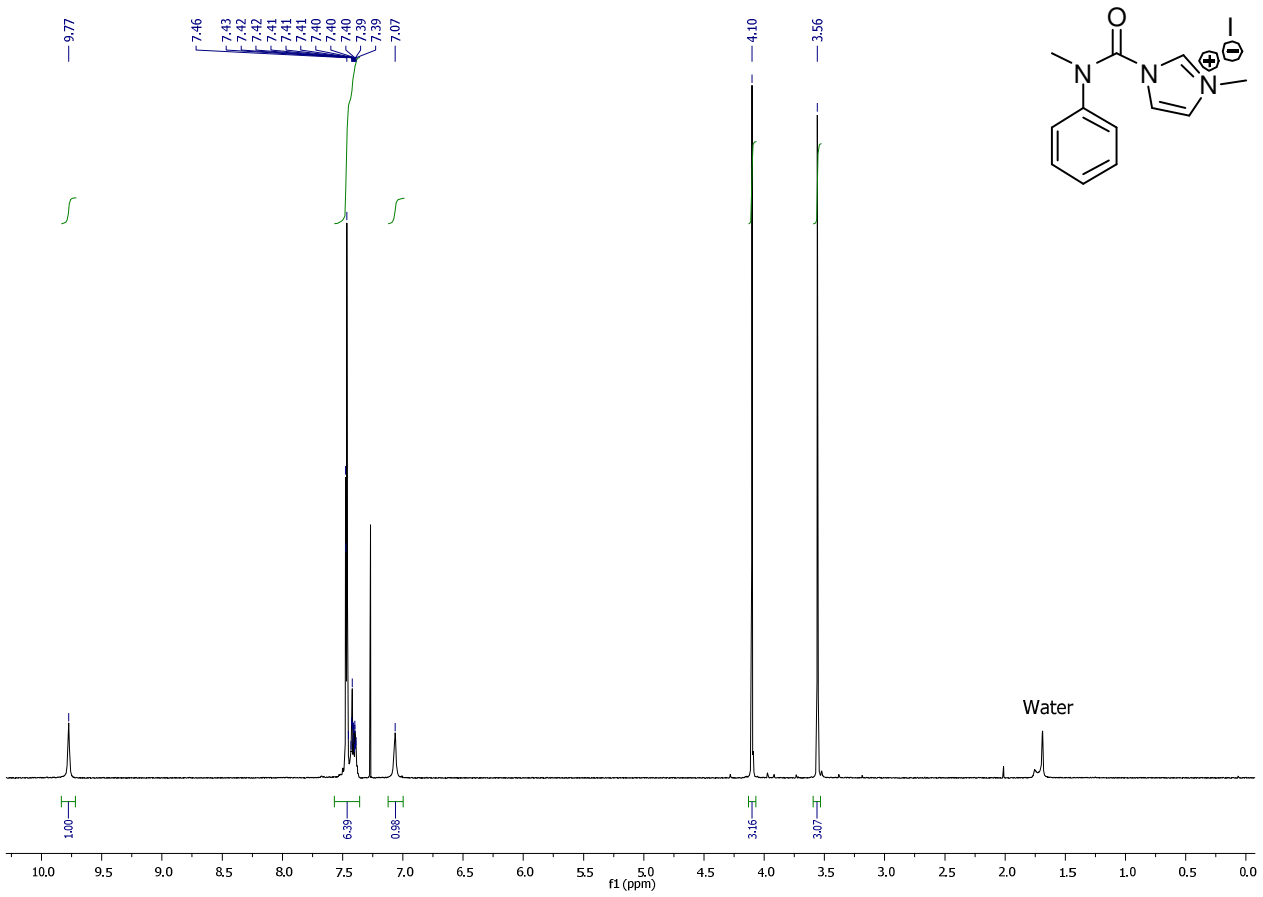


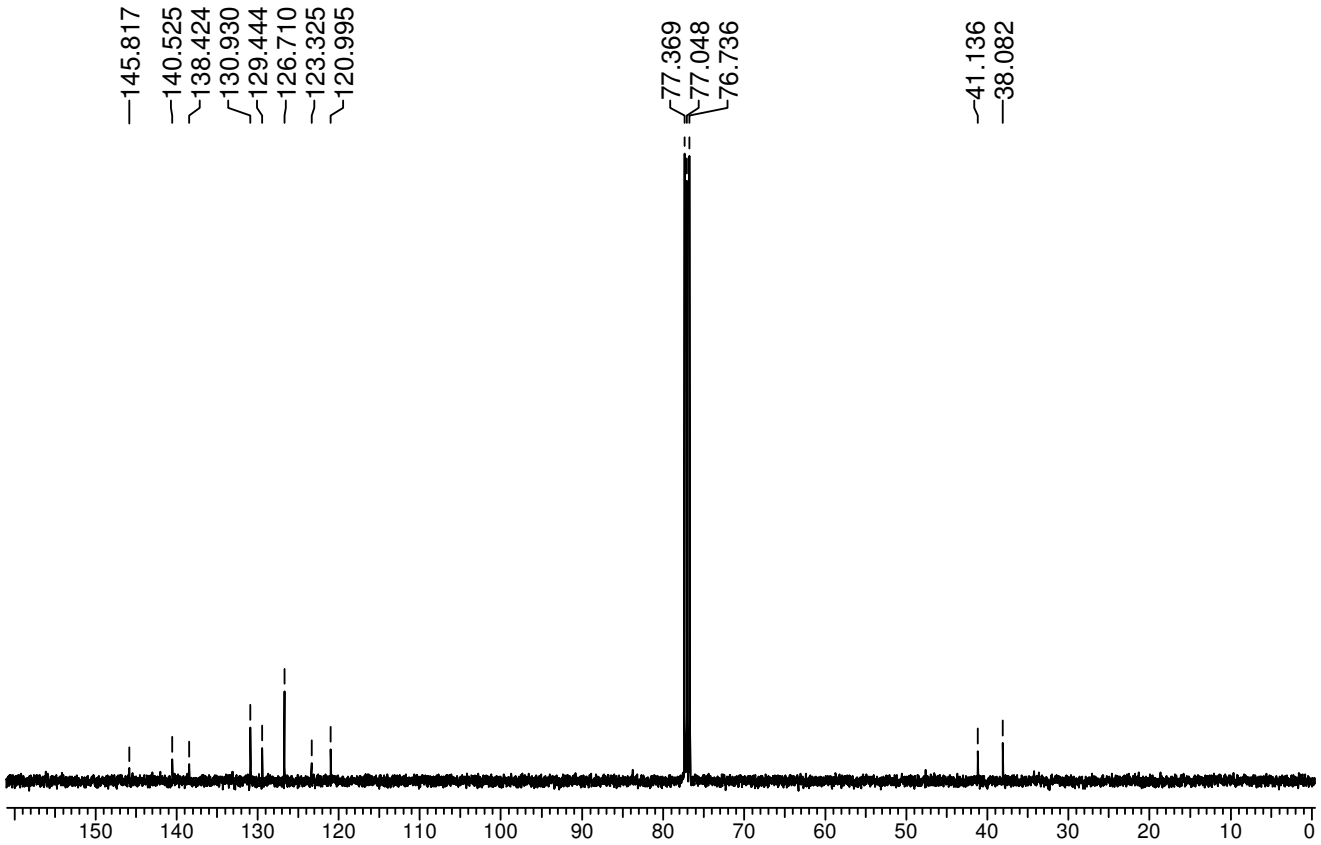
s18: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



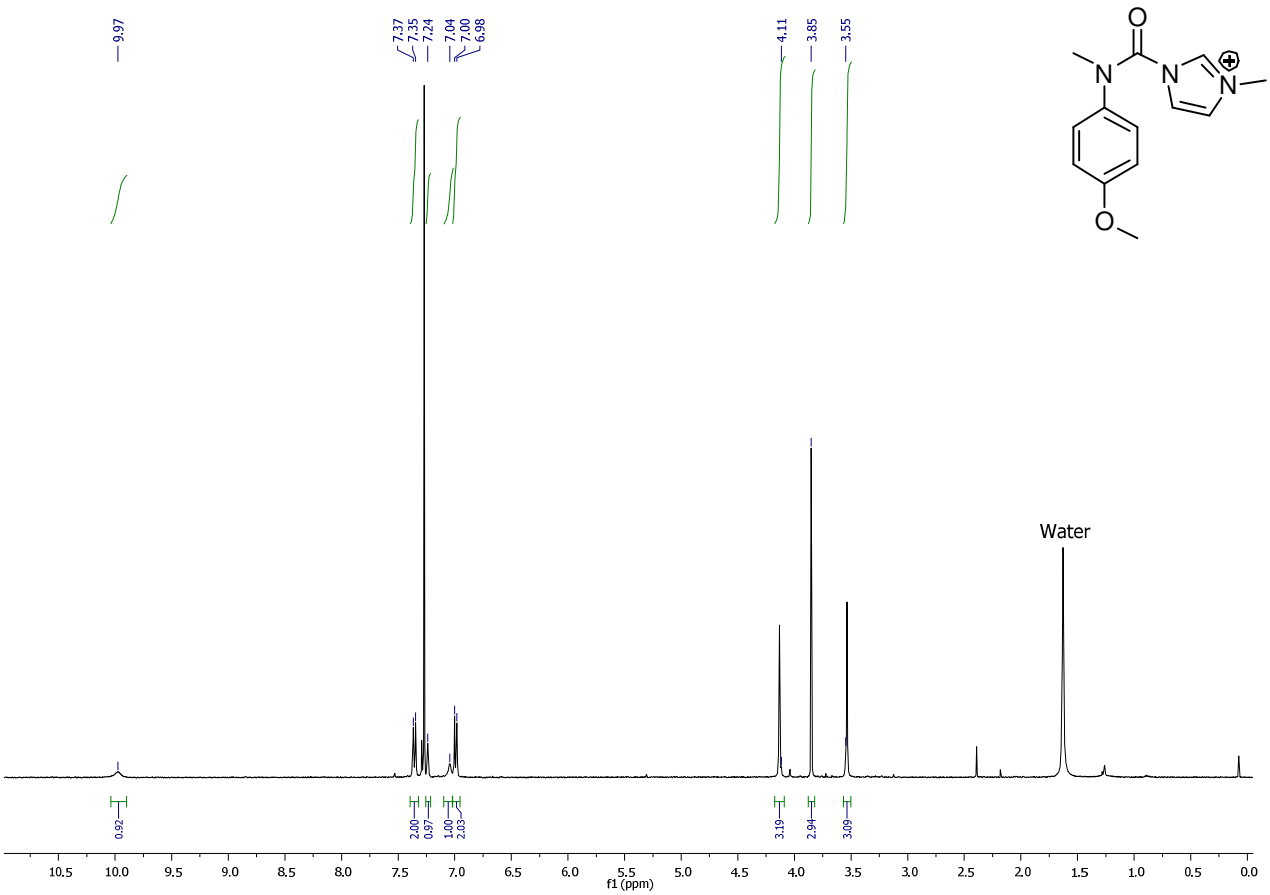


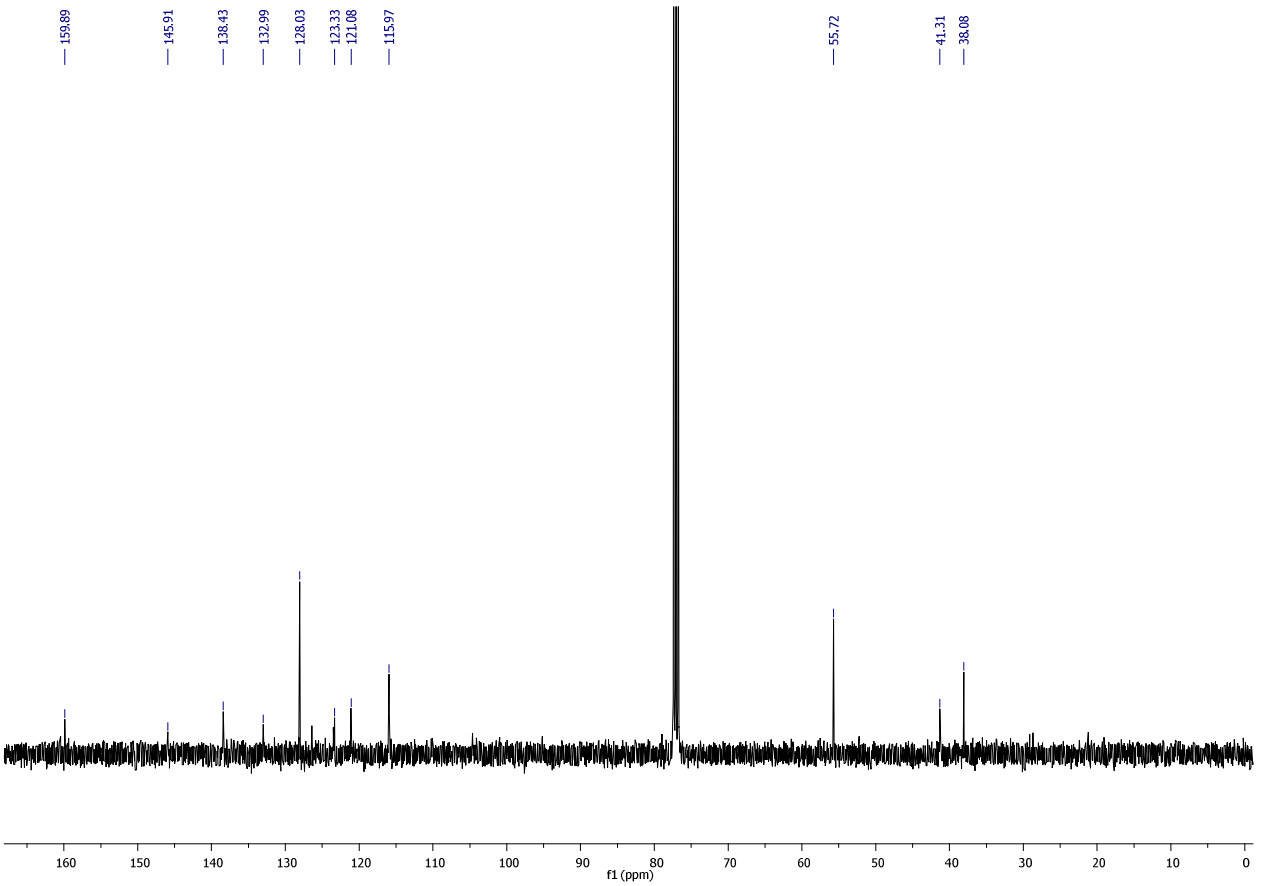
s19: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



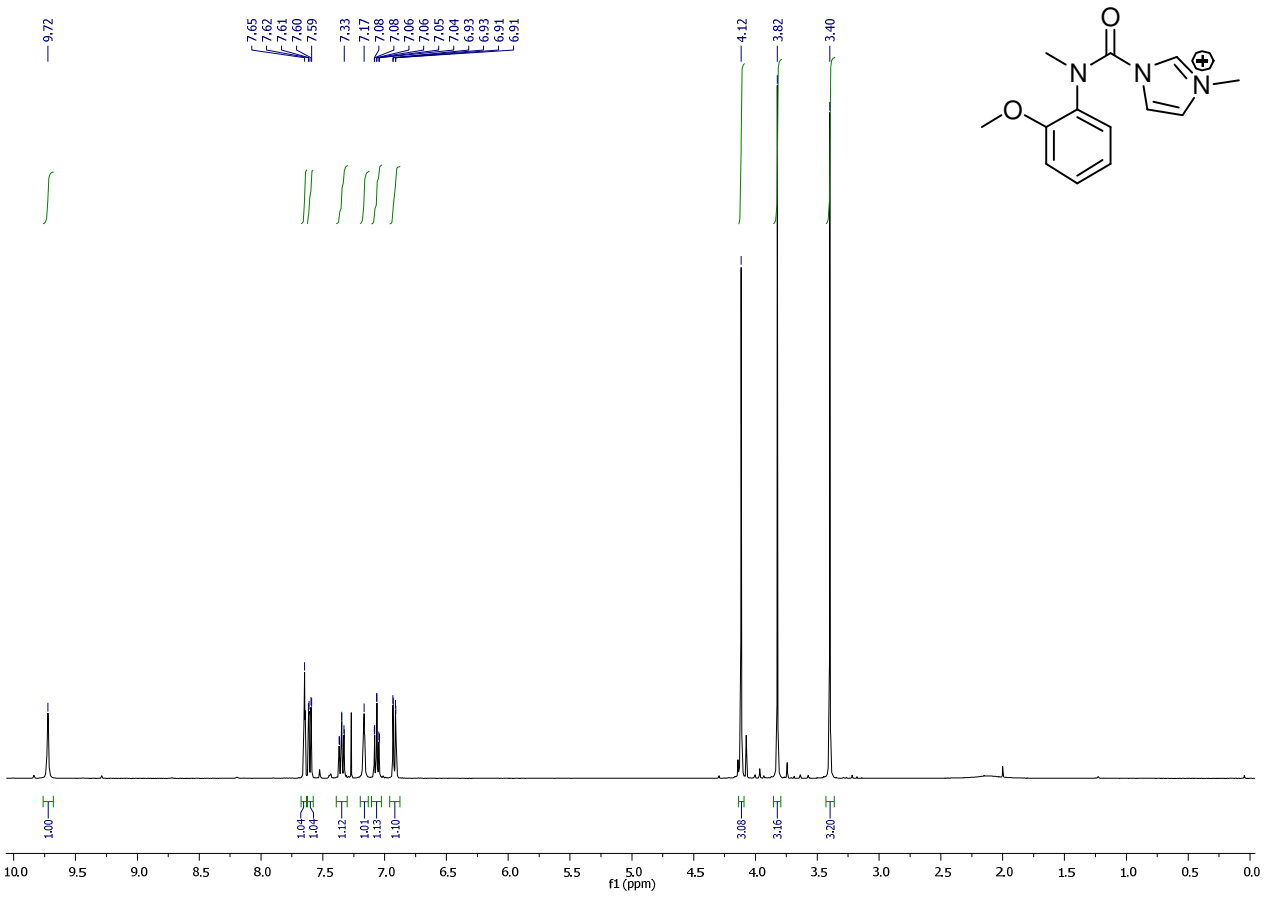


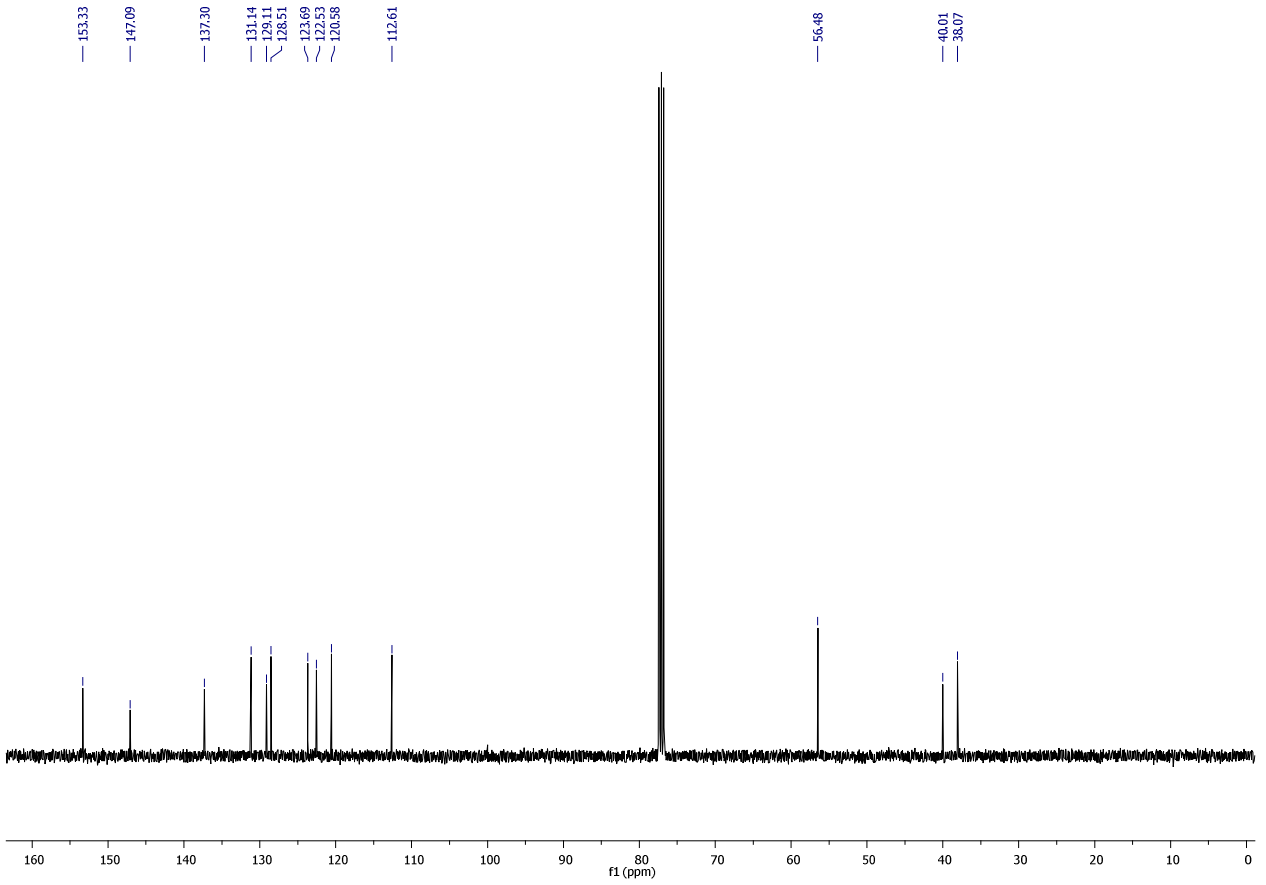
s20: ^{1}H-NMR: 500 MHz, **^{13}C-NMR**: 100 MHz



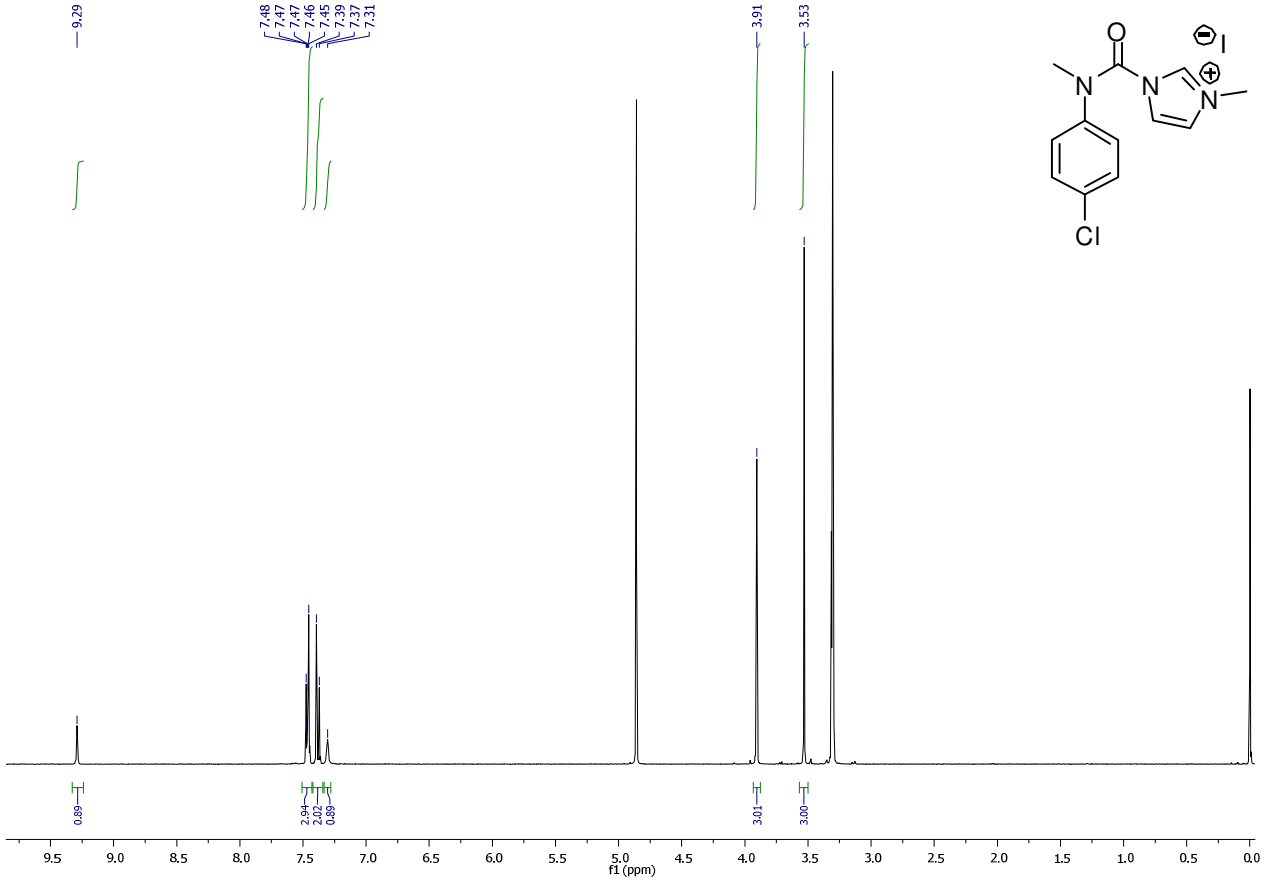


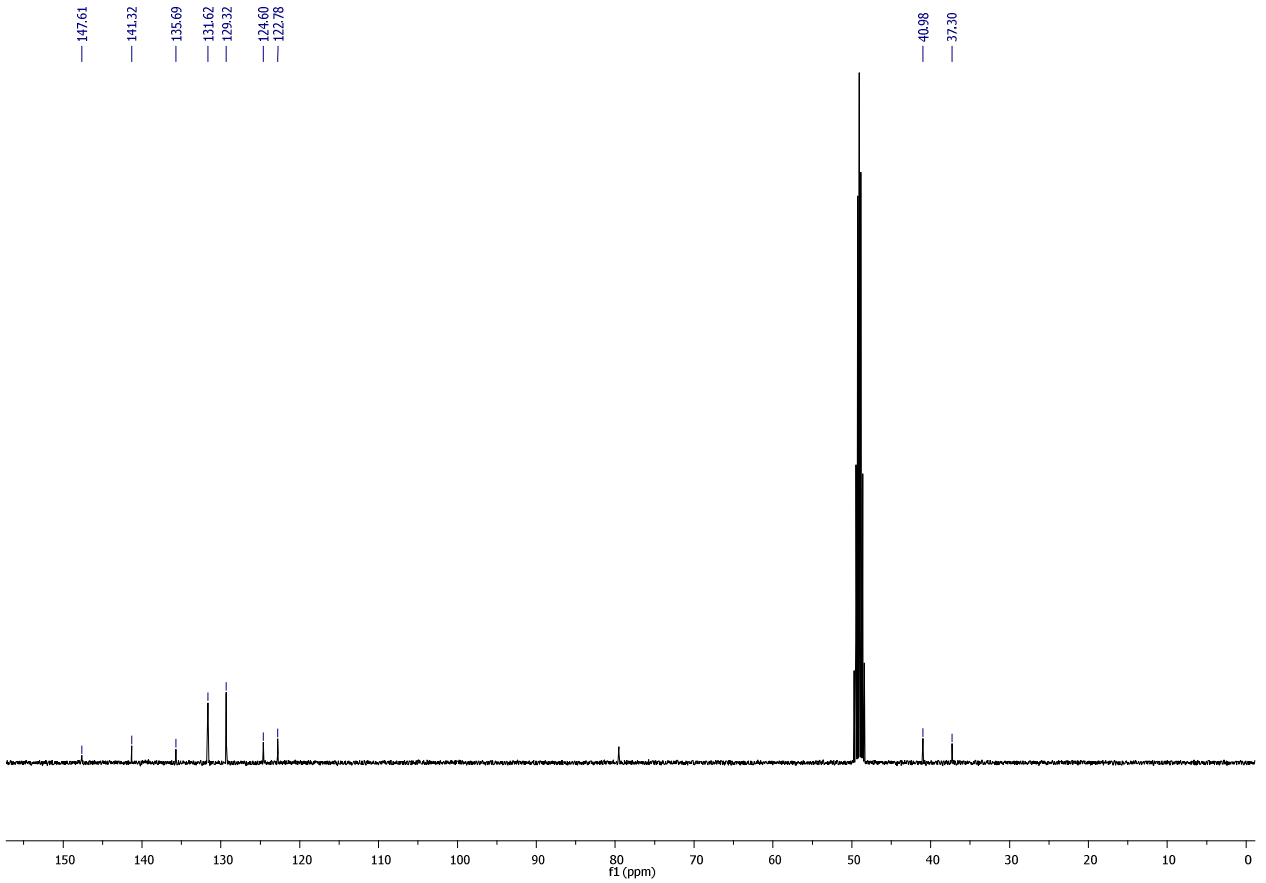
s21: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



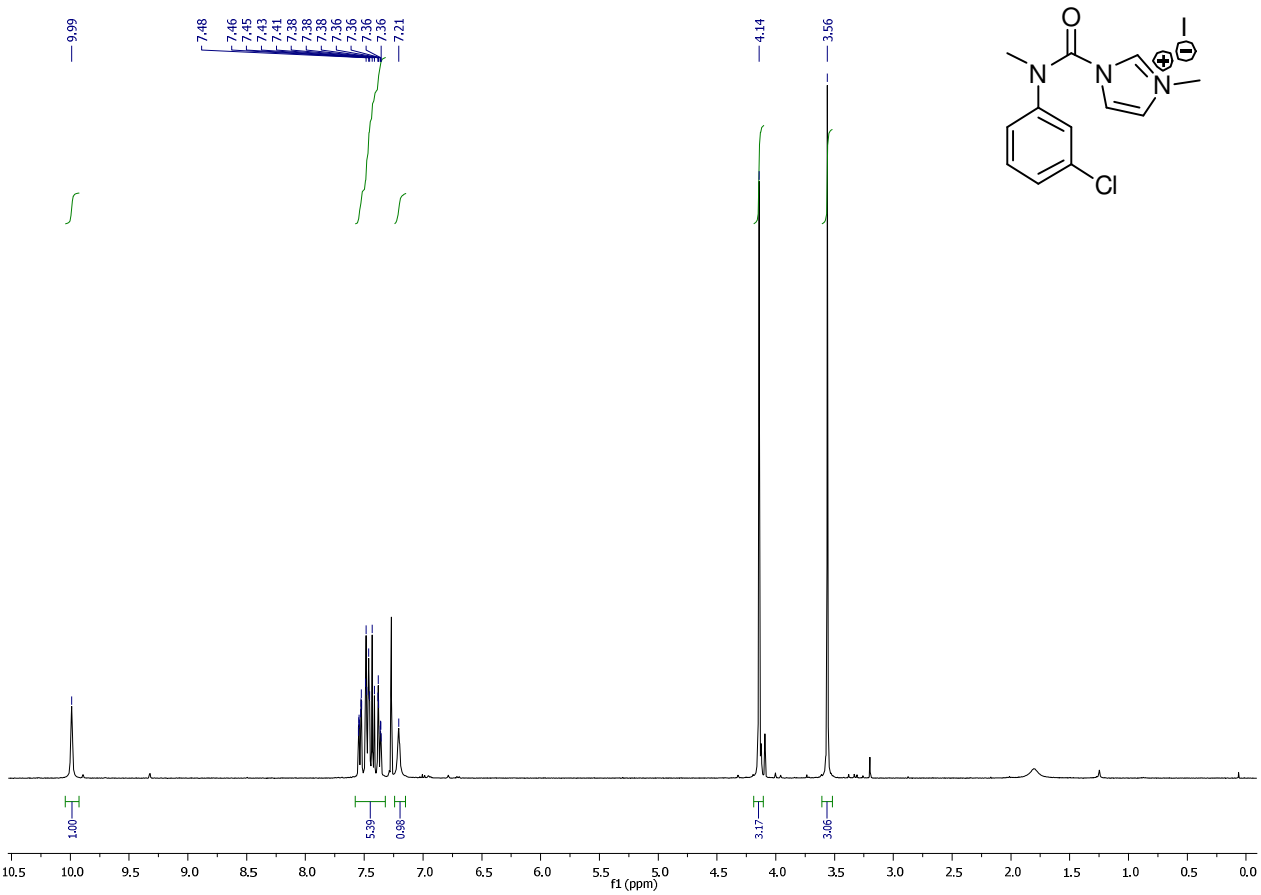


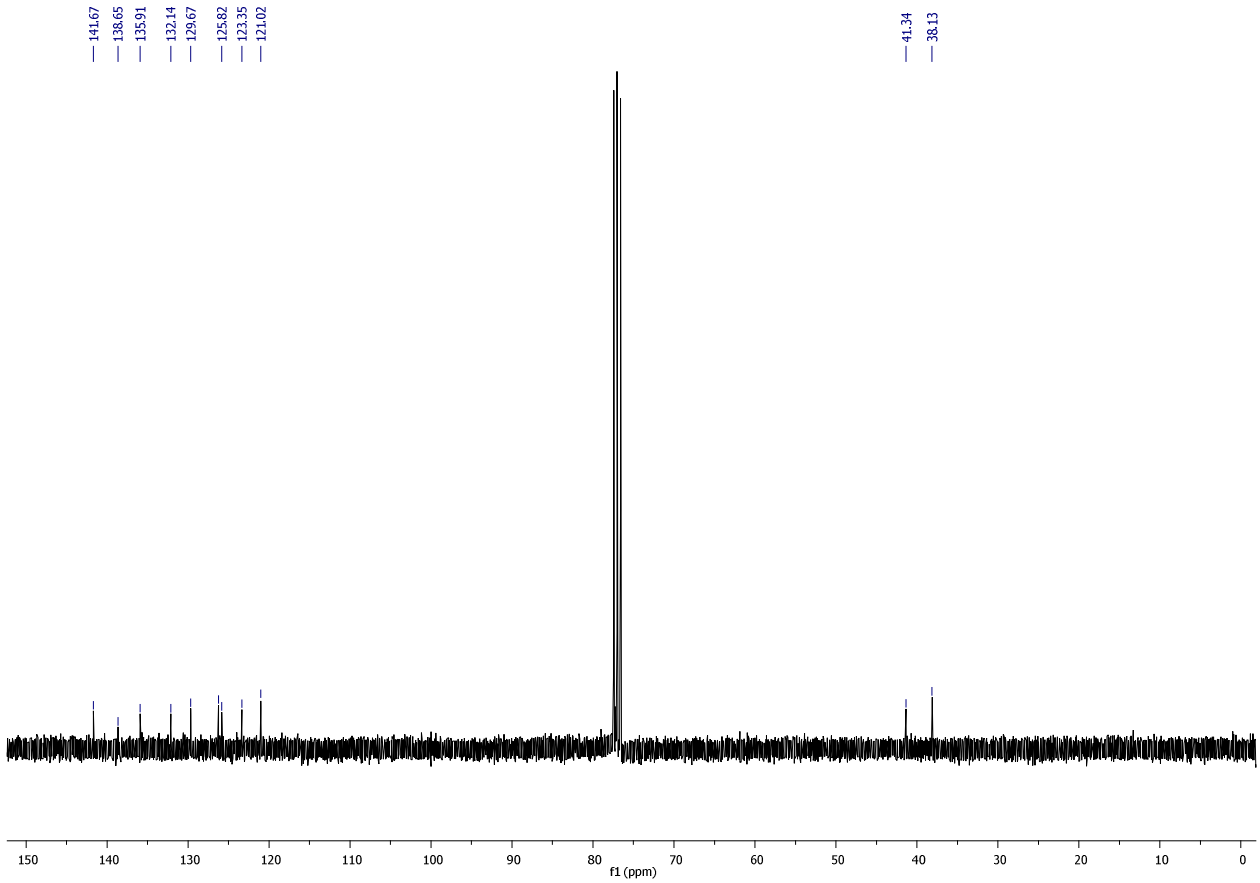
s22: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



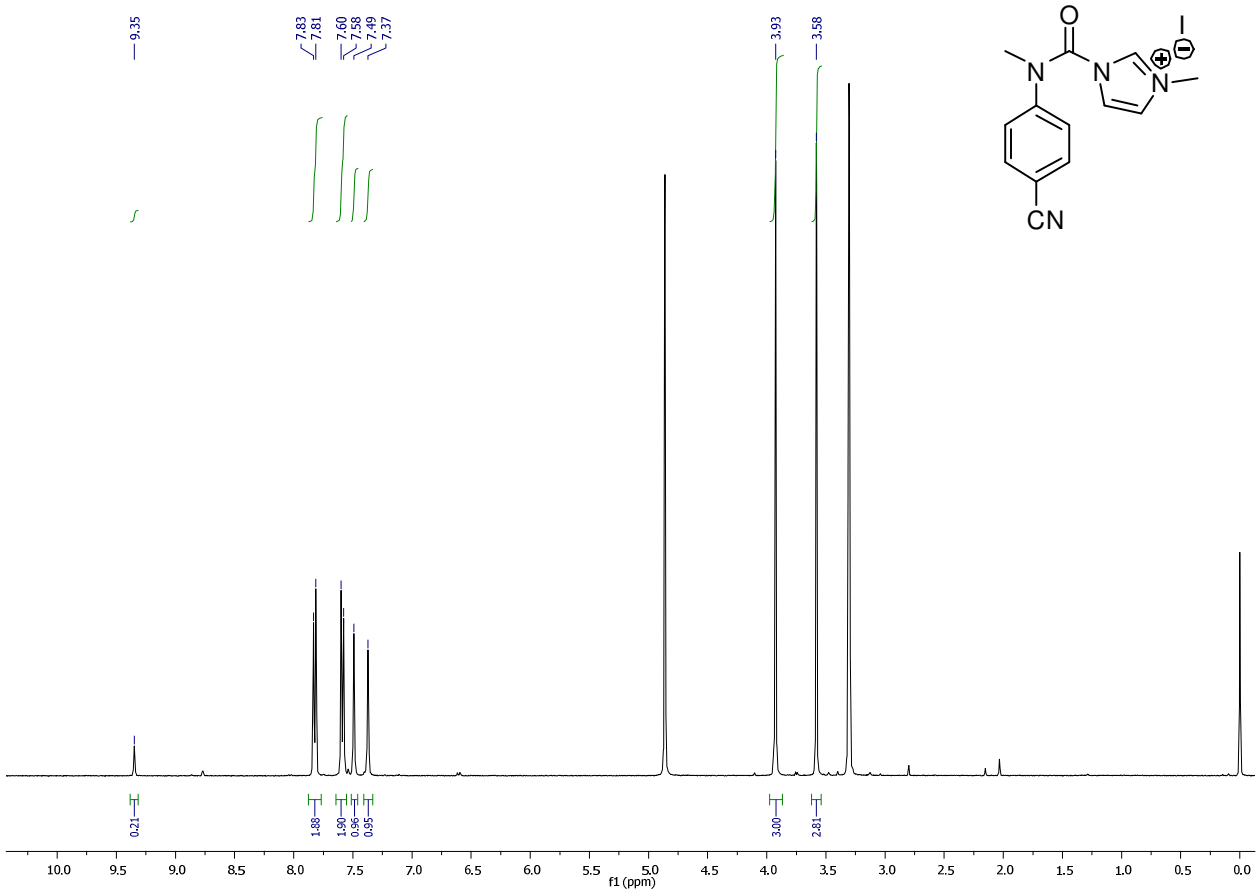


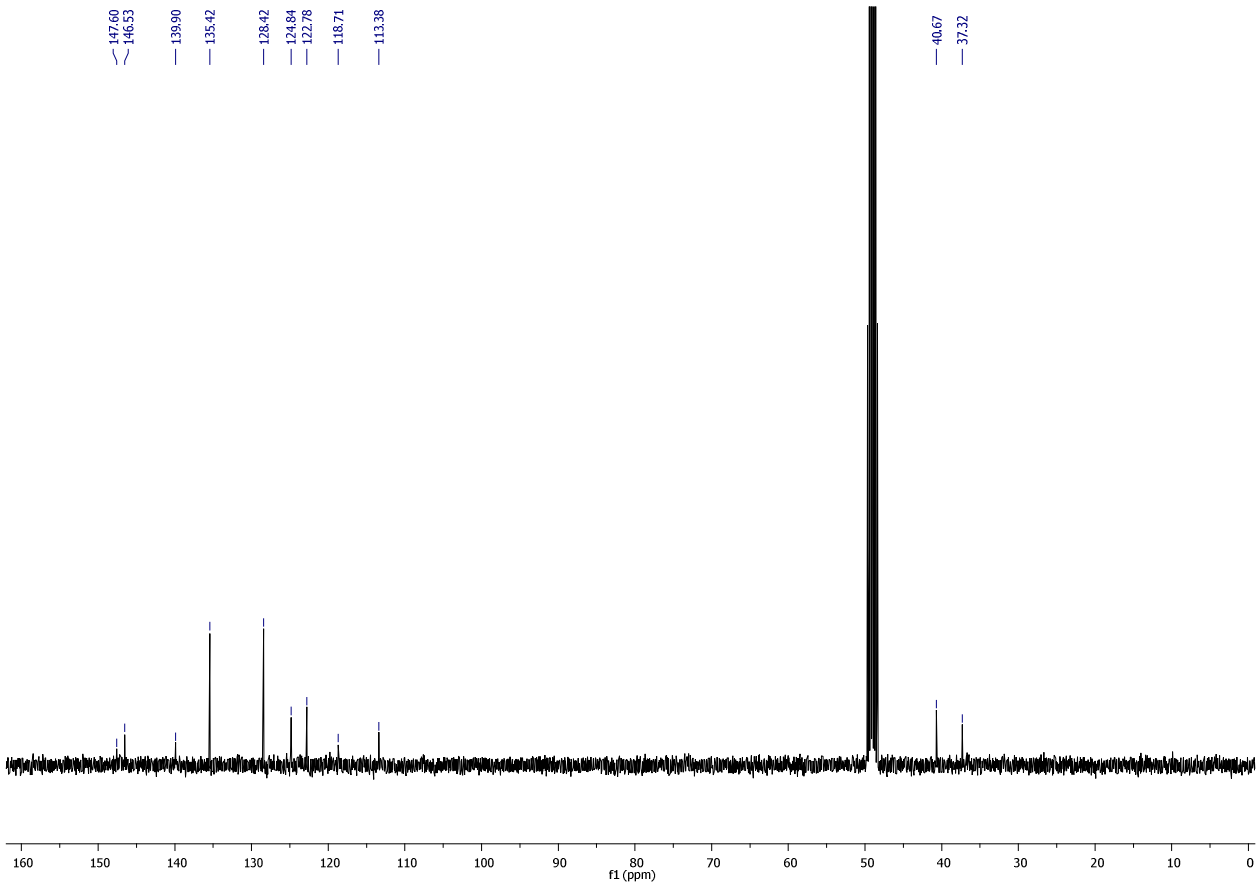
s23: ^{1}H-NMR: 300 MHz, **^{13}C-NMR**: 75 MHz



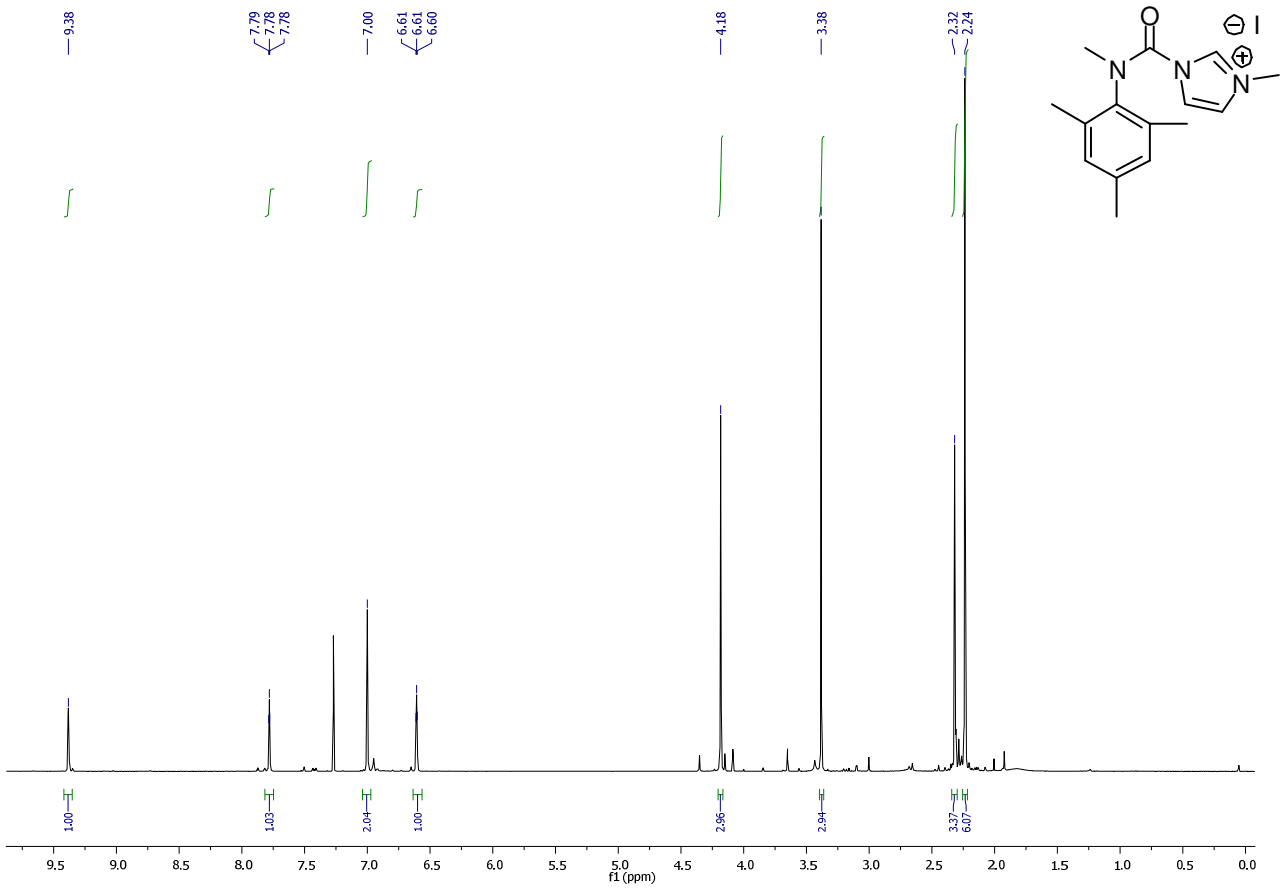


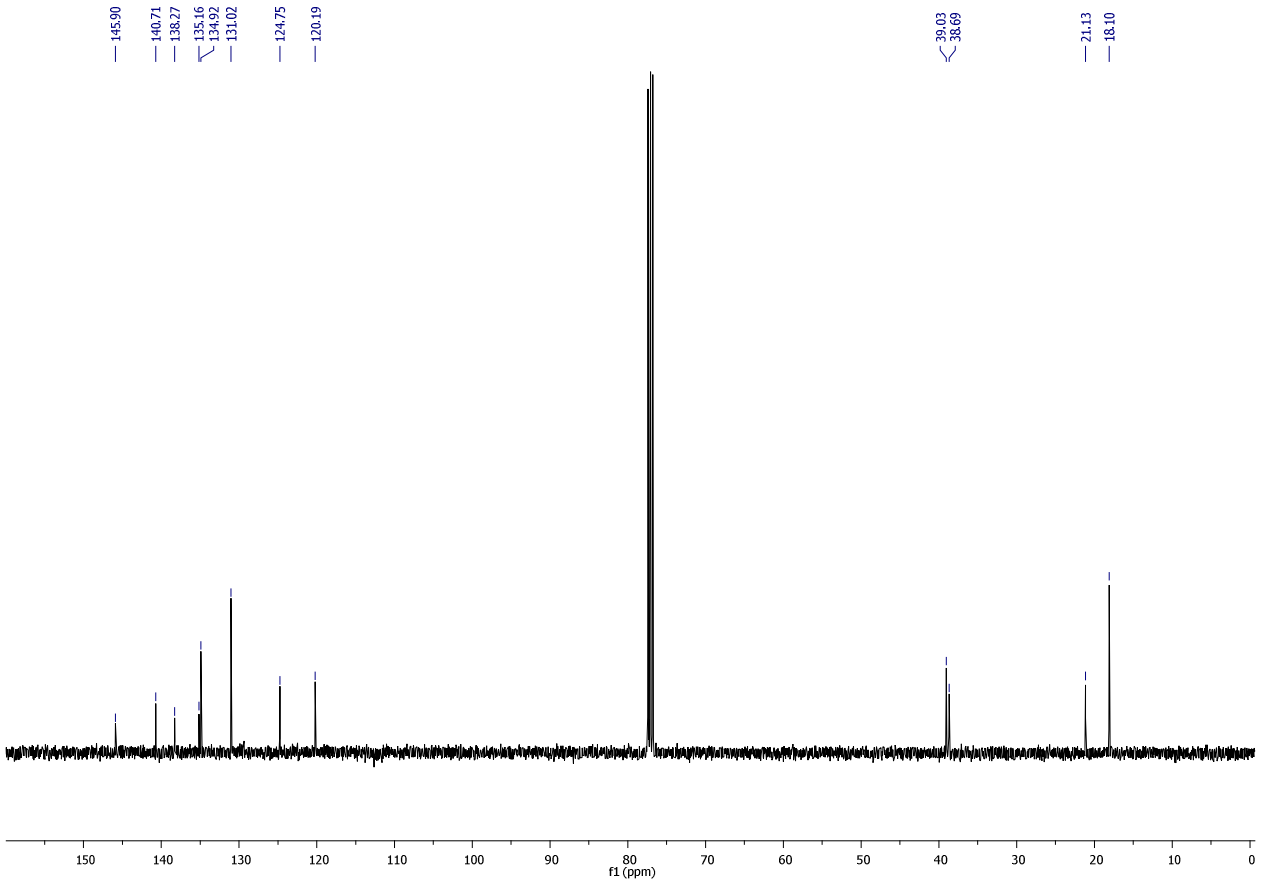
s24: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



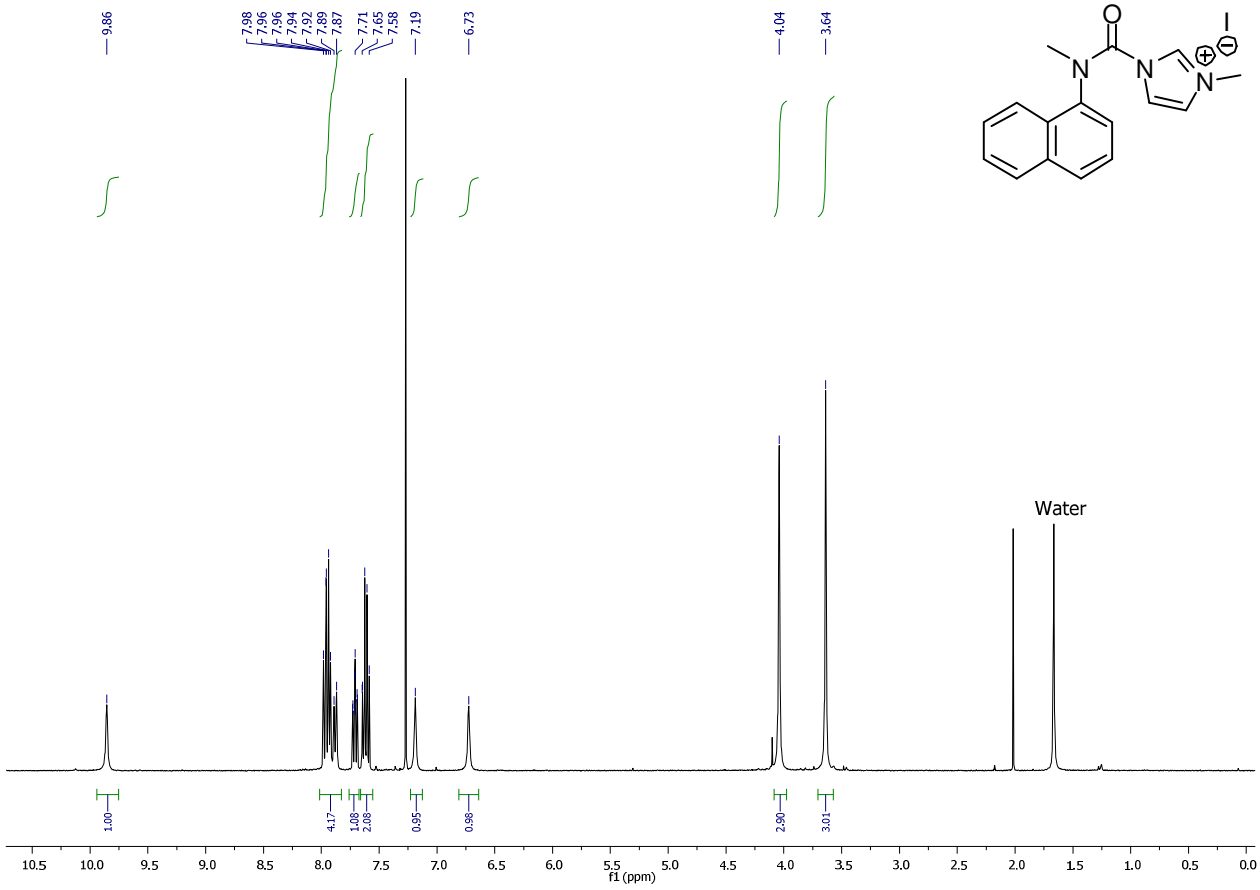


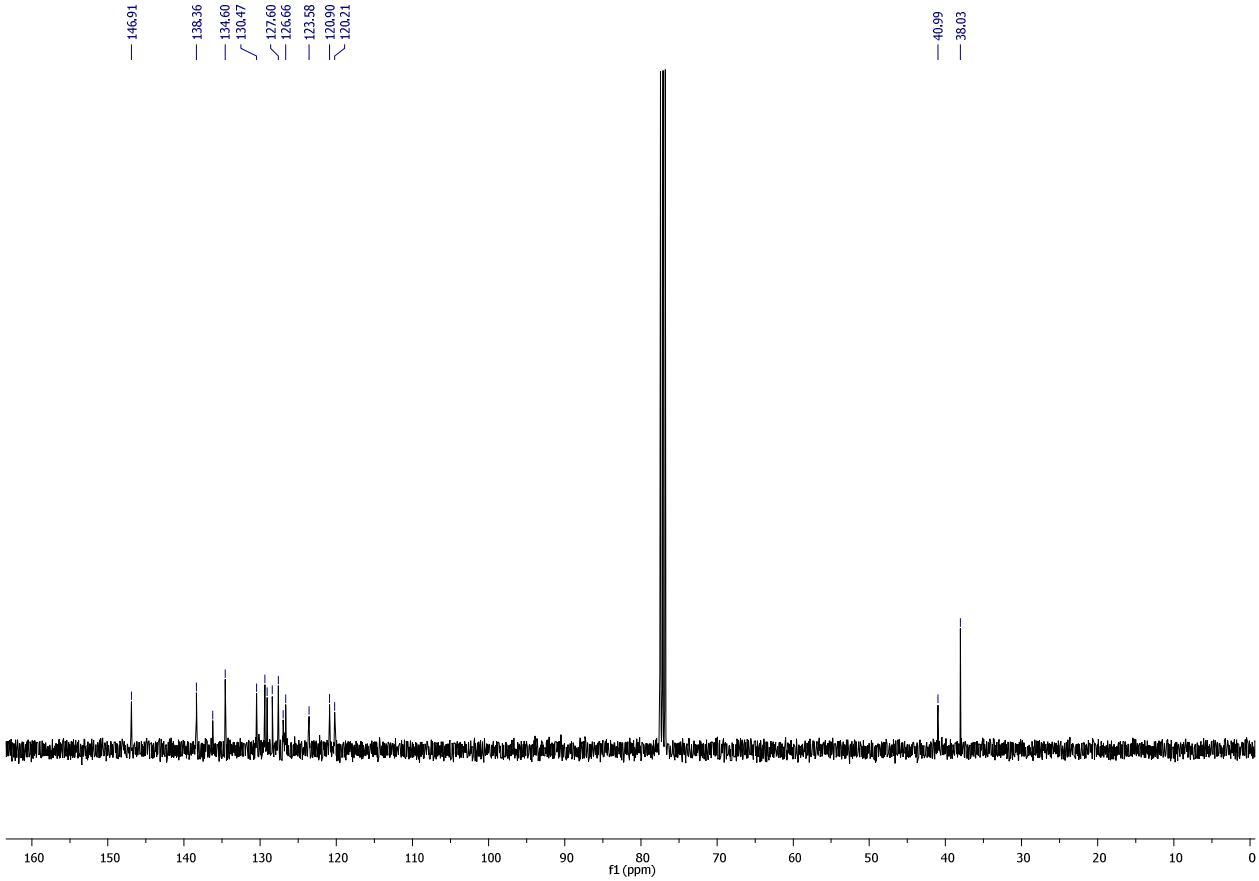
s25: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



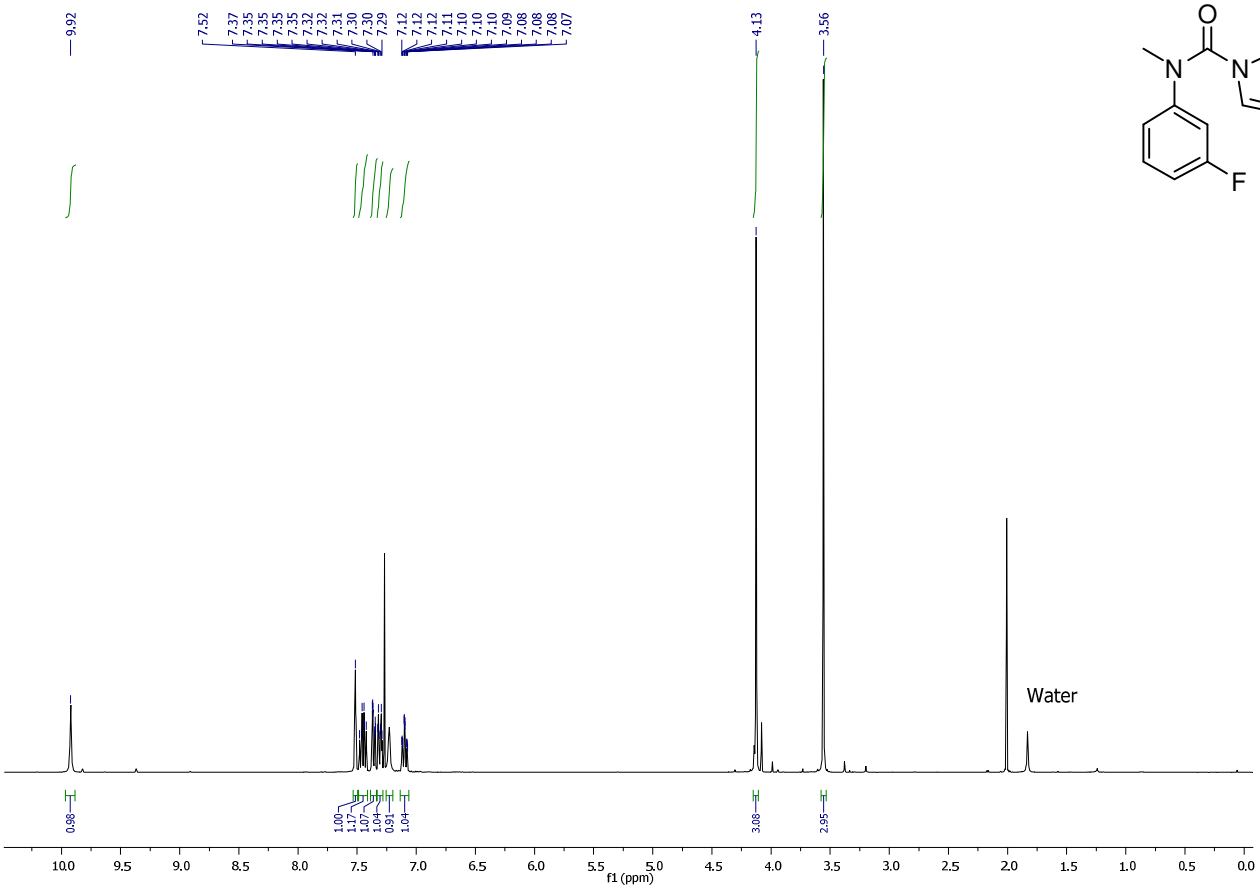


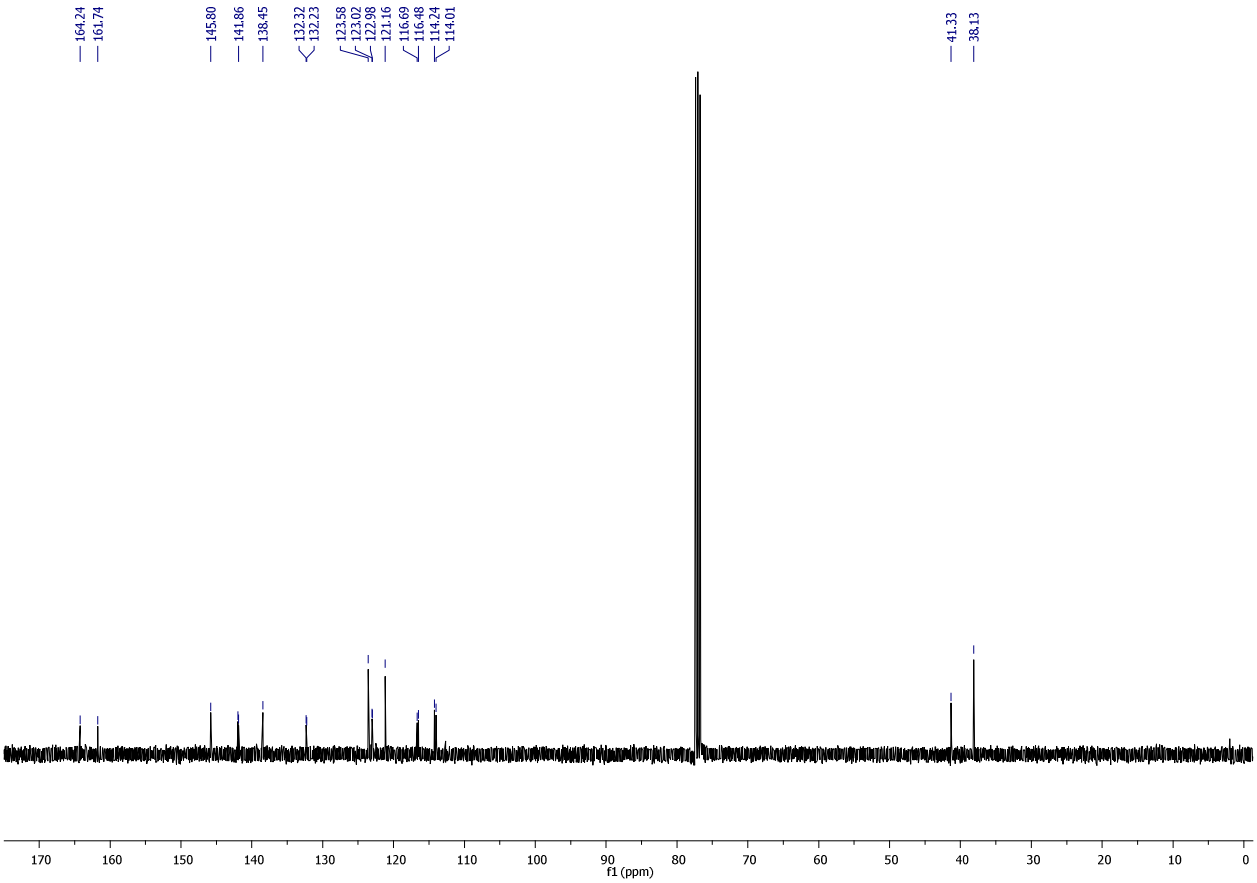
s26: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



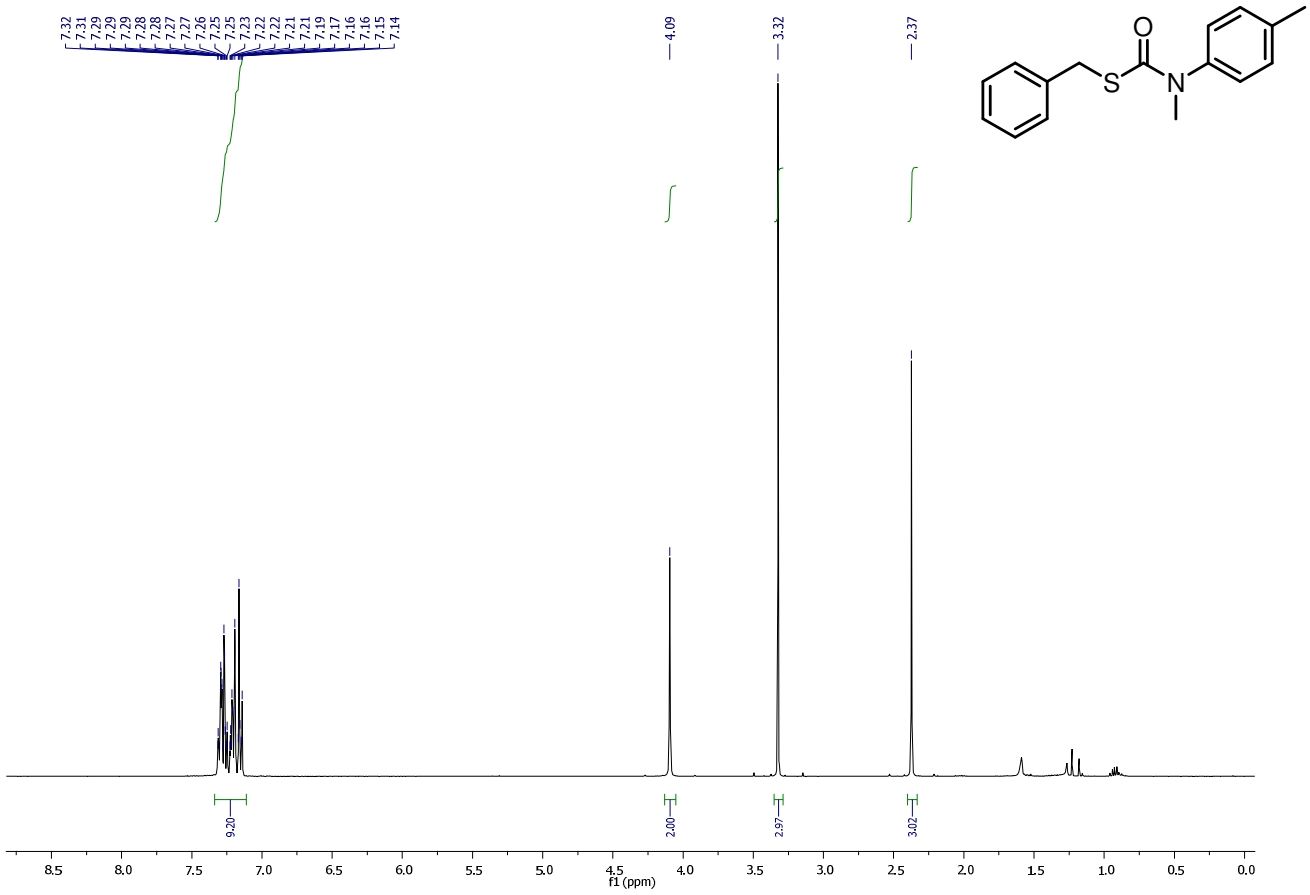


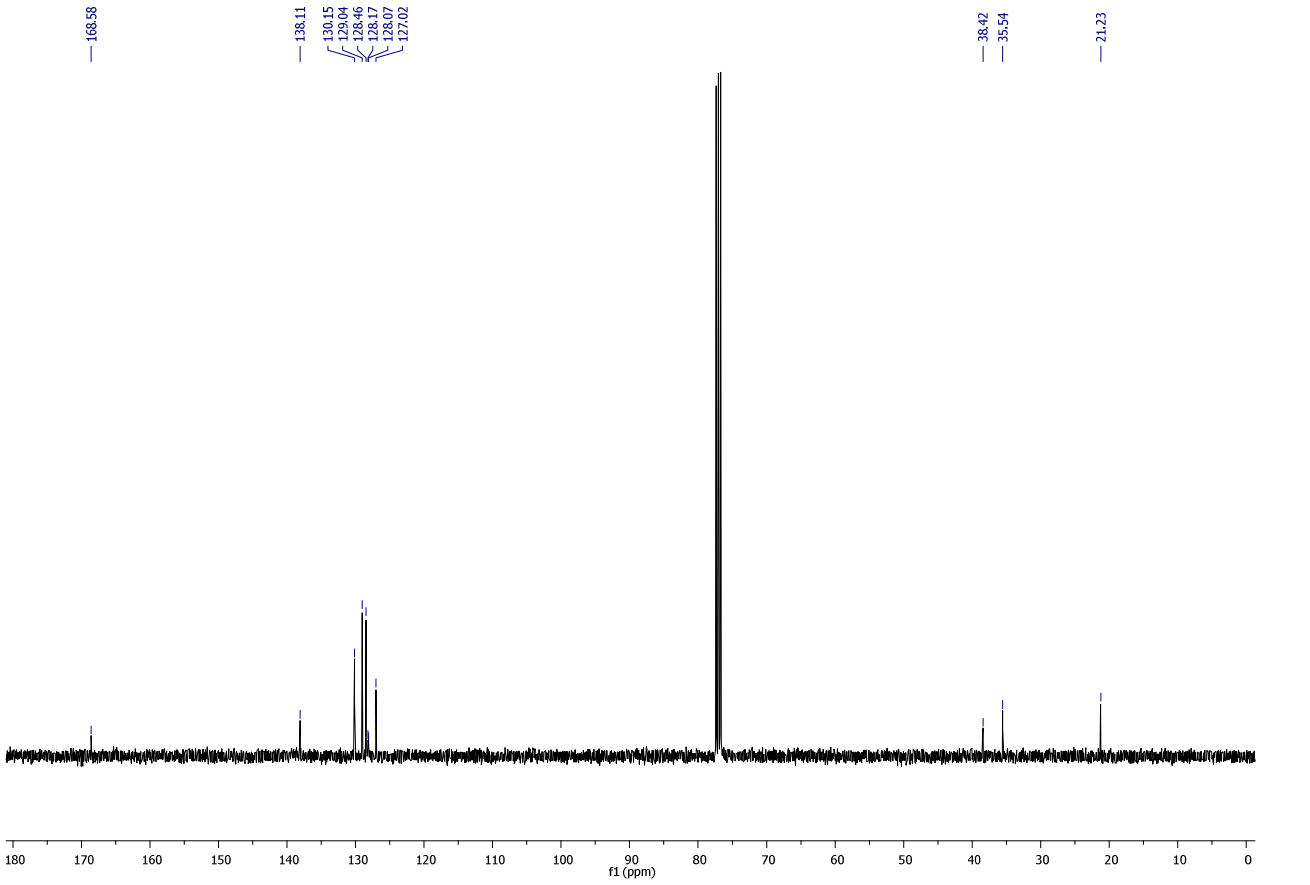
s27: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



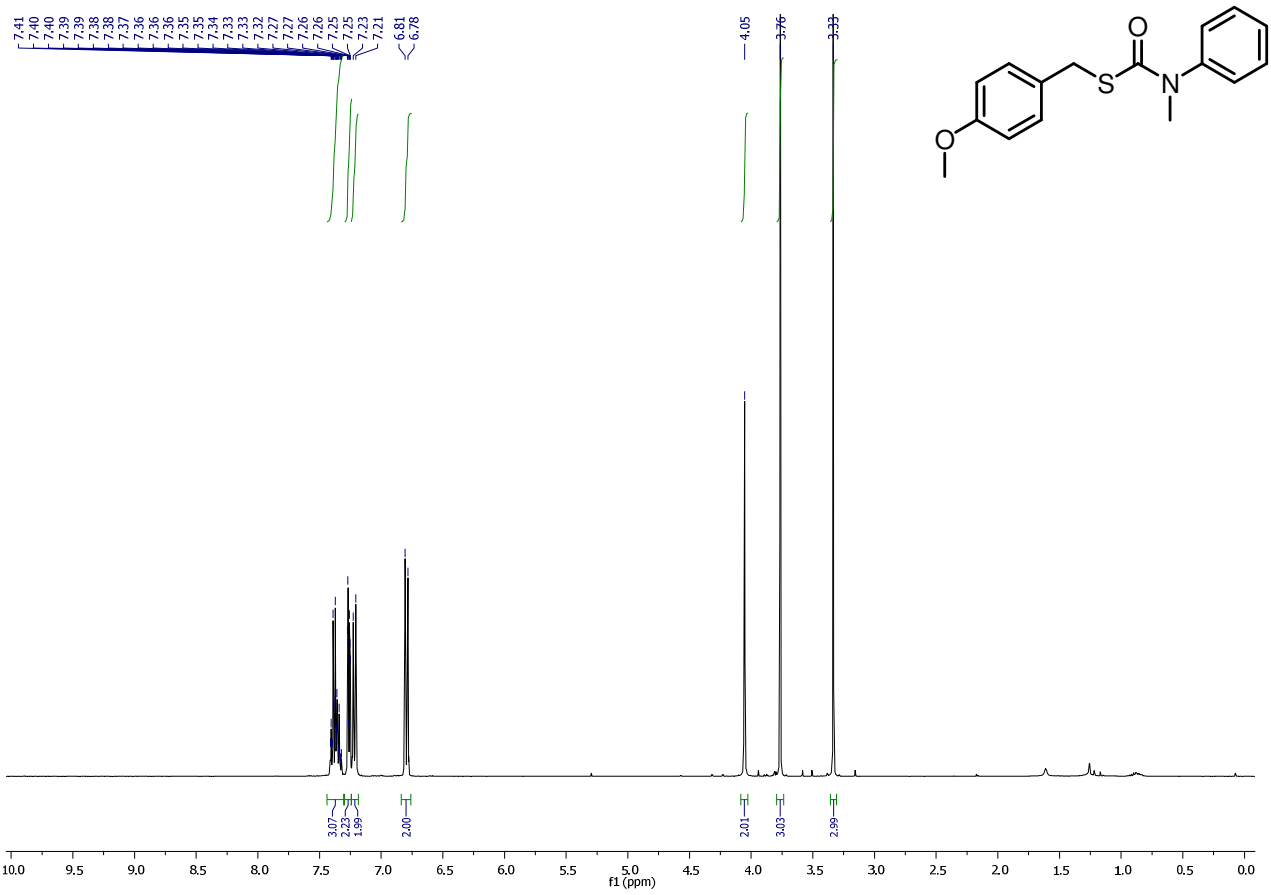


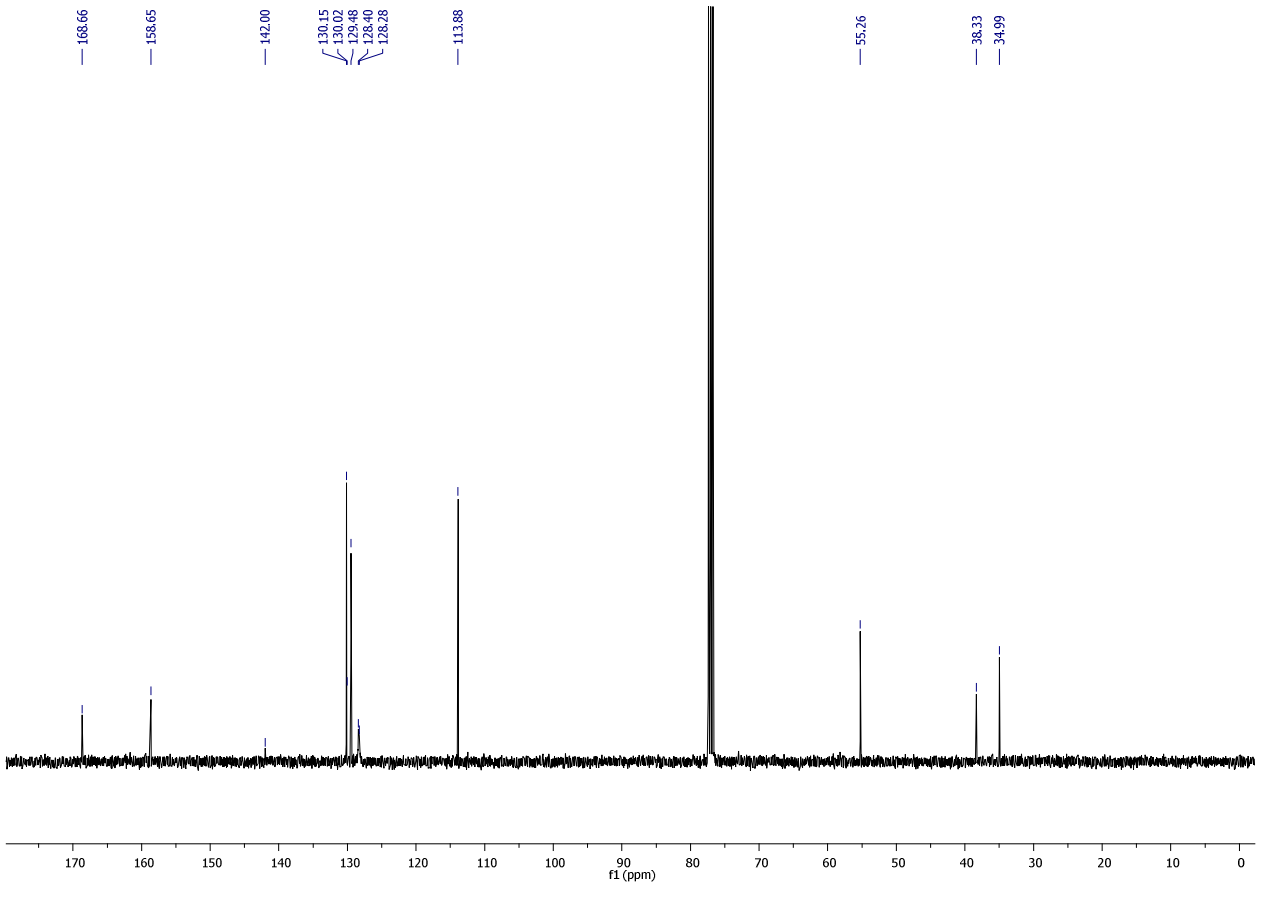
5a: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



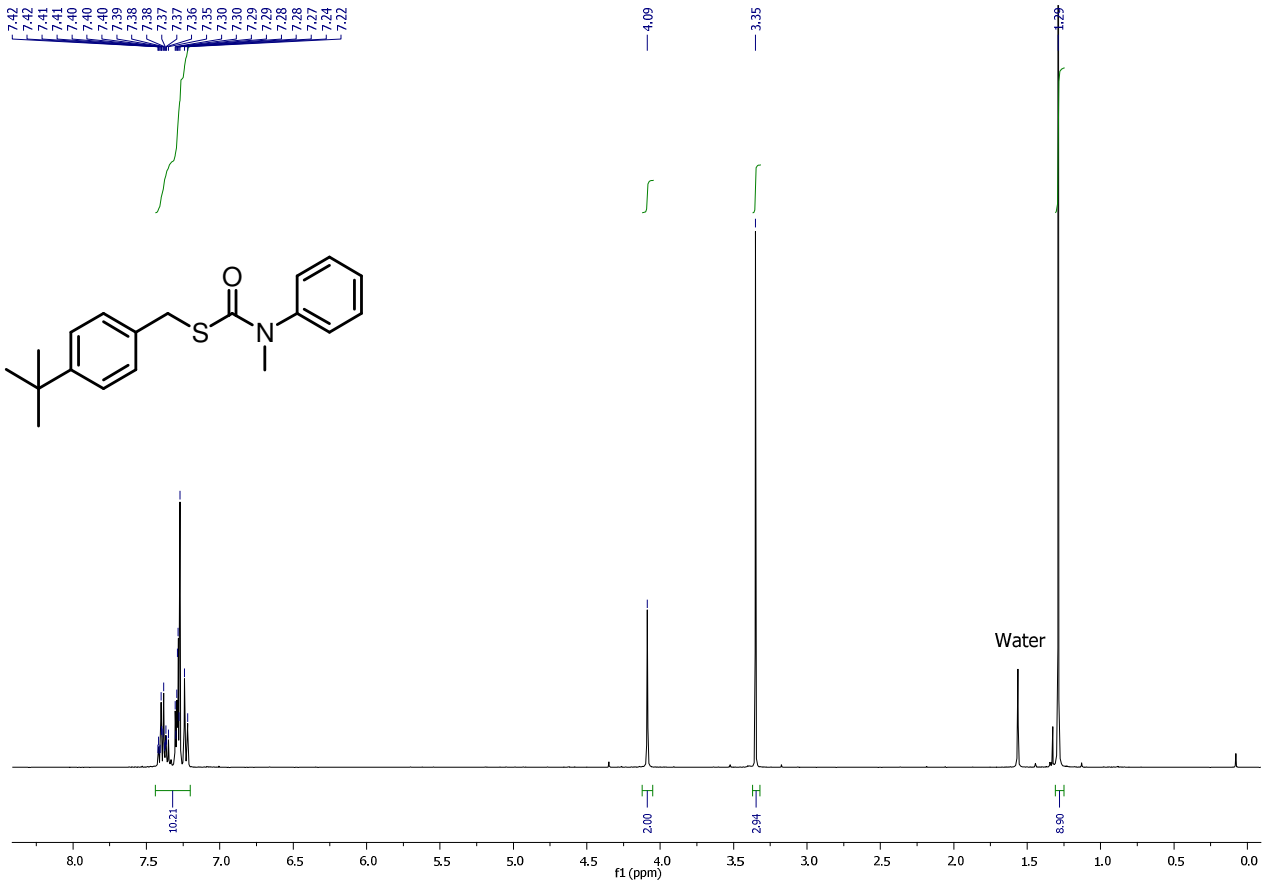


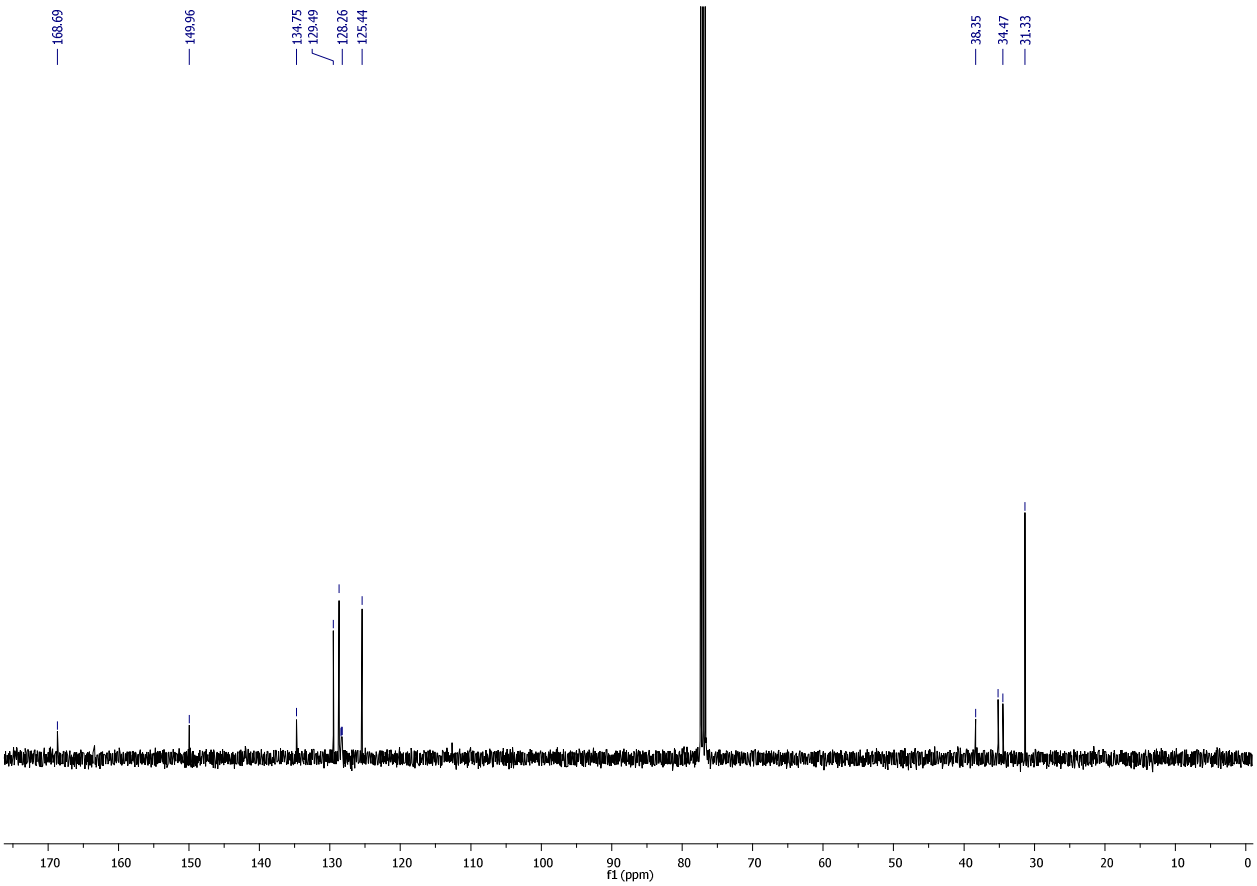
5b: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



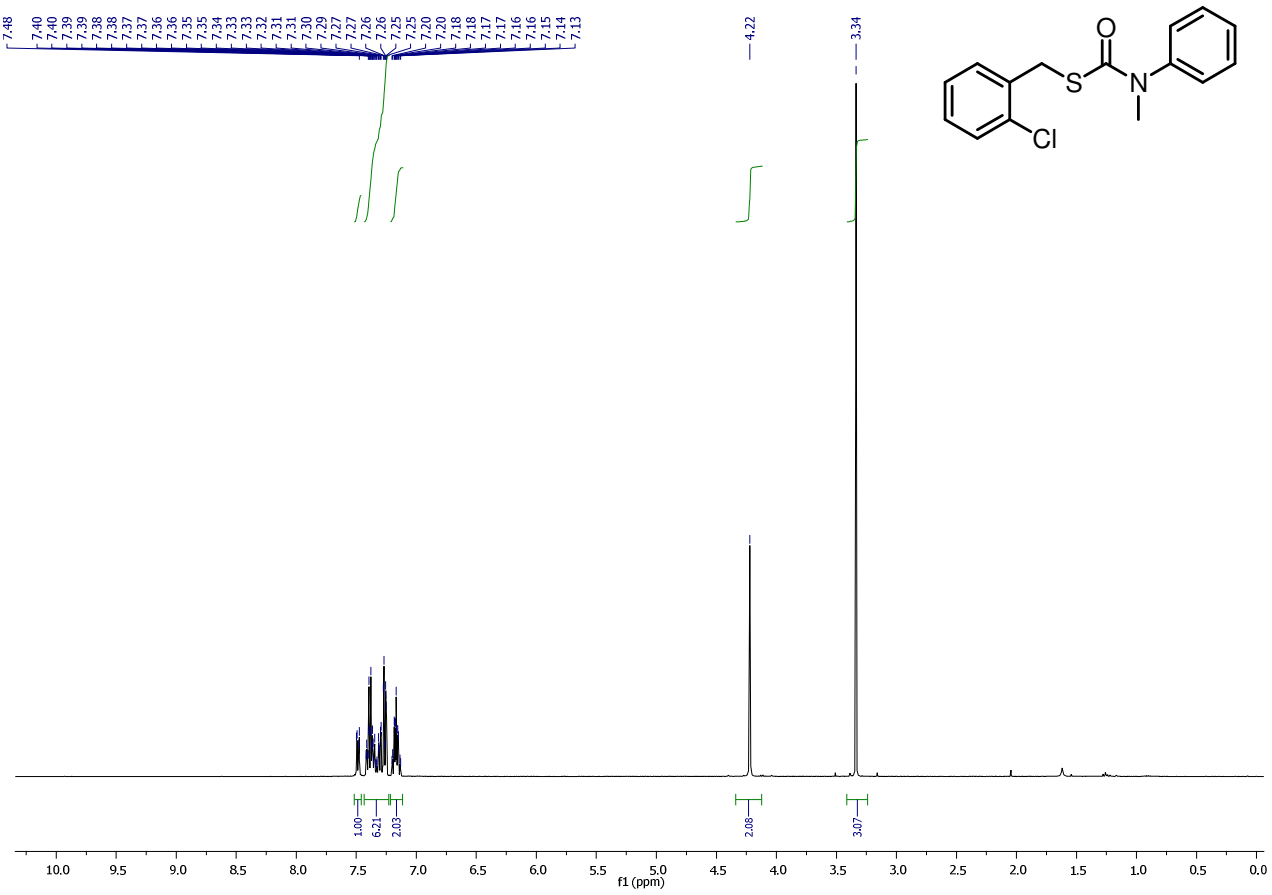


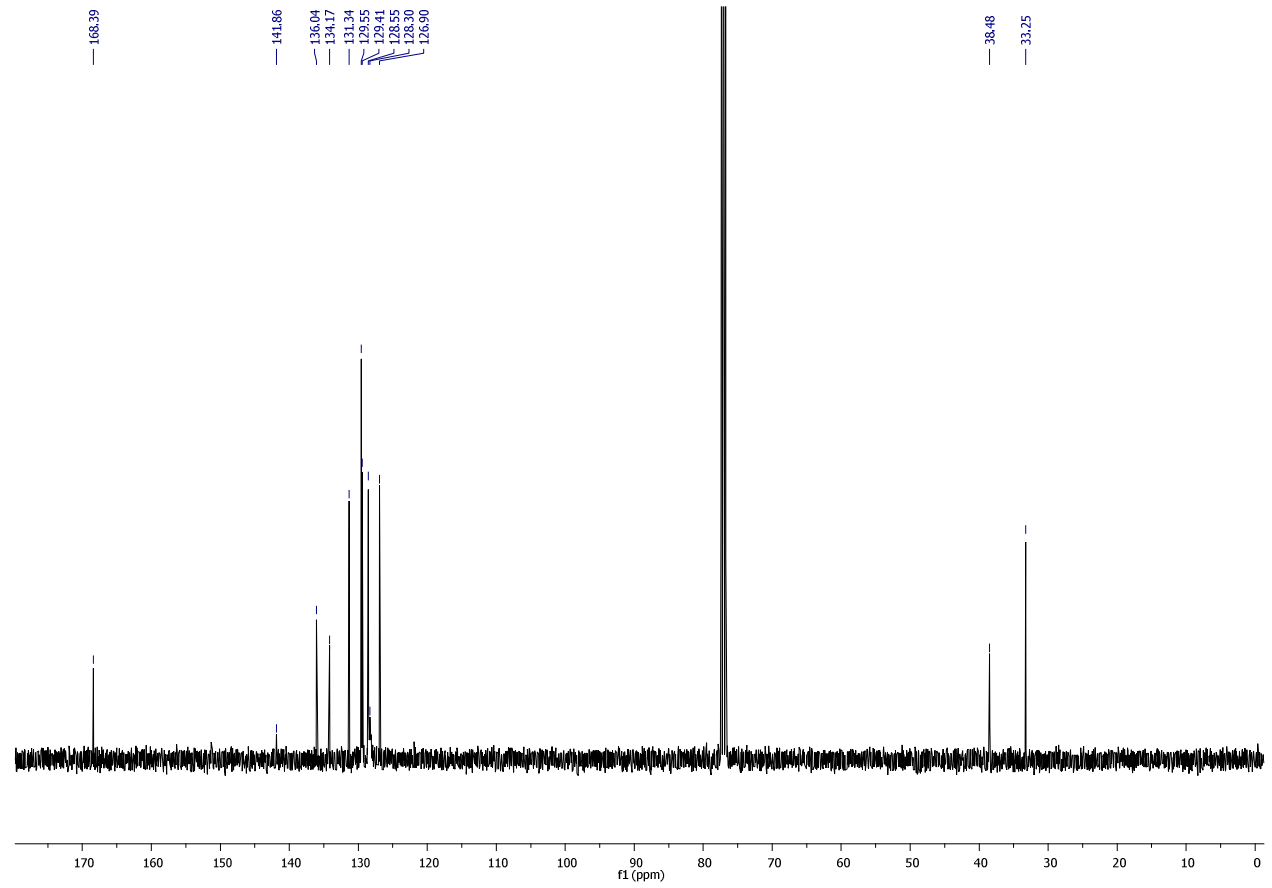
5c: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



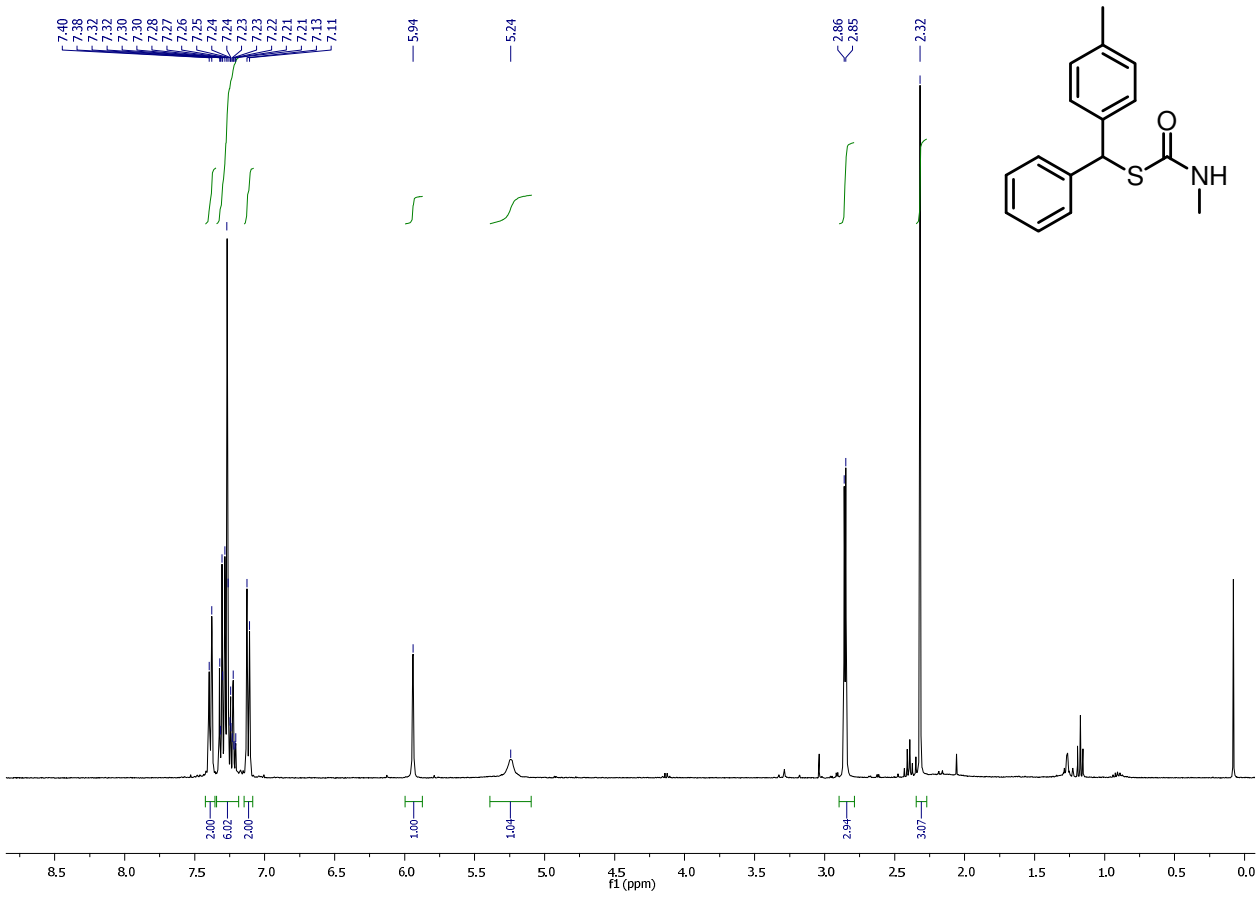


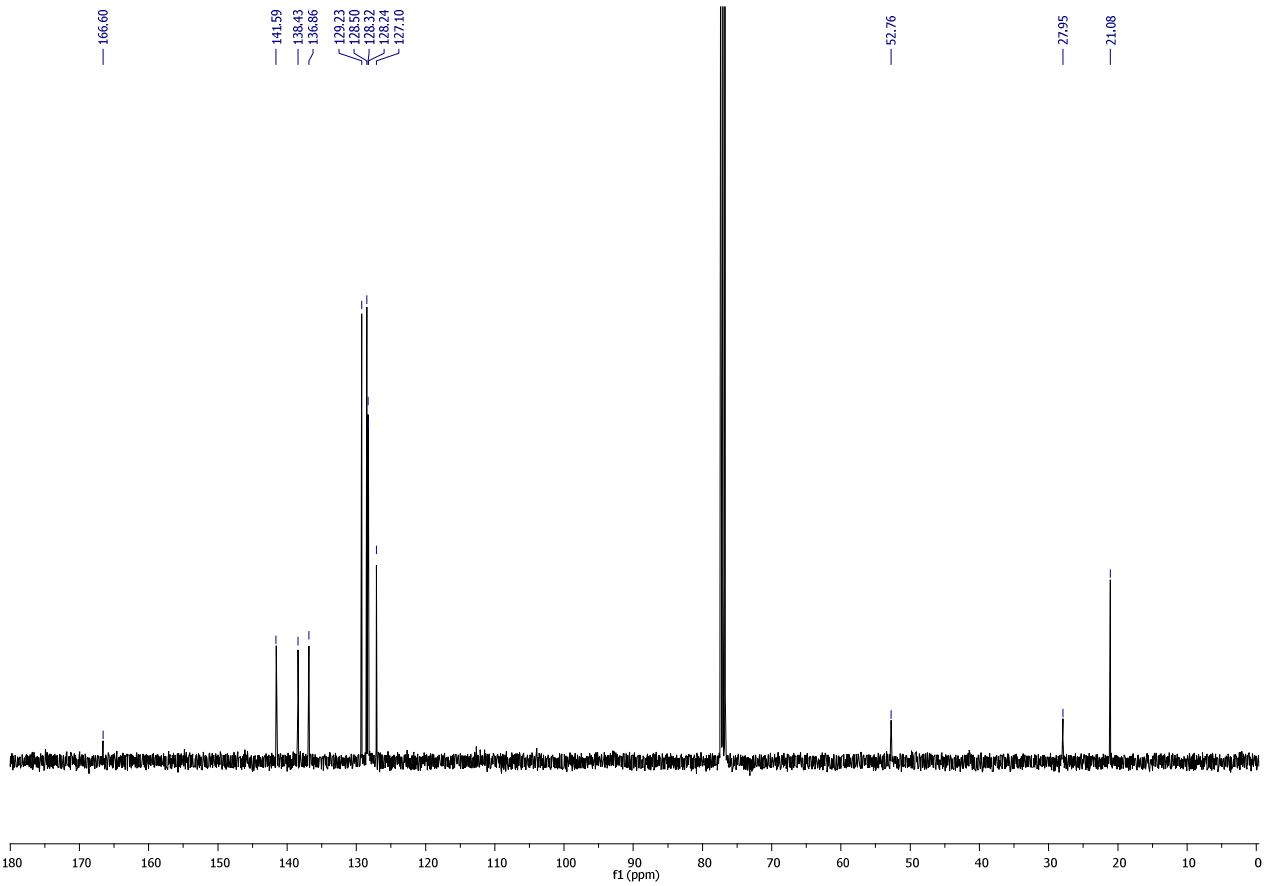
5d: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



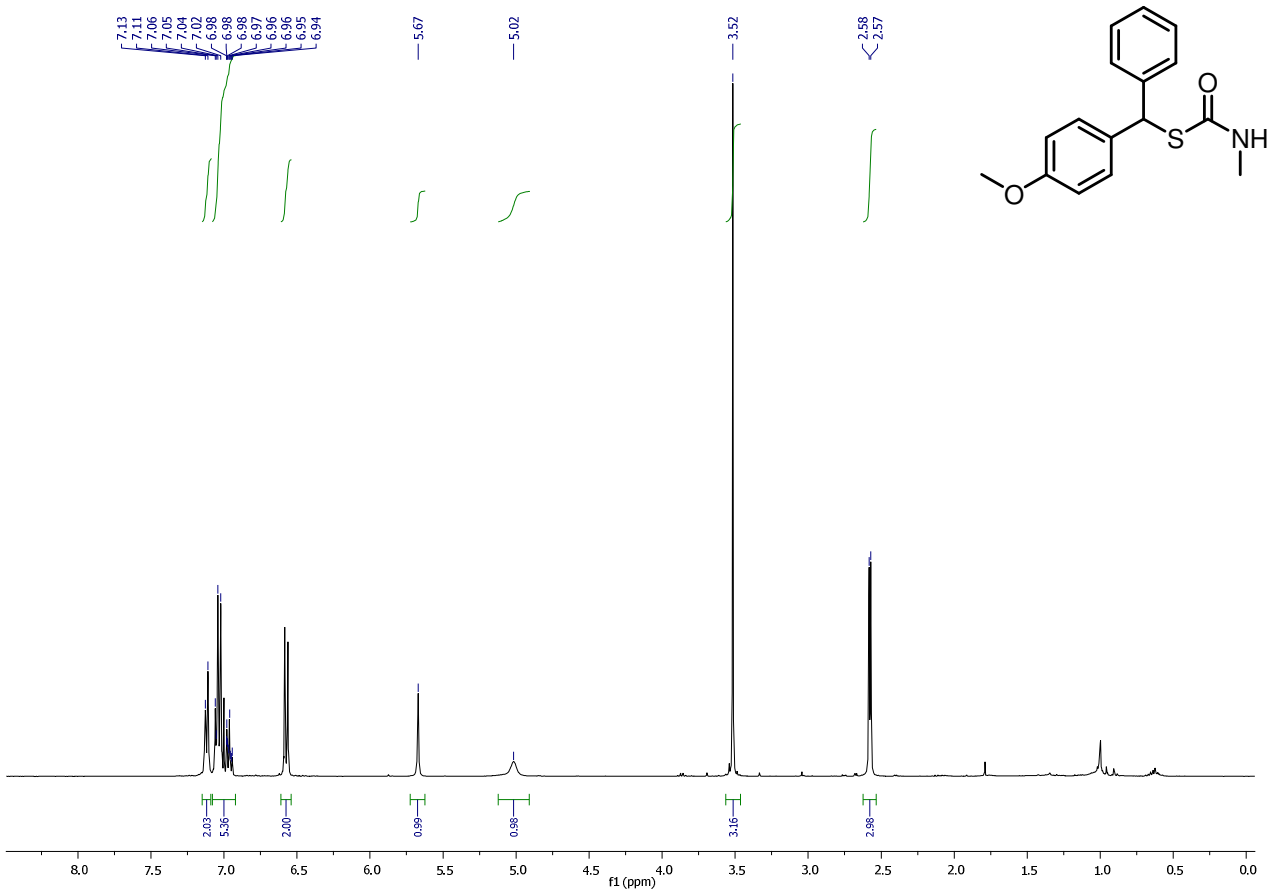


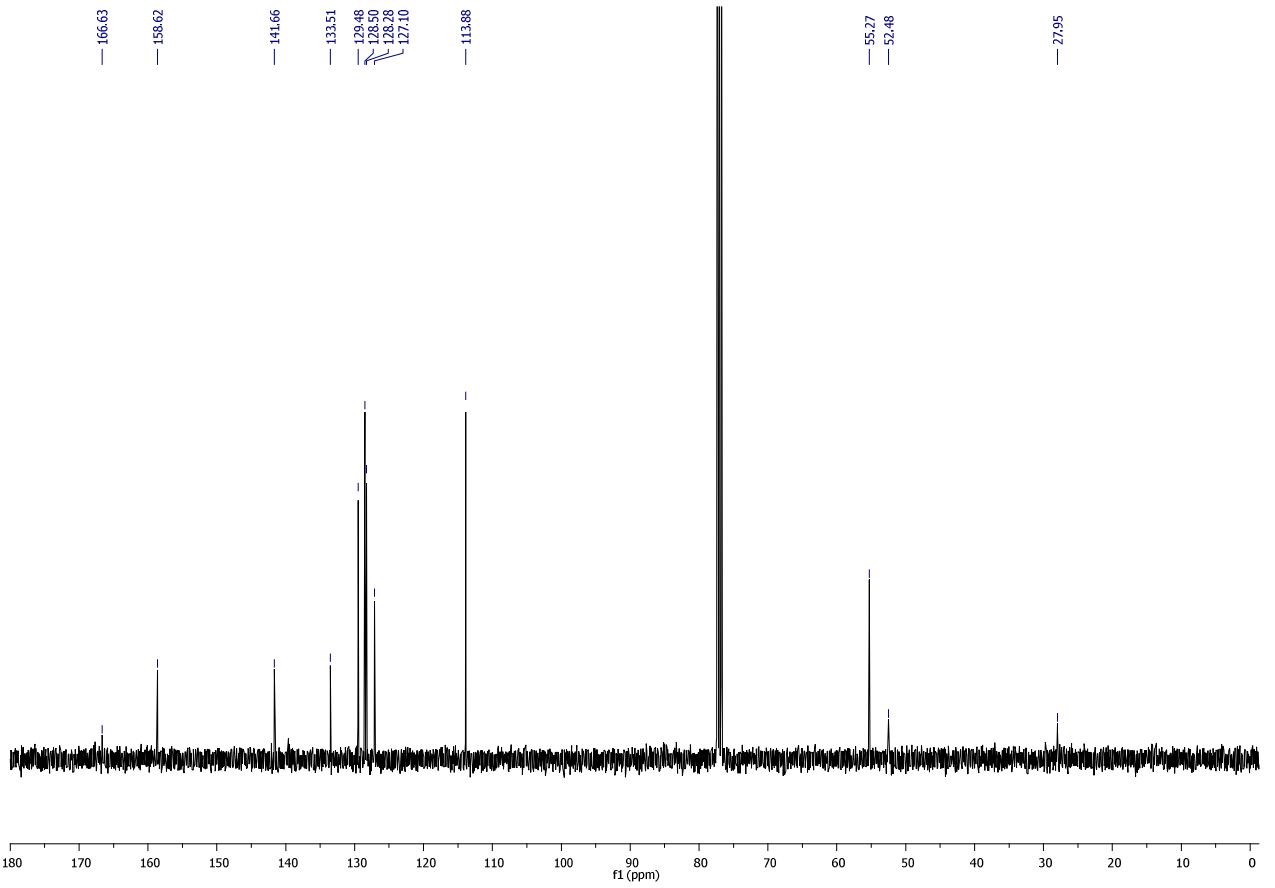
6a: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



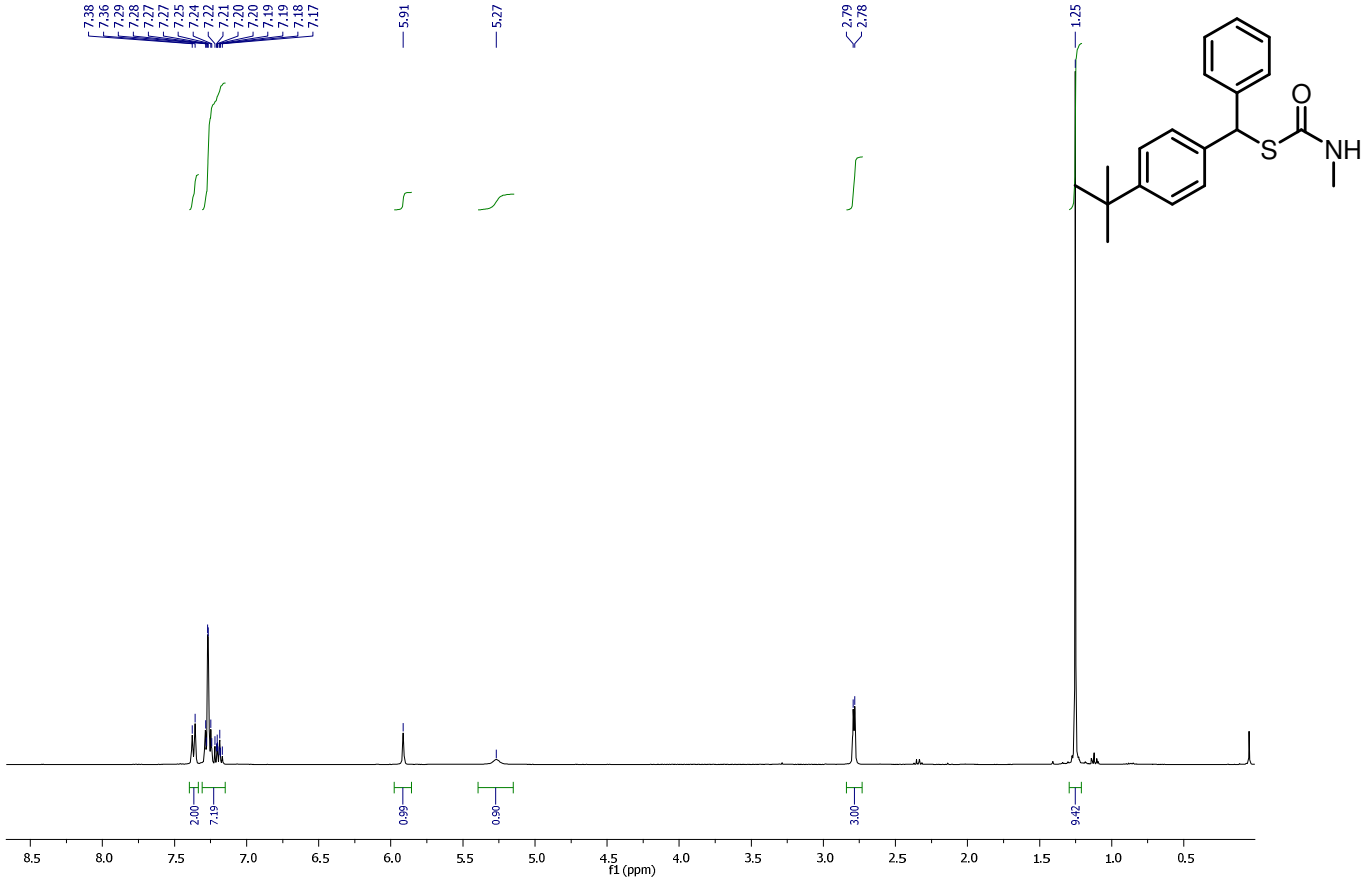


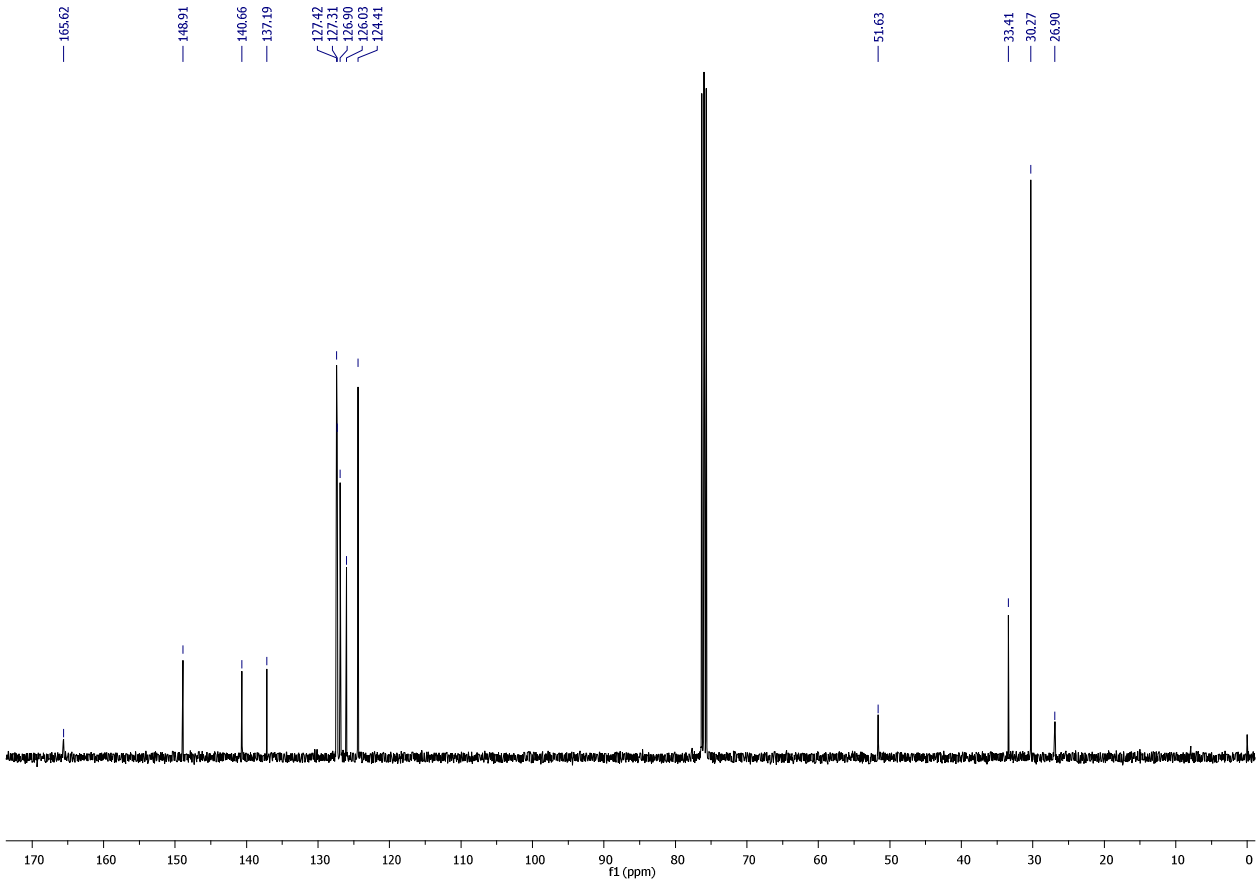
6b: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



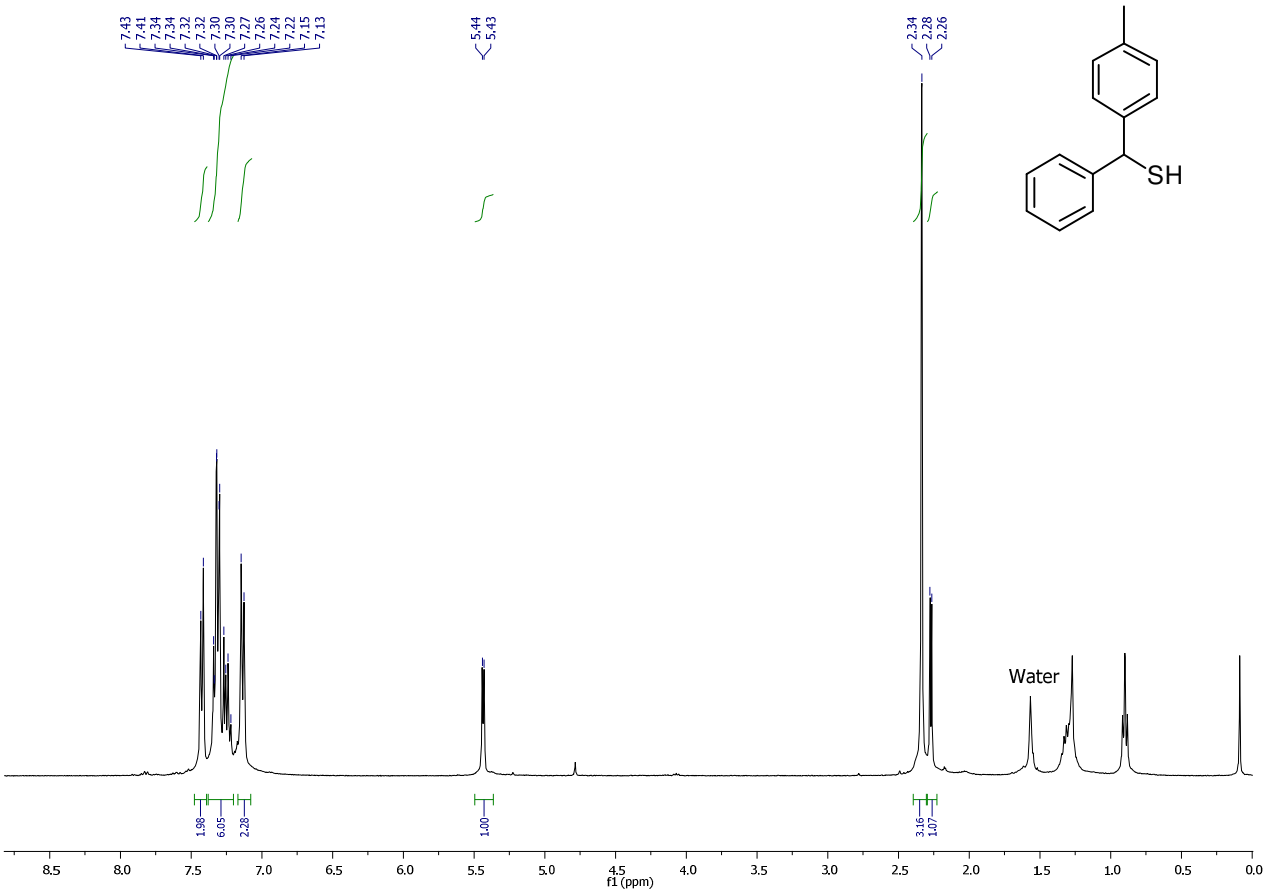


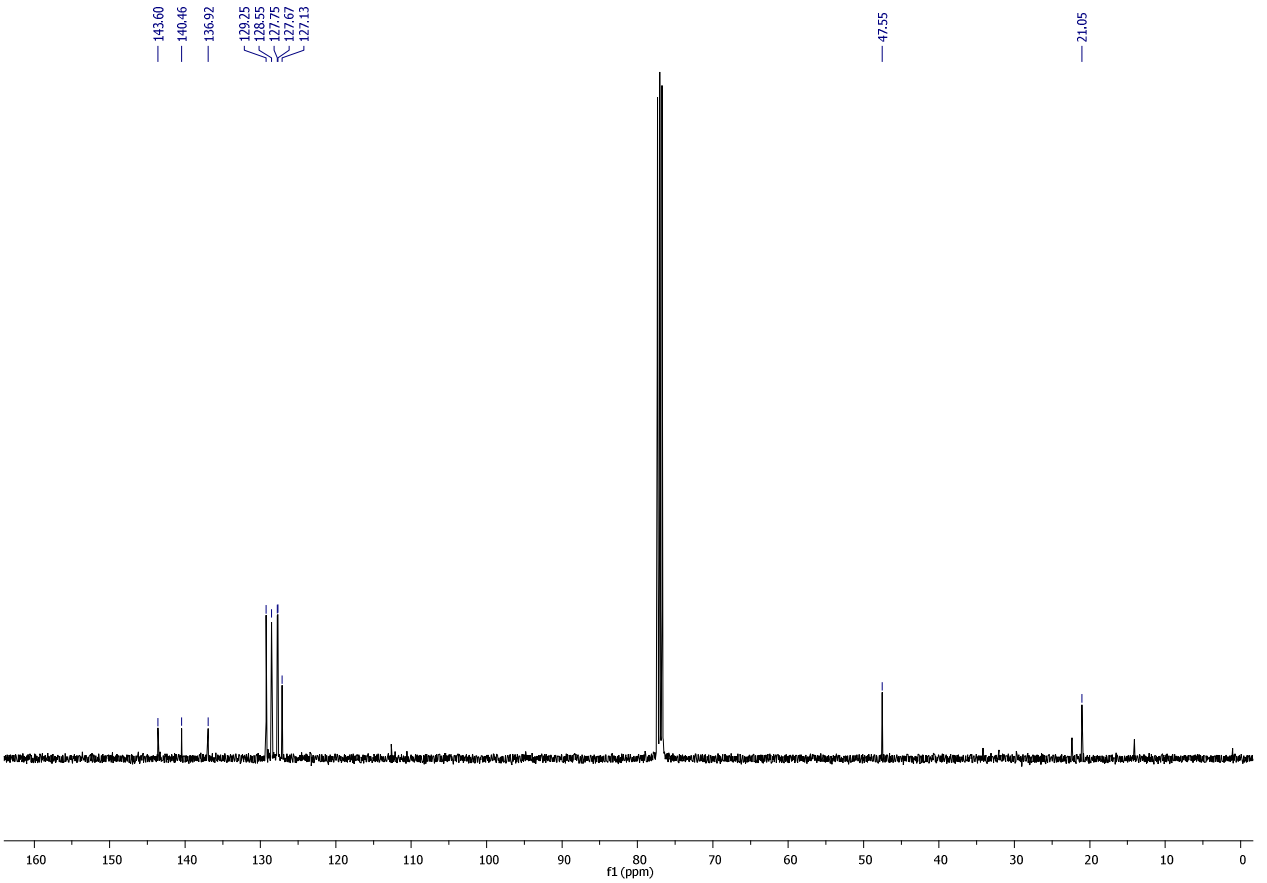
6c: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



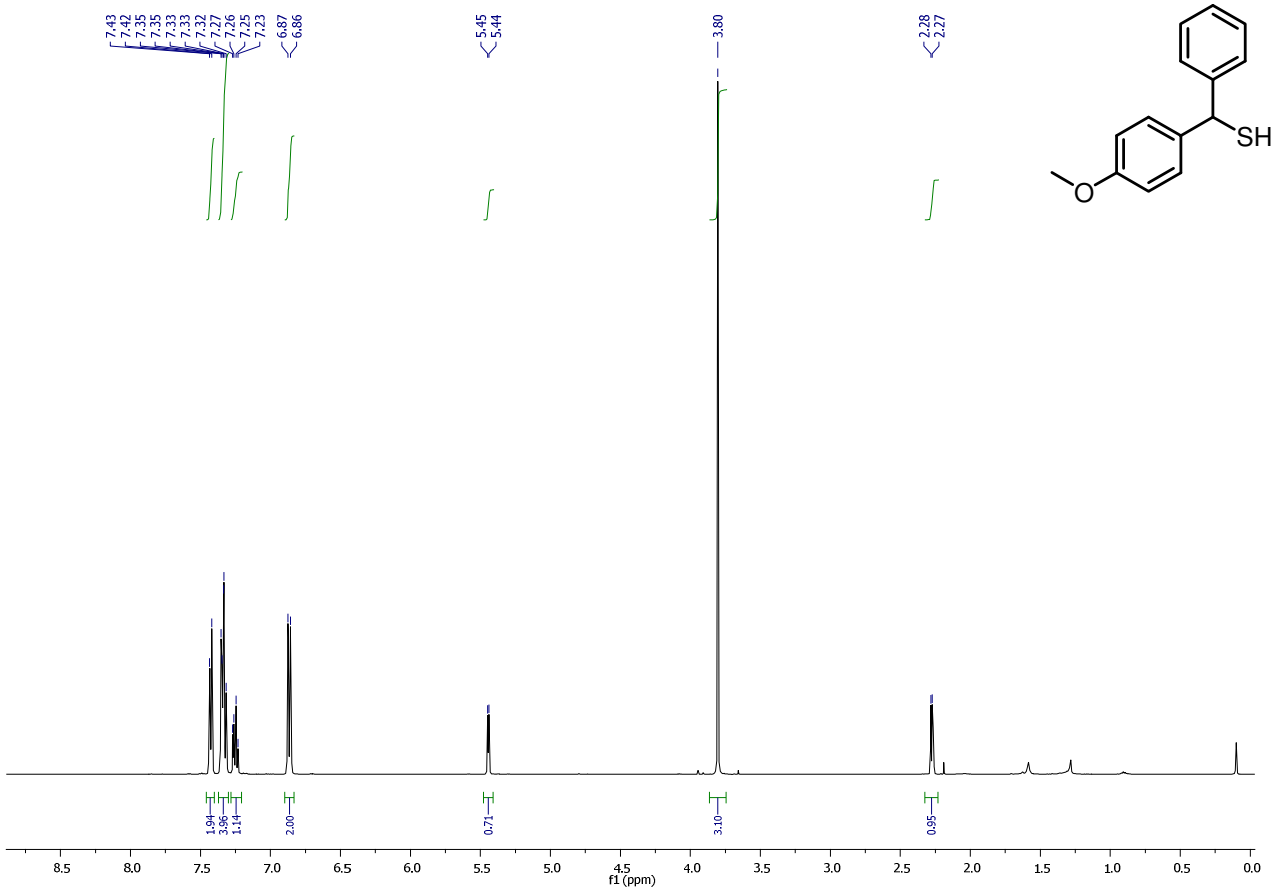


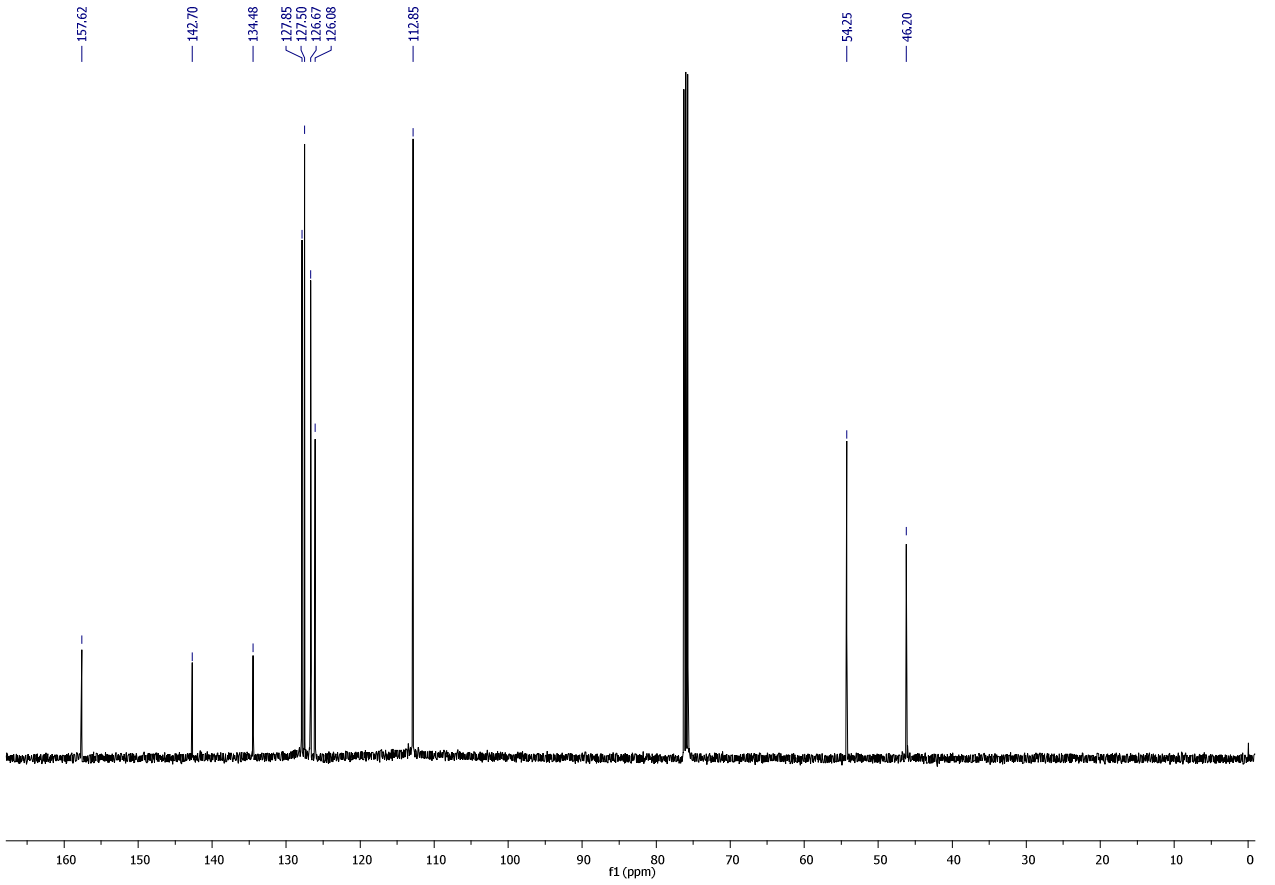
7a: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



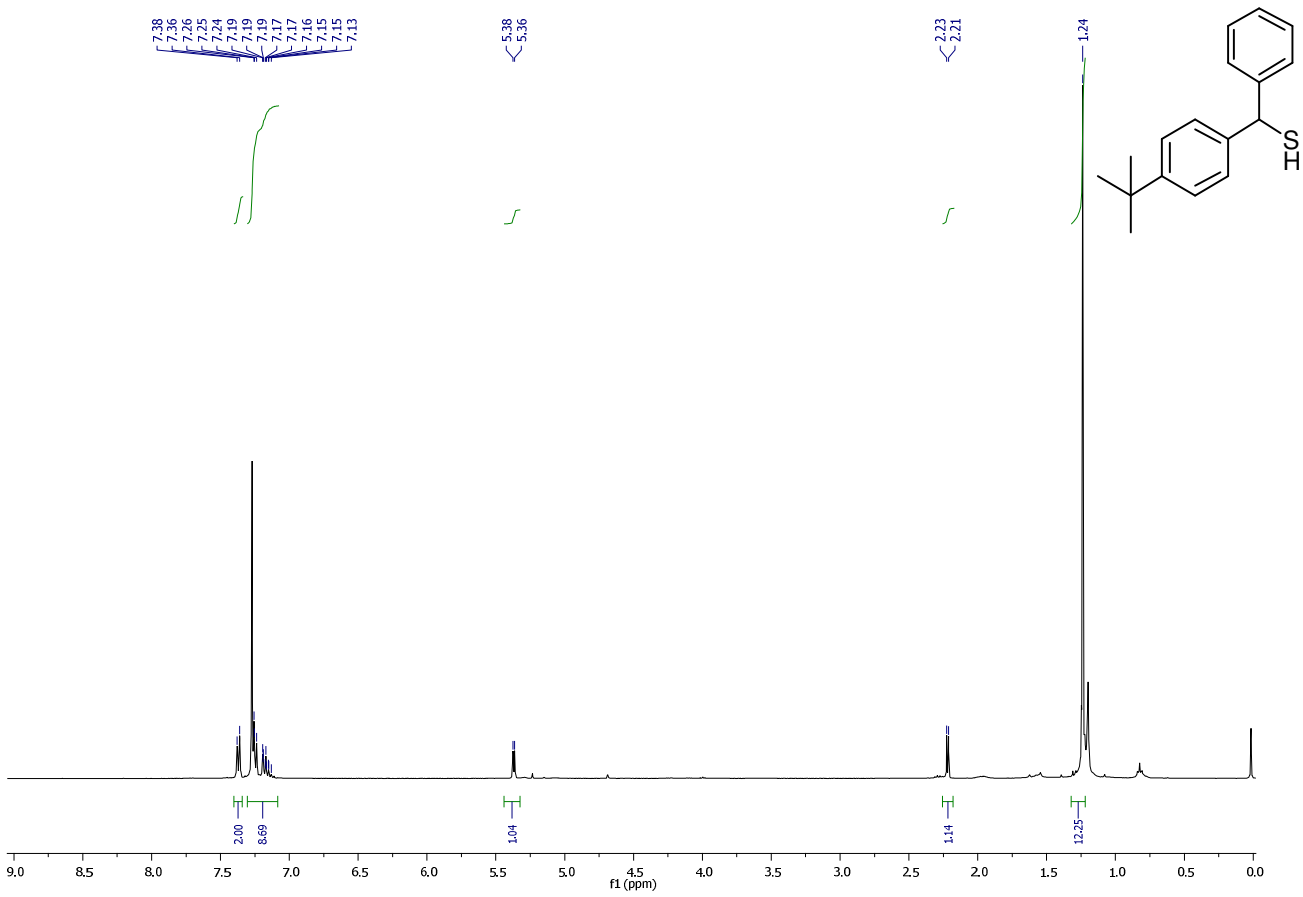


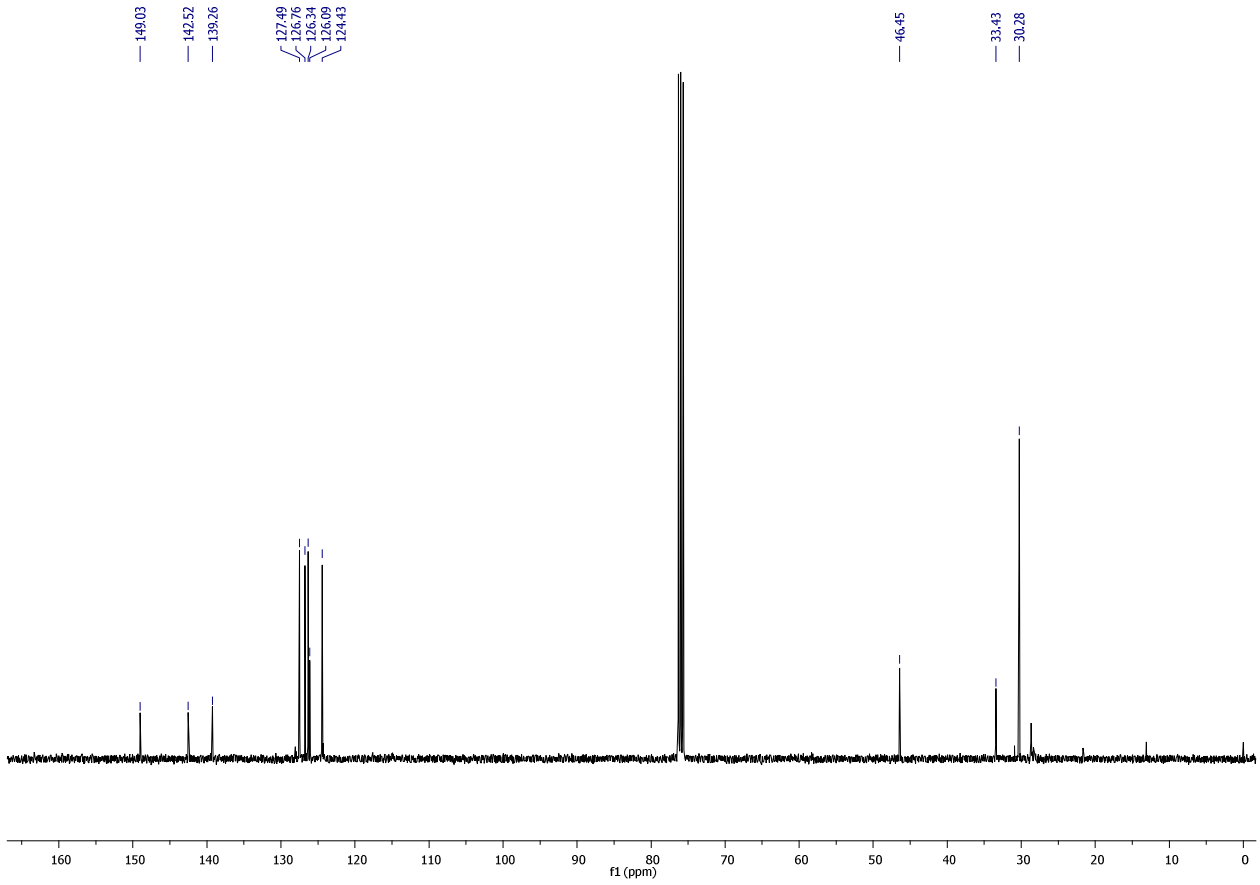
7b: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



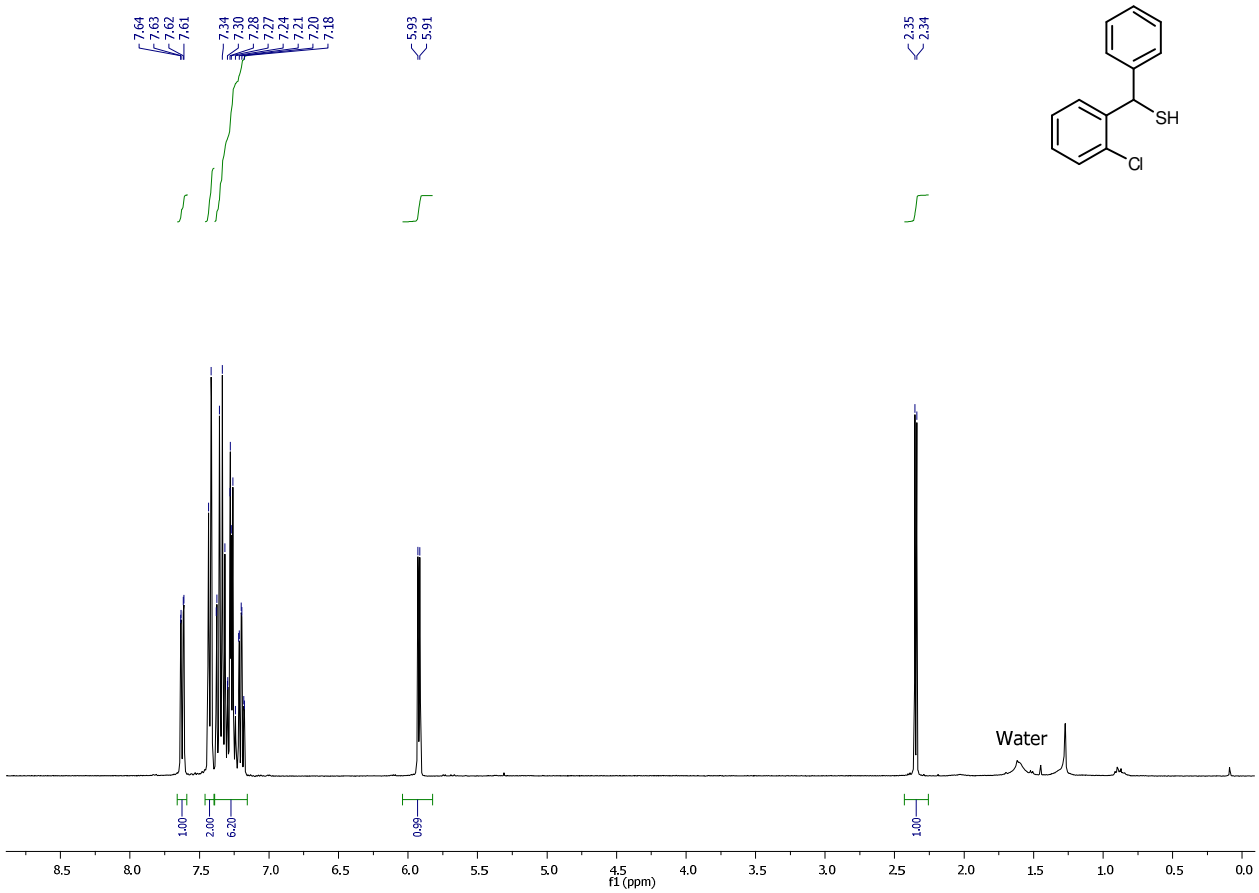


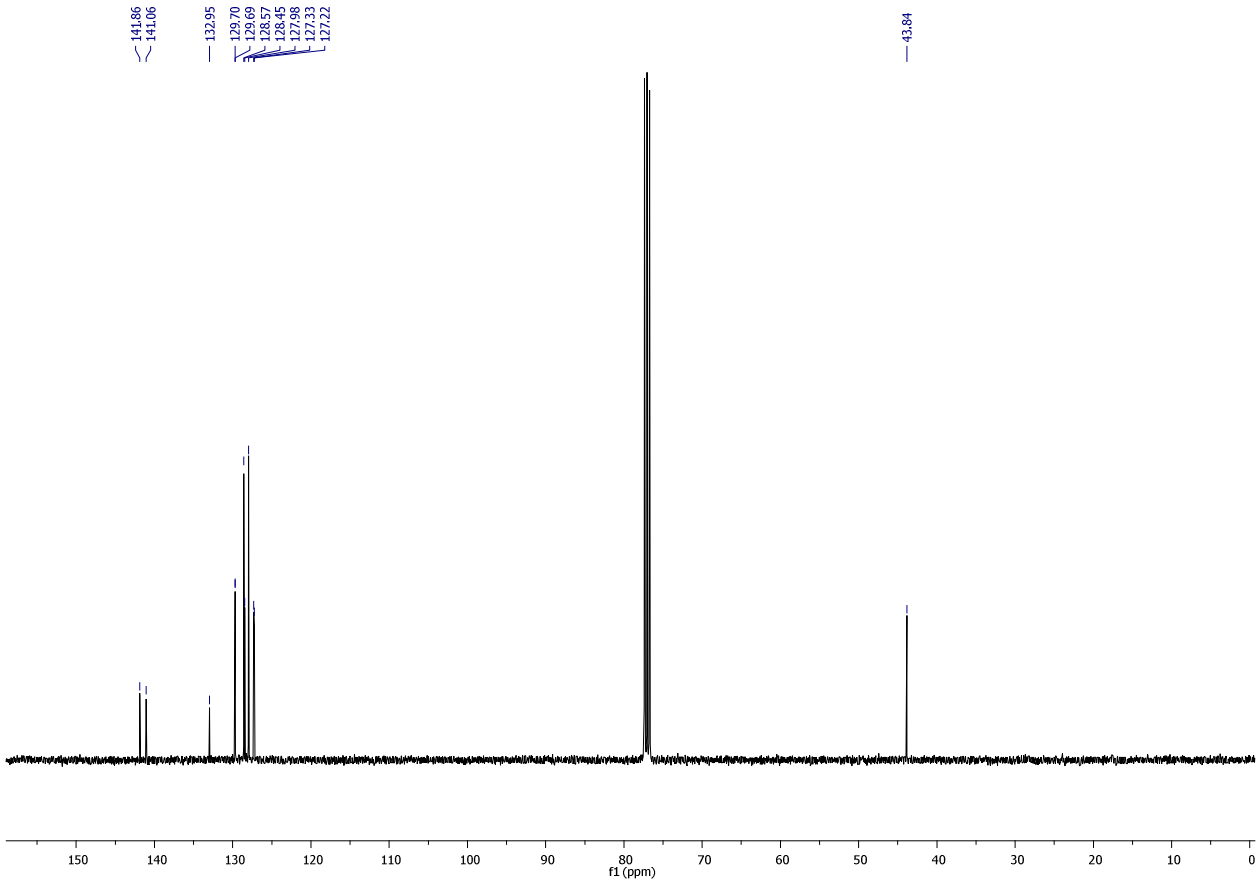
7c: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



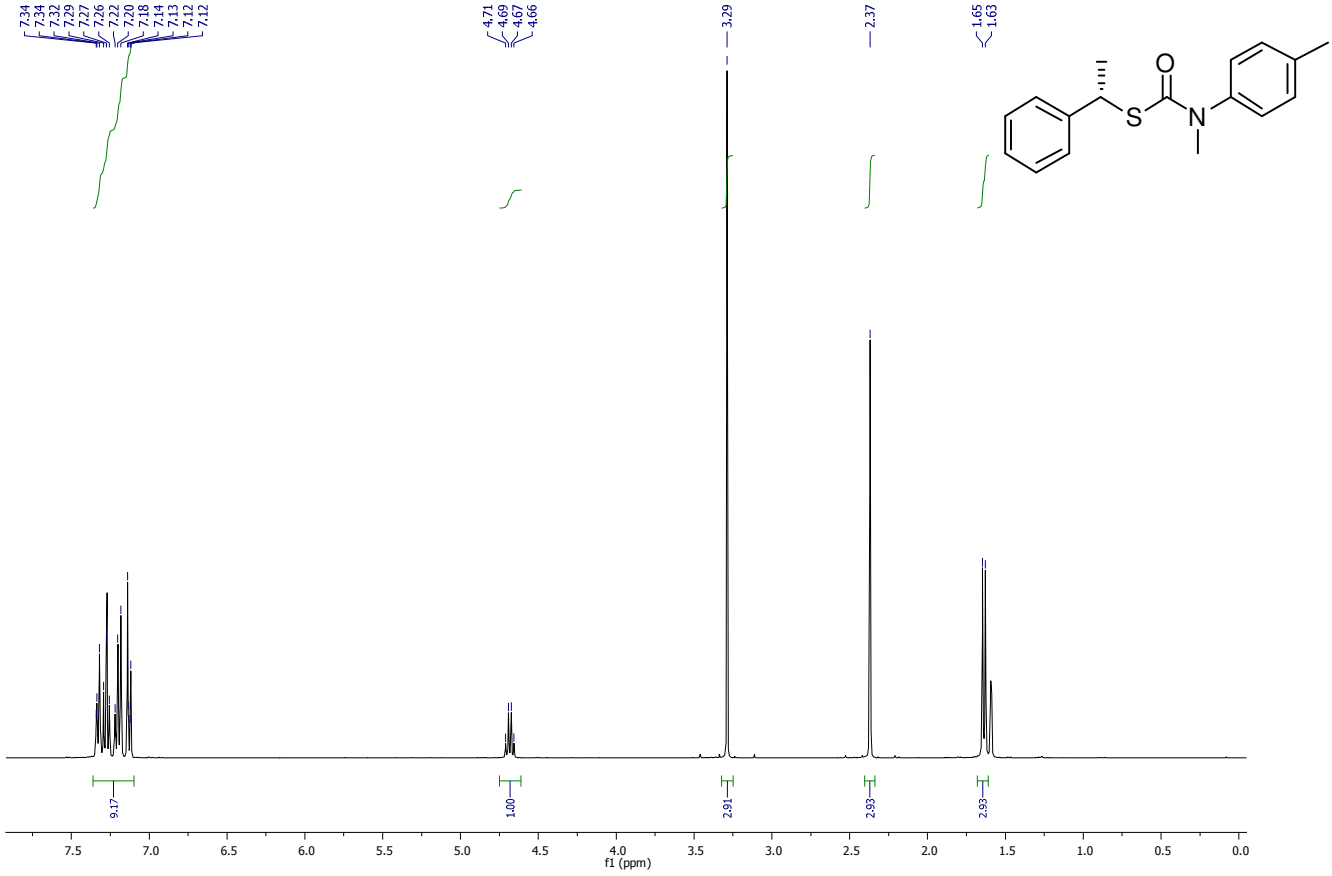


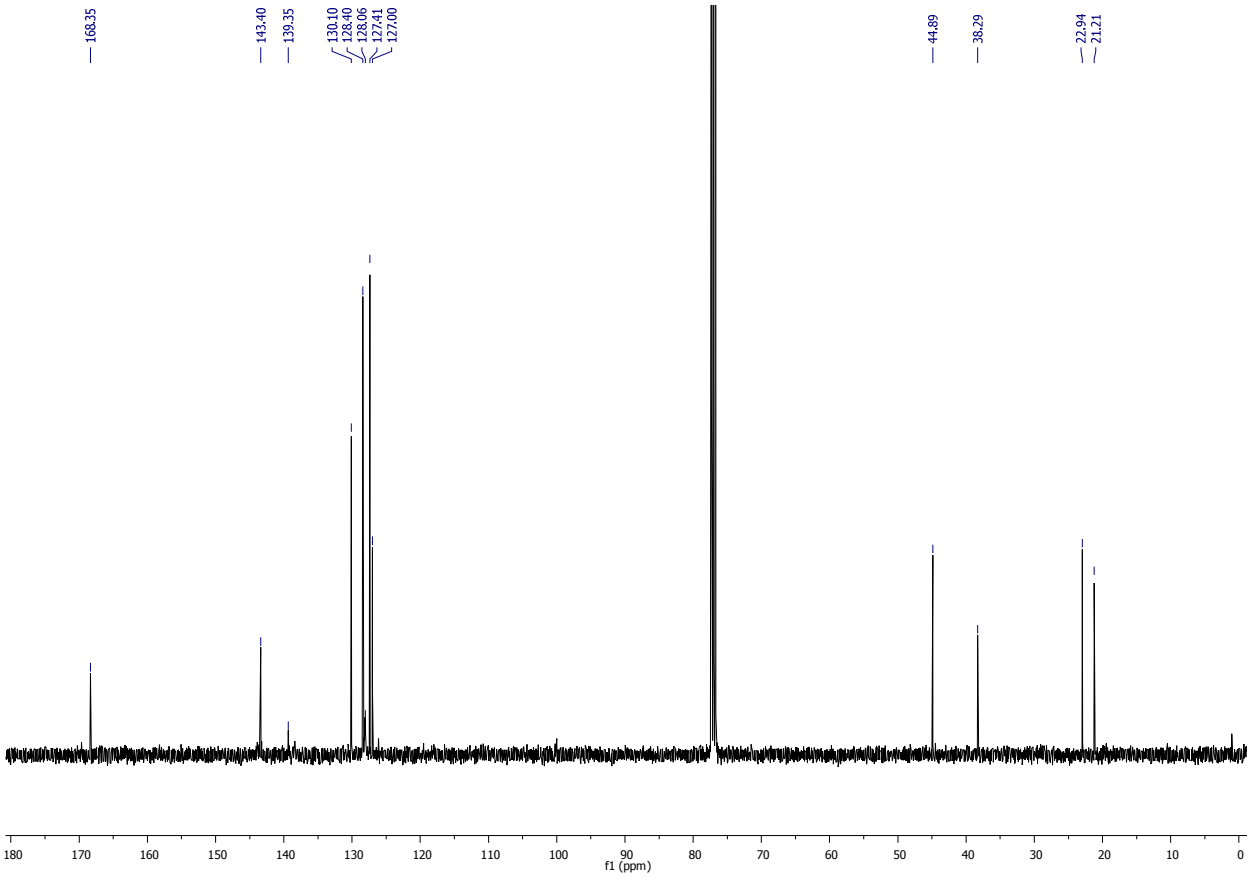
7d: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



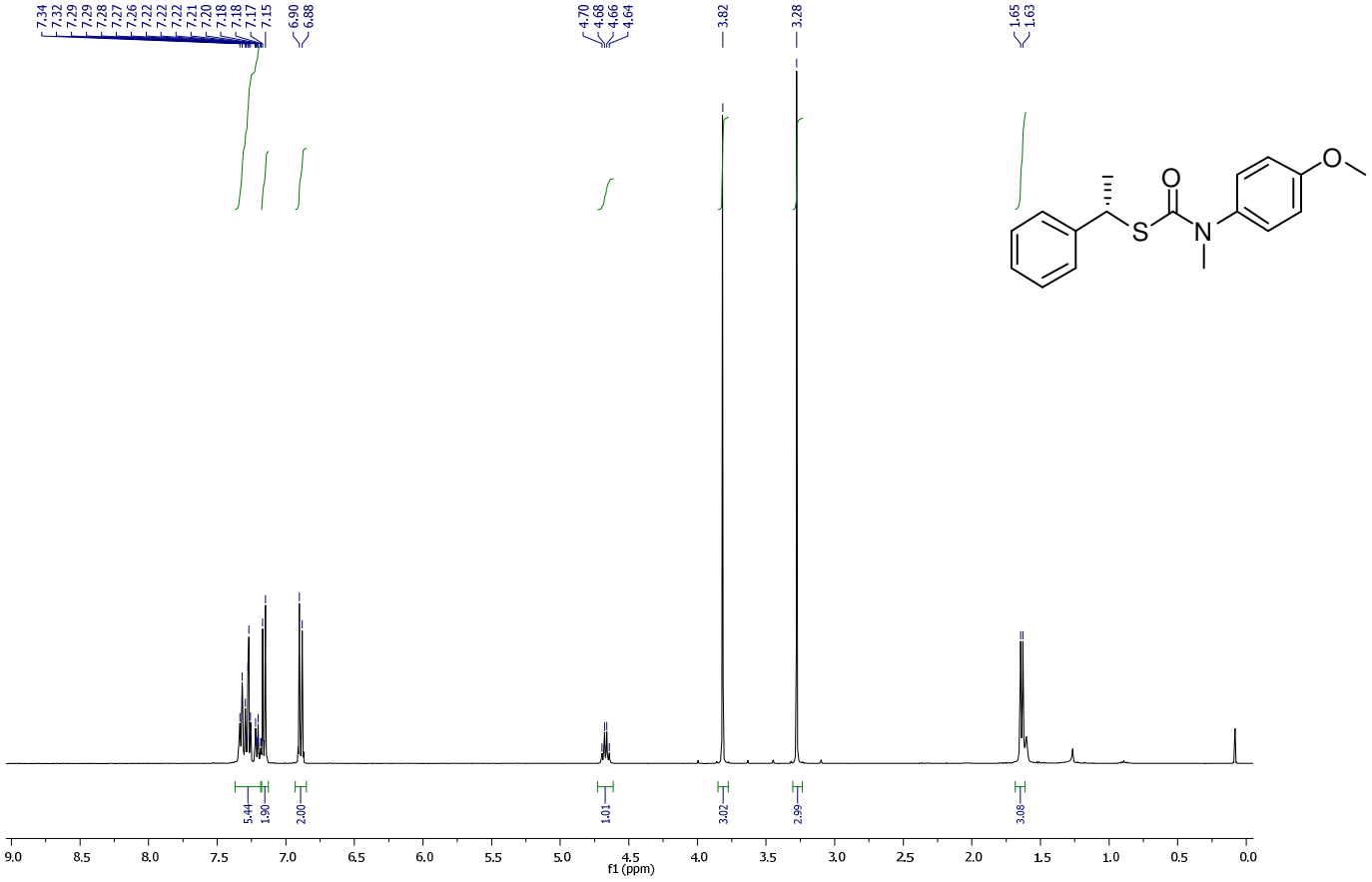


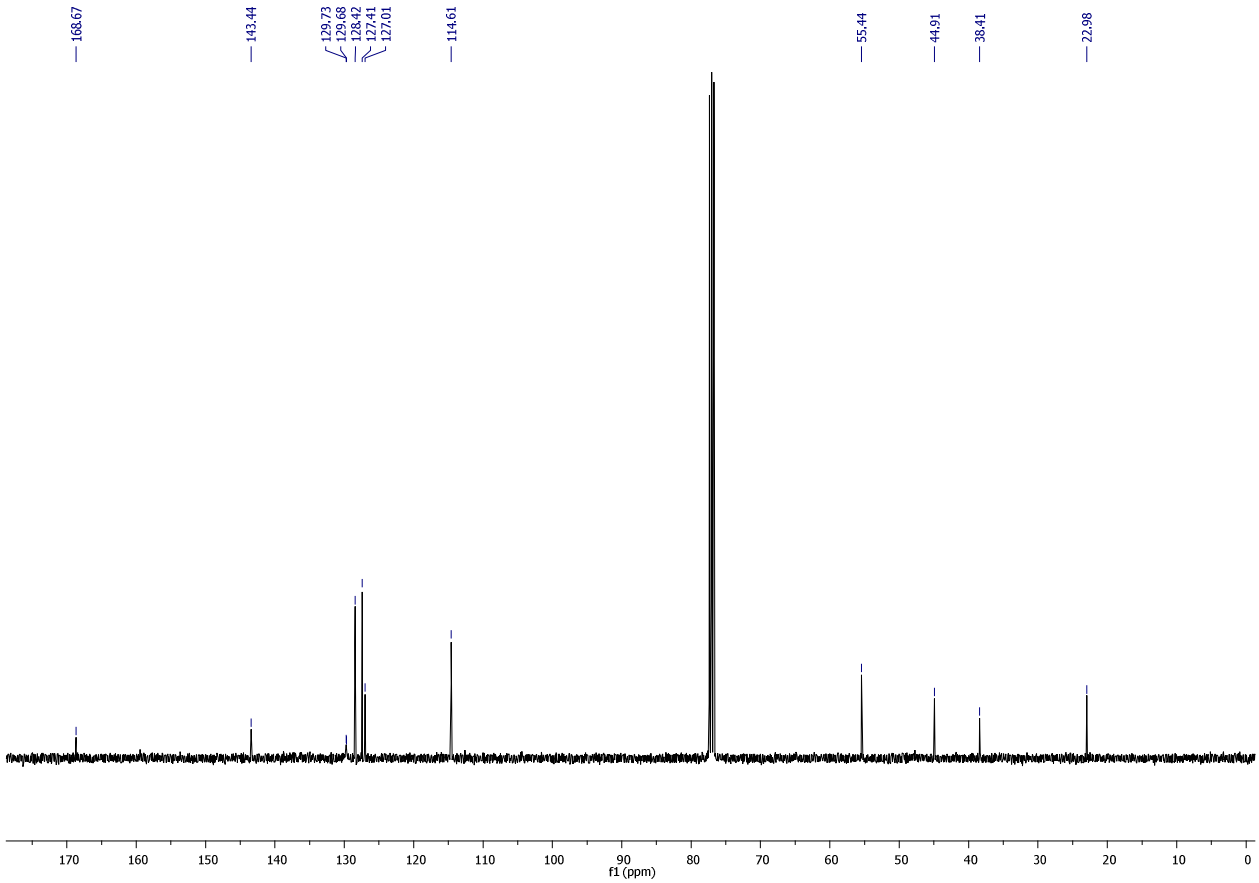
8a: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



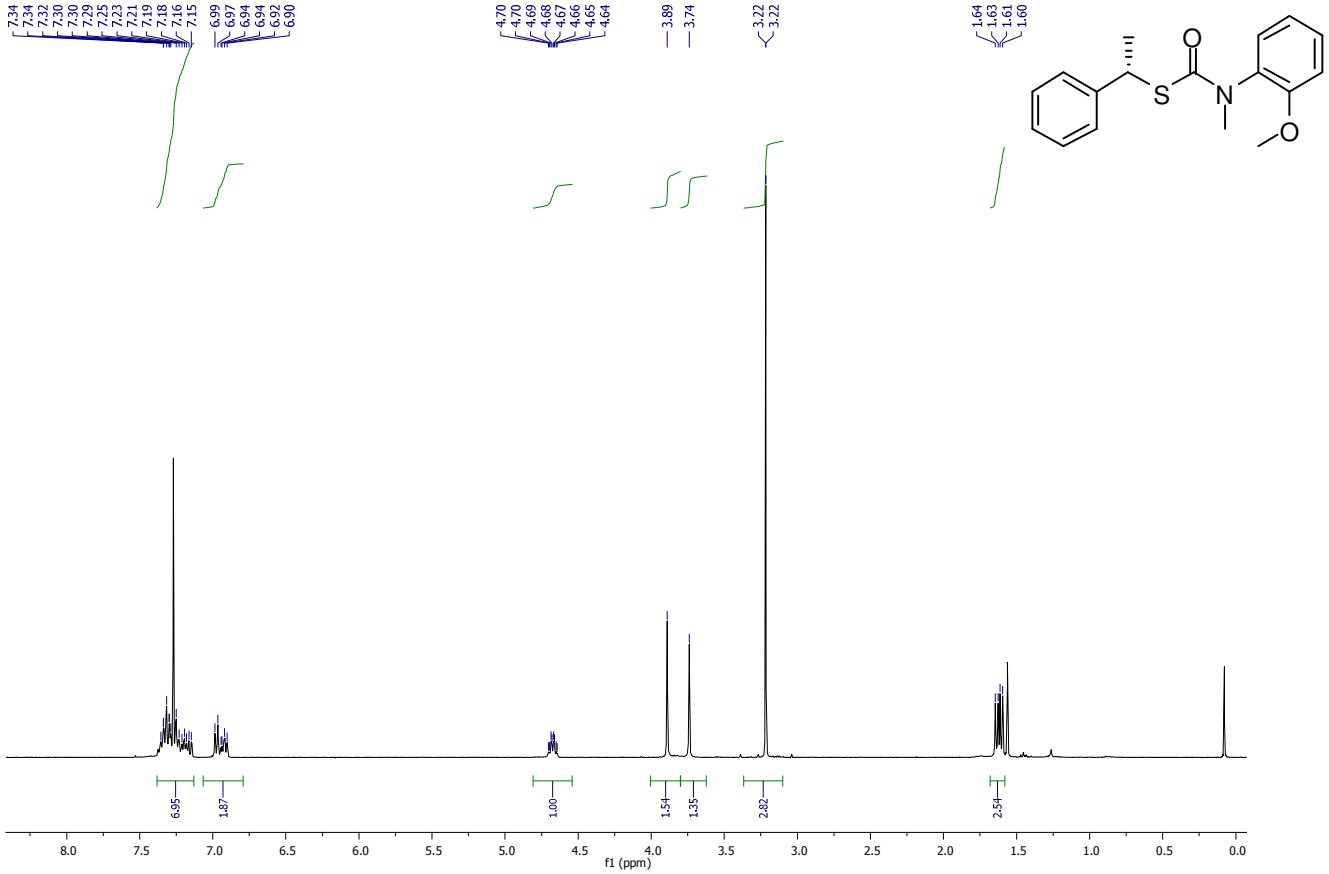


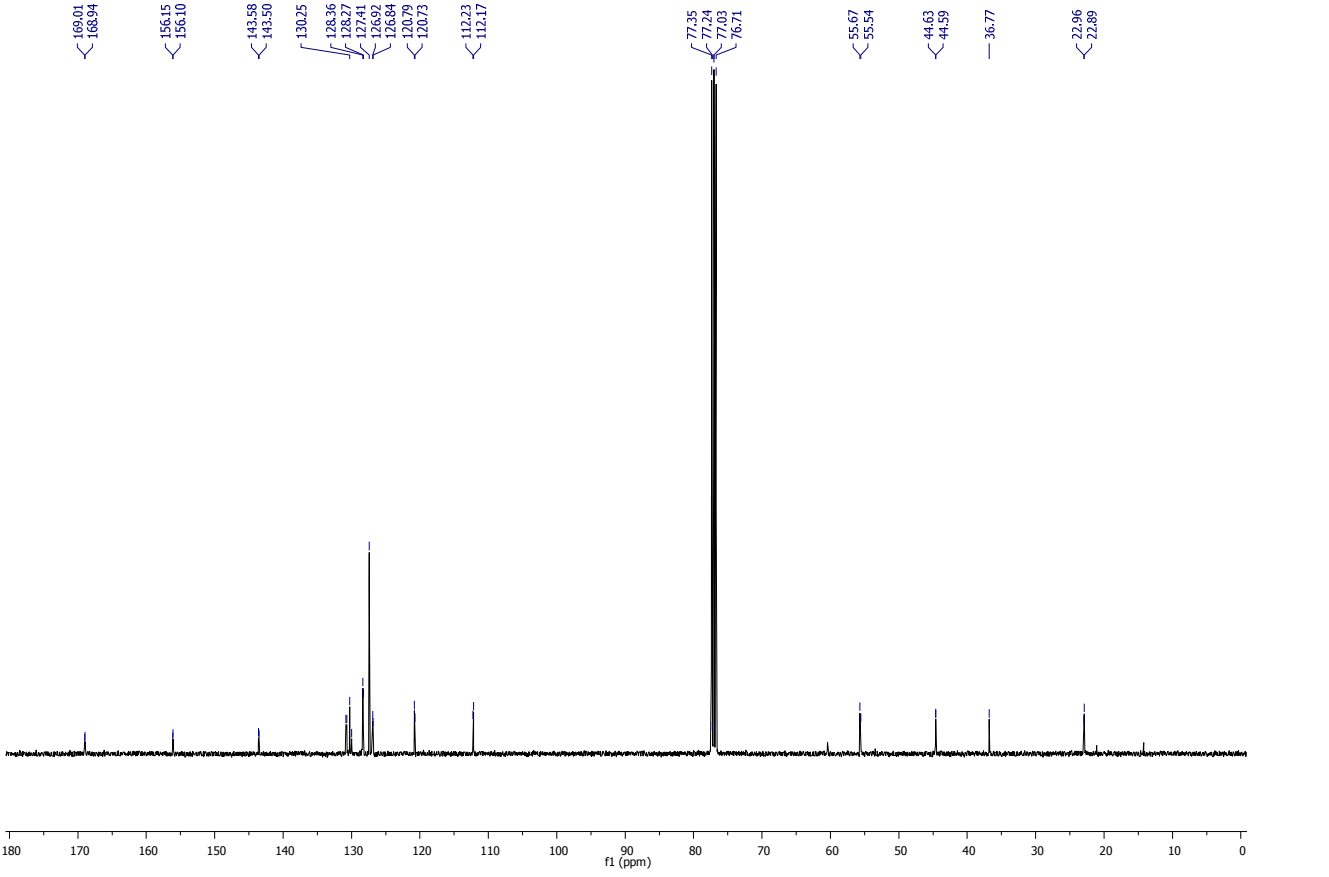
8b: **^{1}H-NMR**: 500 MHz, **^{13}C-NMR**: 100 MHz



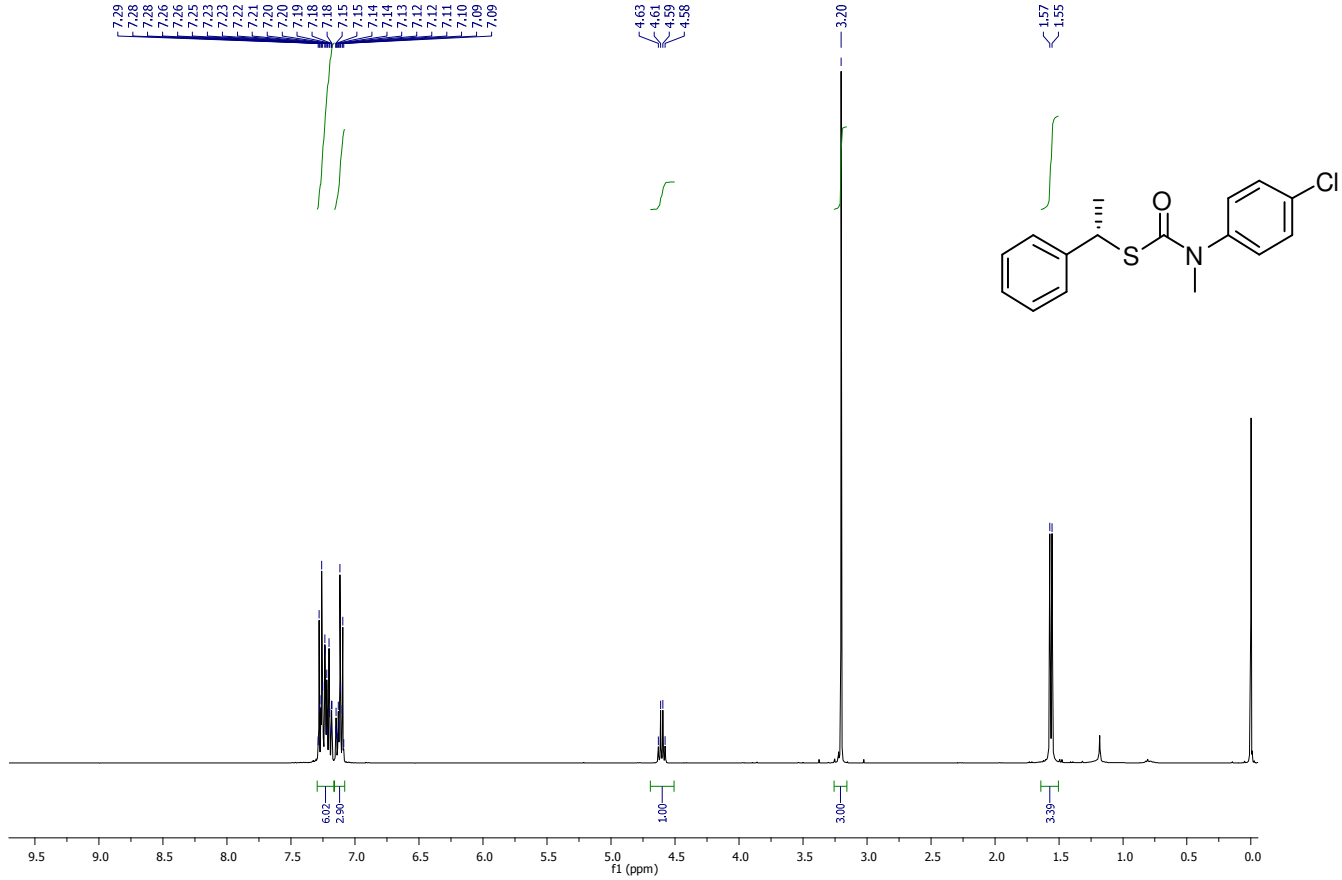


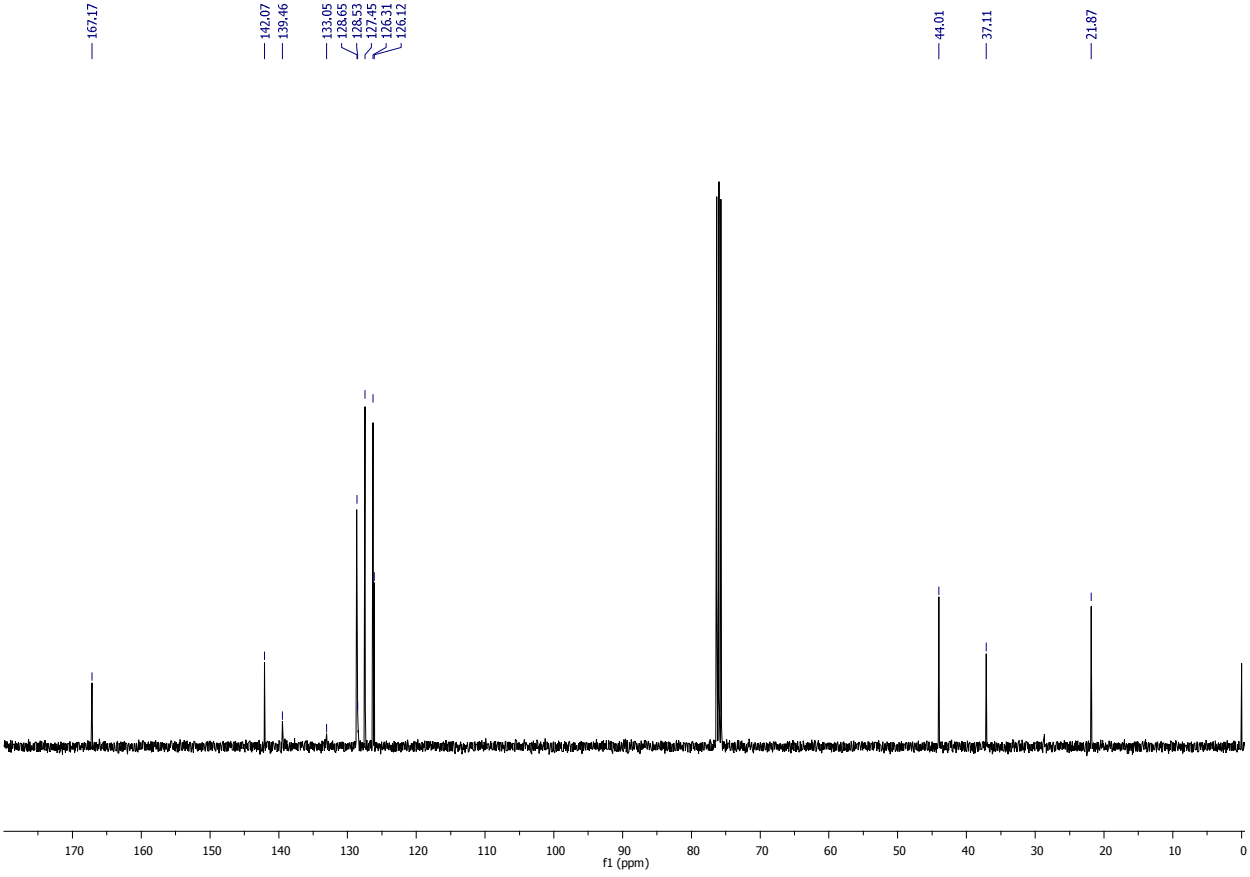
8c: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



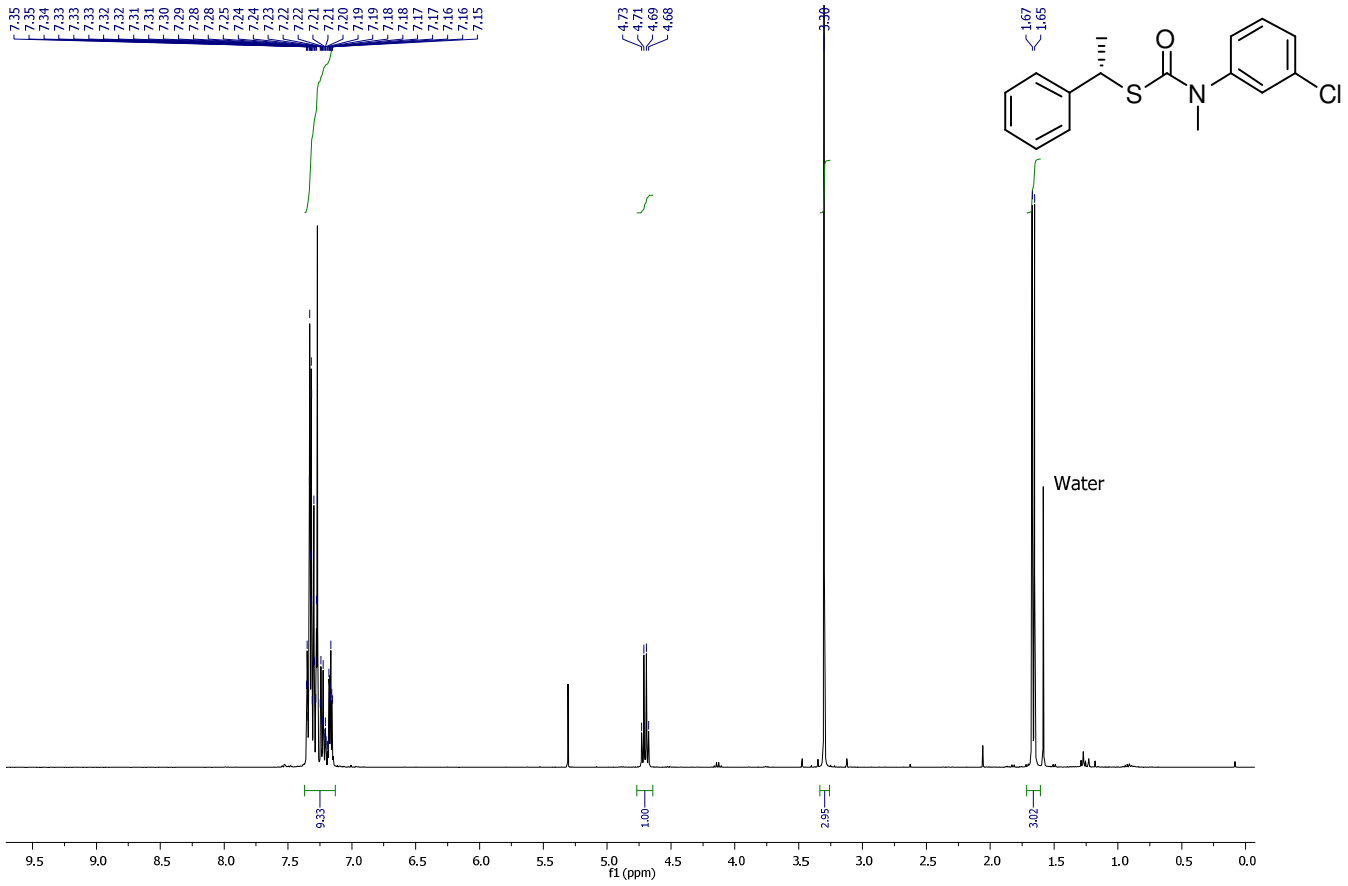


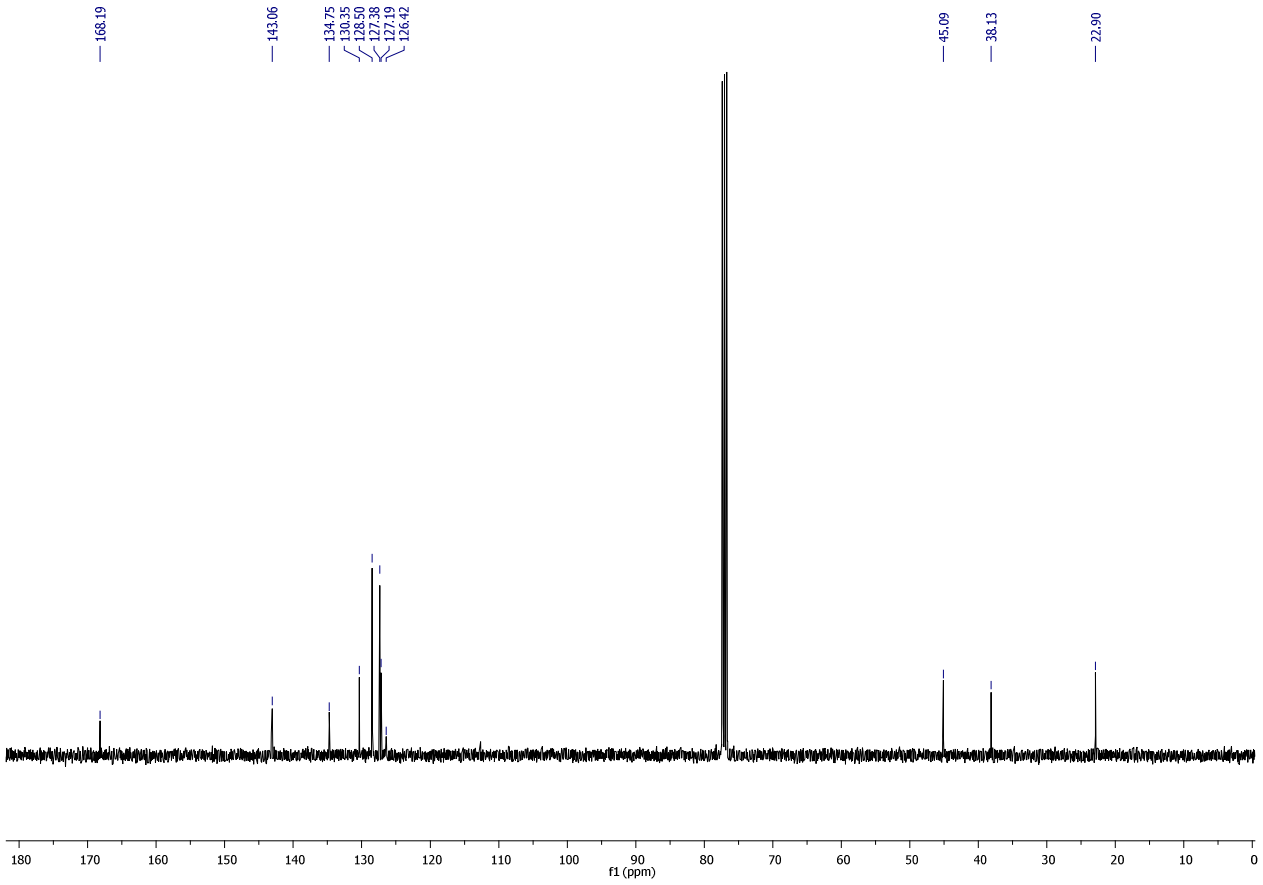
8d: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



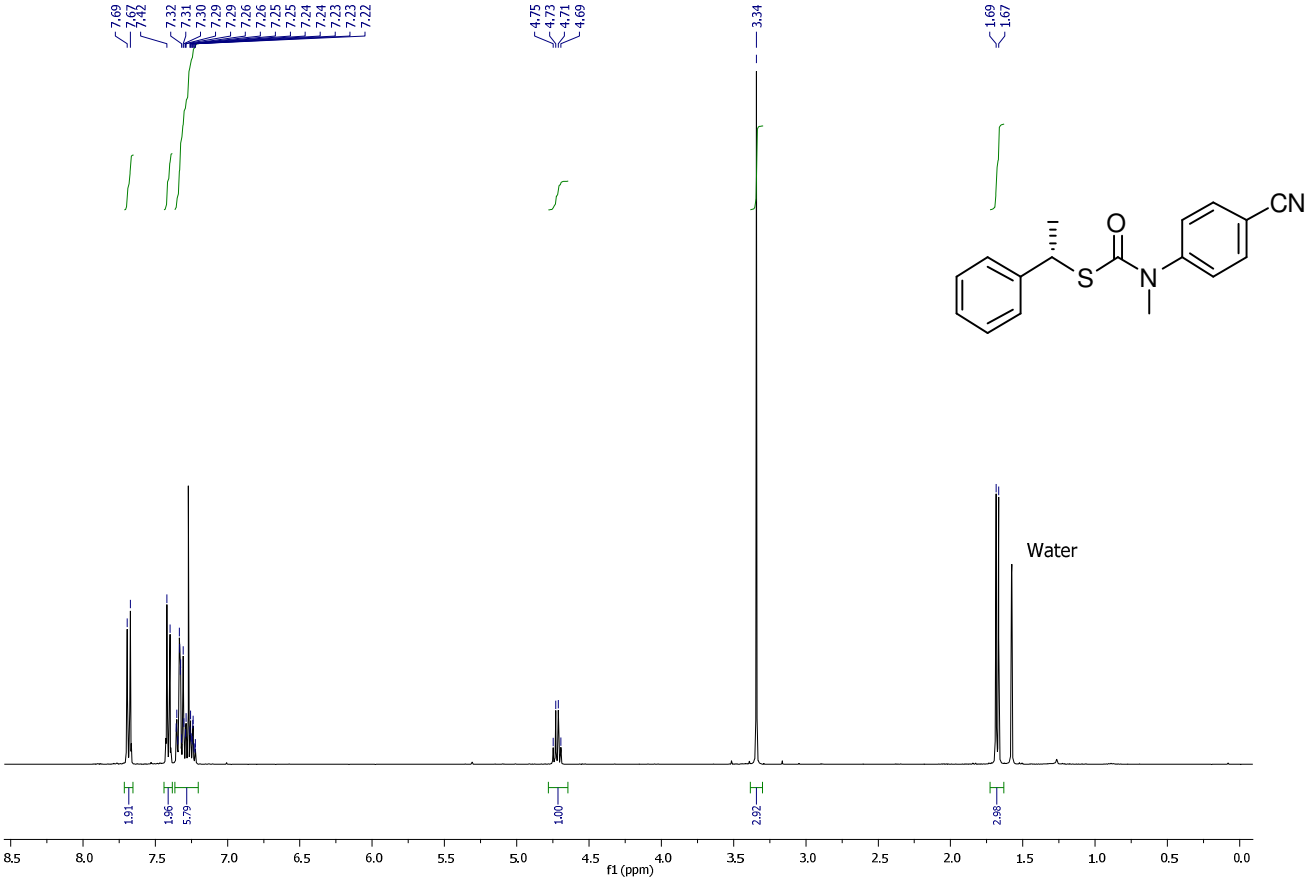


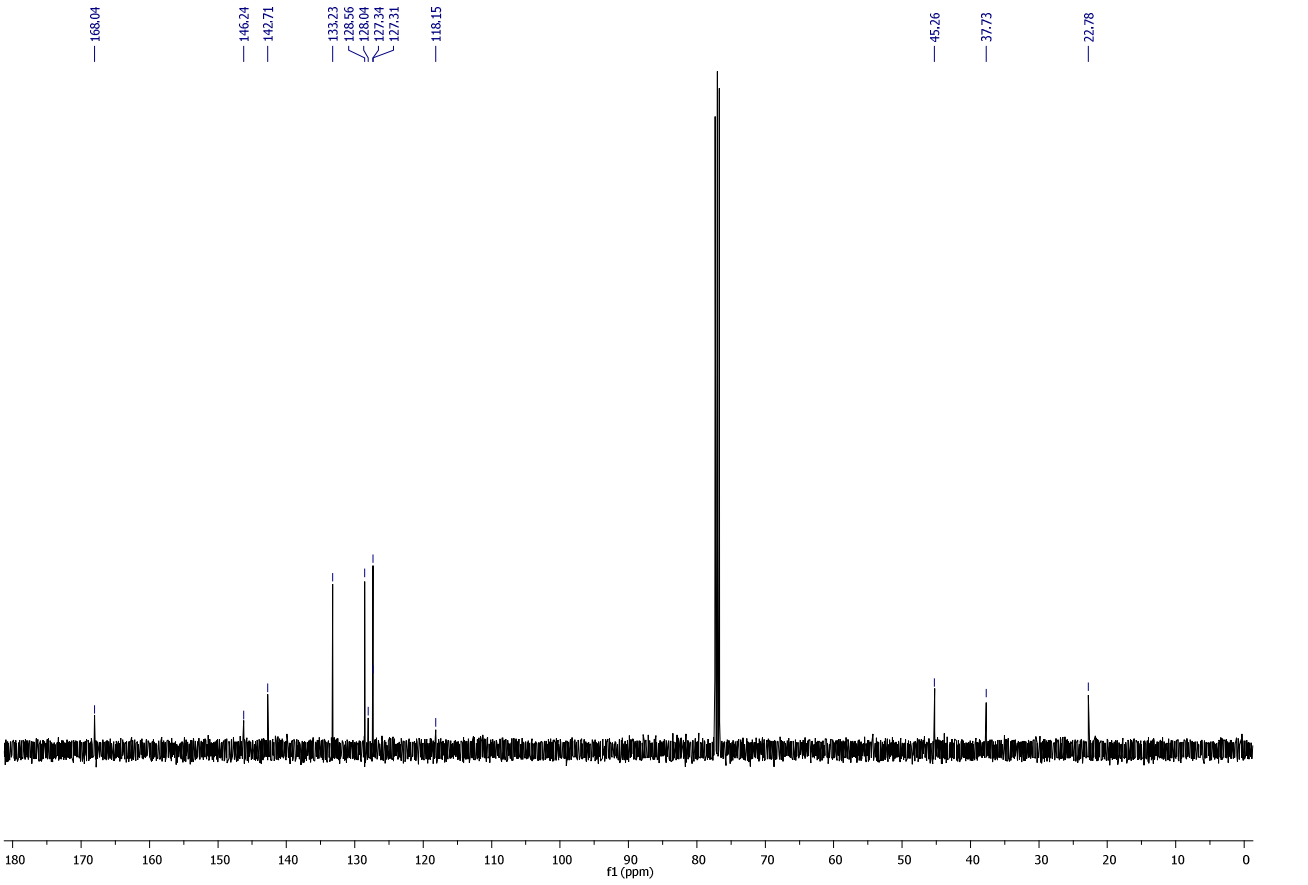
8e: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



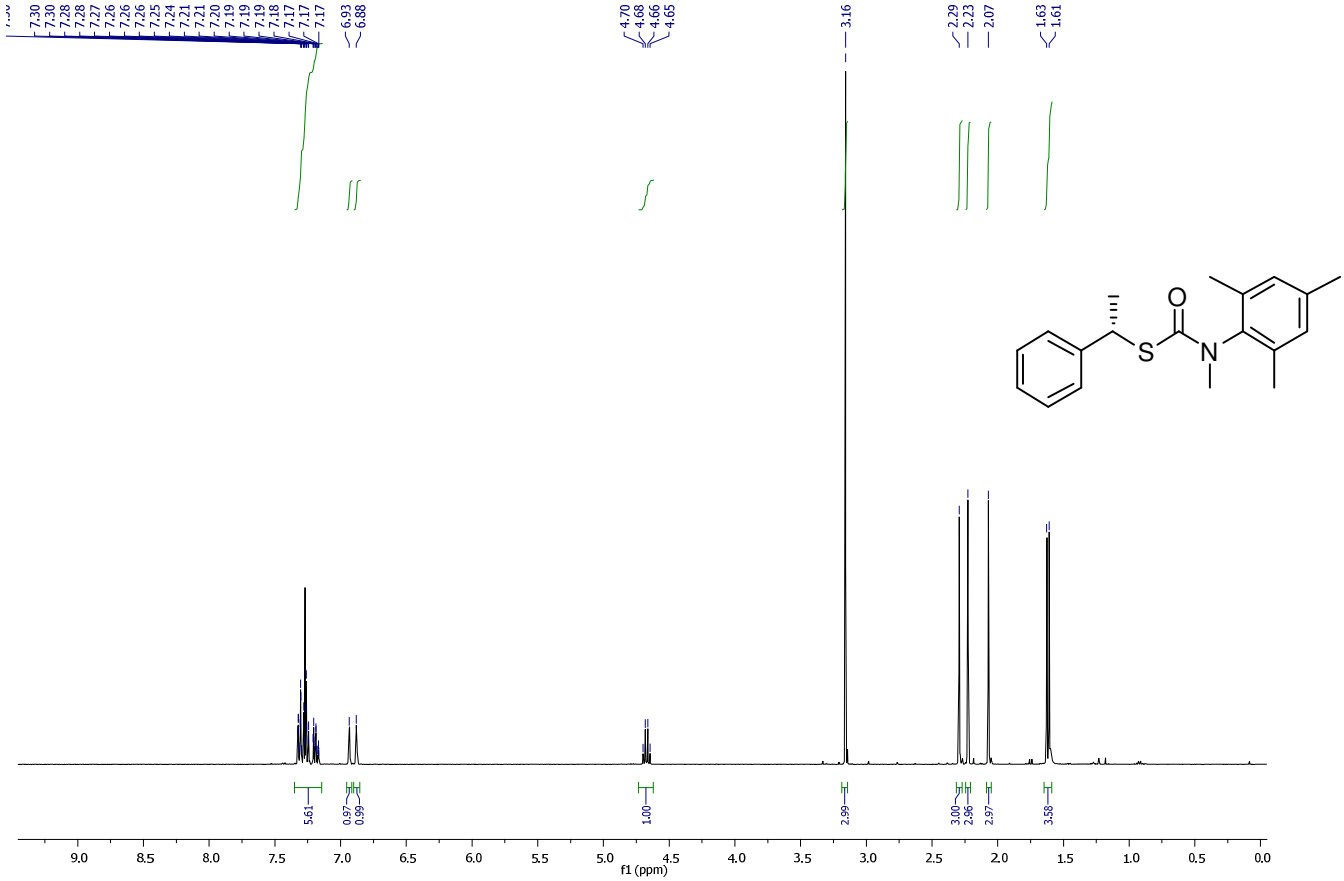


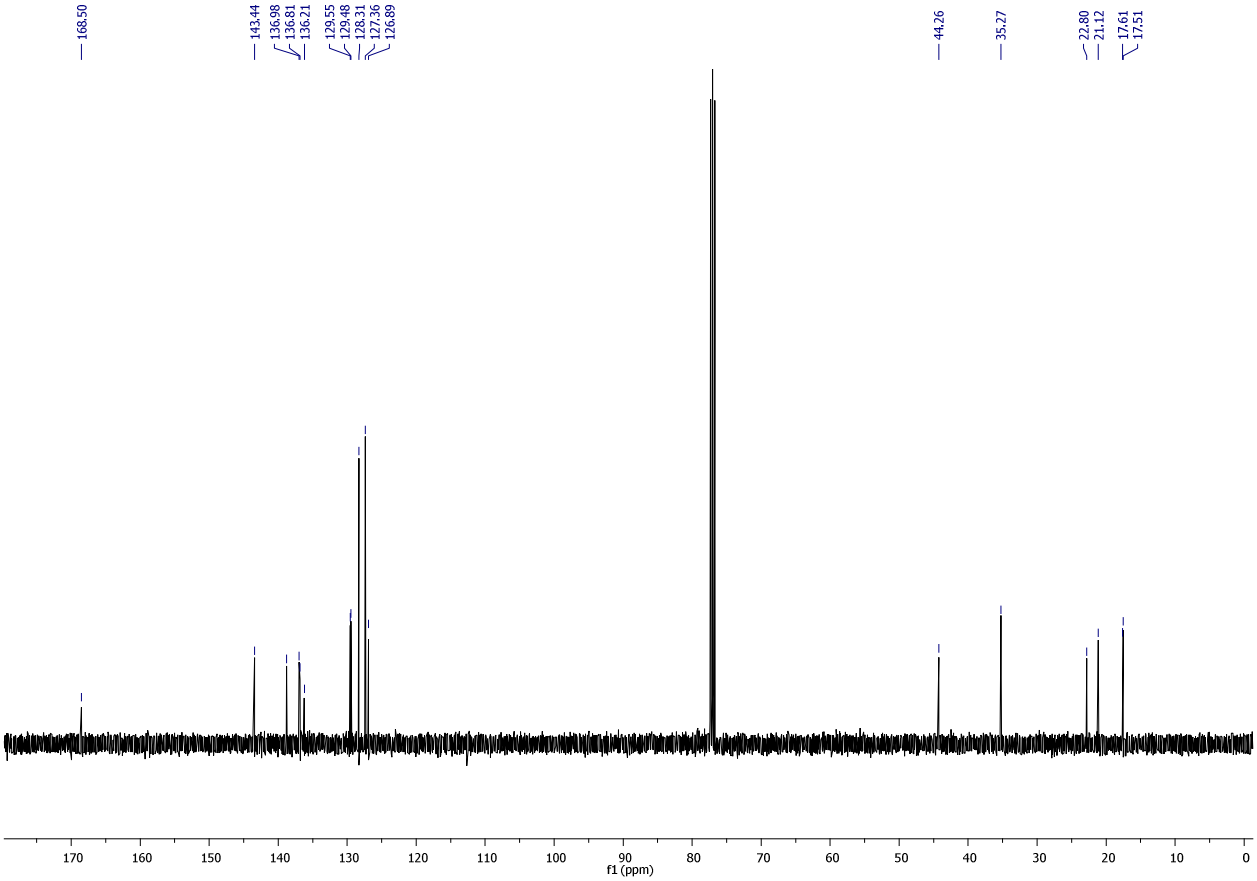
8f: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



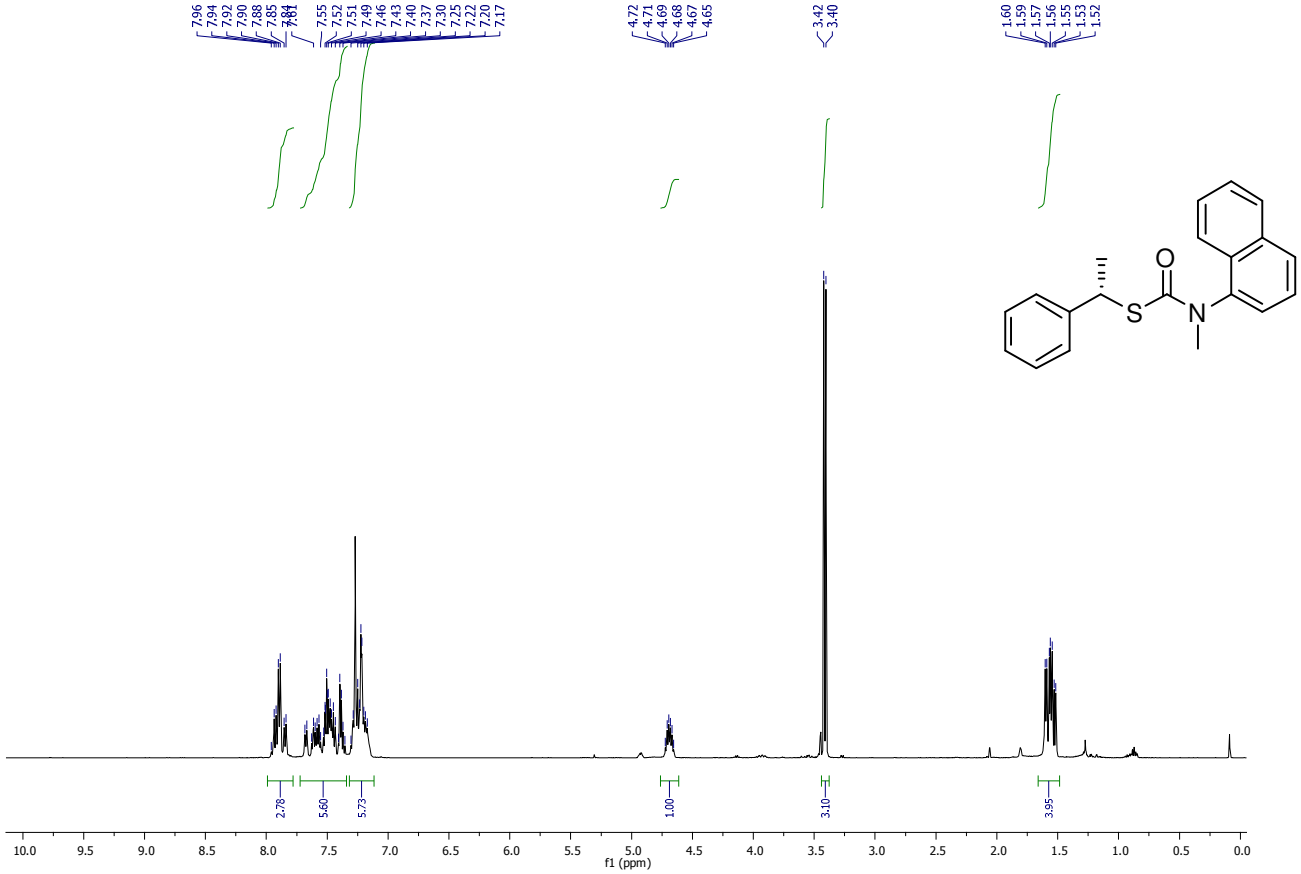


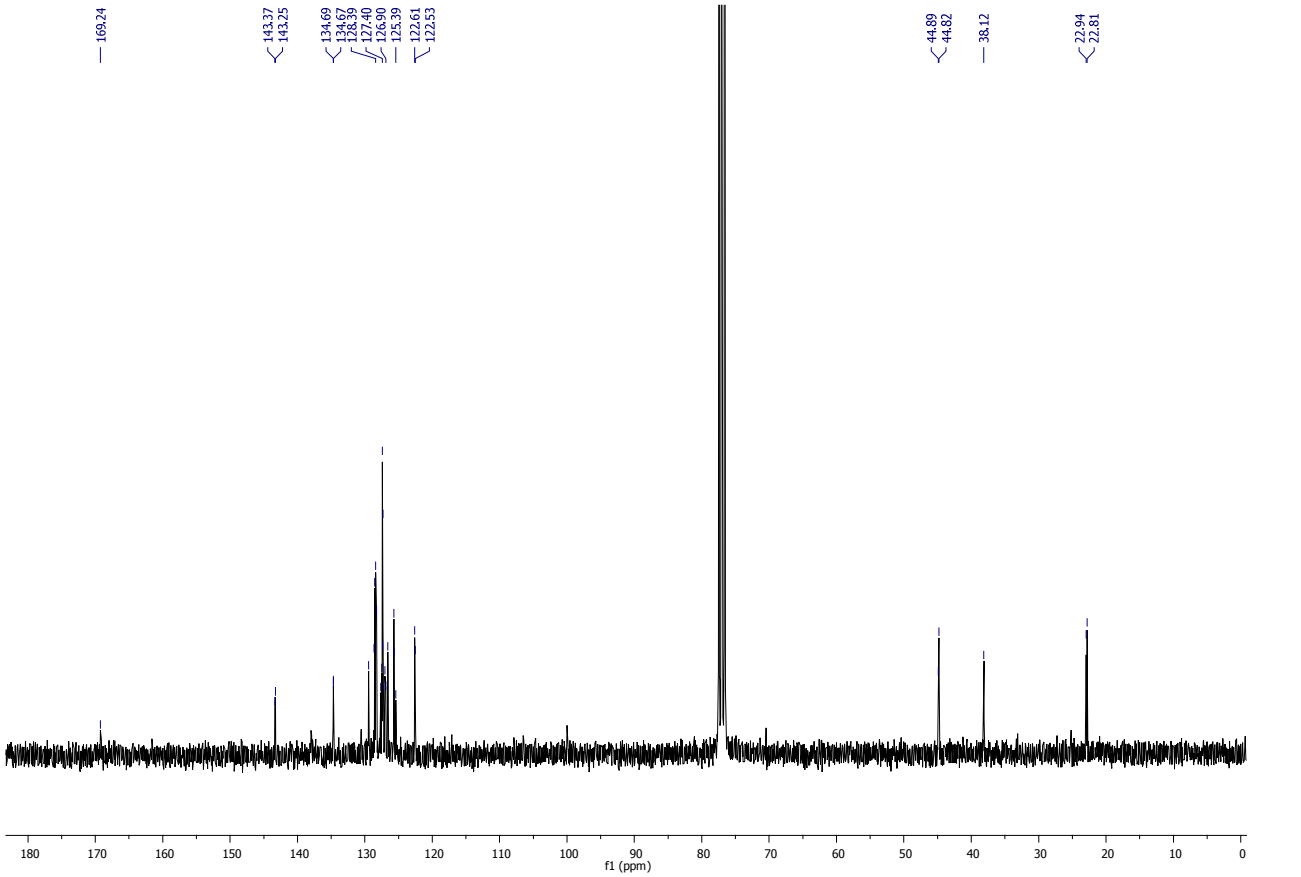
8g: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



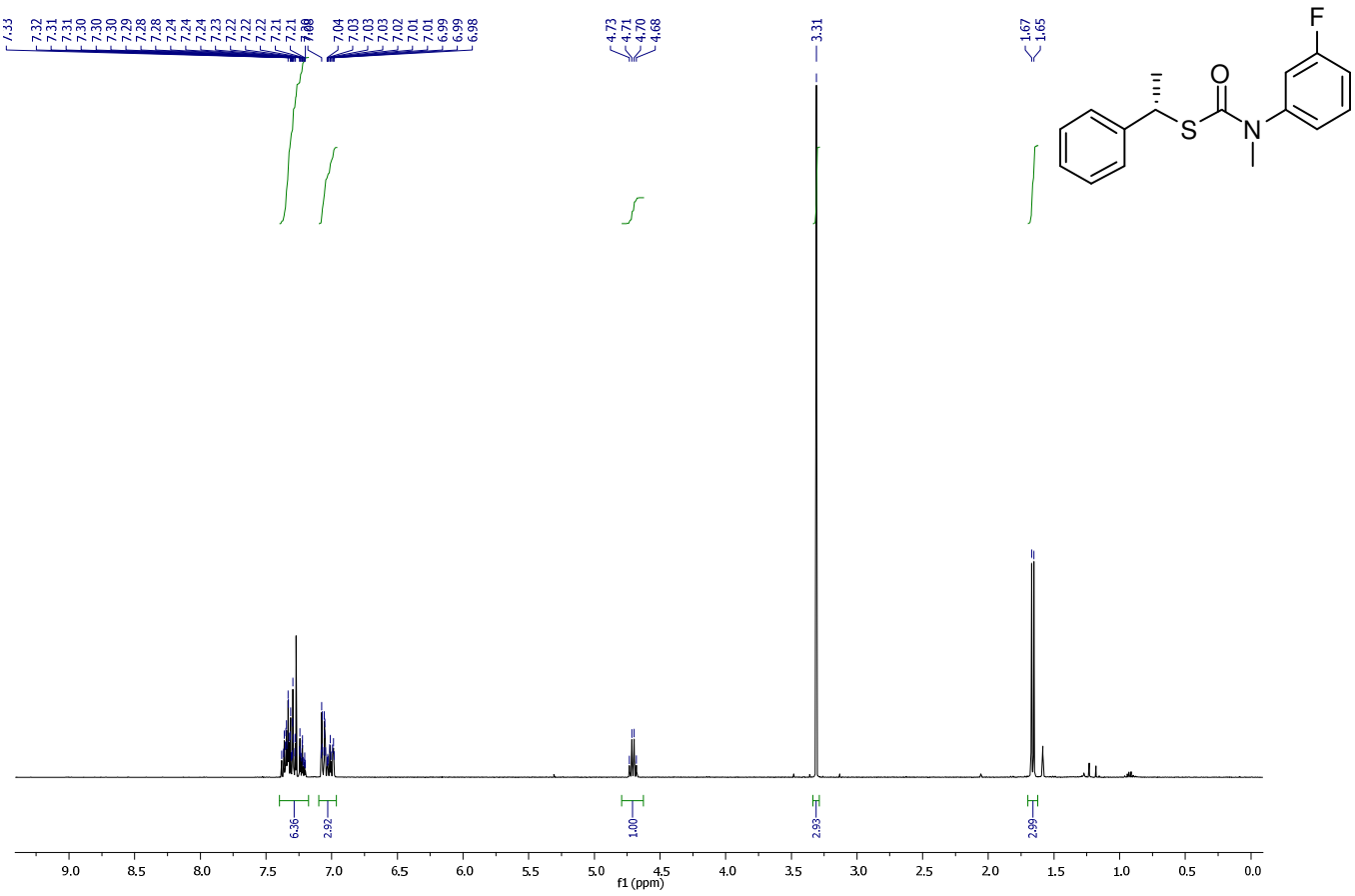


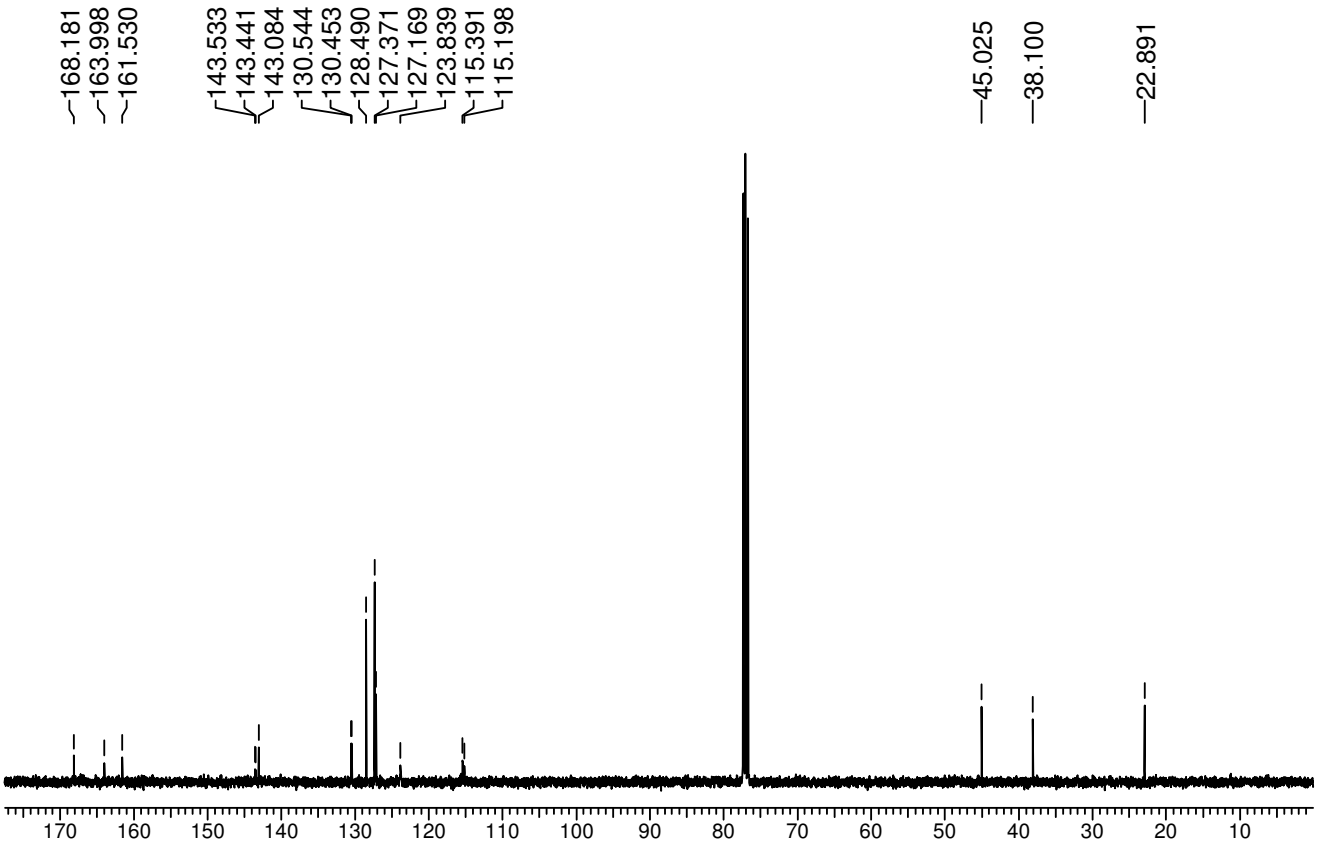
8h: ^{1}H-NMR: 500 MHz, **^{13}C-NMR**: 75.5 MHz



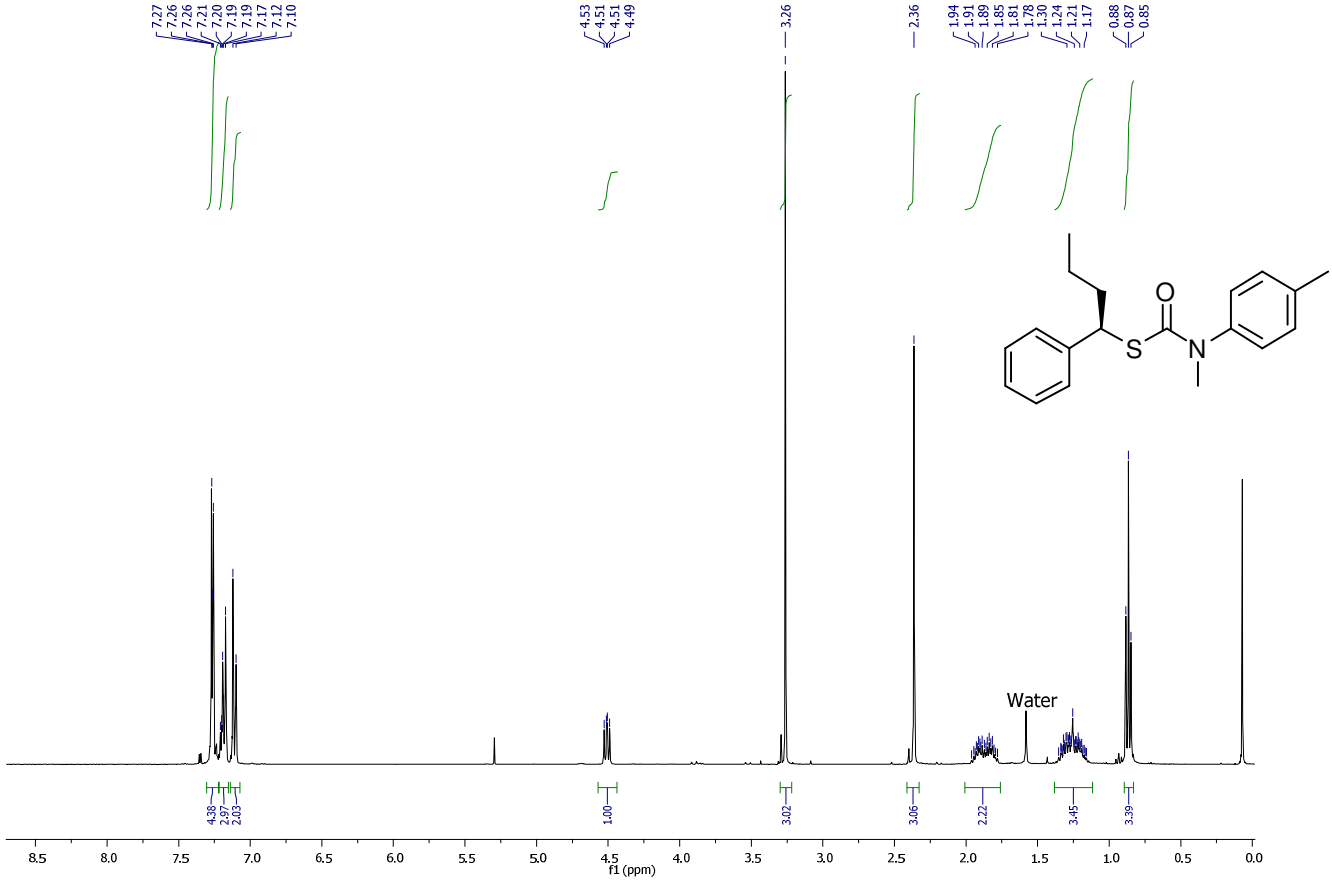


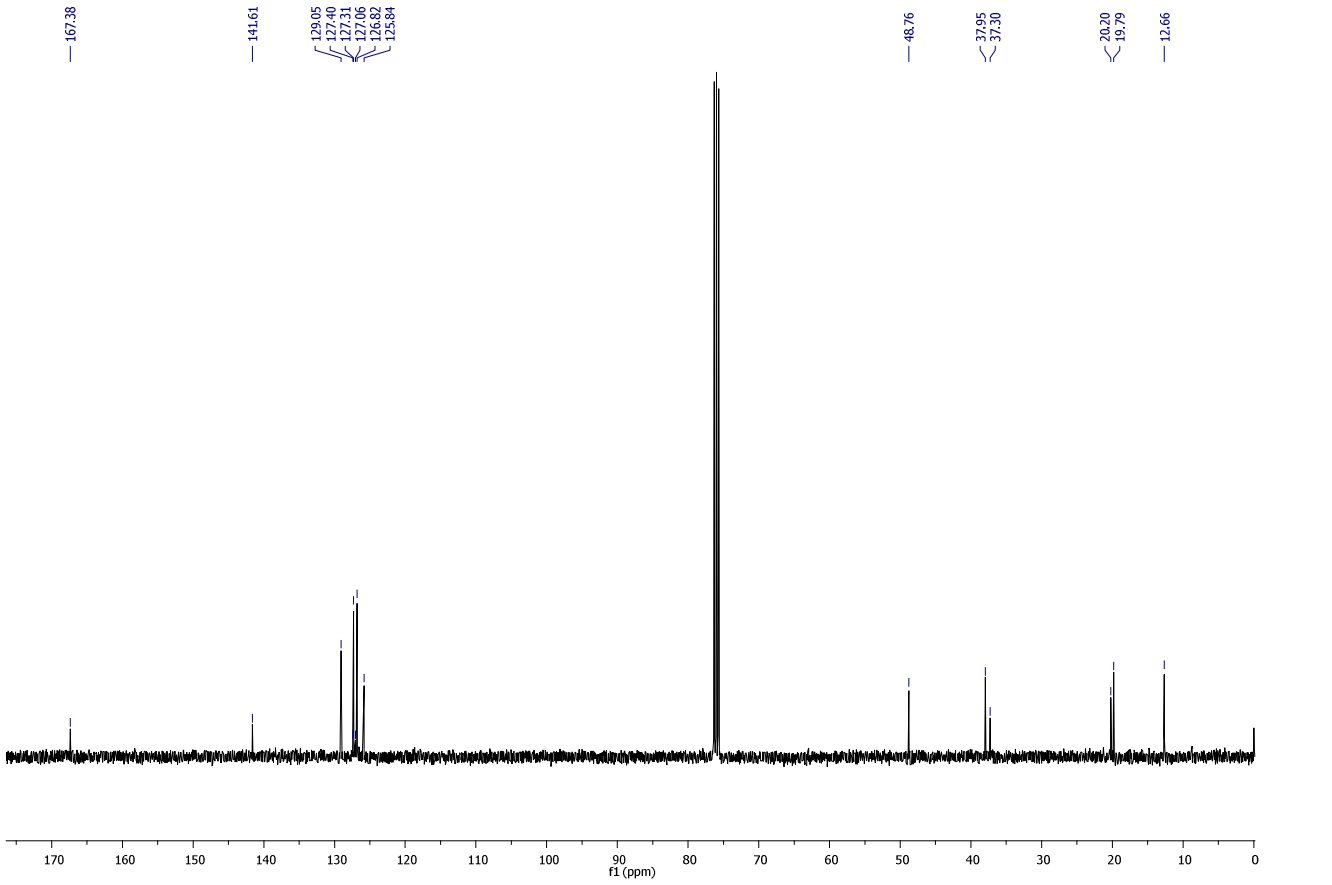
8i: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



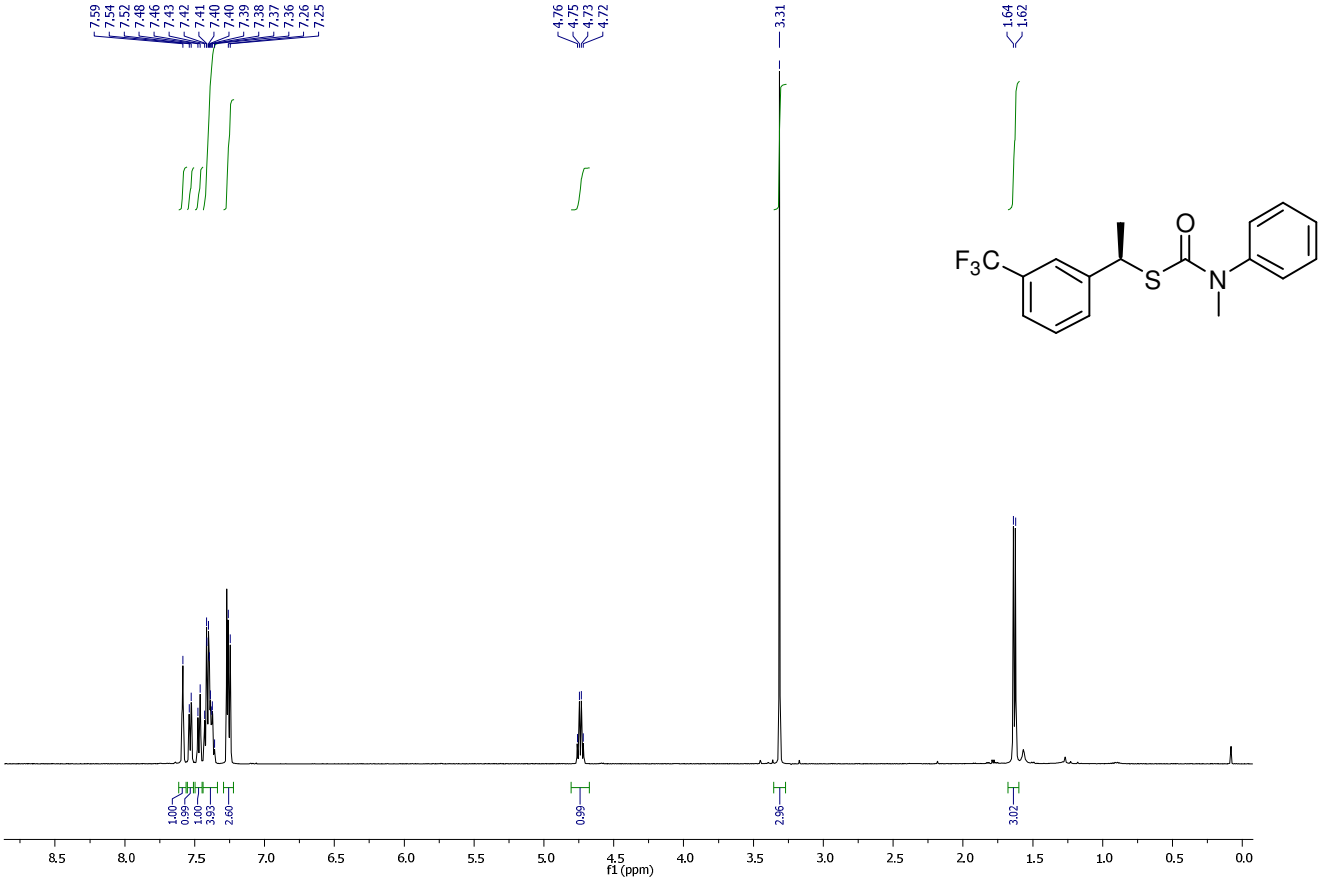


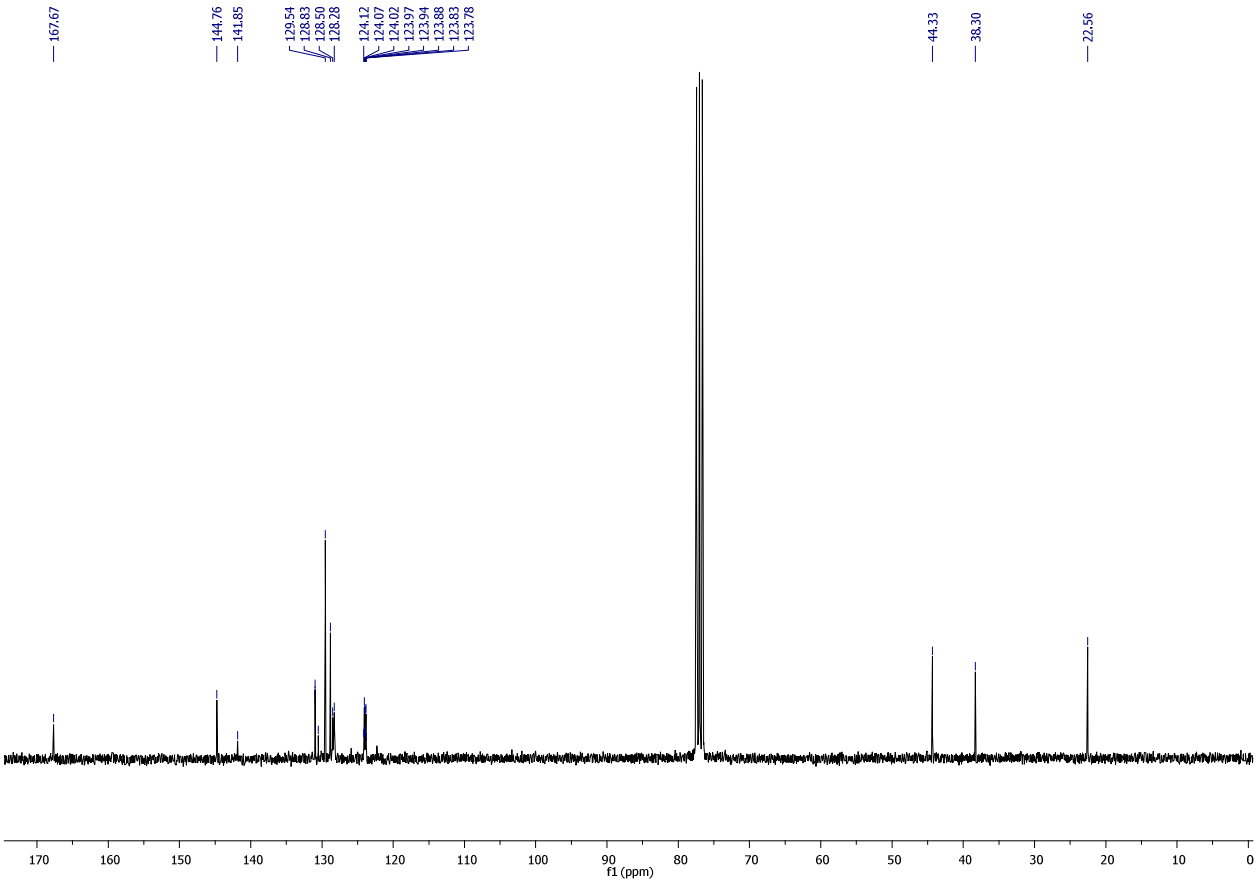
8j: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



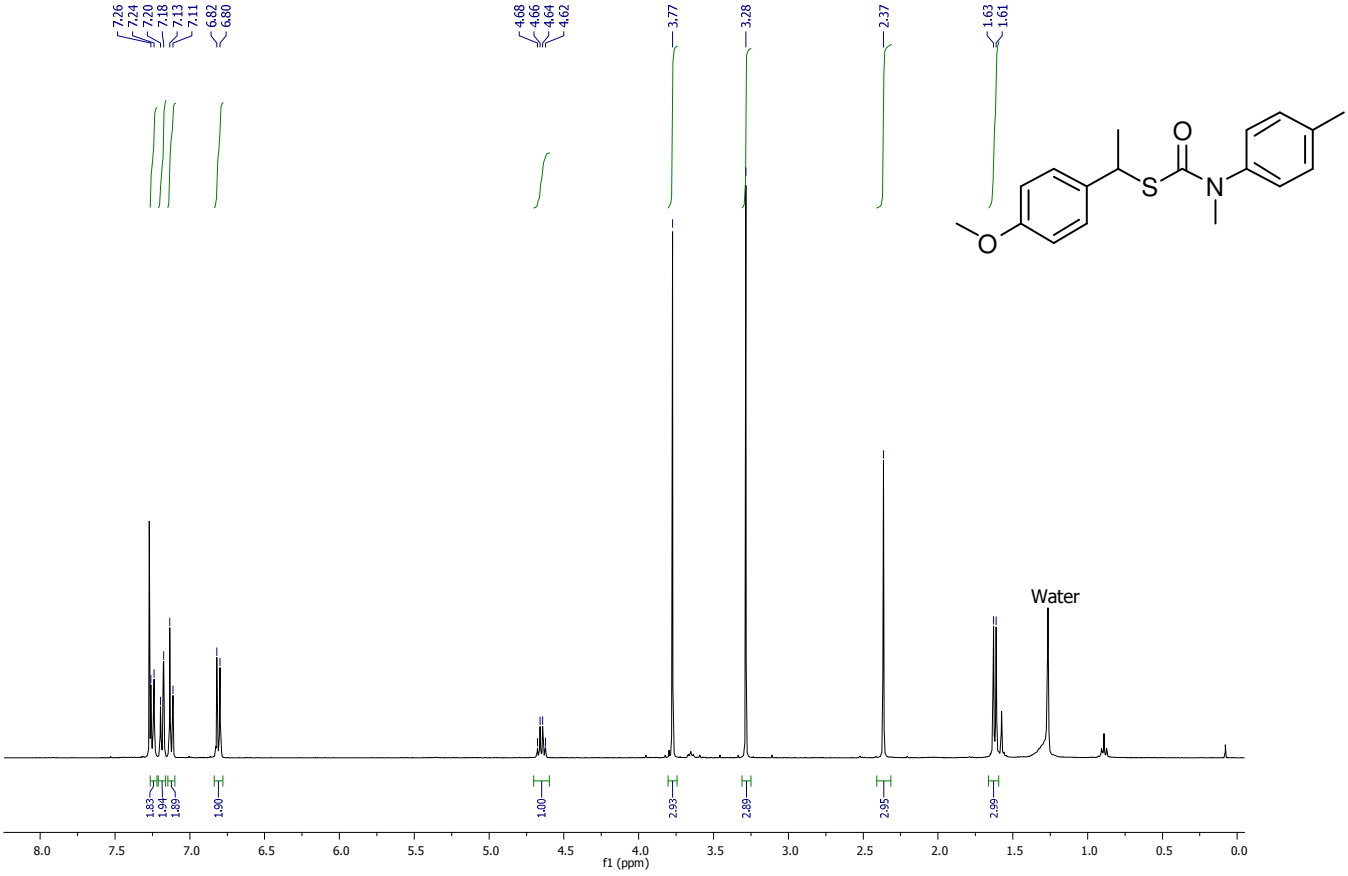


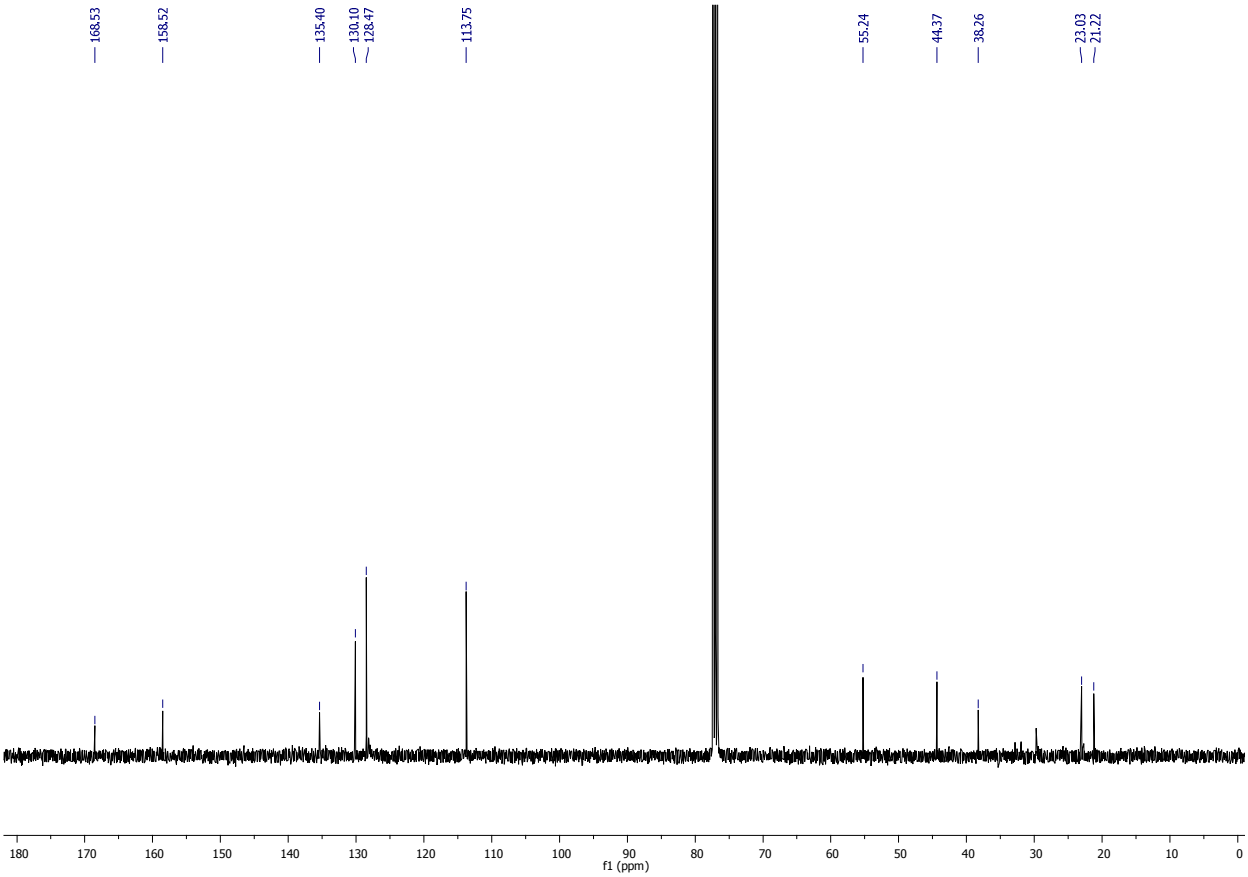
8k: **^{1}H-NMR**: 500 MHz, **^{13}C-NMR**: 75.5 MHz



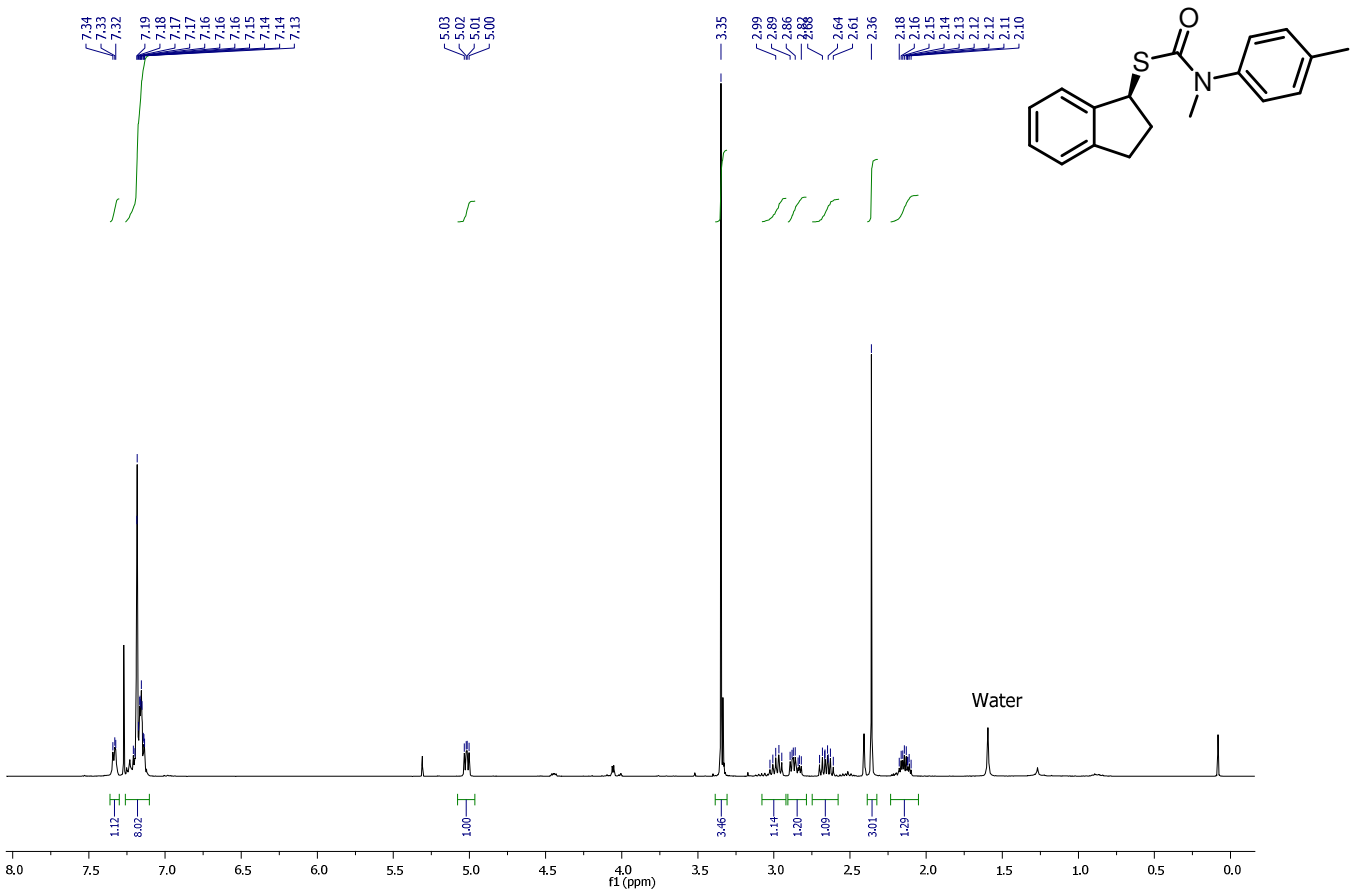


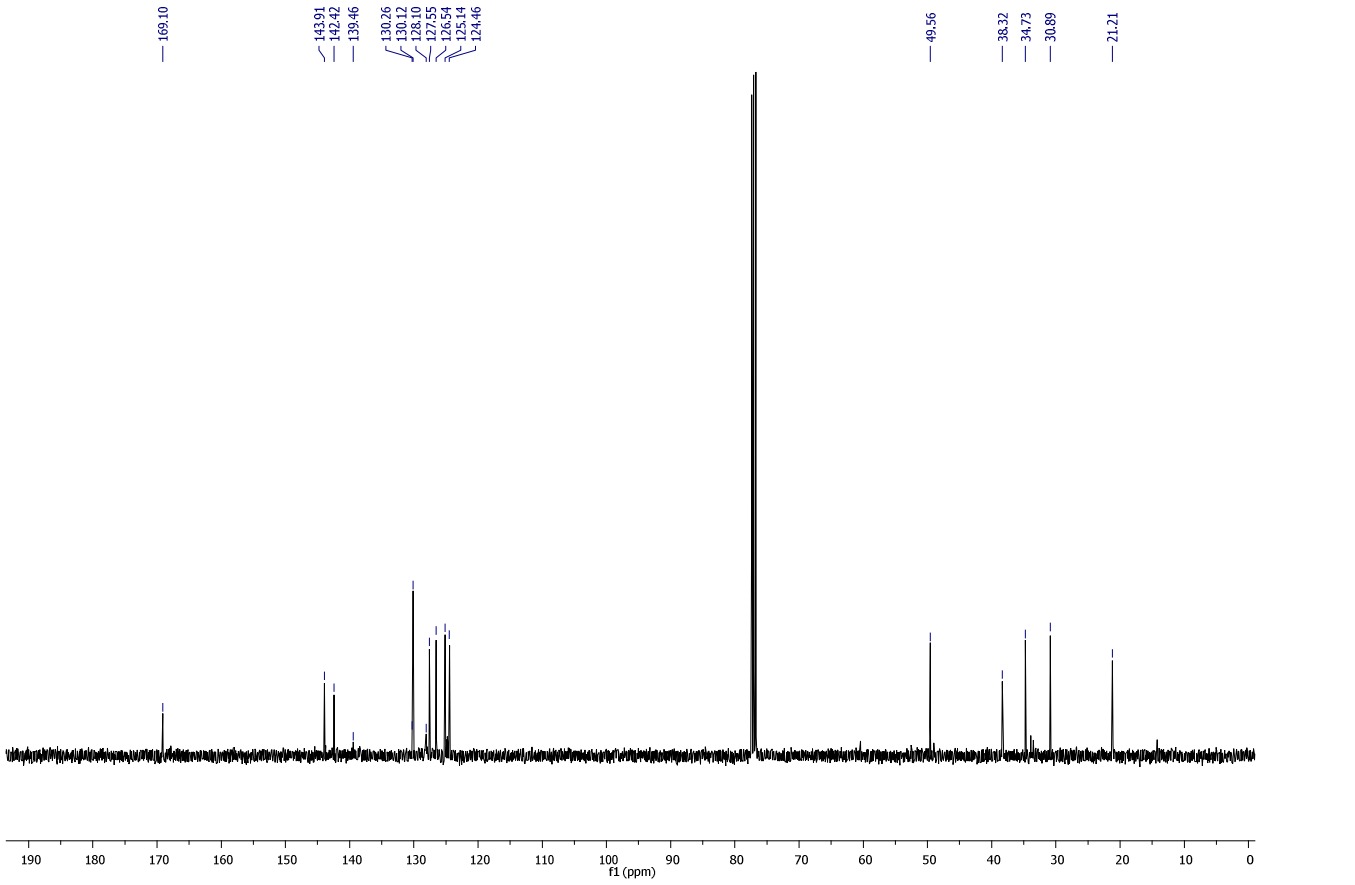
8l: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 75.5 MHz



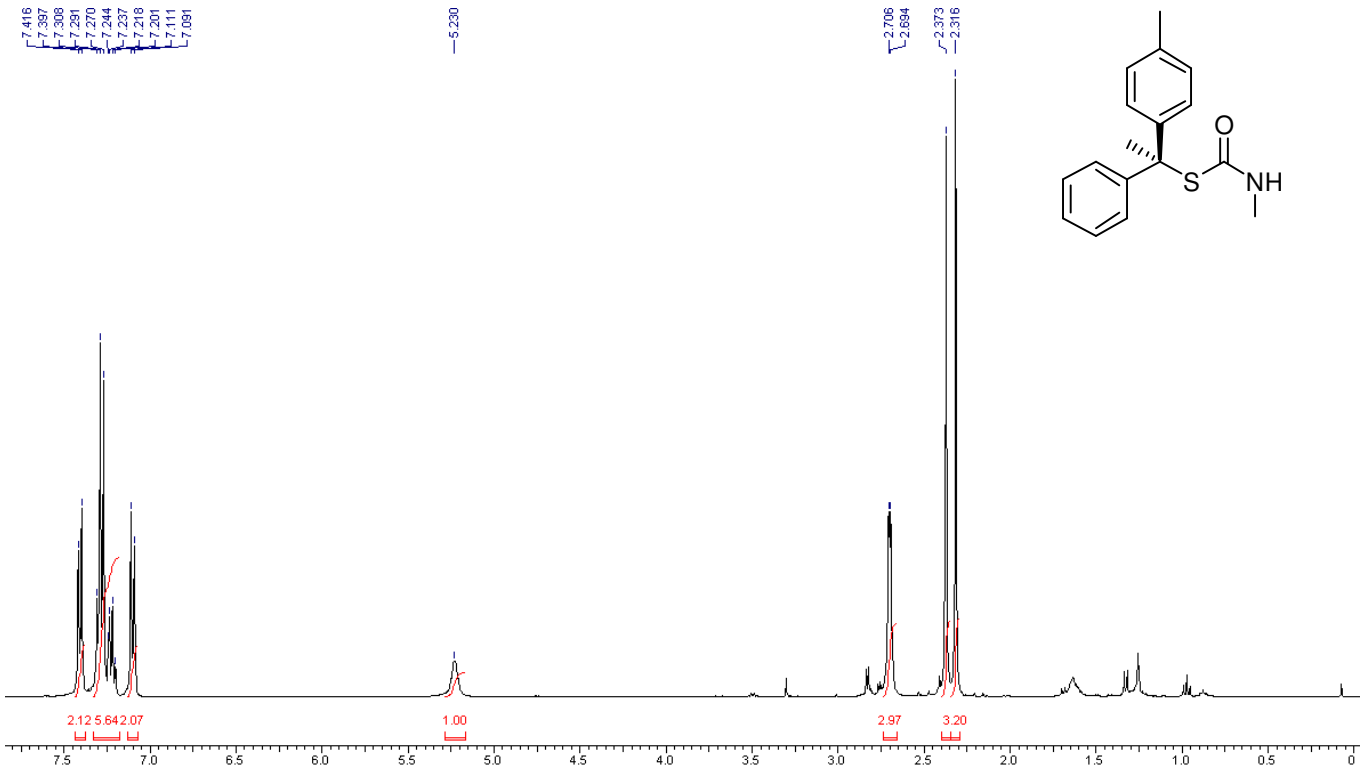


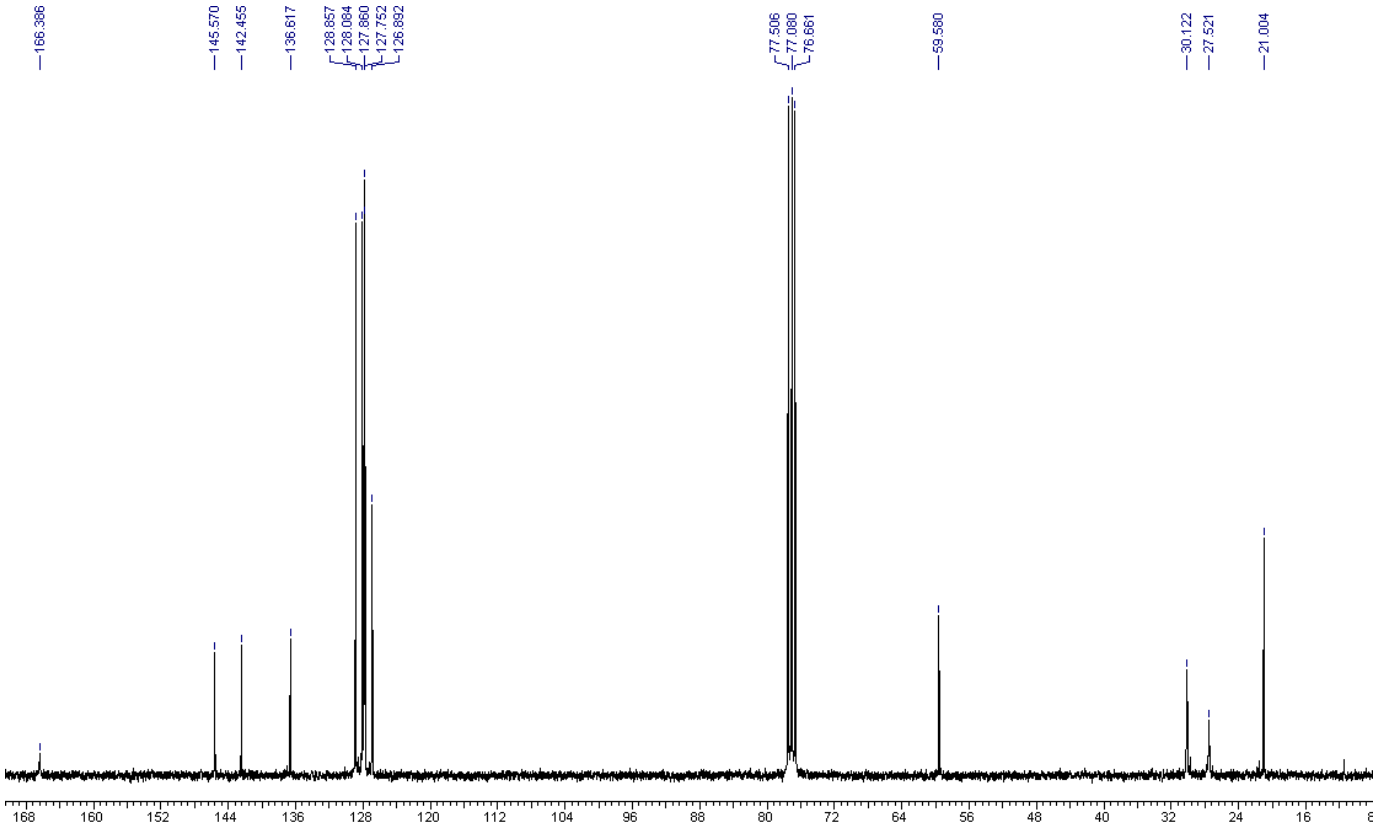
8m: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



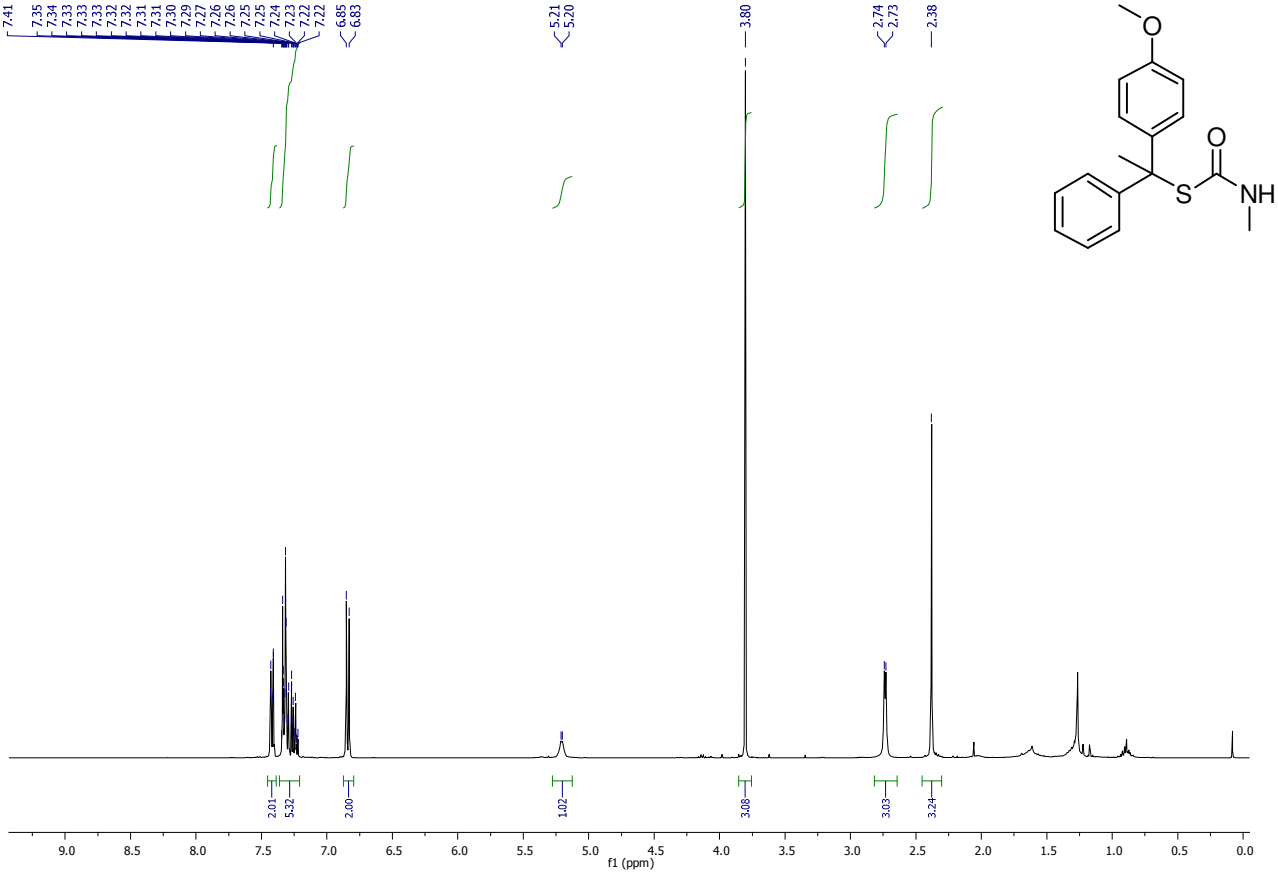


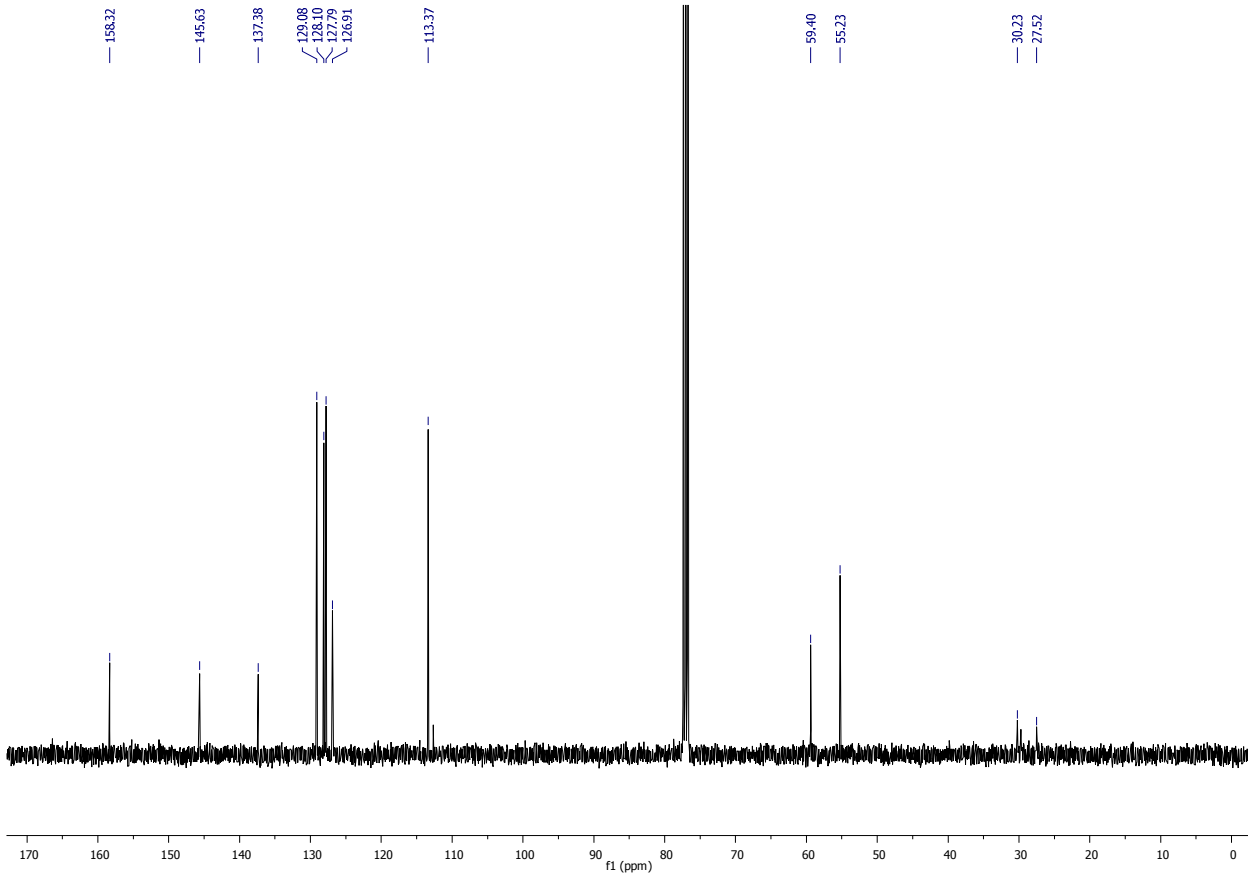
9a: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 75.5 MHz



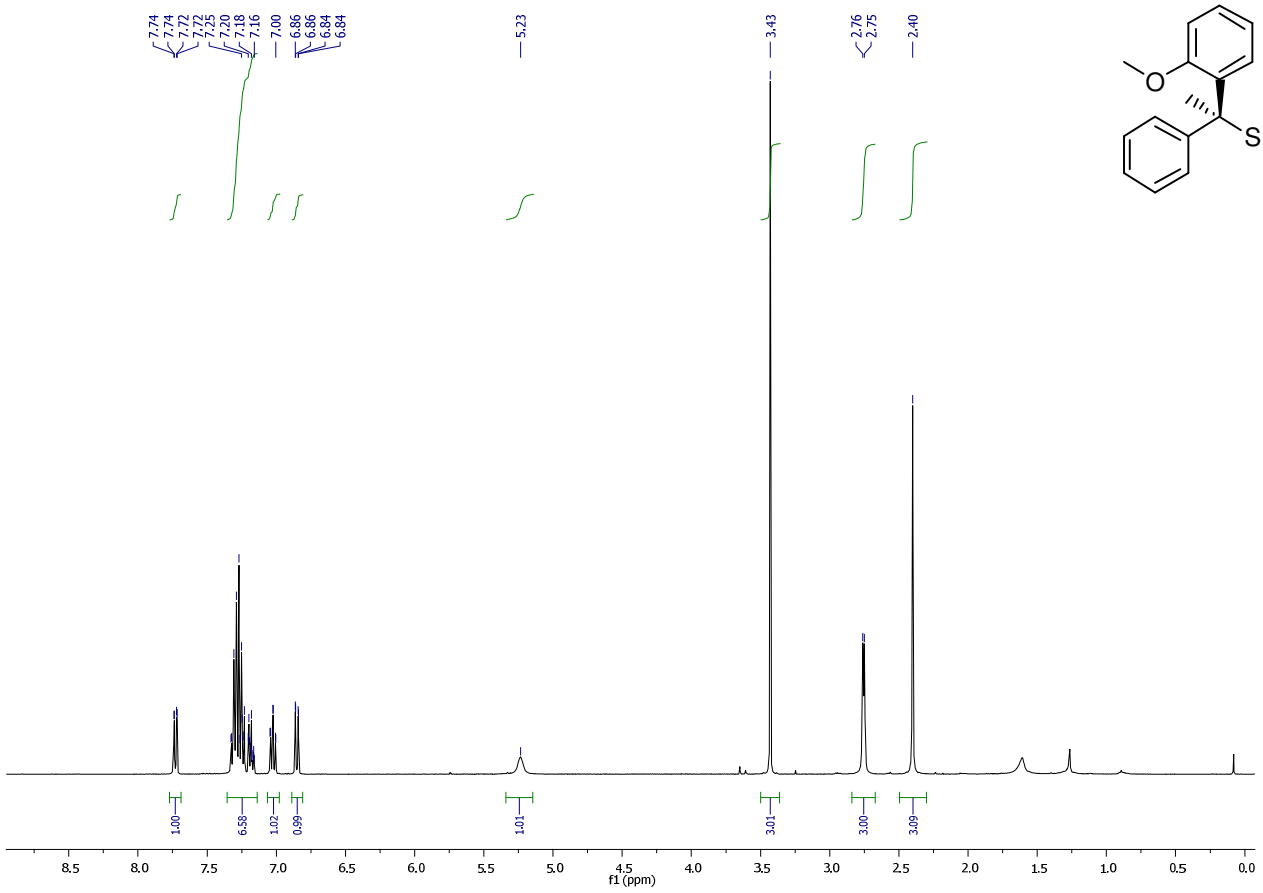


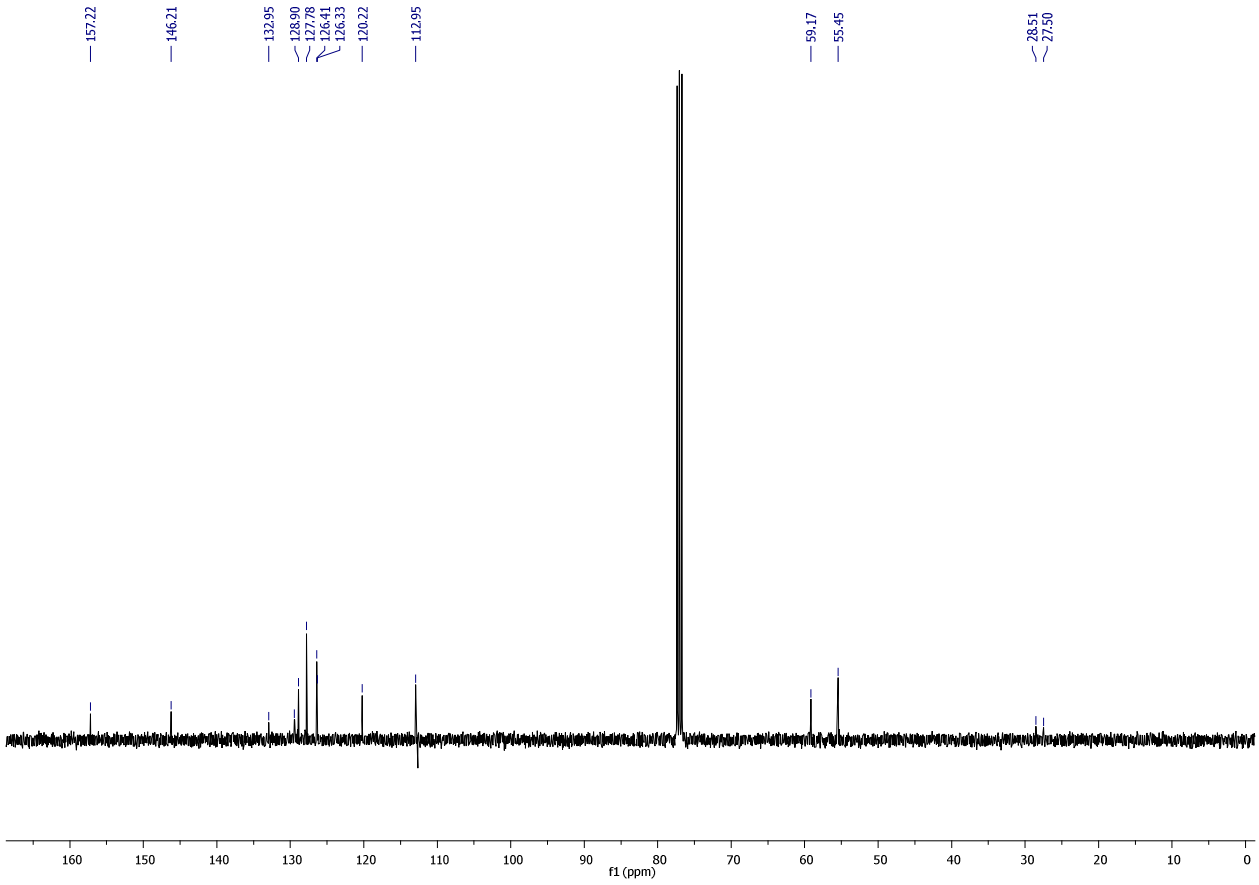
9b: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



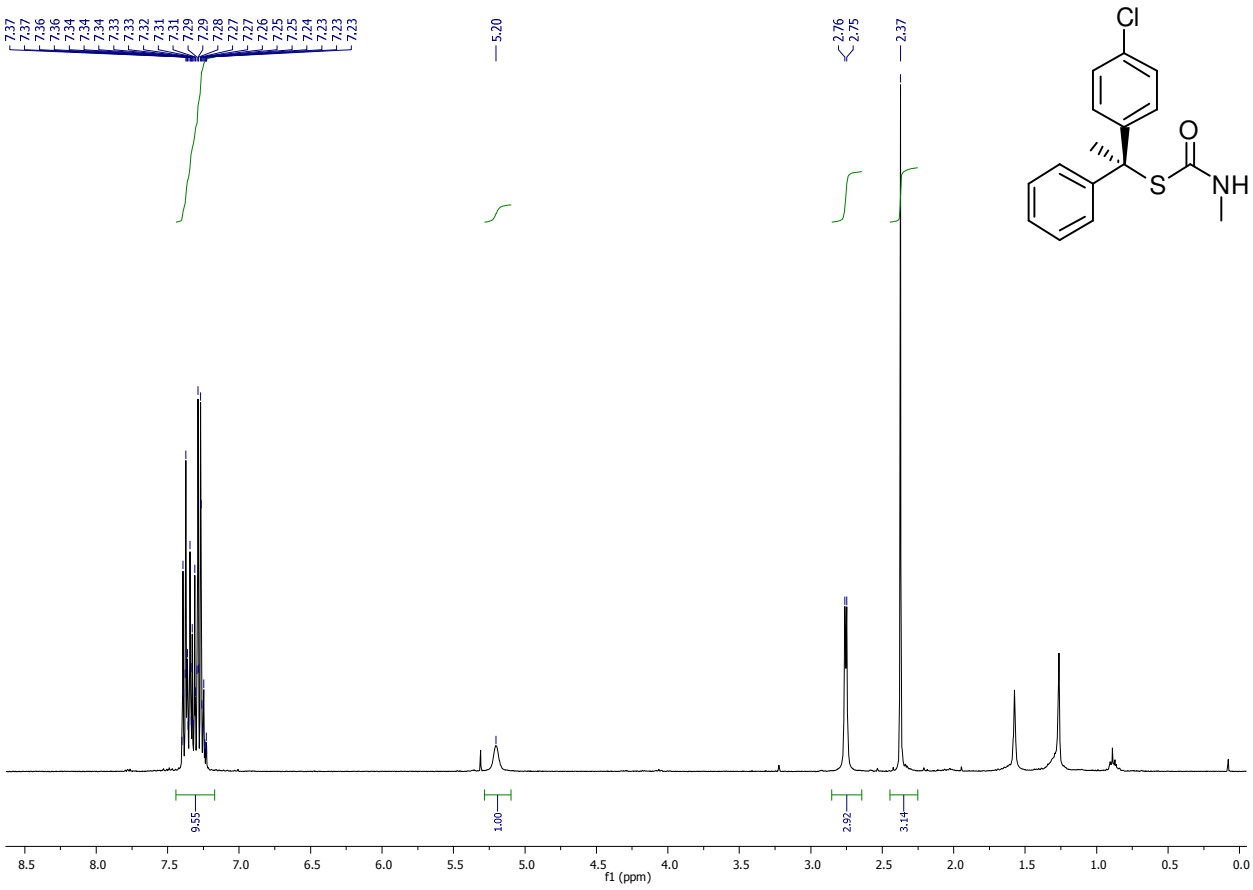


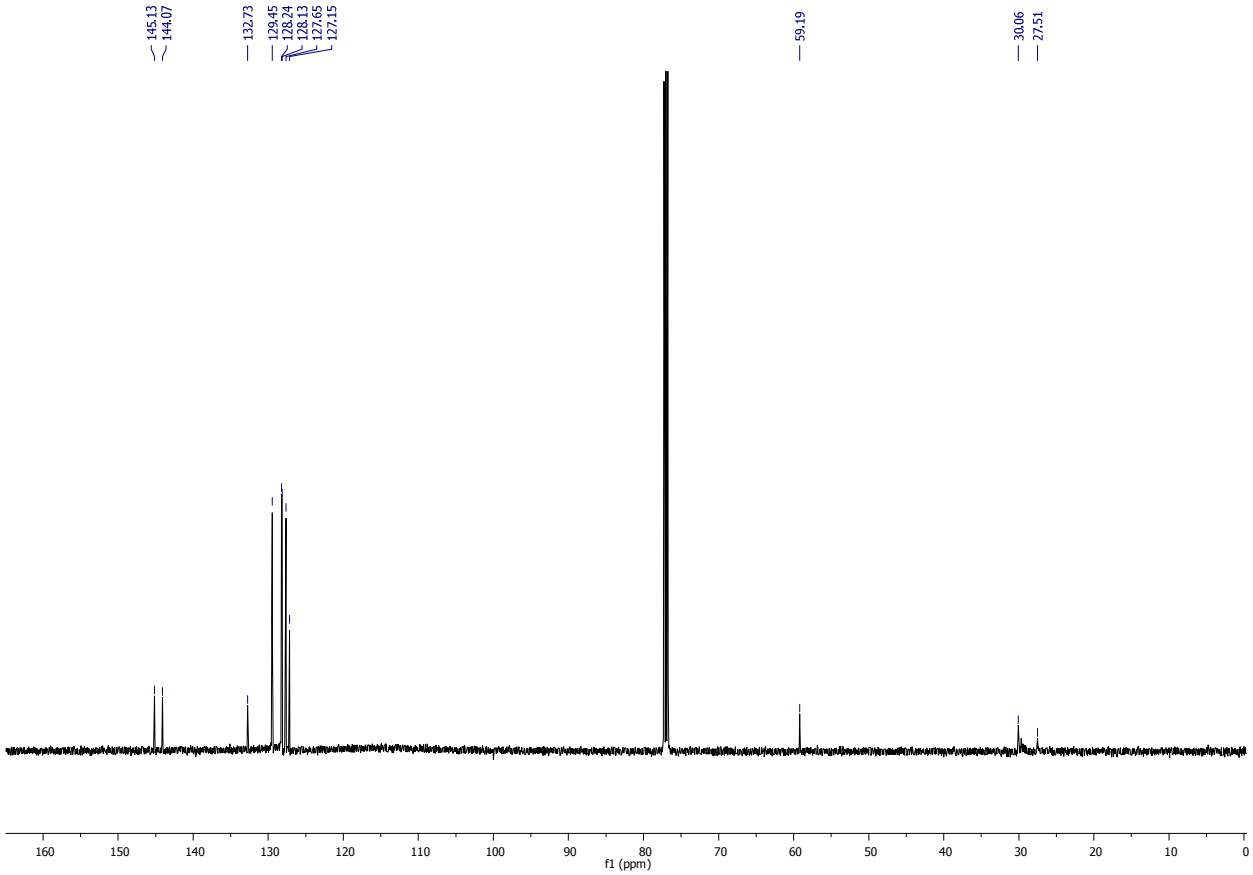
9c: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



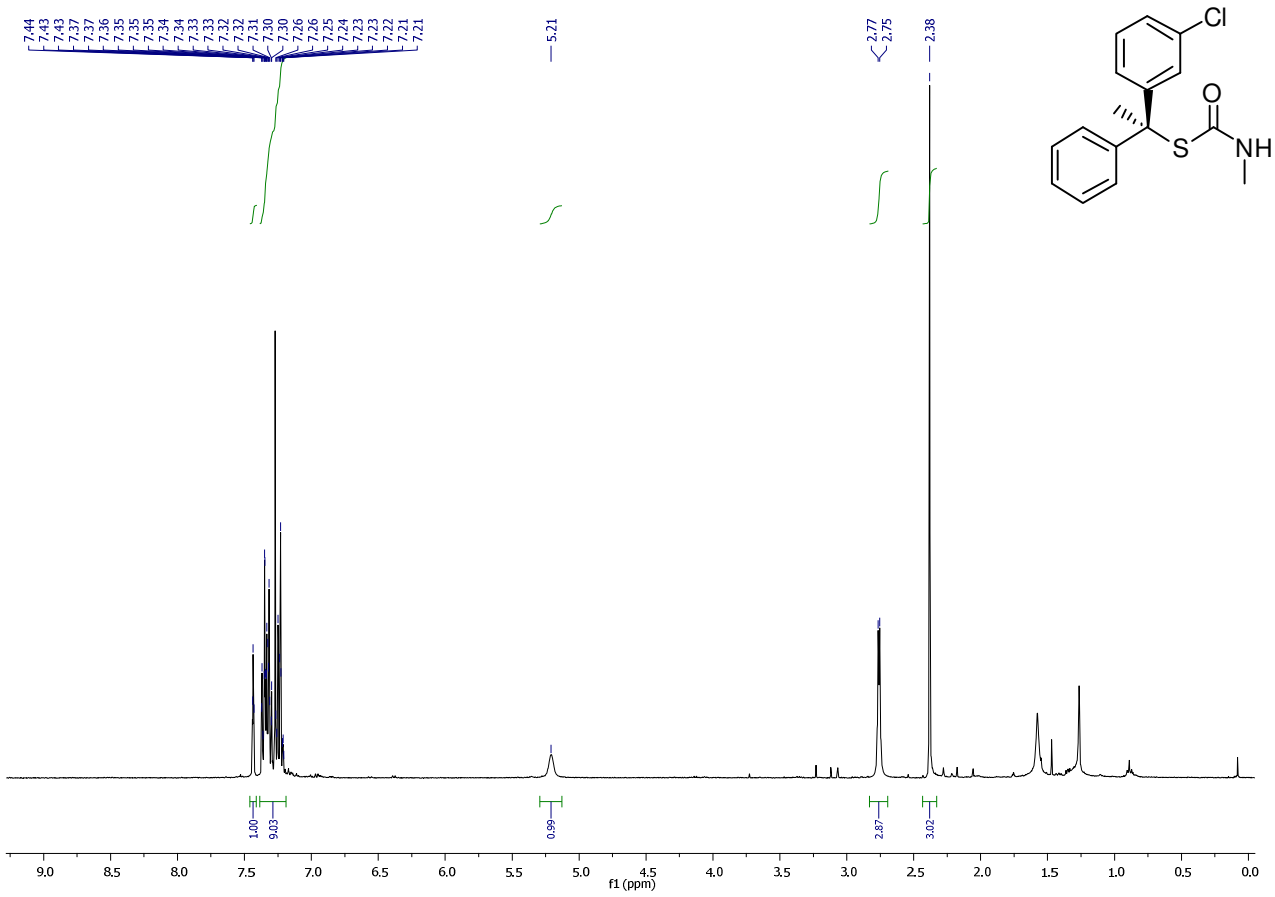


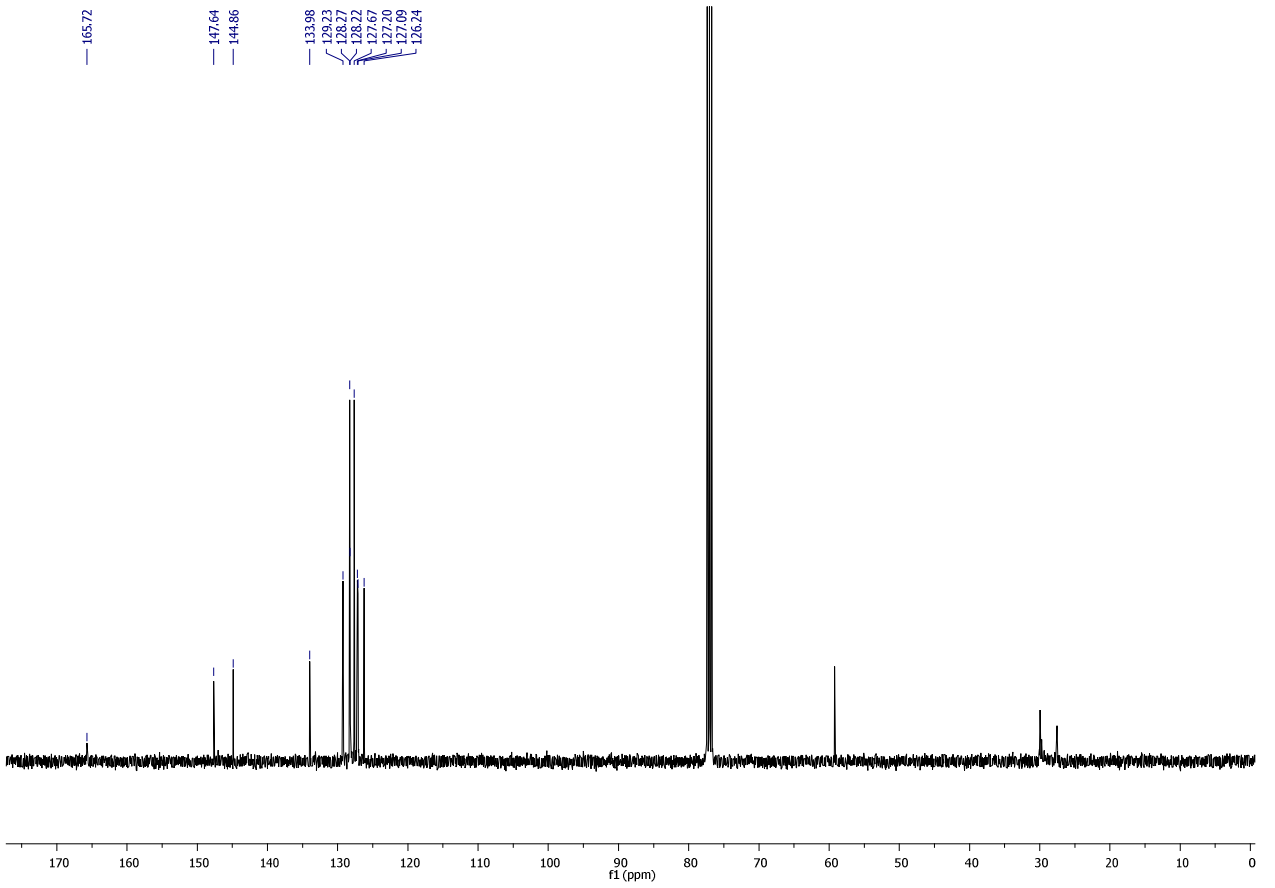
9d: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 125 MHz



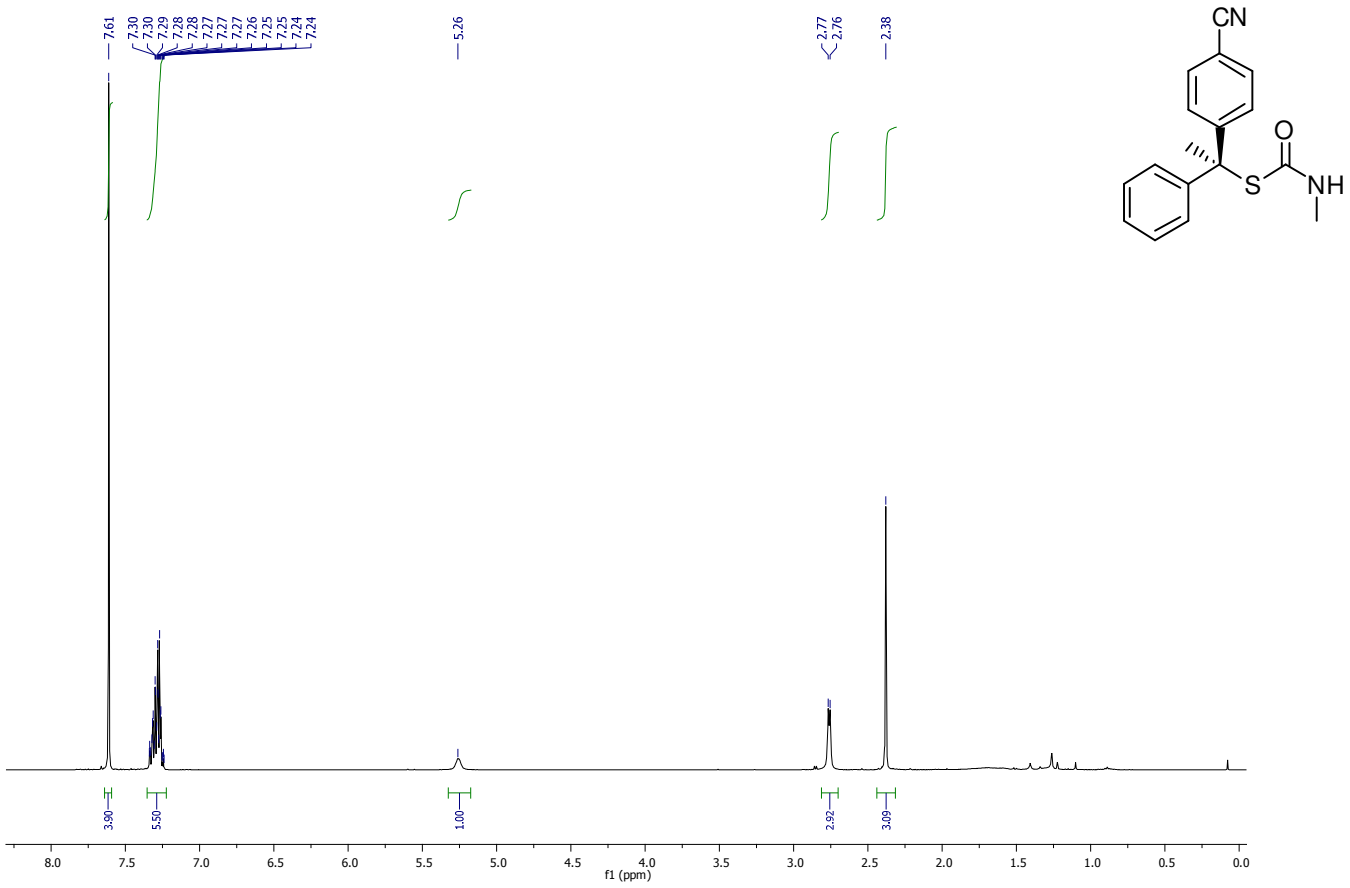


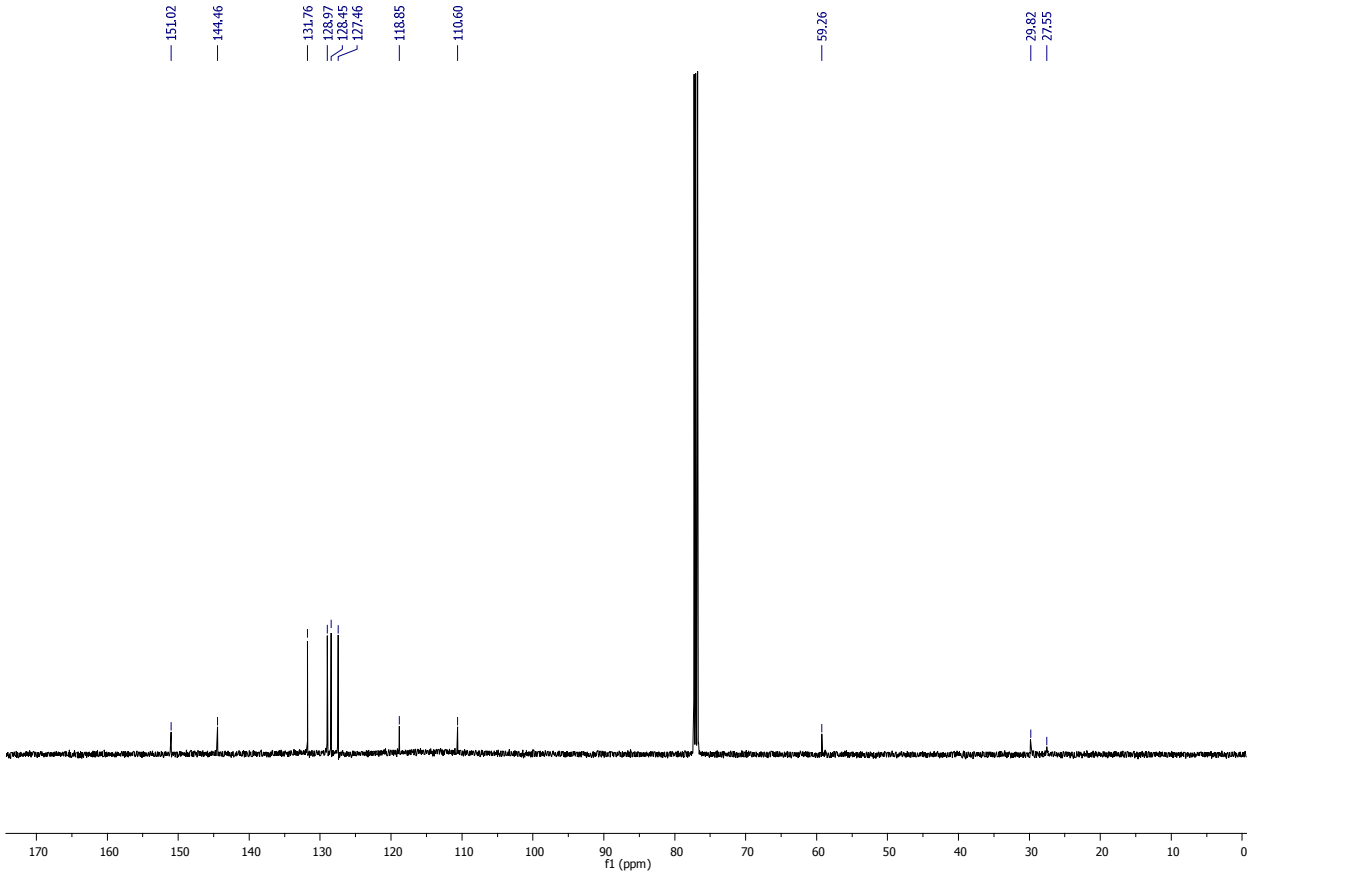
9e: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 75.5 MHz



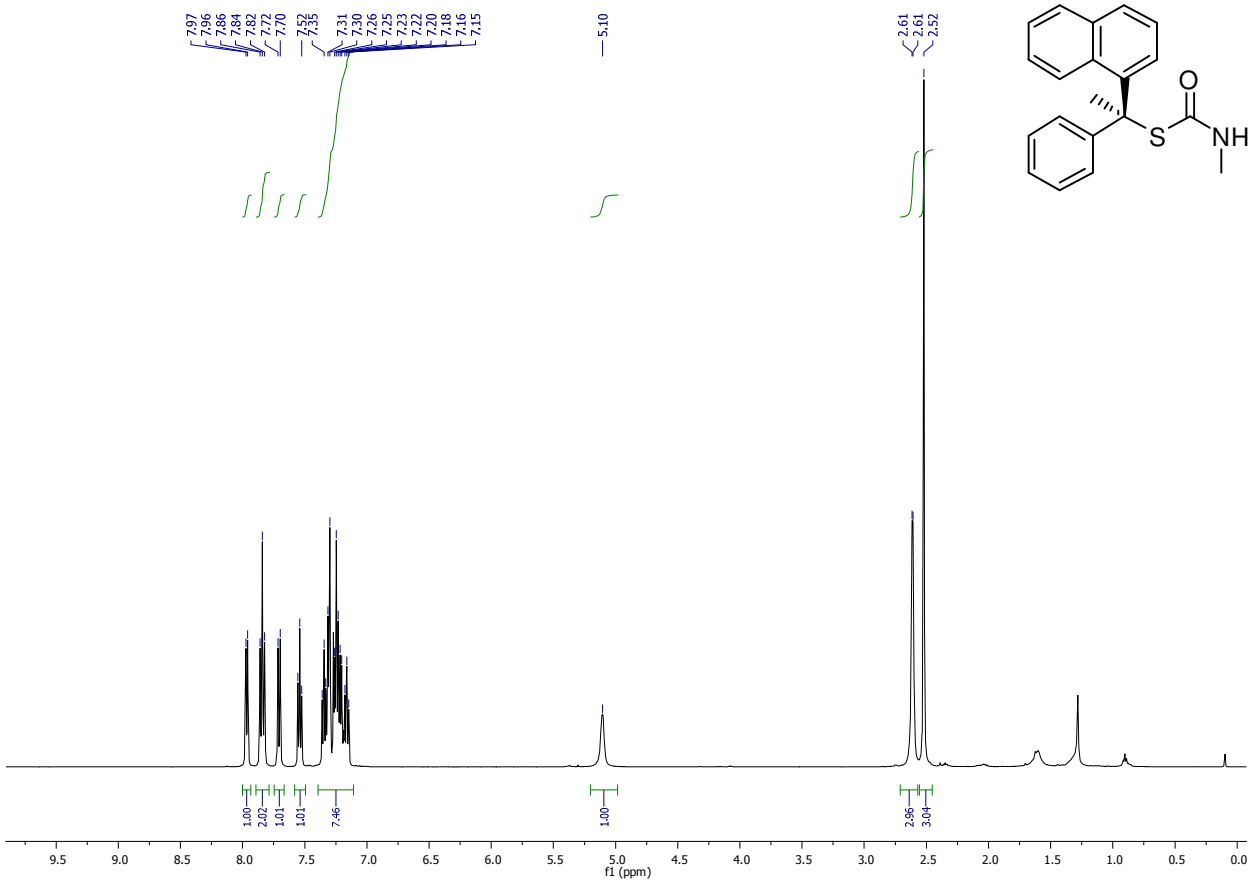


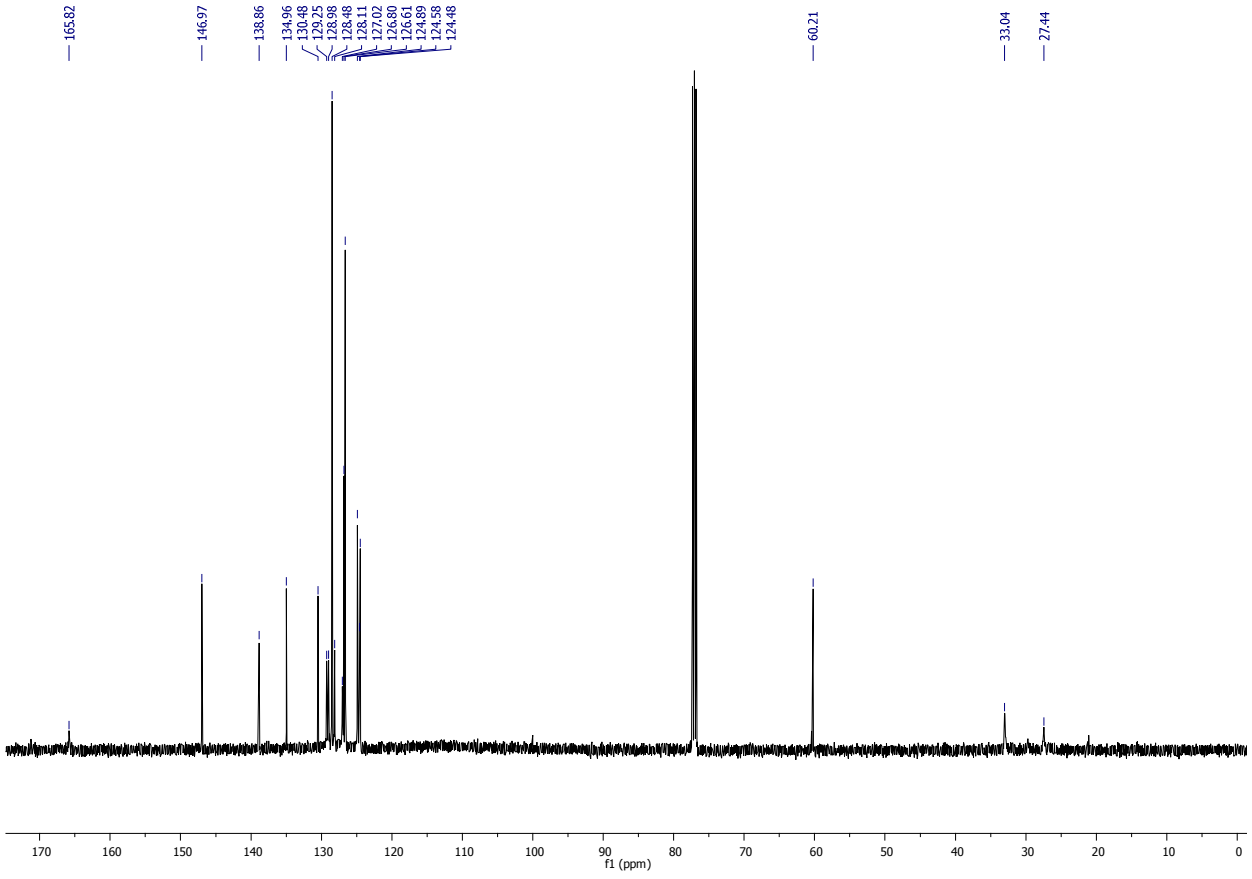
9f: ^{1}H-NMR: 500 MHz, **^{13}C-NMR**: 125 MHz



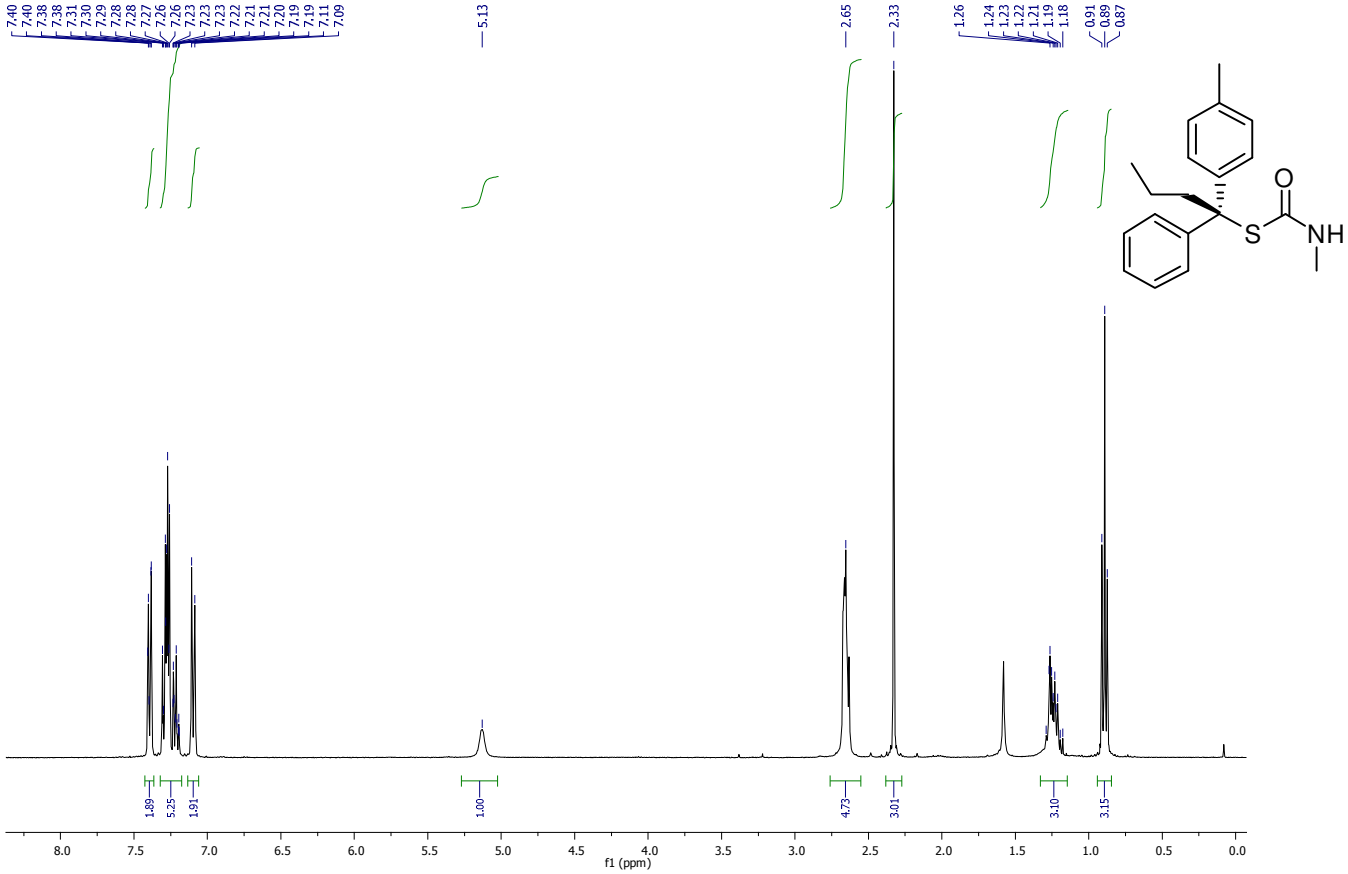


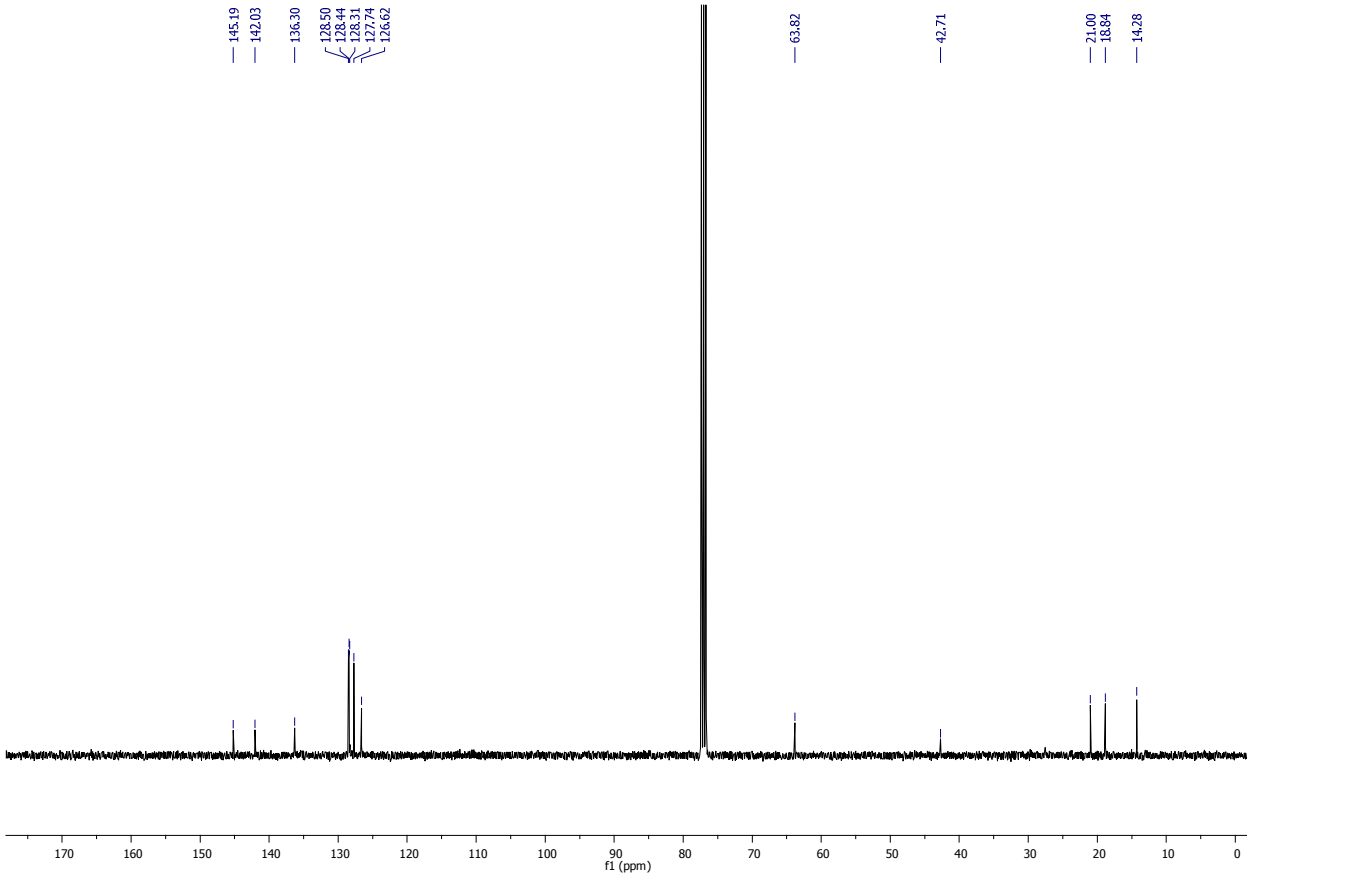
9h: ^{1}H-NMR: 500 MHz, **^{13}C-NMR**: 125 MHz



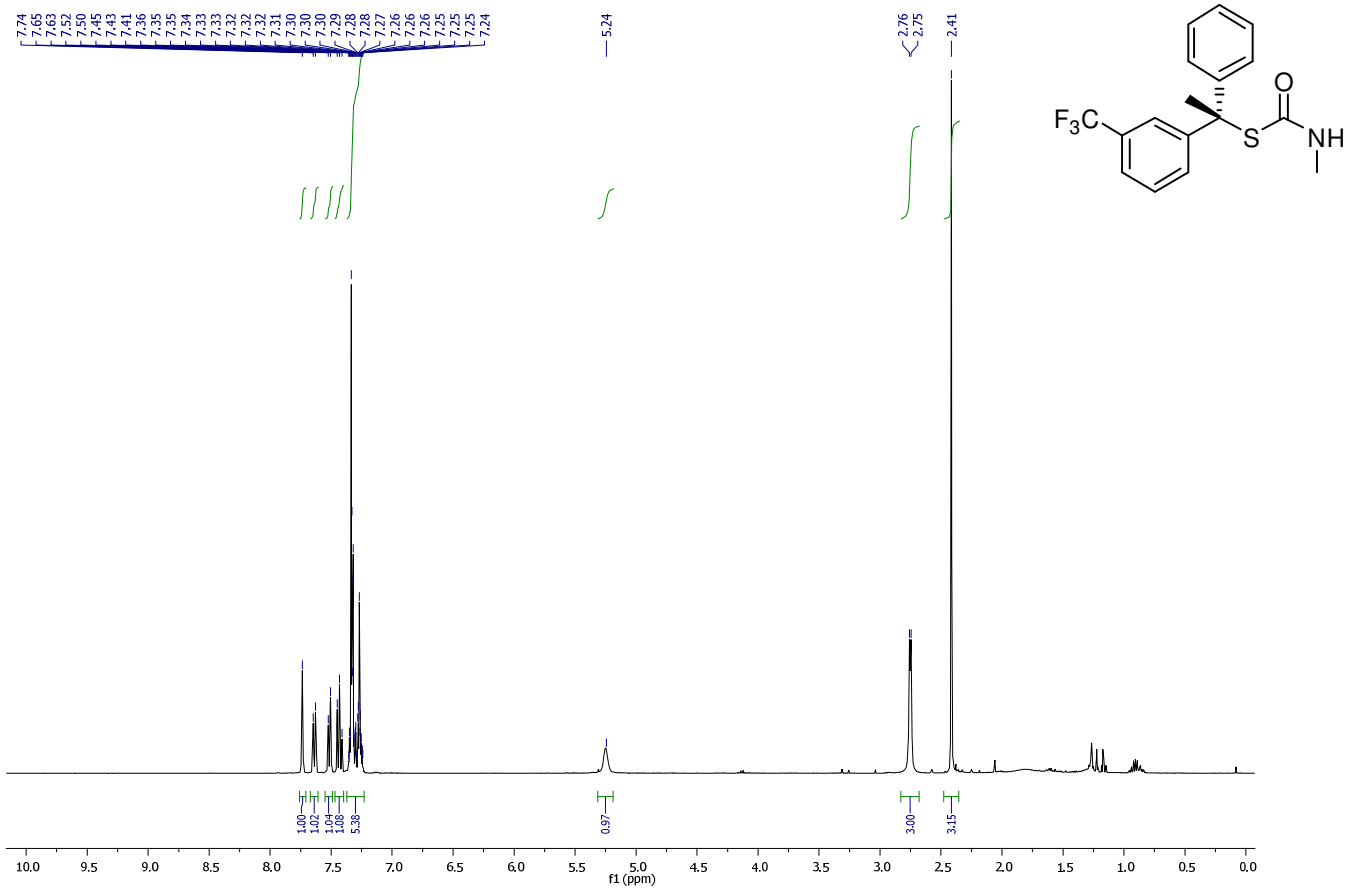


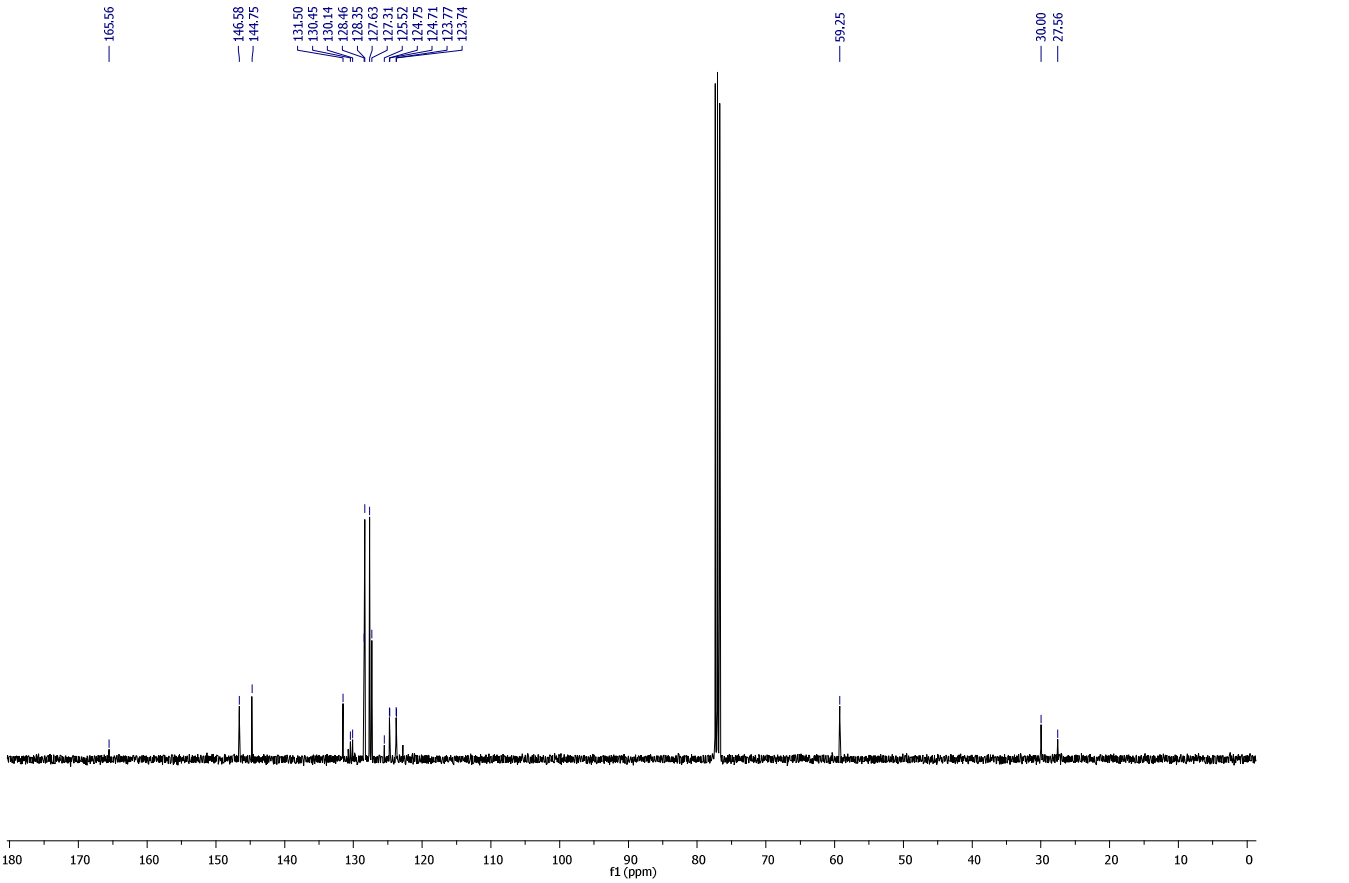
9j: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



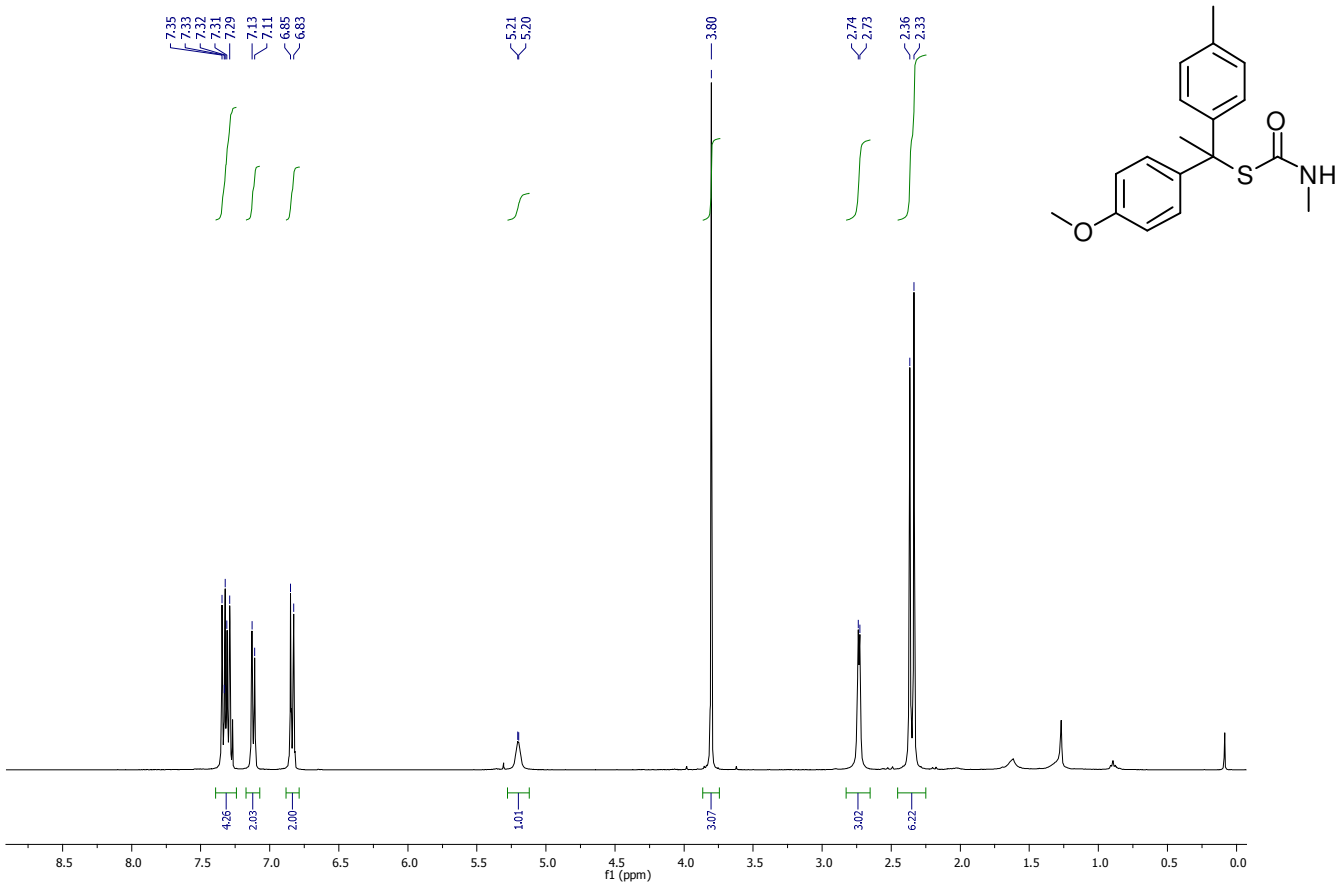


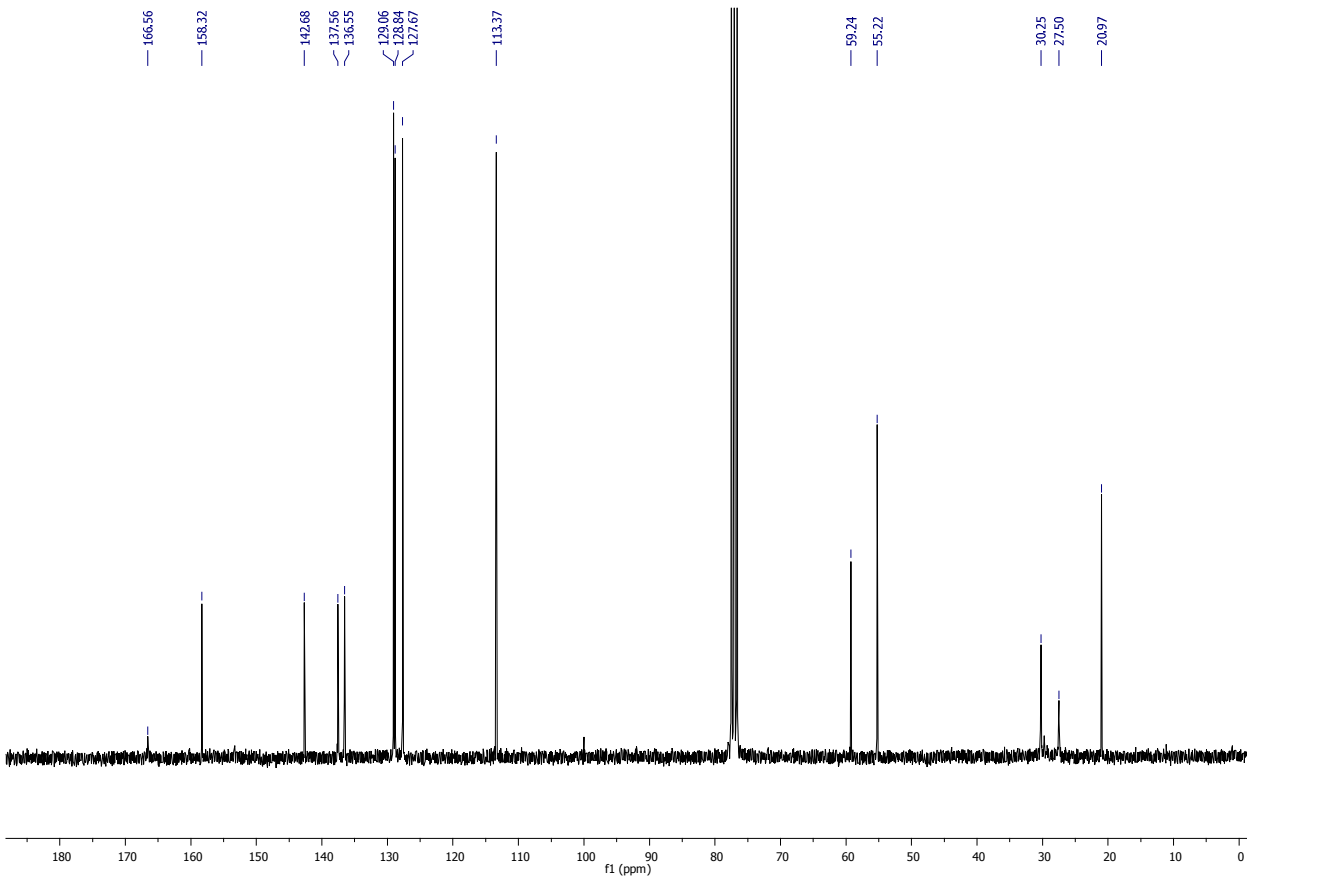
9k: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 75.5 MHz



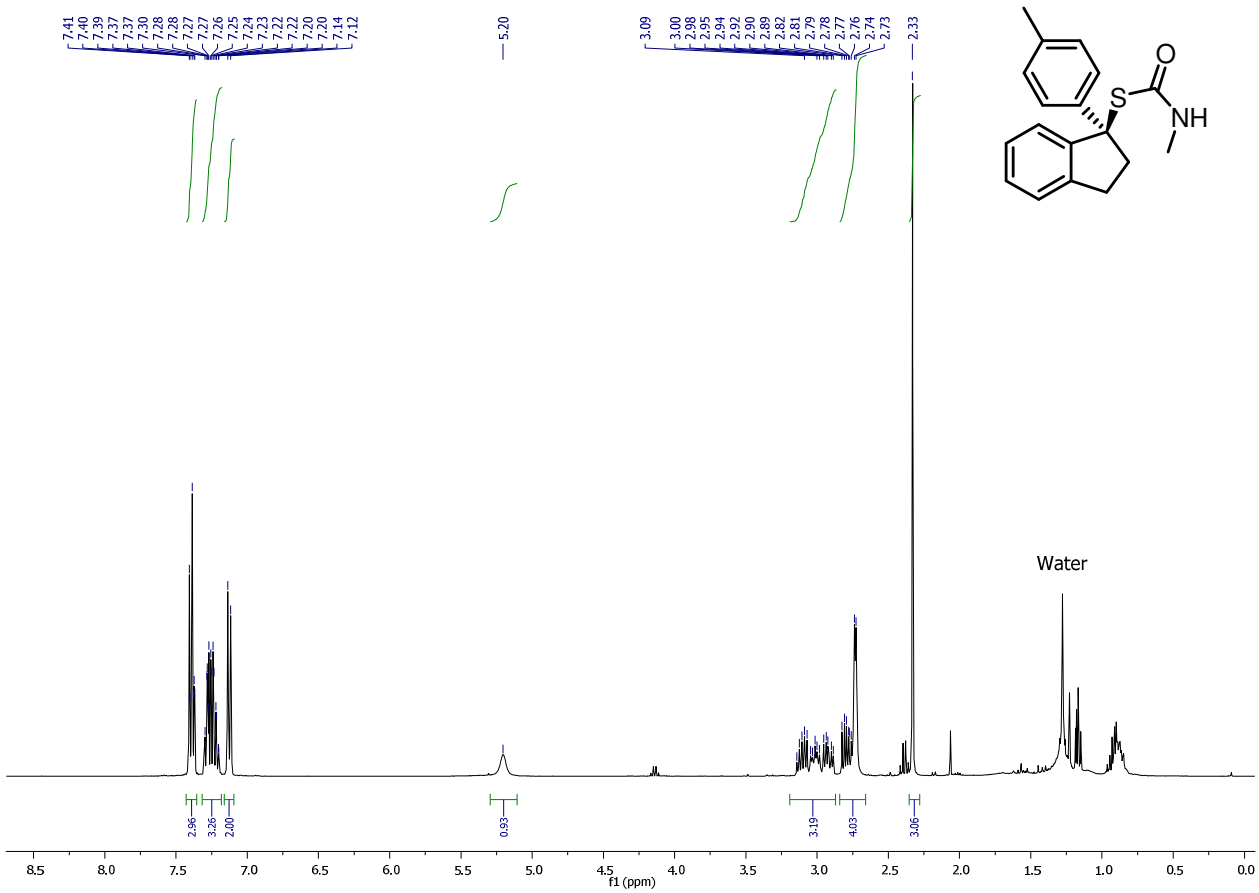


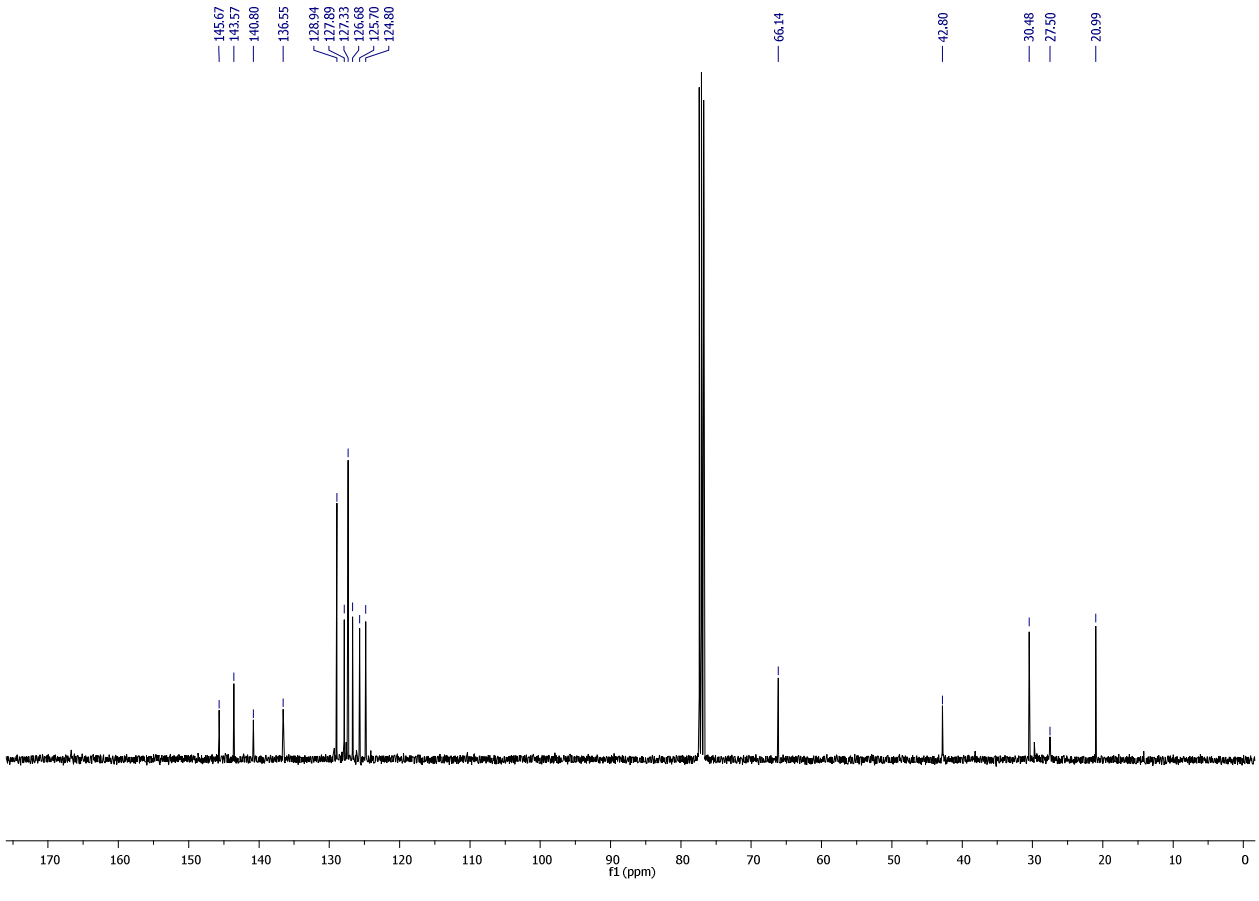
9l: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 75.5 MHz



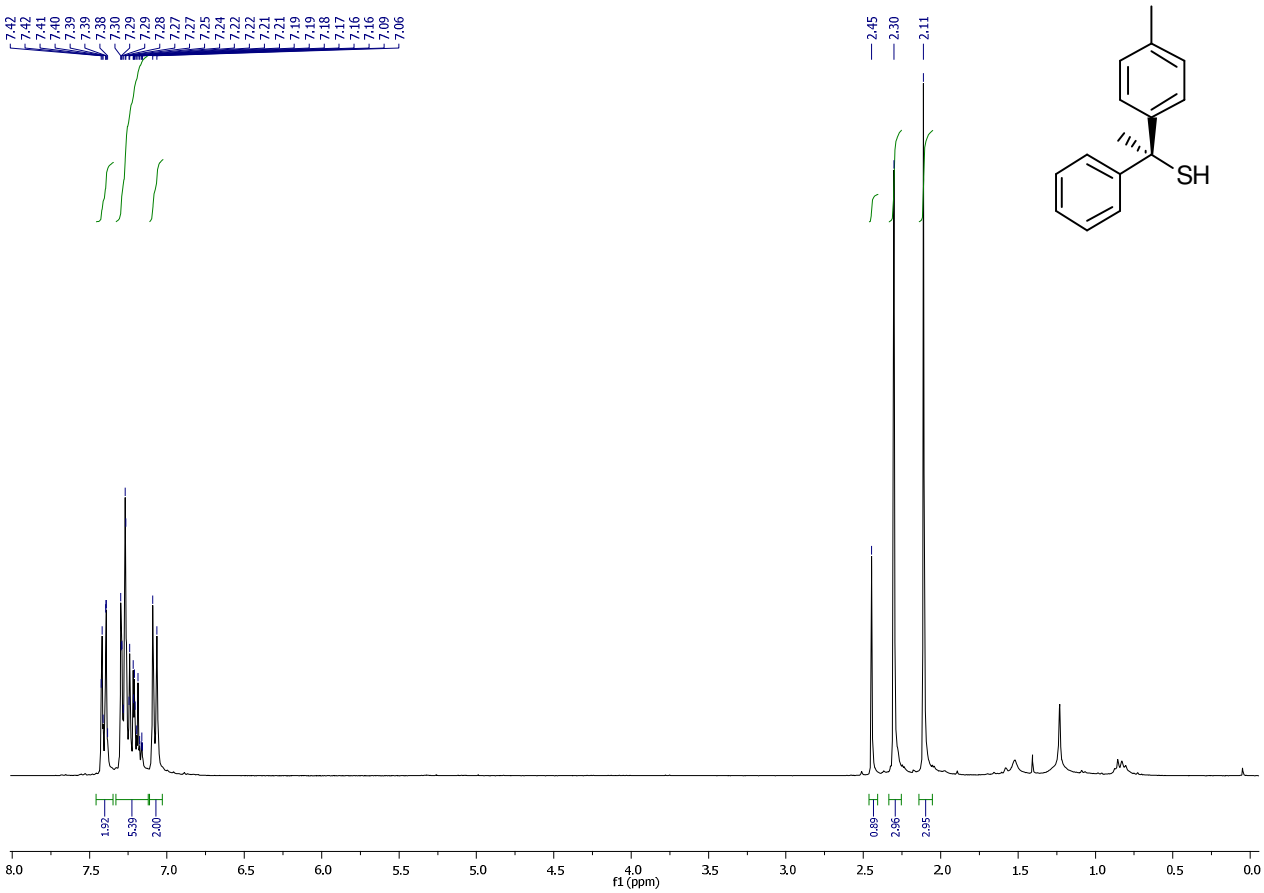


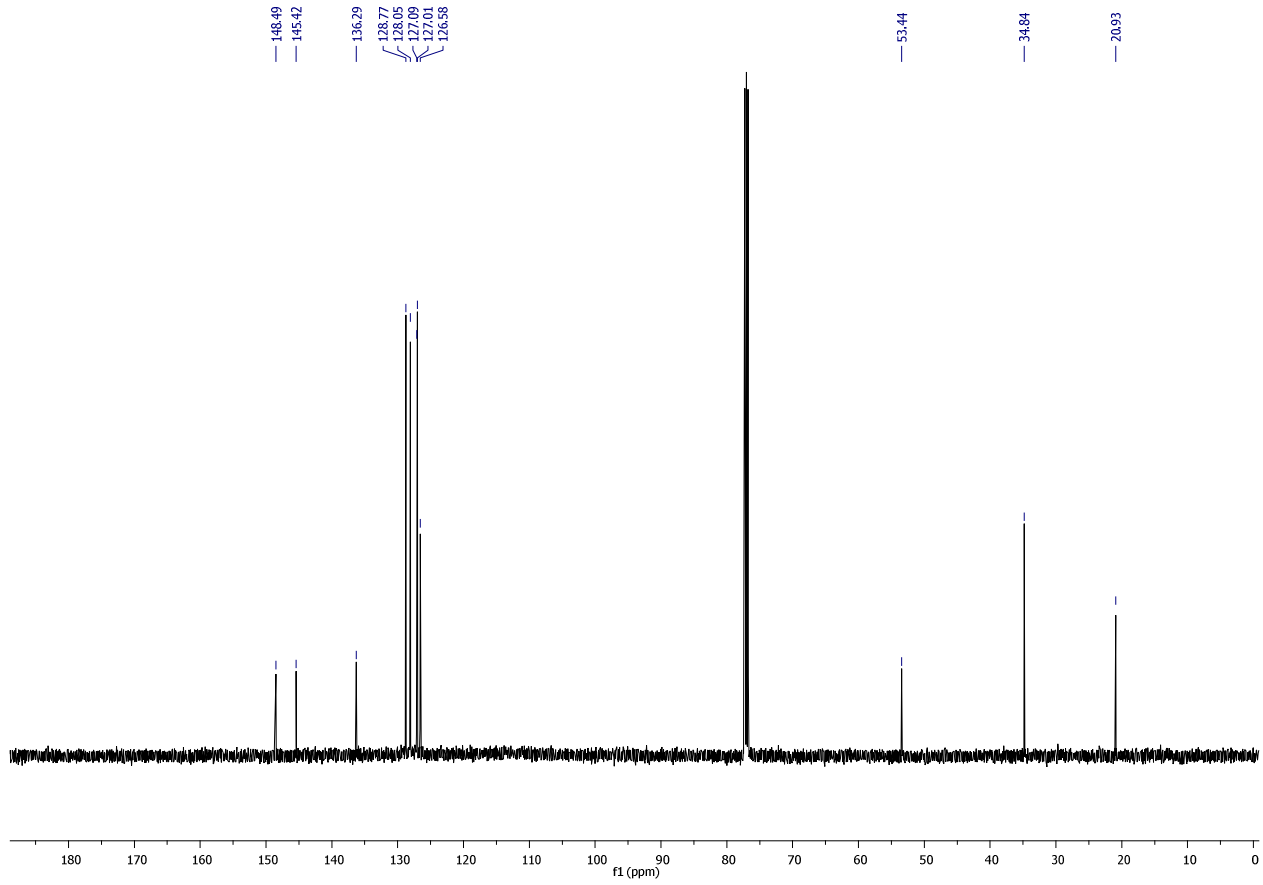
9m: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



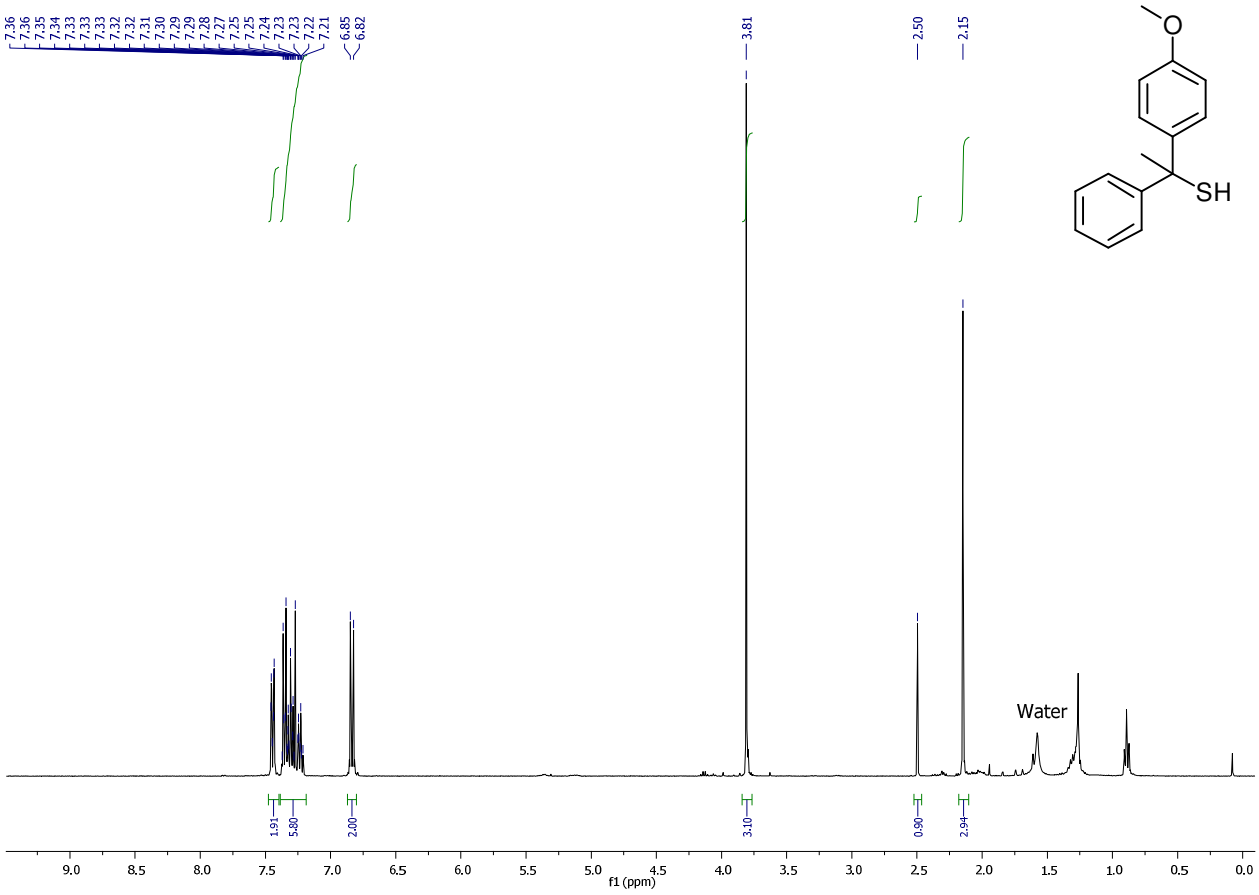


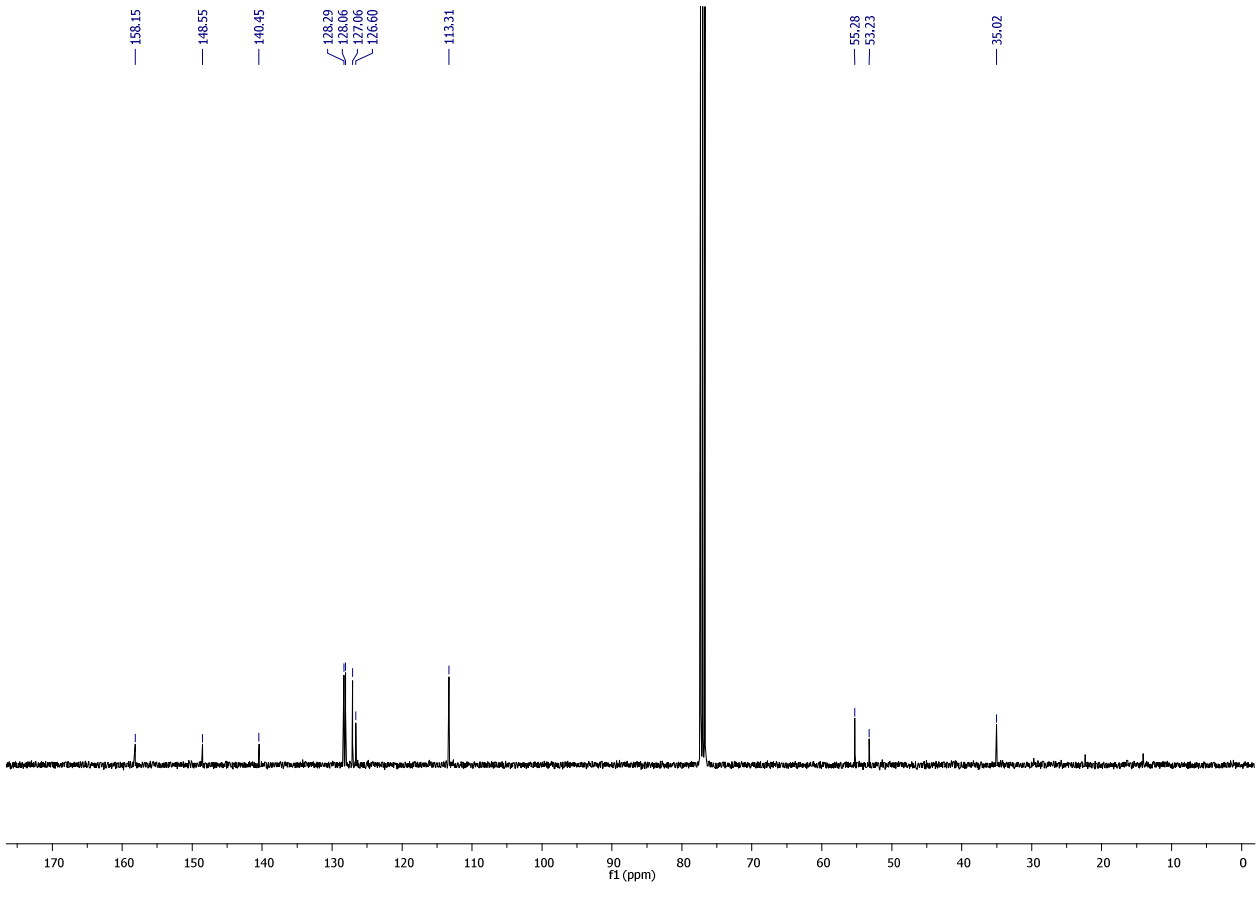
10a: **^{1}H-NMR**: 300 MHz, **^{13}C-NMR**: 125 MHz



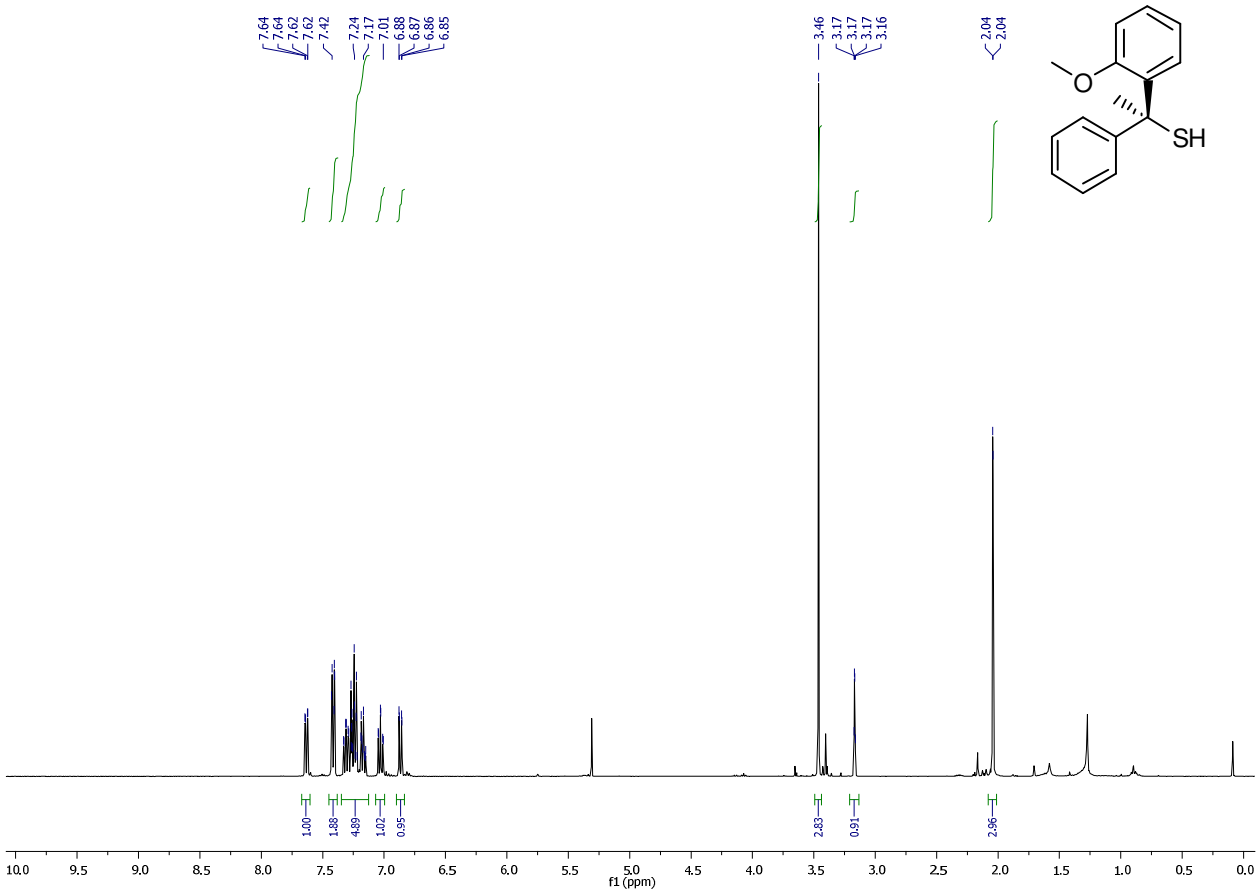


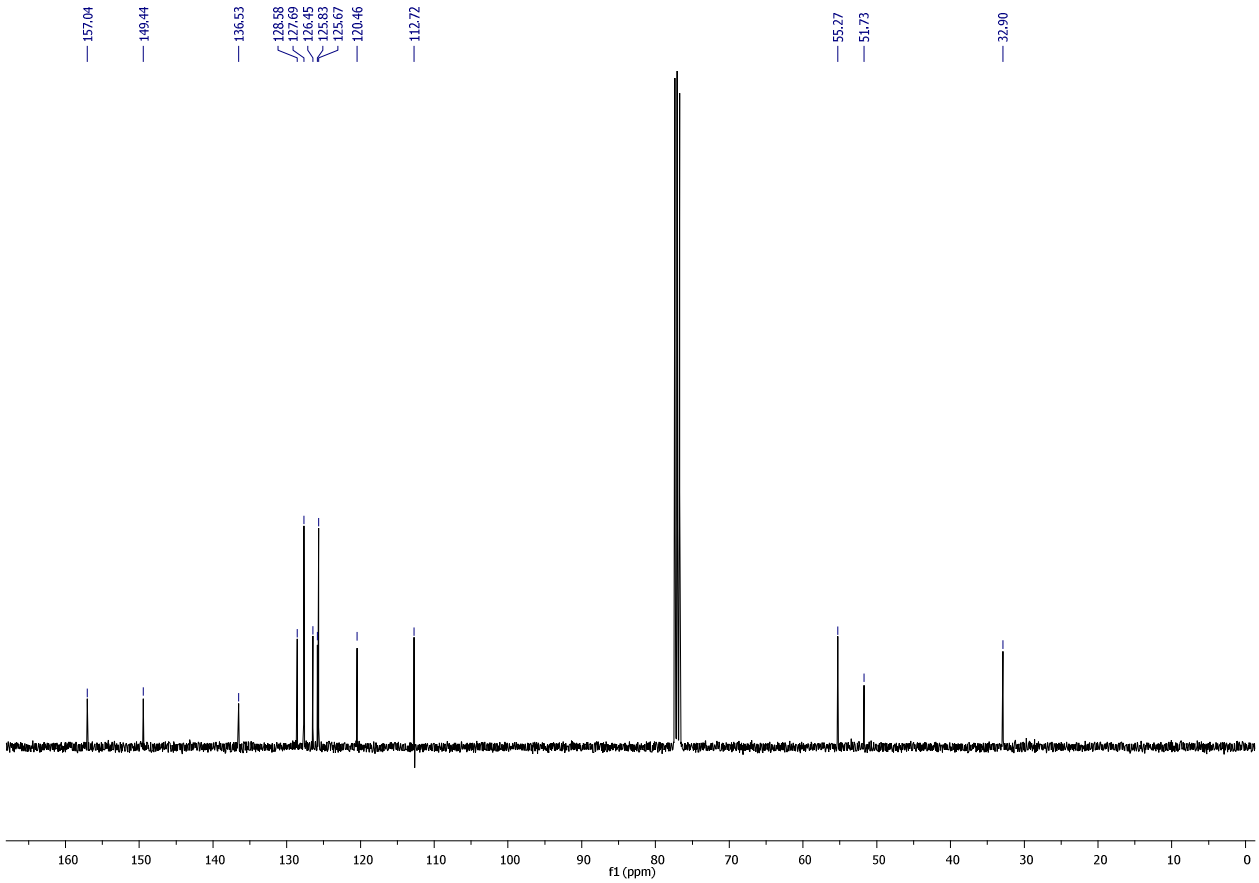
10b: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



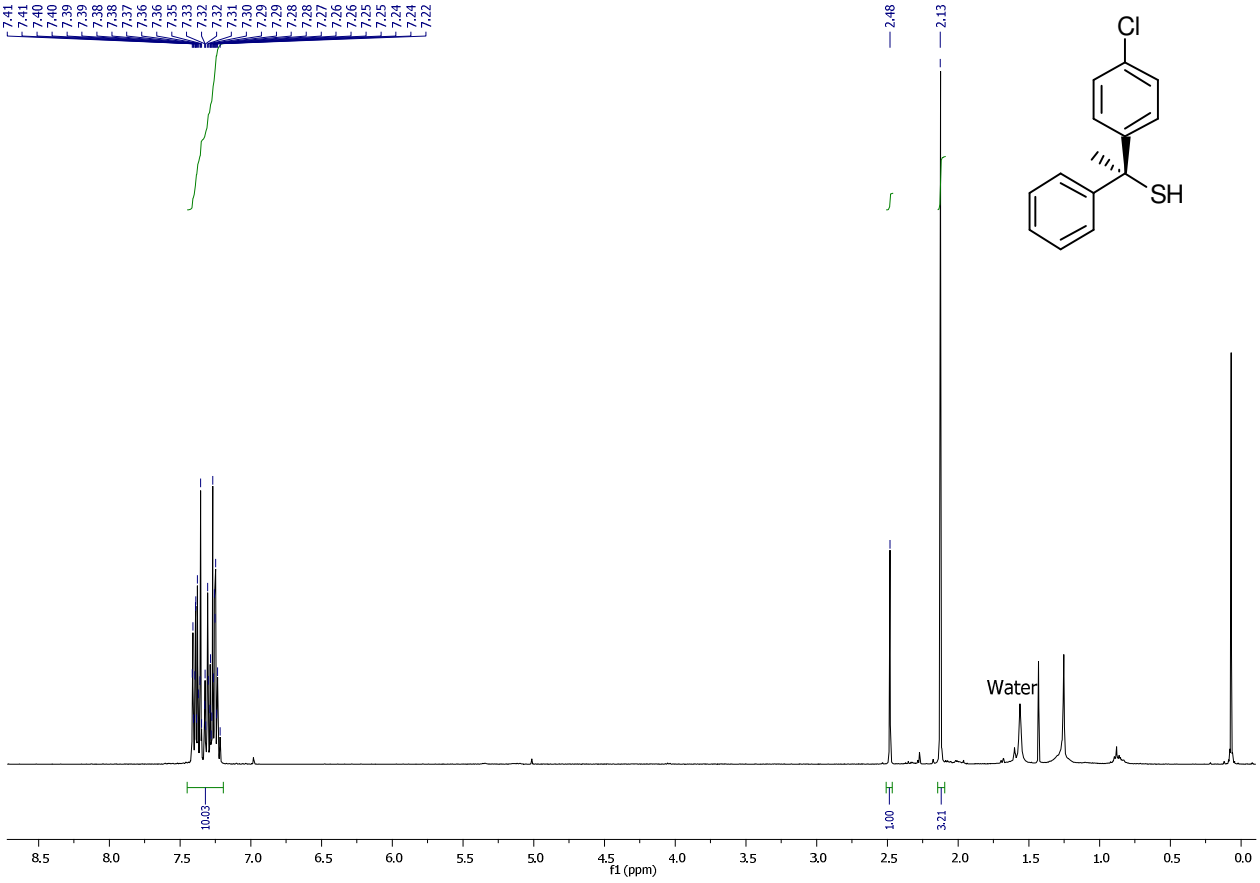


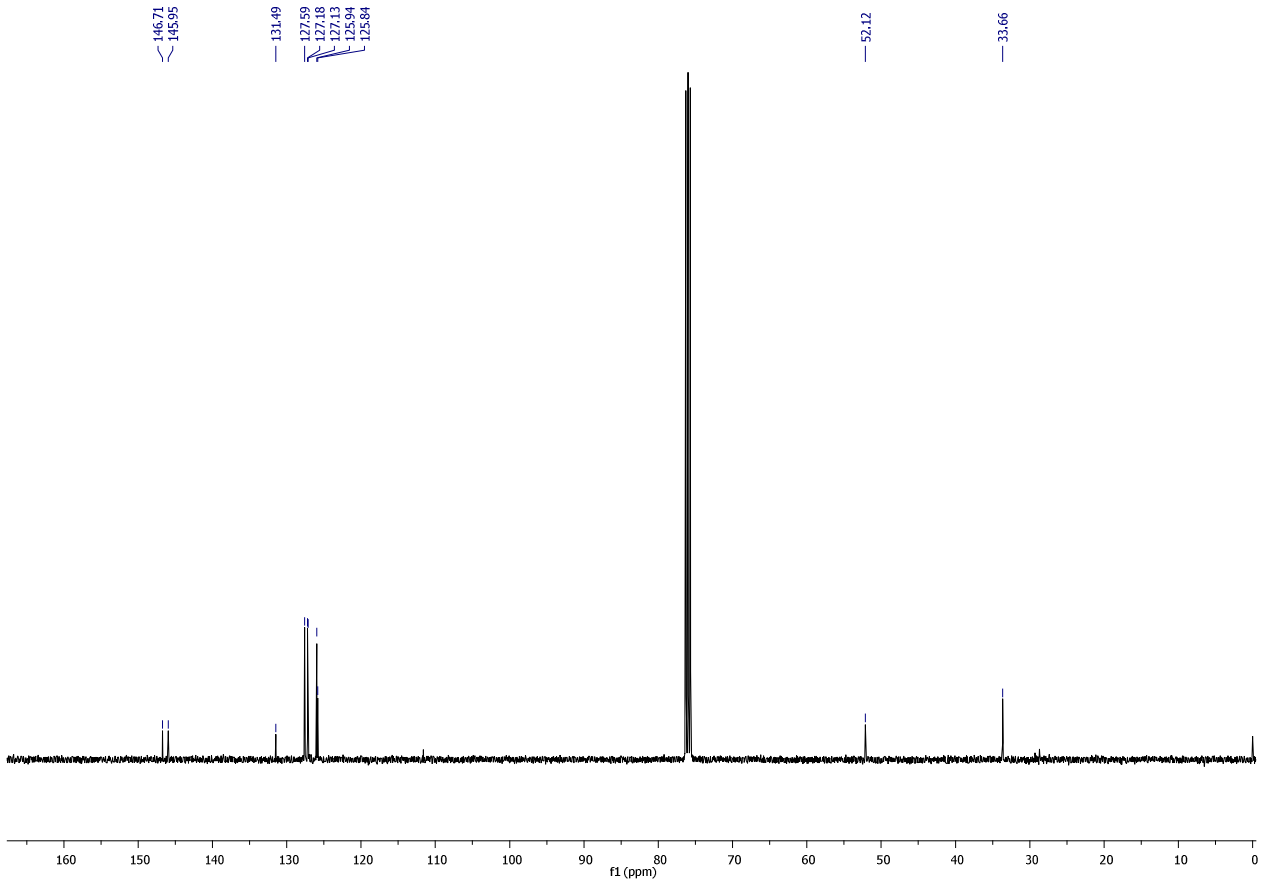
10c: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 100 MHz



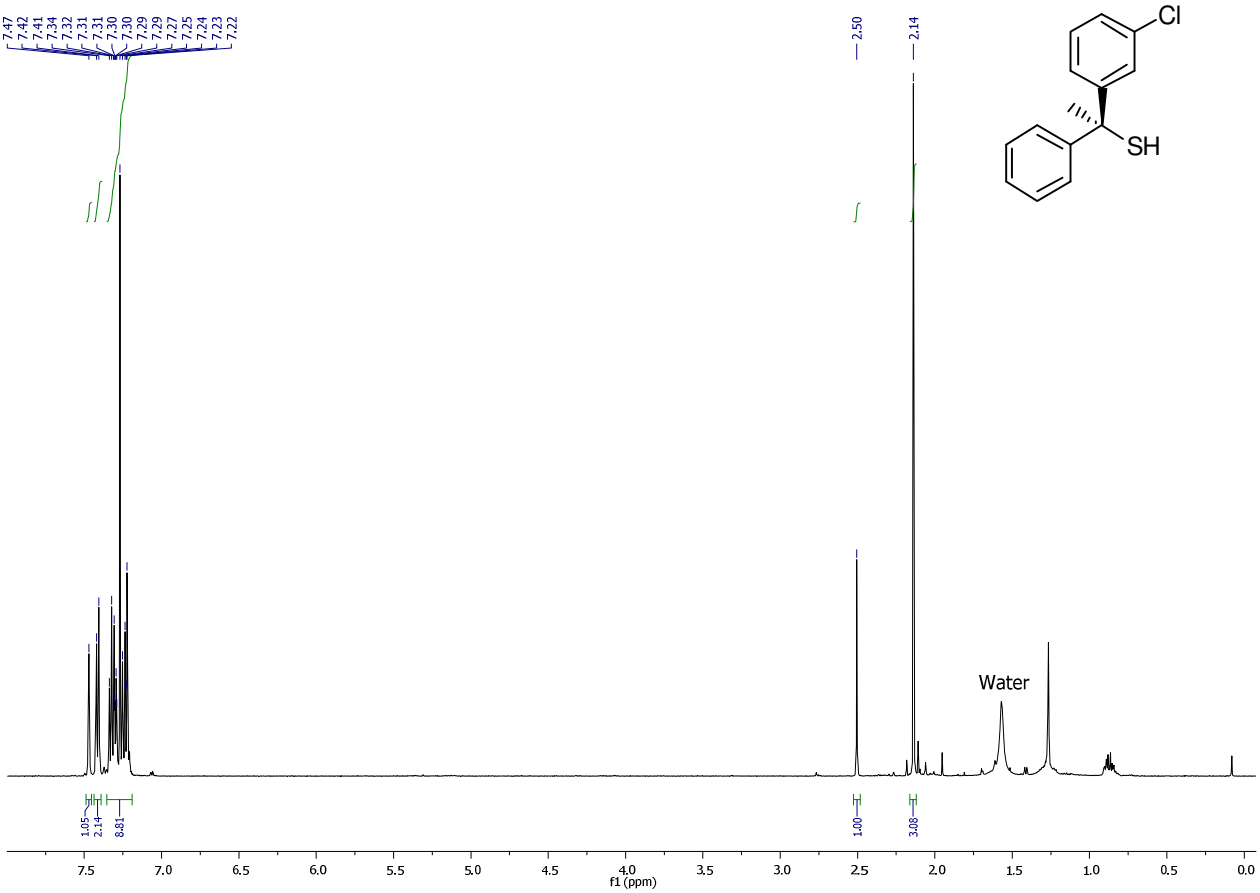


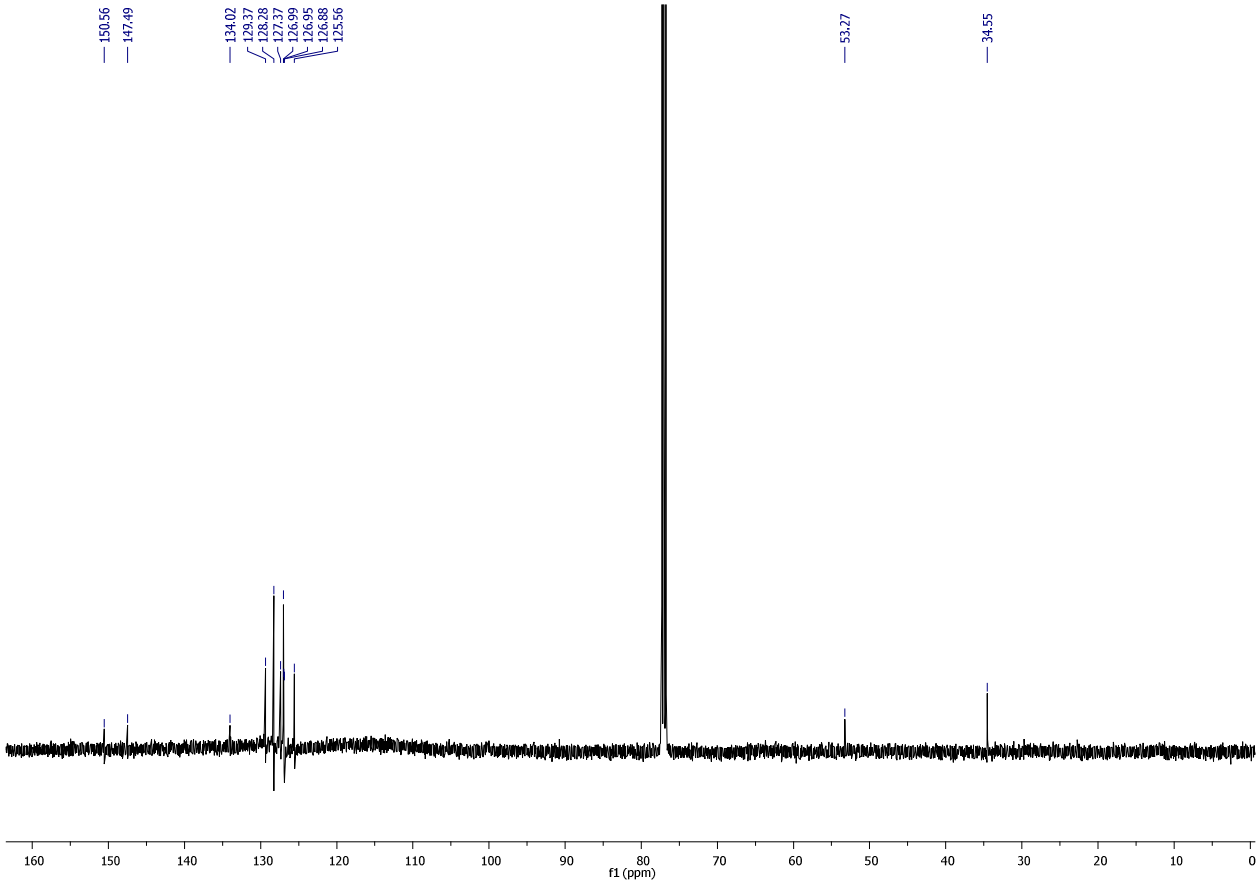
10d: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



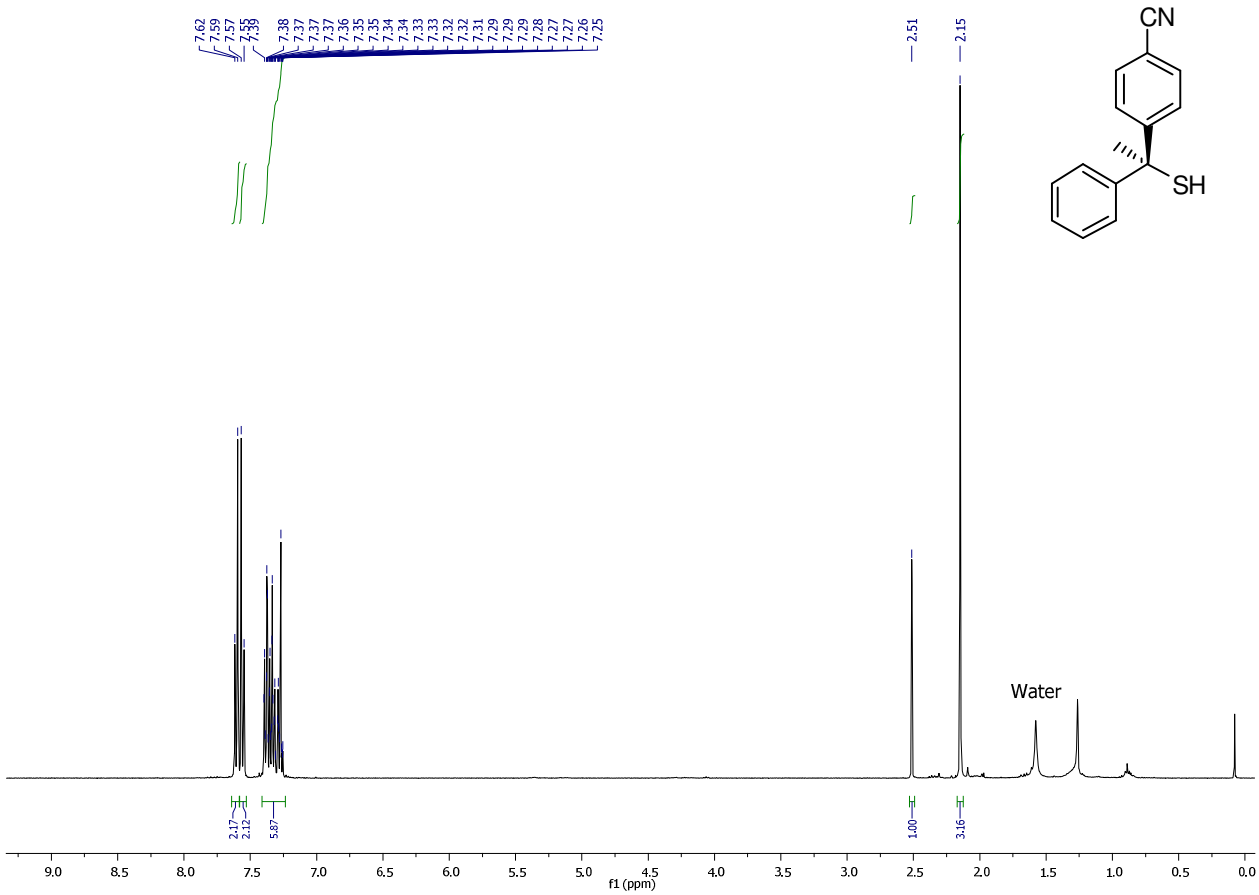


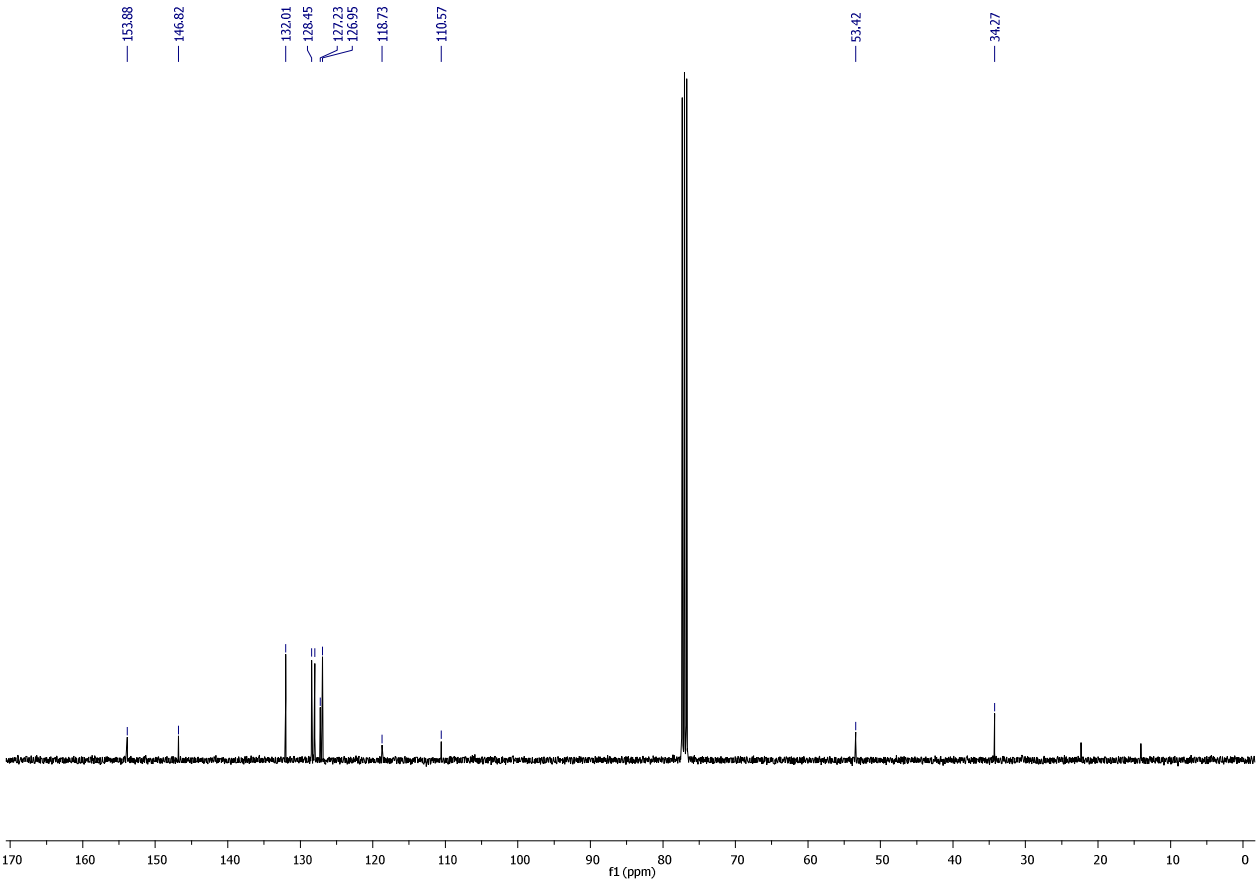
10e: ^{1}H-NMR: 500 MHz, **^{13}C-NMR**: 100 MHz



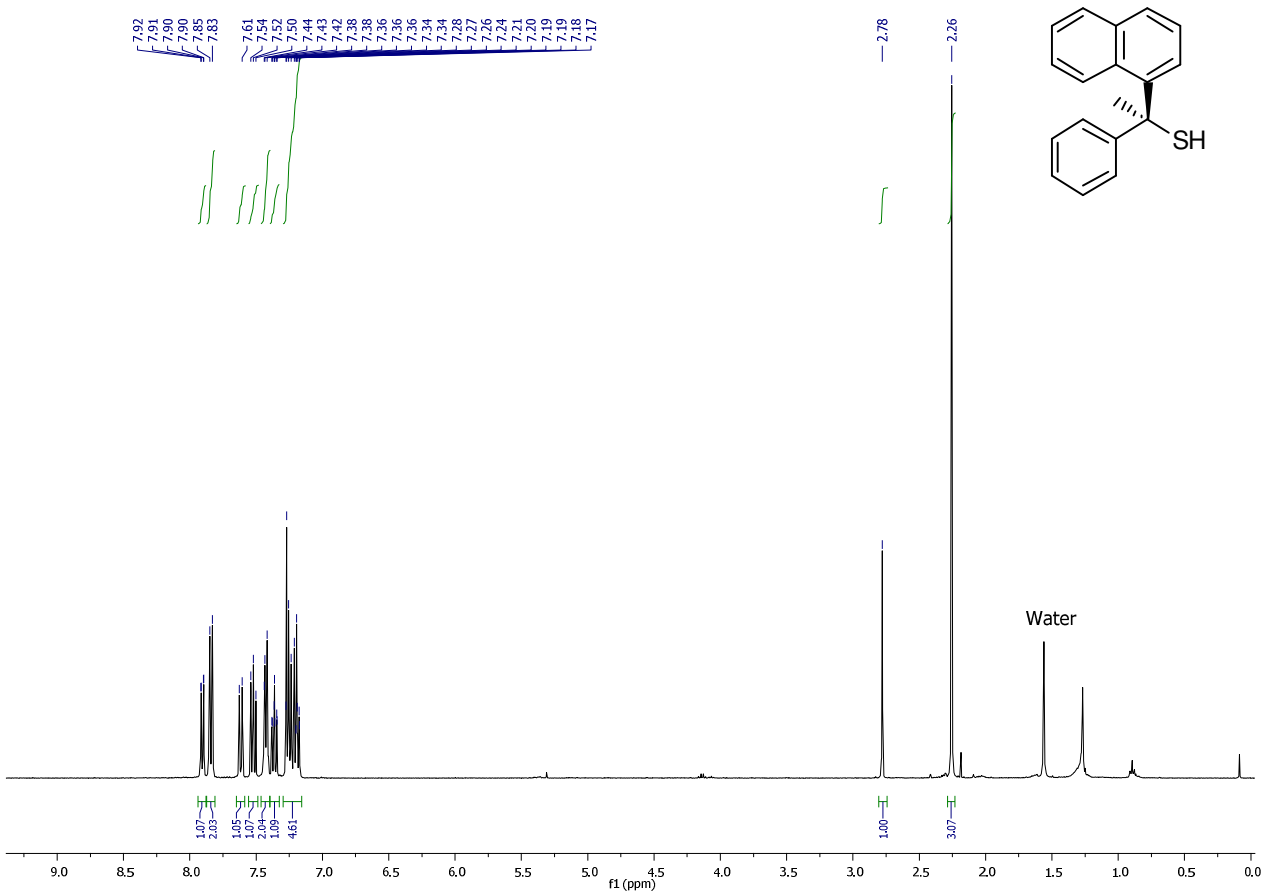


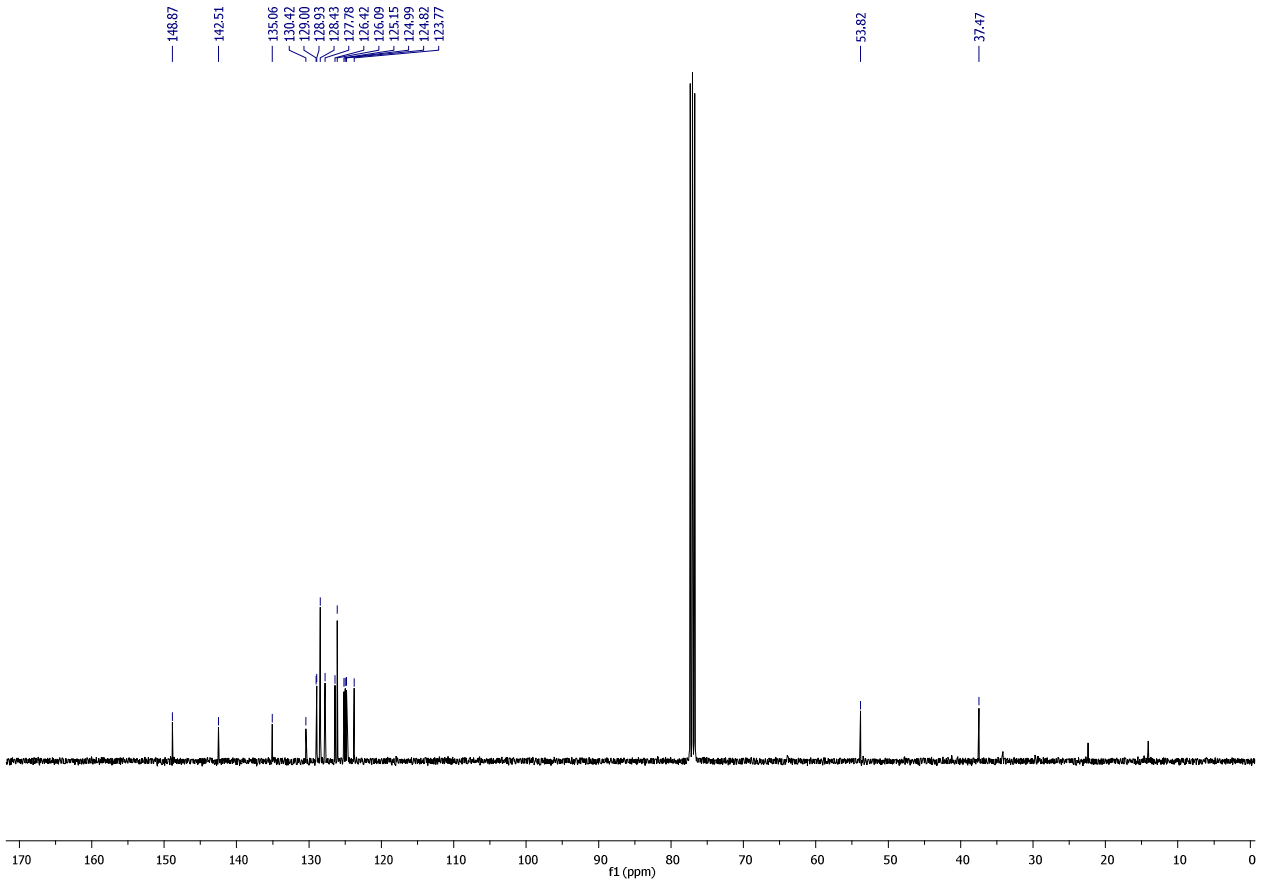
10f: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



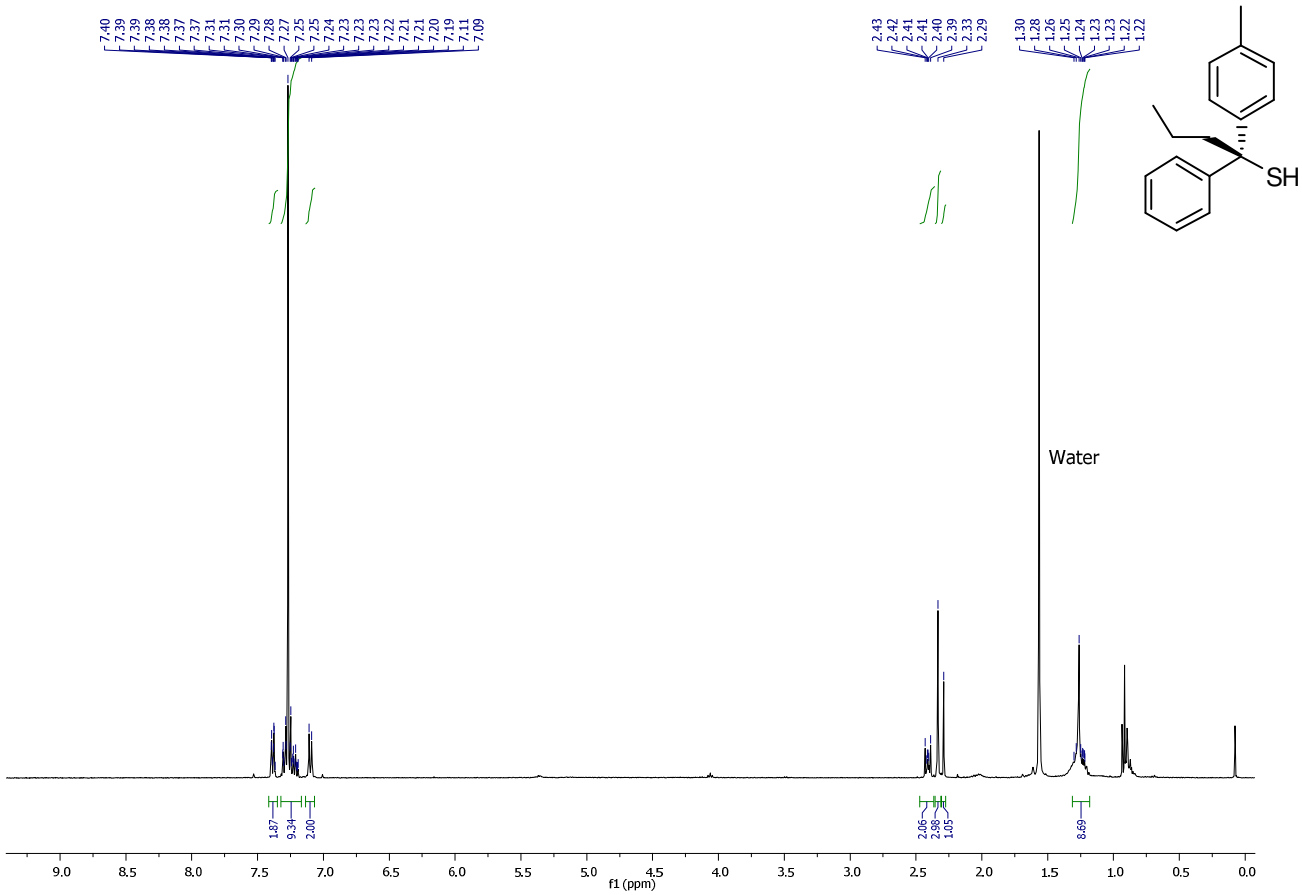


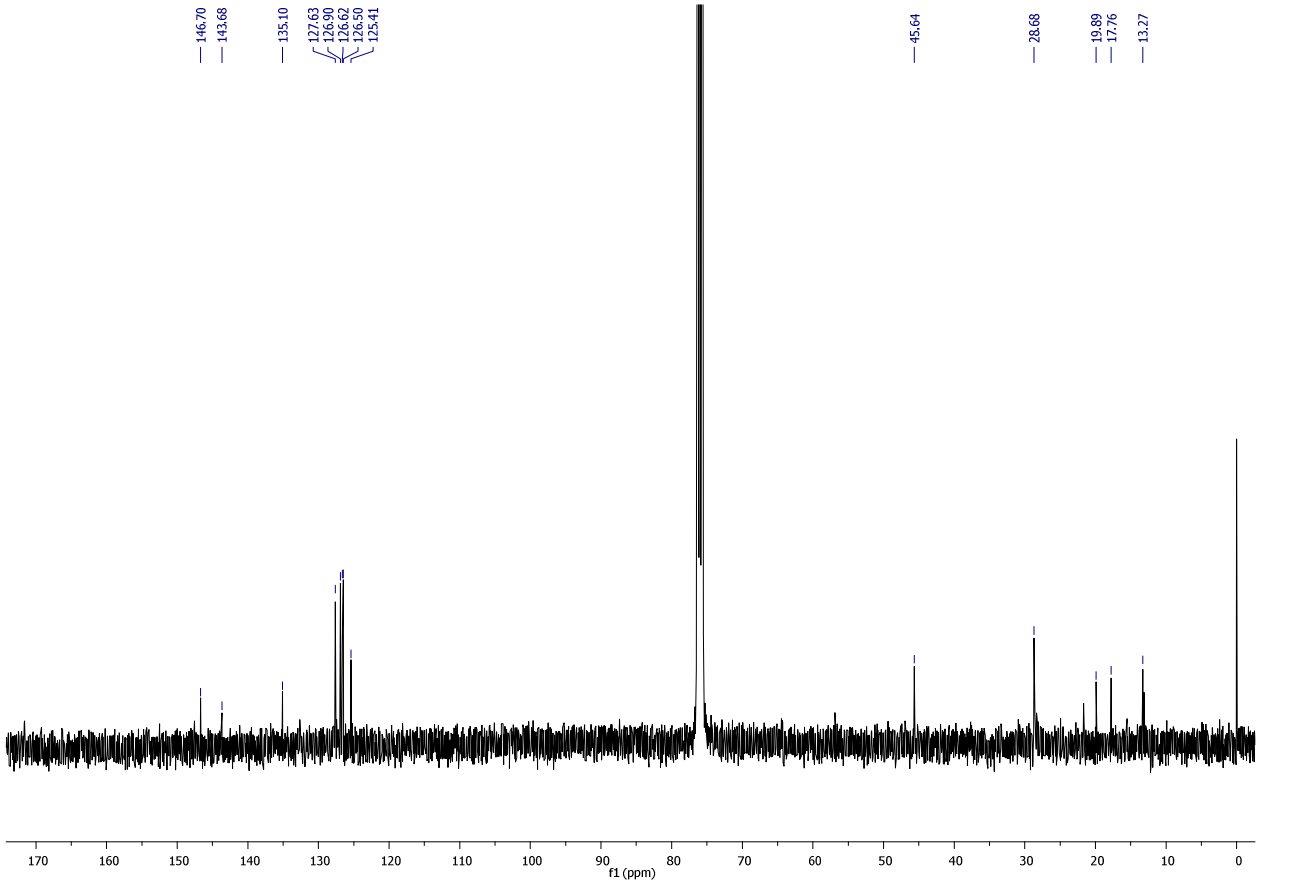
10h: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



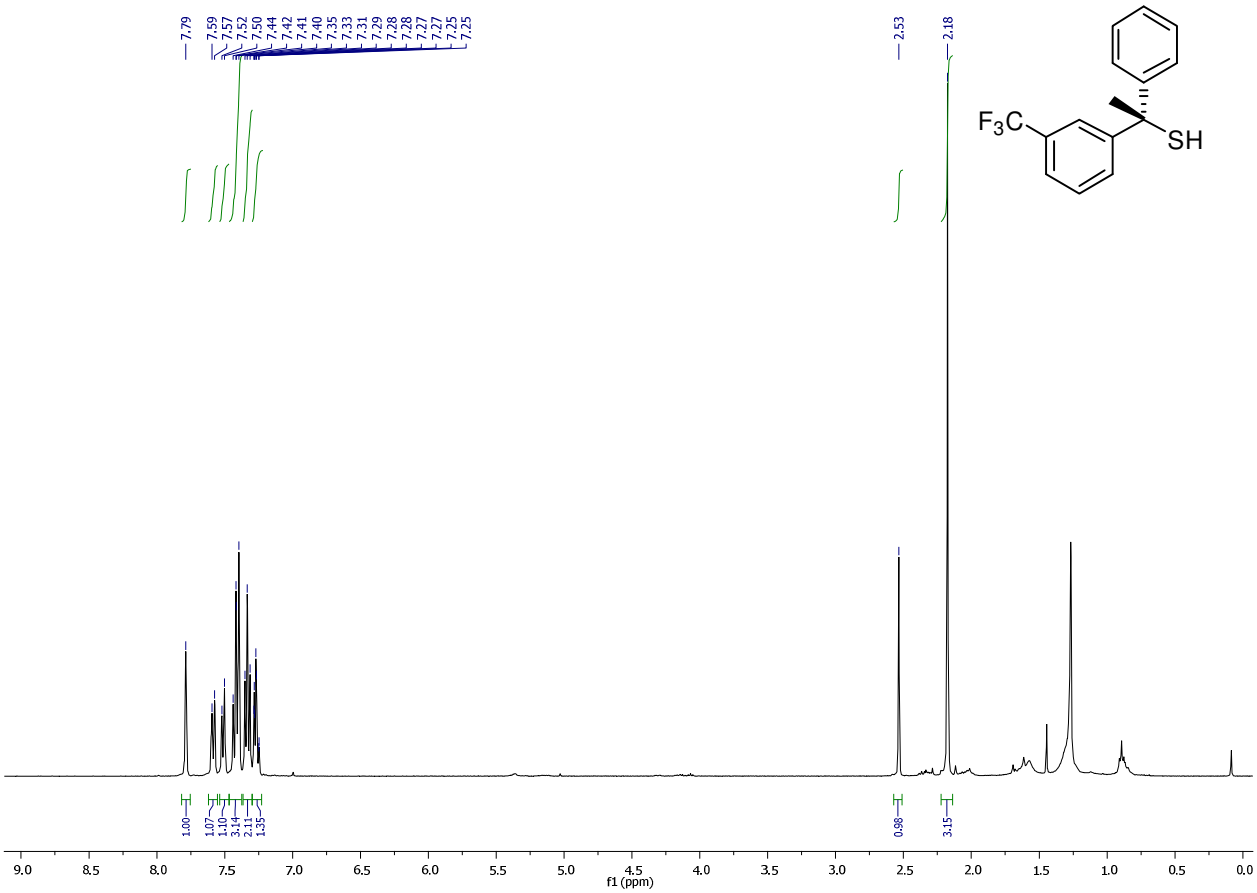


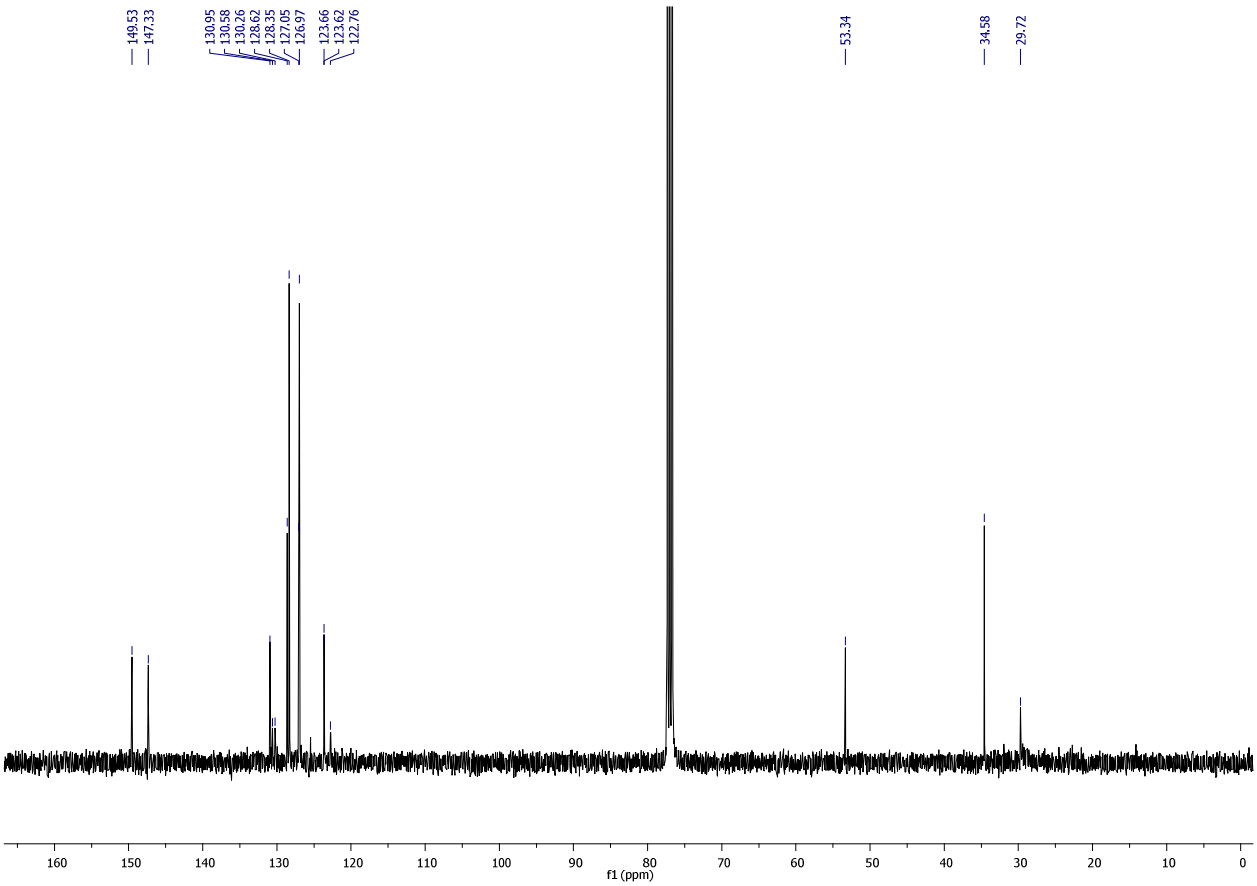
10j: ^{1}H-NMR: 500 MHz, **^{13}C-NMR**: 100 MHz



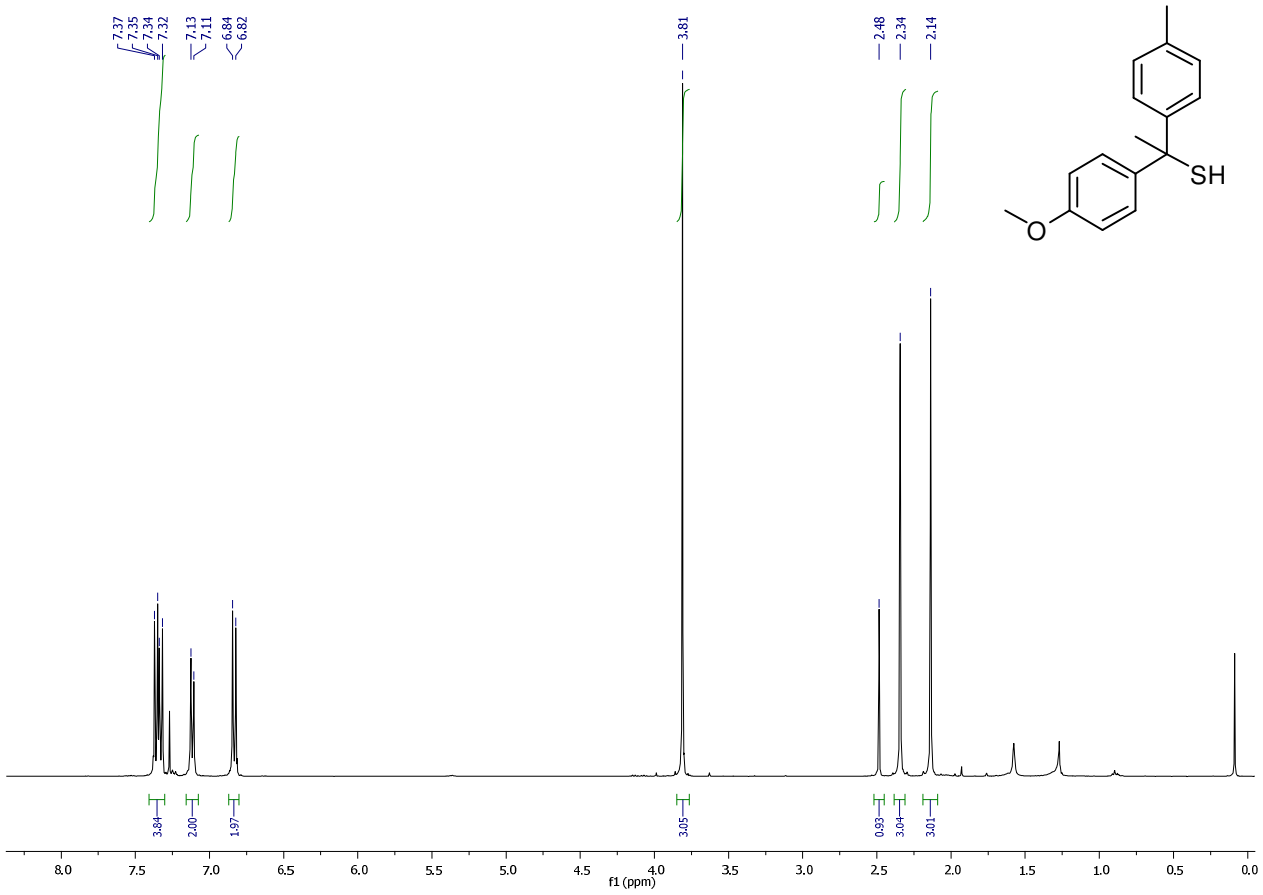


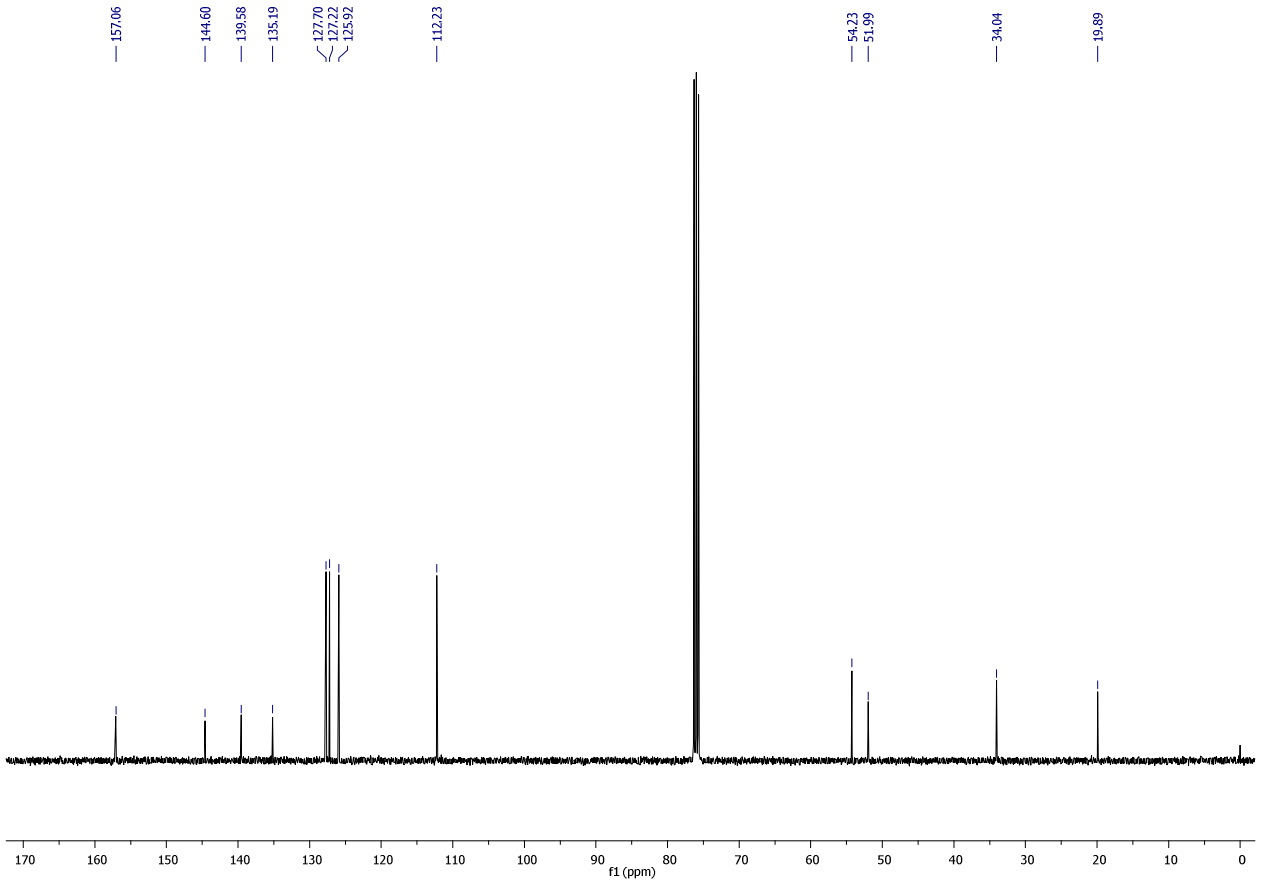
10k: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



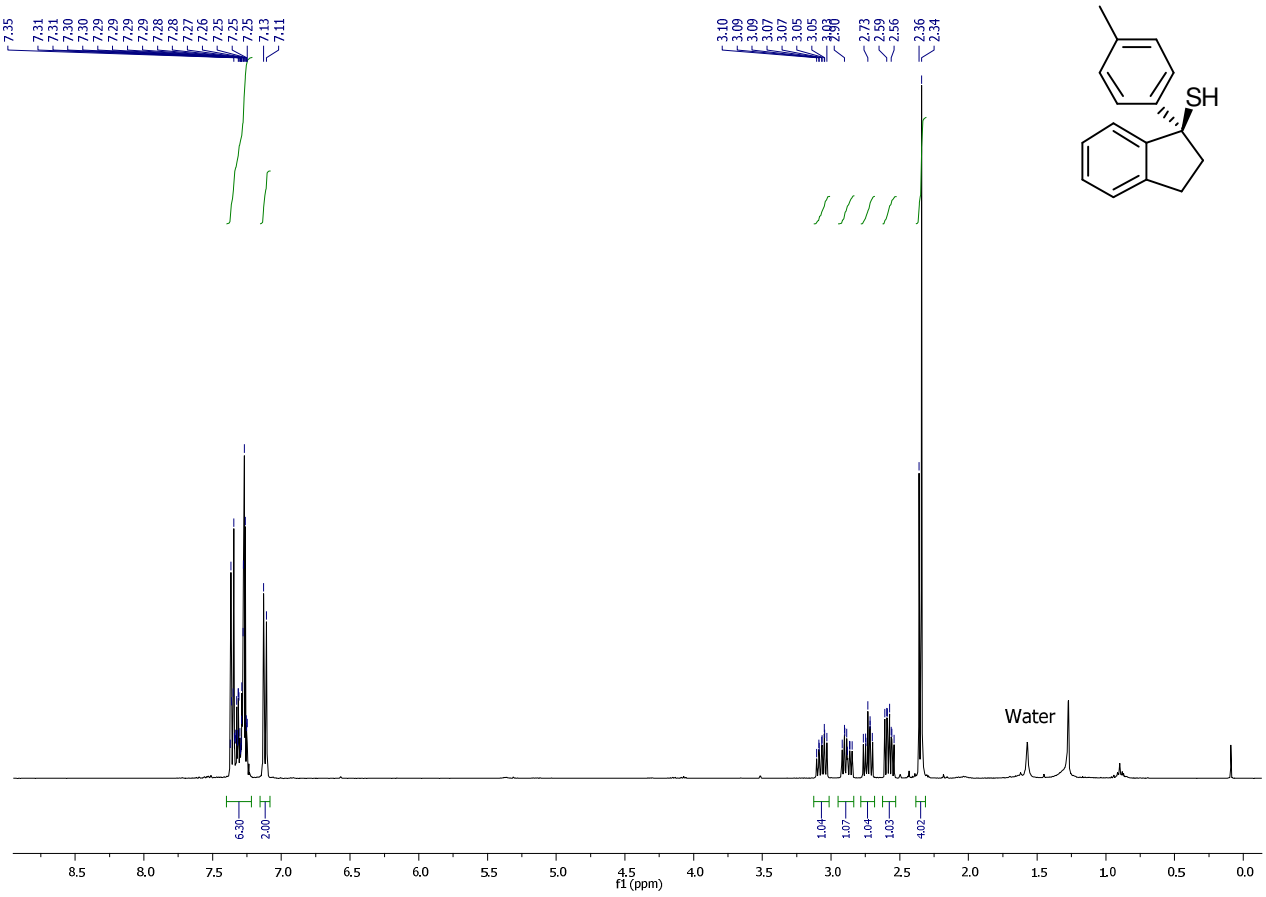


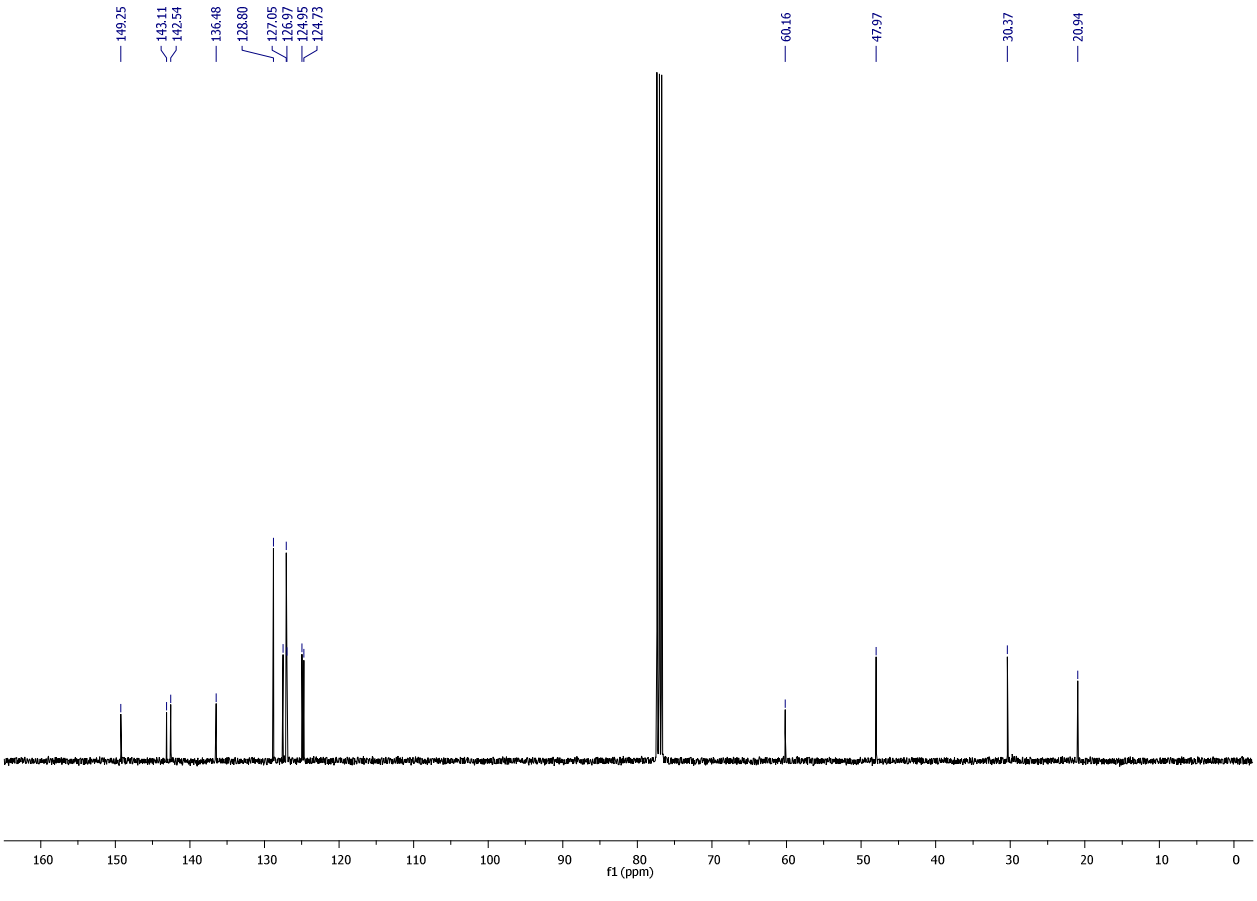
10l: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



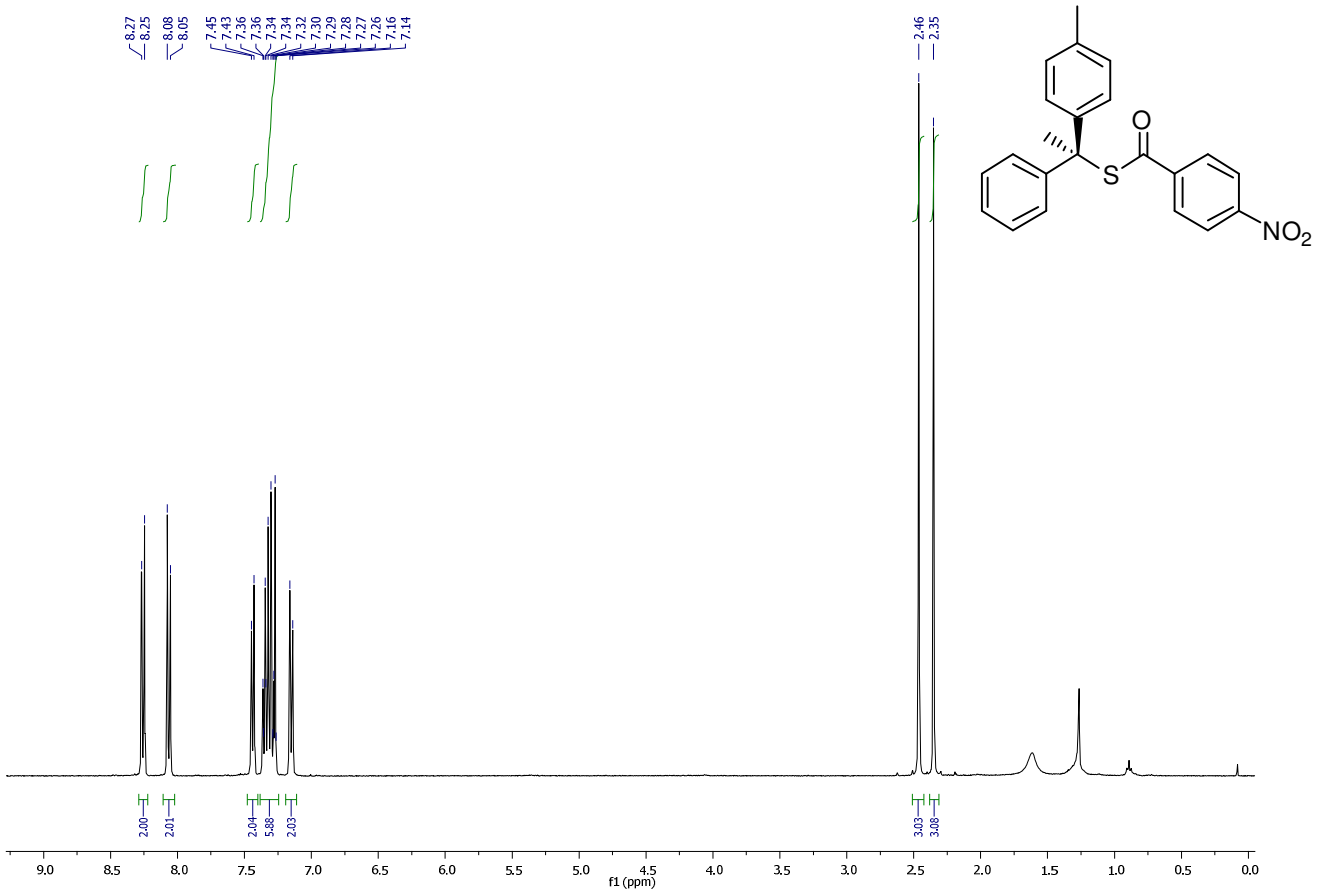


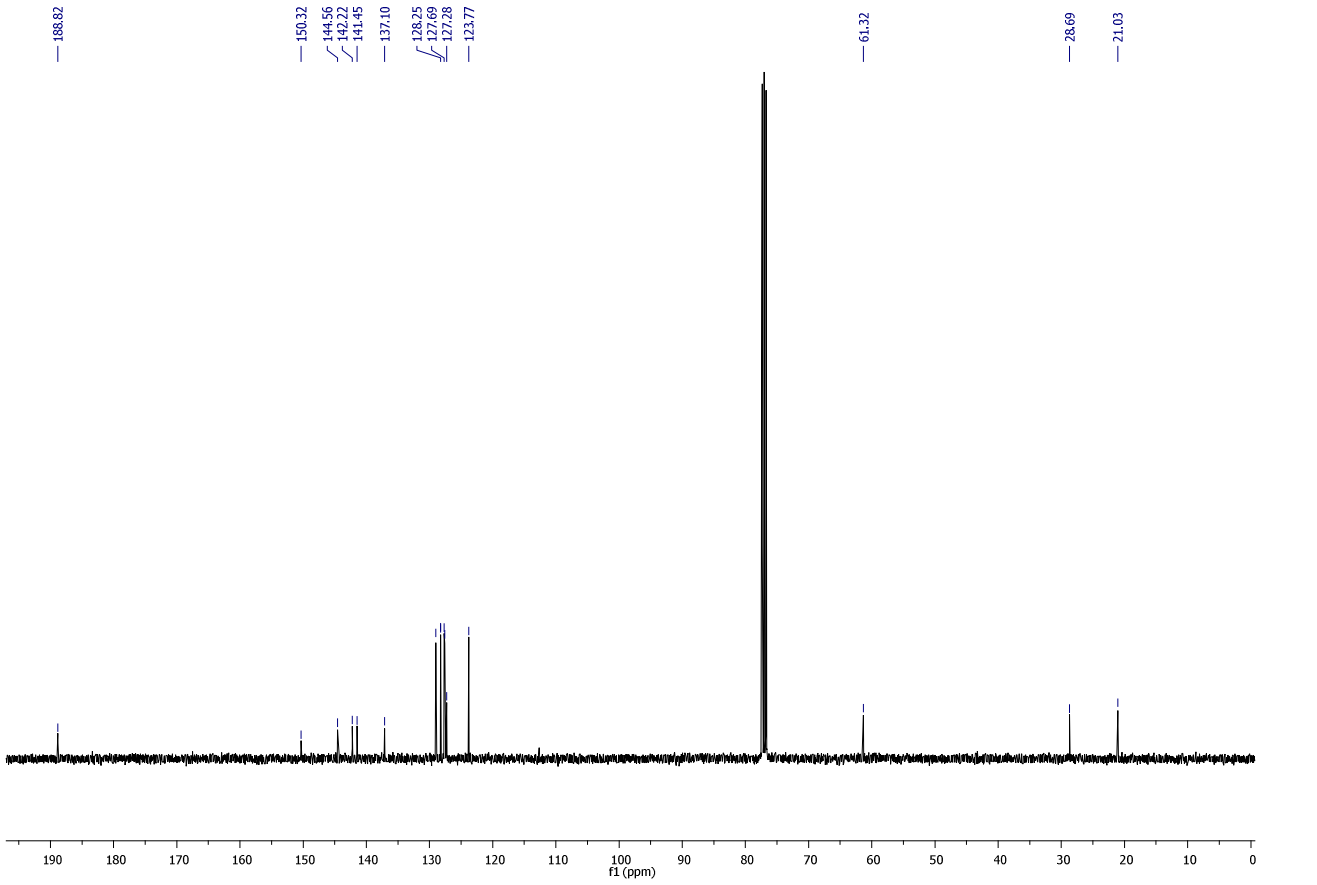
10m: ^{1}H-NMR: 400 MHz, **^{13}C-NMR**: 100 MHz



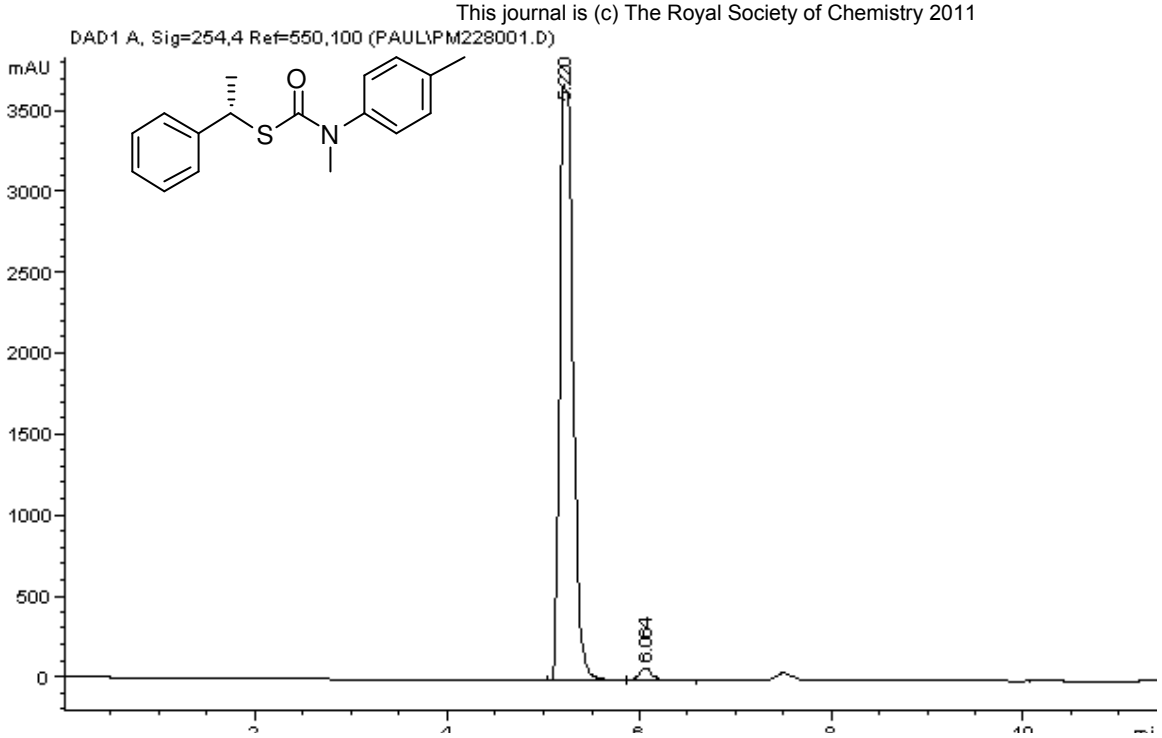


11: **^{1}H-NMR**: 400 MHz, **^{13}C-NMR**: 75.5 MHz



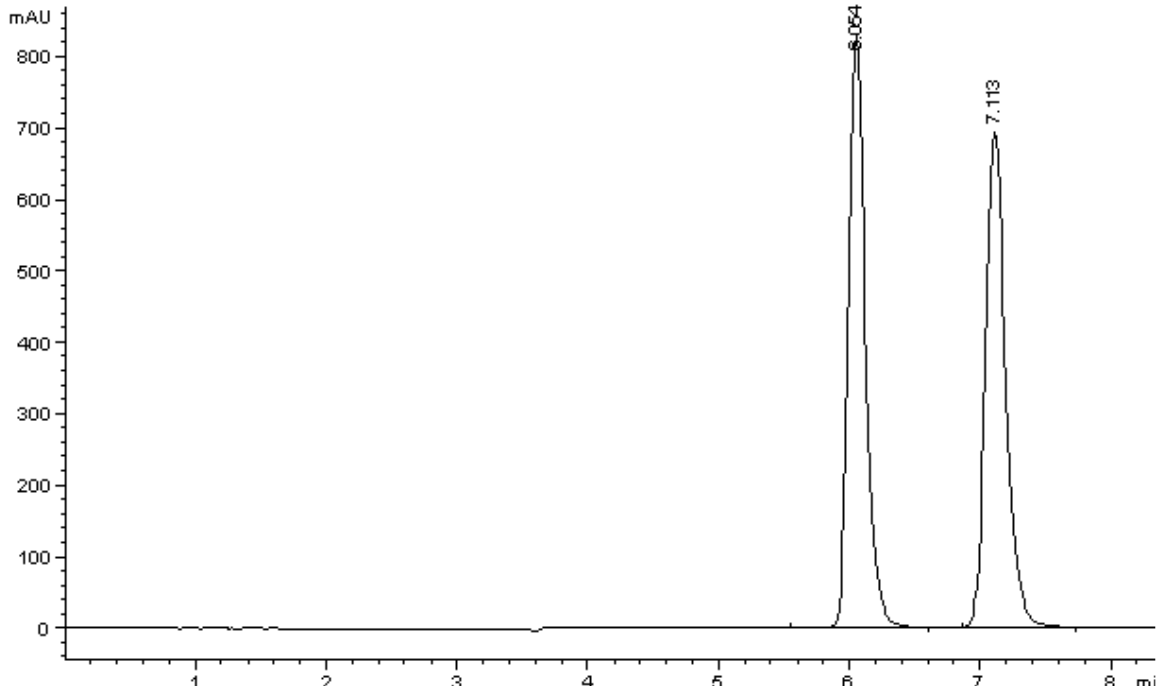


8a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.220	BV	0.1317	3.51665e4	3674.12085	98.0432
2	6.064	VB	0.1432	701.86371	76.35201	1.9568

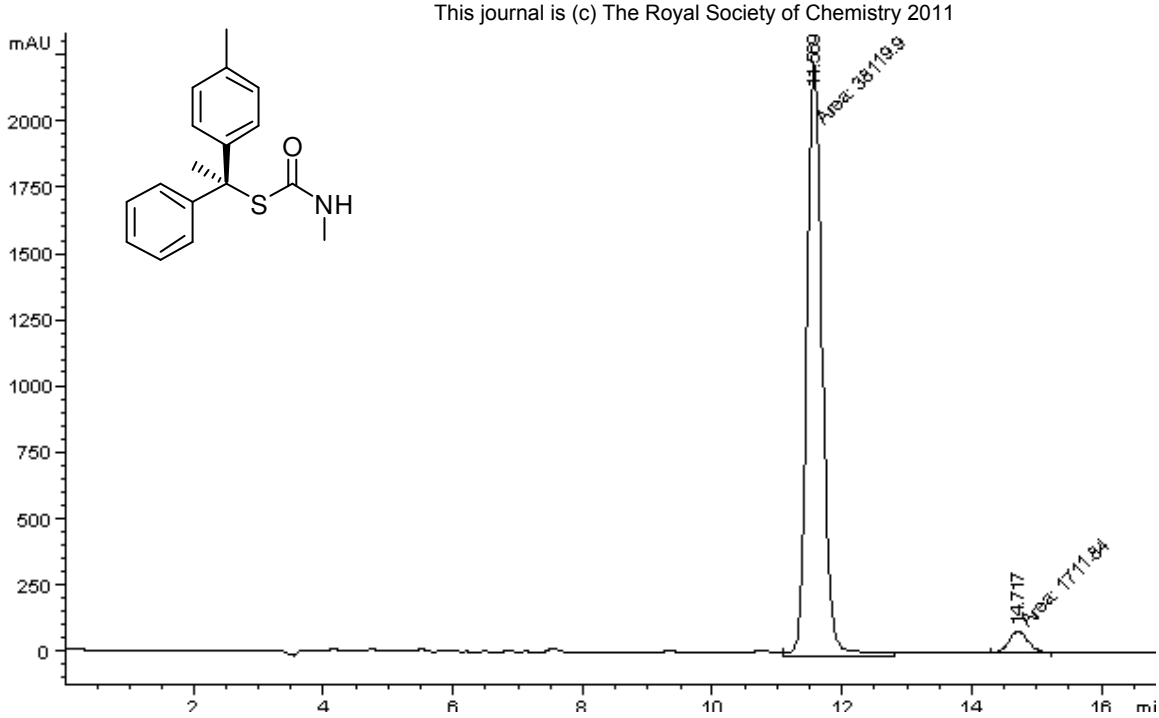
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.054	VB	0.1364	7417.34375	828.77435	49.9656
2	7.113	PB	0.1647	7427.54932	694.90533	50.0344

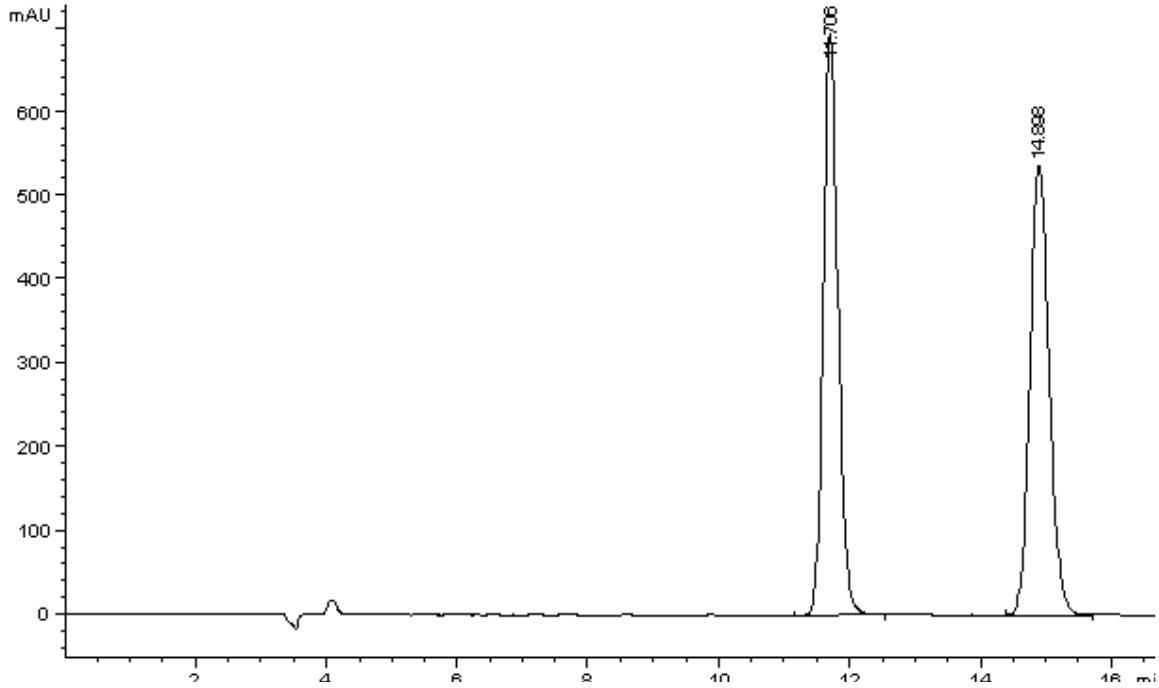
9a



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.569	MM	0.2822	3.81199e4	2251.11377	95.7023
2	14.717	MM	0.3422	1711.84241	83.38615	4.2977

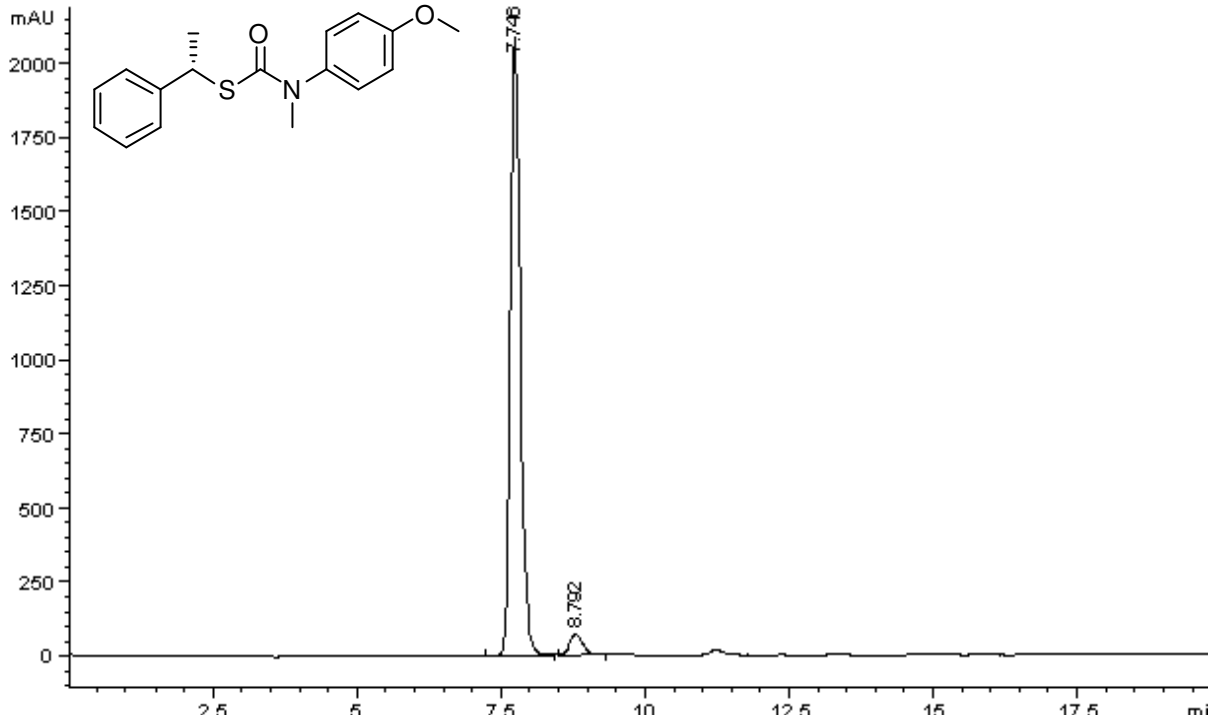
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.706	PB	0.2454	1.10593e4	696.09546	50.0059
2	14.898	BB	0.3199	1.10567e4	537.80151	49.9941

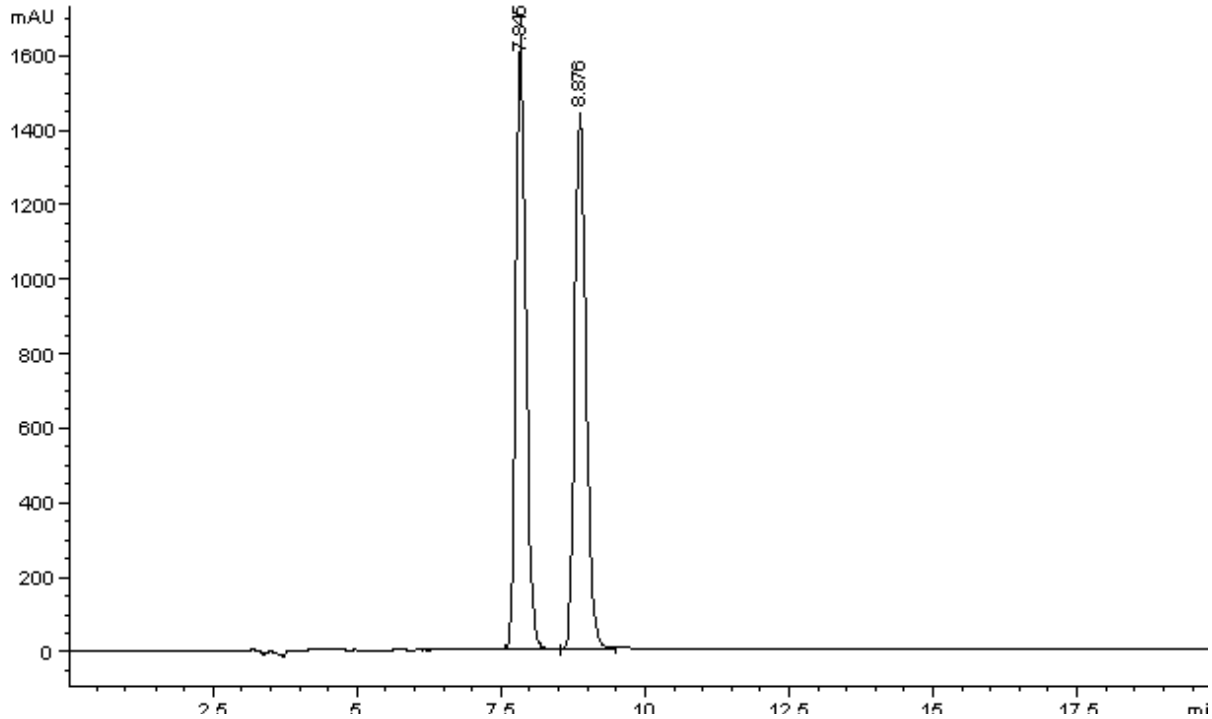
8b



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.746	BB	0.1901	2.55153e4	2095.47119	95.7928
2	8.792	BB	0.2515	1120.62744	69.72172	4.2072

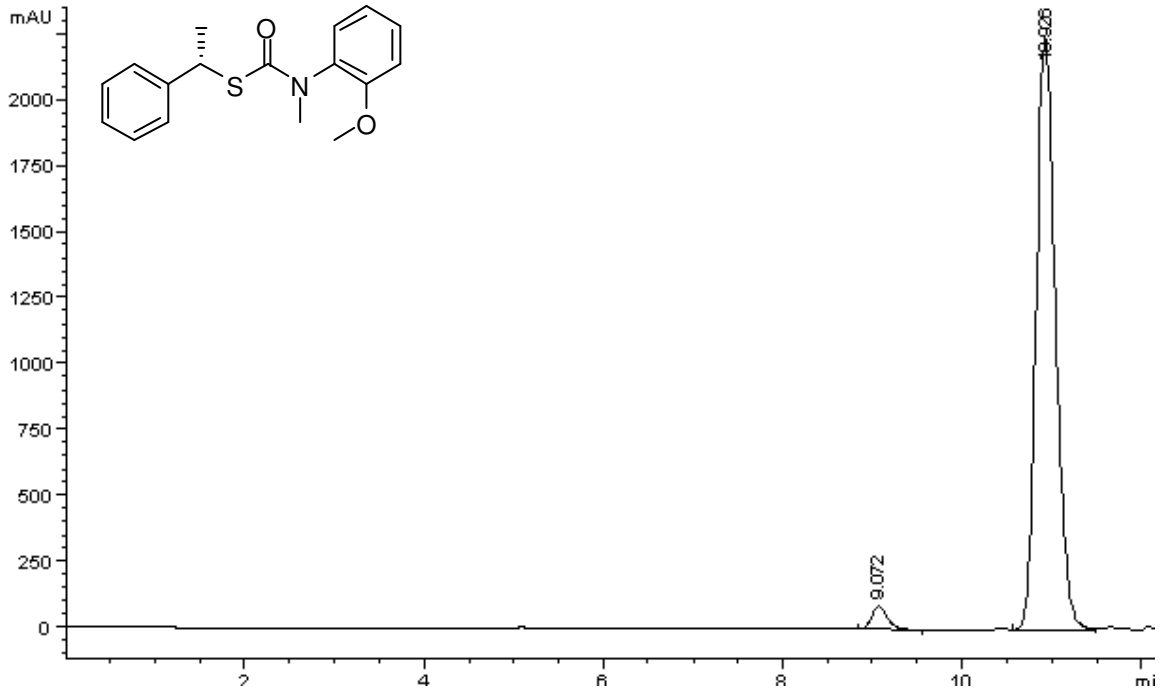
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.845	PP	0.1847	1.98794e4	1648.81665	50.0121
2	8.876	VV	0.2135	1.98698e4	1435.23914	49.9879

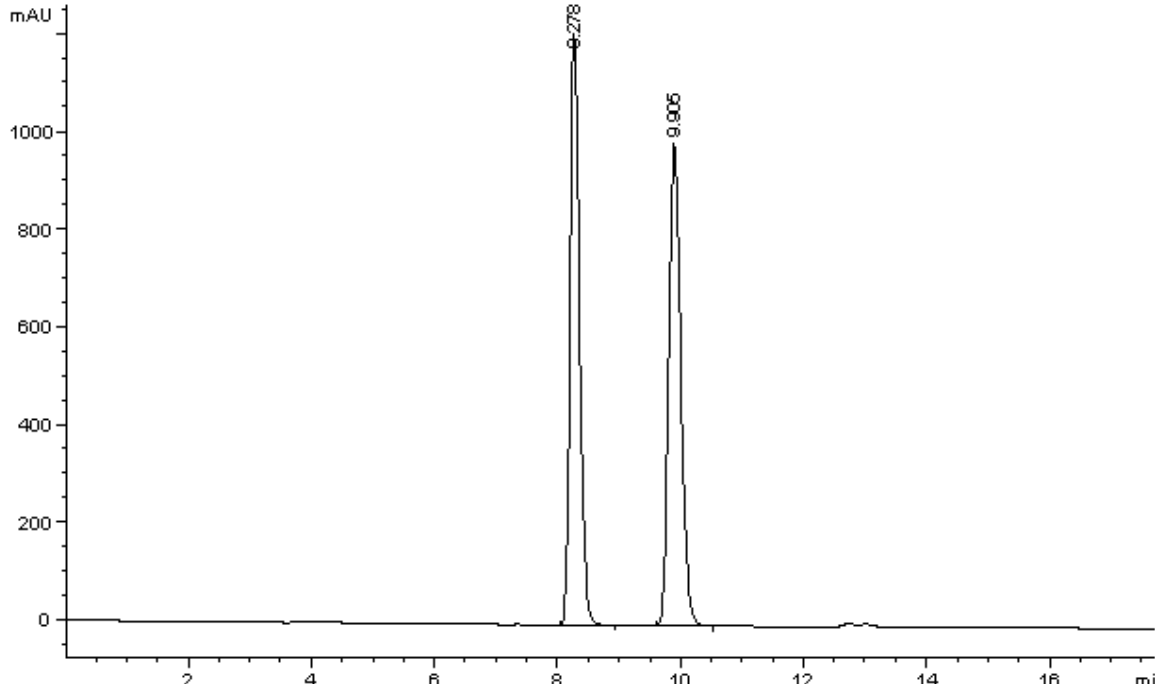
8c



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.072	BP	0.1830	1025.82043	86.08256	2.9283
2	10.926	VV	0.2361	3.40056e4	2253.46045	97.0717

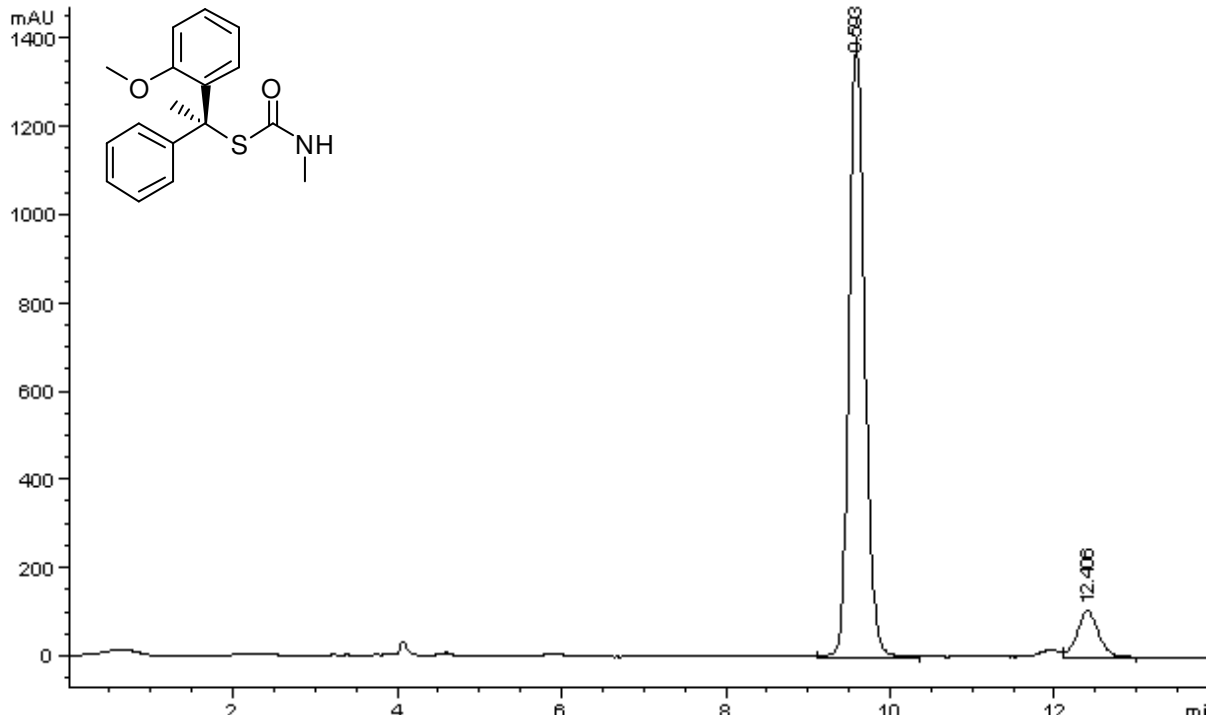
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.278	BB	0.1712	1.32093e4	1211.24646	50.0643
2	9.905	BB	0.2079	1.31753e4	986.13293	49.9357

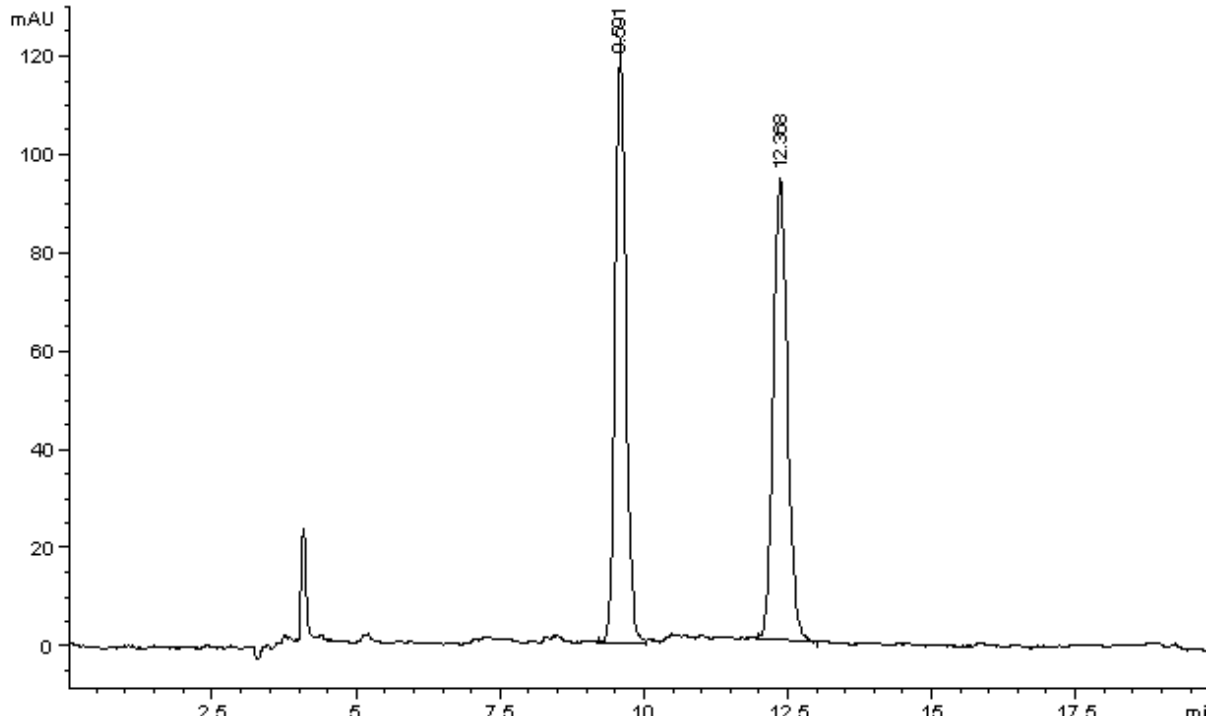
9c



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.593	BB	0.2027	1.86374e4	1405.98096	91.0293
2	12.406	VB	0.2728	1836.66443	104.64954	8.9707

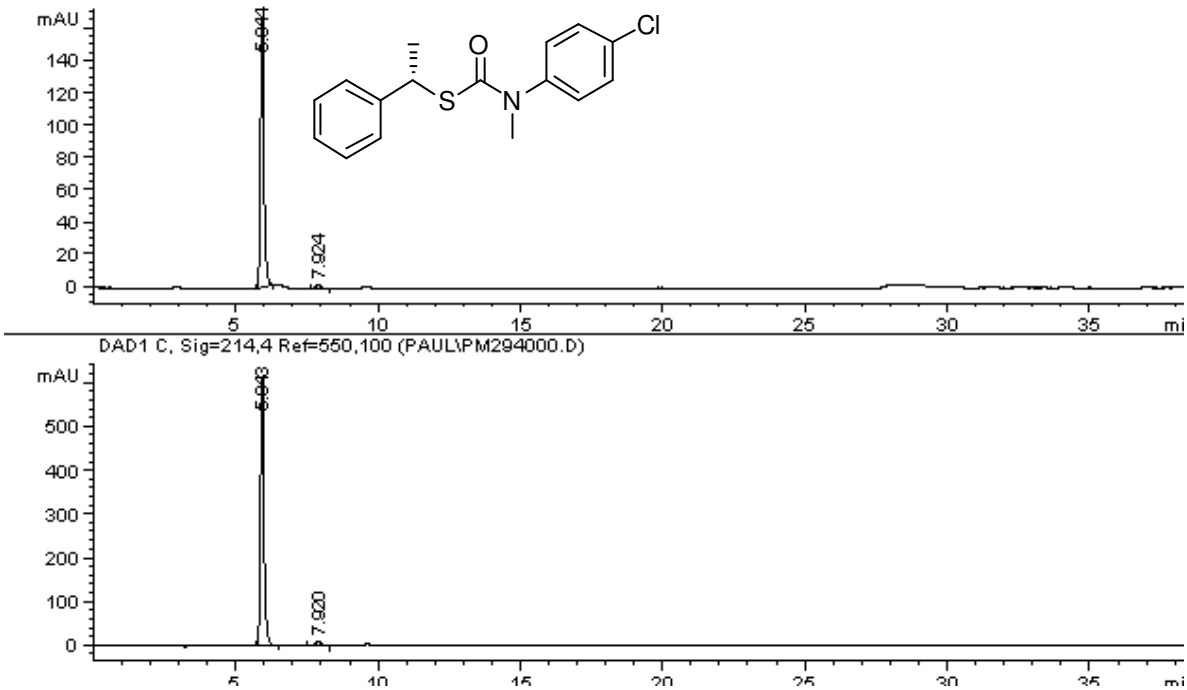
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.591	VV	0.1995	1599.88586	123.22392	50.0838
2	12.368	BP	0.2574	1594.53088	94.25573	49.9162

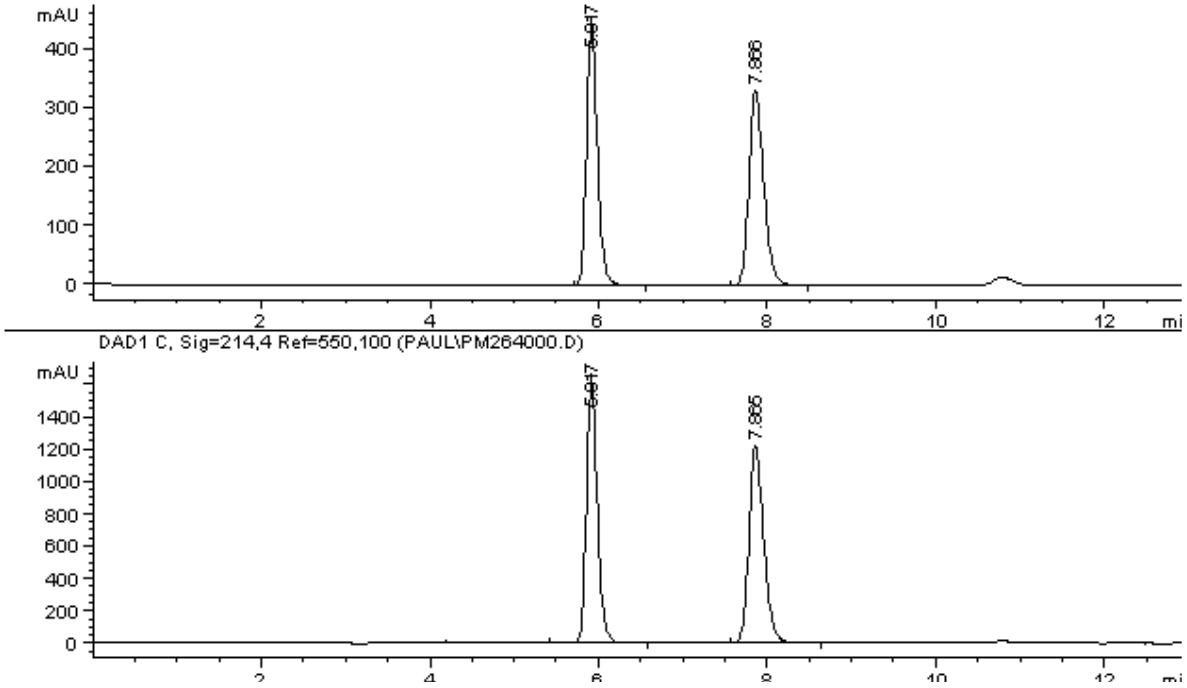
8d



Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.944	PB	0.1347	1459.14587	165.68994	97.9949
2	7.924	BP	0.1764	29.85662	2.55404	2.0051

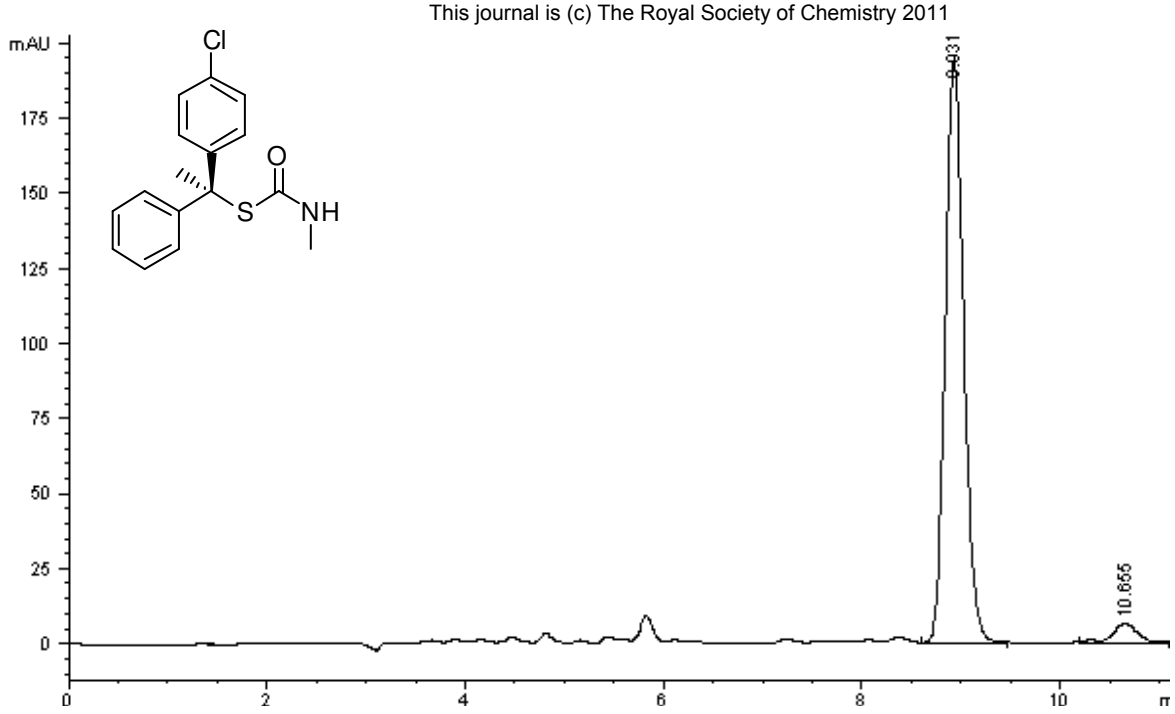
Racemic standard:



Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.917	BB	0.1351	4043.82666	457.61426	49.9791
2	7.866	BB	0.1908	4047.20630	330.75778	50.0209

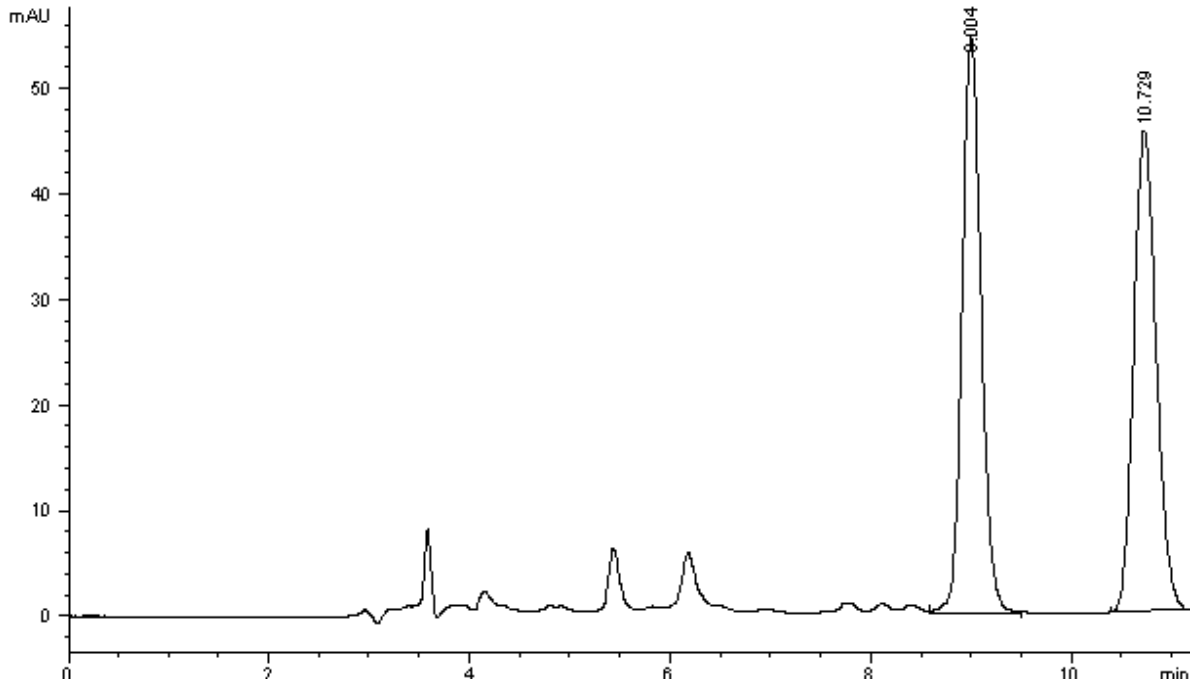
9d



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.931	VB	0.1992	2505.80054	193.30365	95.9564
2	10.655	BB	0.2528	105.59557	6.39132	4.0436

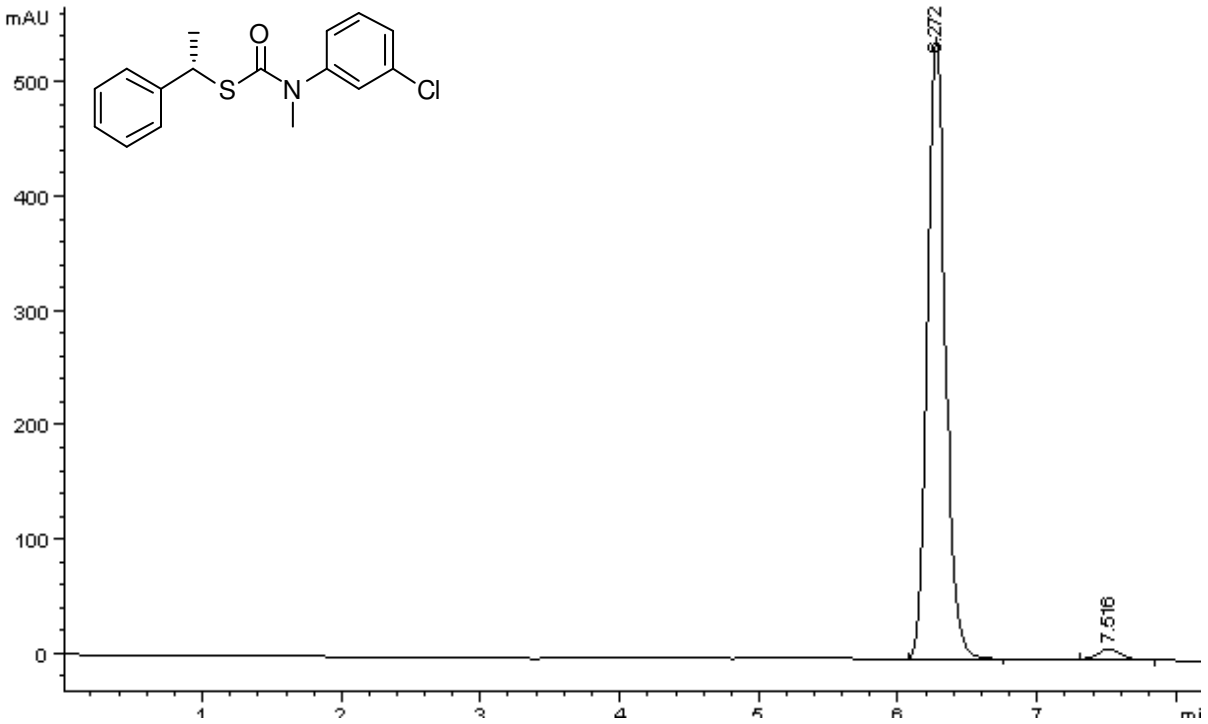
Racemic standard:



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.004	VB	0.2027	720.47180	54.69103	50.4221
2	10.729	BBA	0.2425	708.40808	45.52840	49.5779

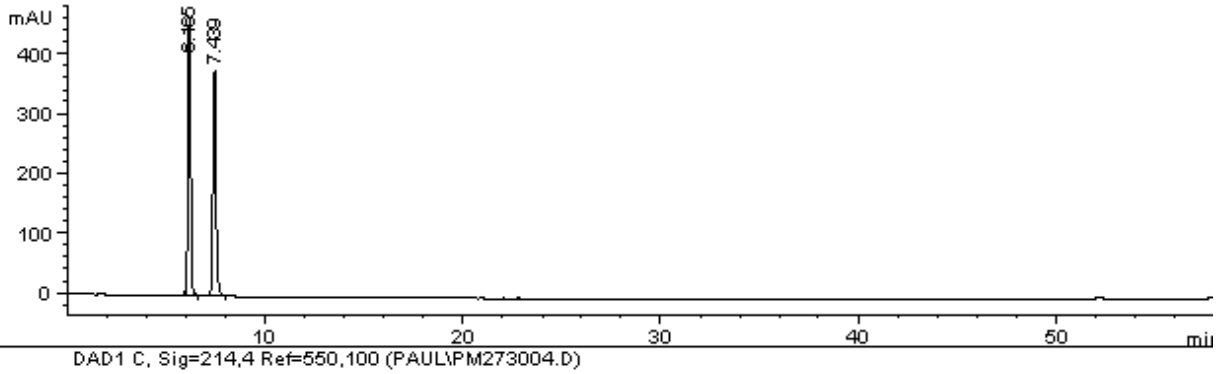
8e



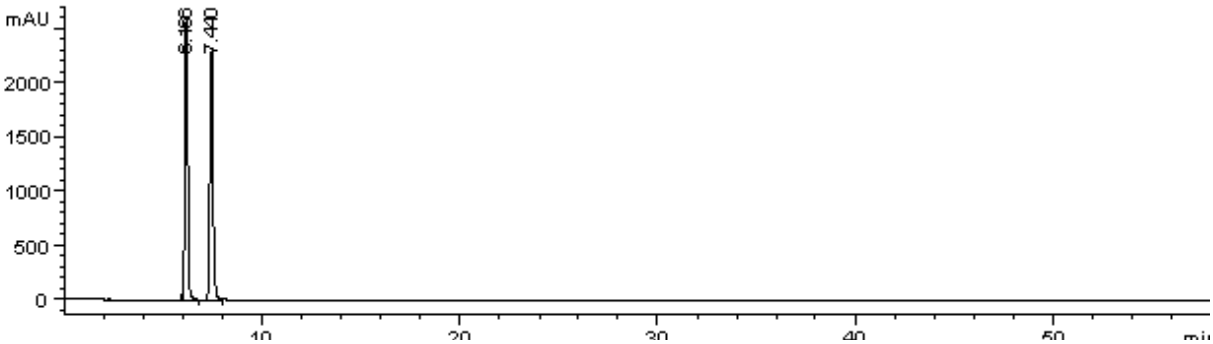
Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.272	BP	0.1411	4898.31836	543.63306	97.9129
2	7.516	BP	0.1816	104.41408	9.11720	2.0871

Racemic standard:



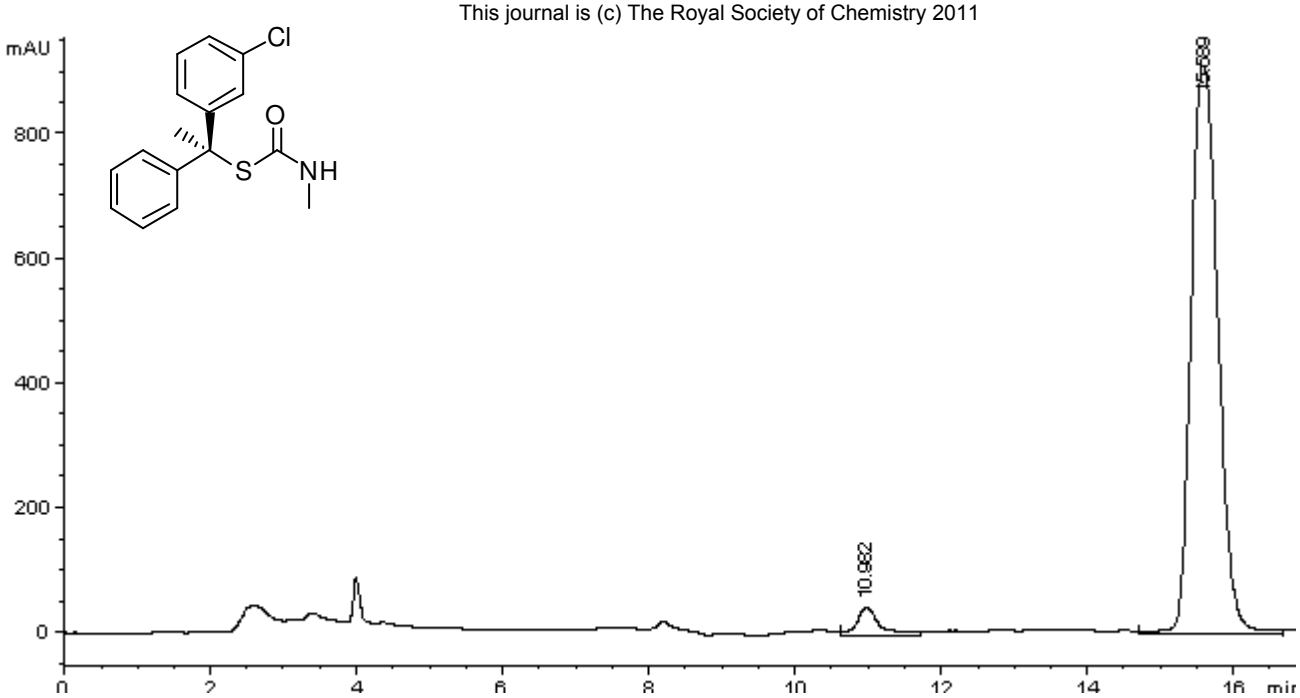
DAD1 C, Sig=214,4 Ref=550,100 (PAUL\PM273004.D)



Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.165	BB	0.1433	4255.04102	462.60983	49.9863
2	7.439	BB	0.1759	4257.36865	376.61154	50.0137

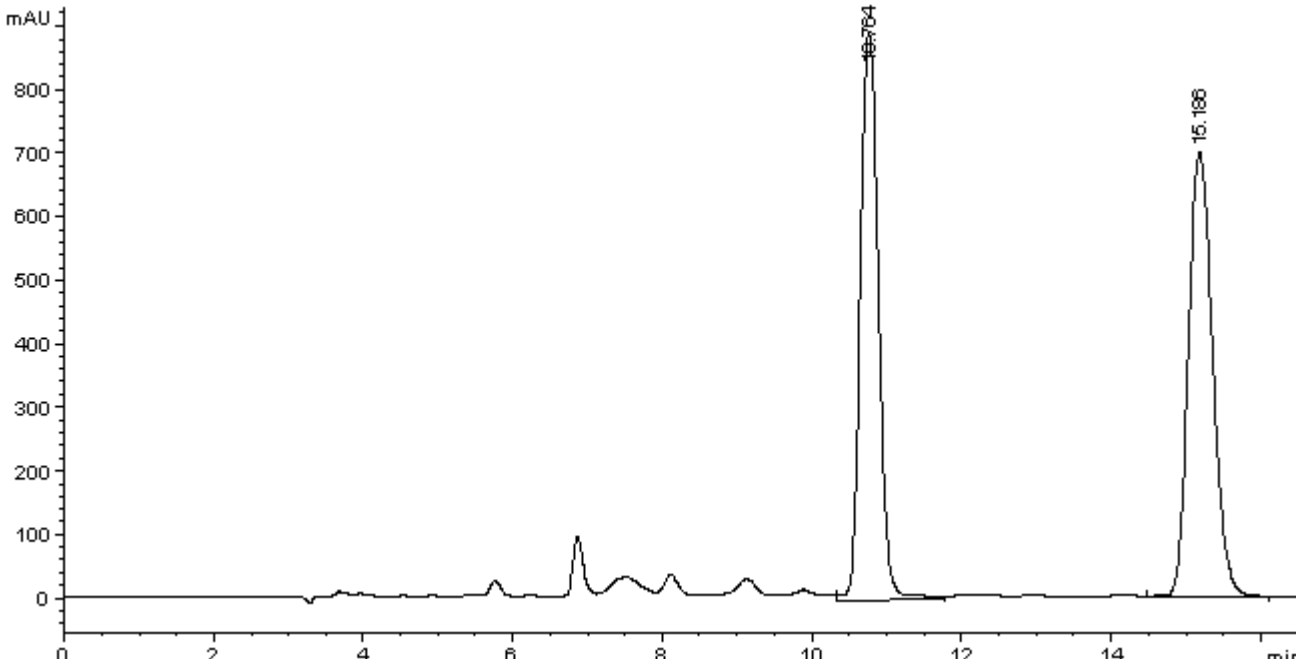
9e



Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.982	VB	0.3134	1004.04181	44.98306	4.1493
2	15.589	VV	0.4020	2.31939e4	911.10040	95.8507

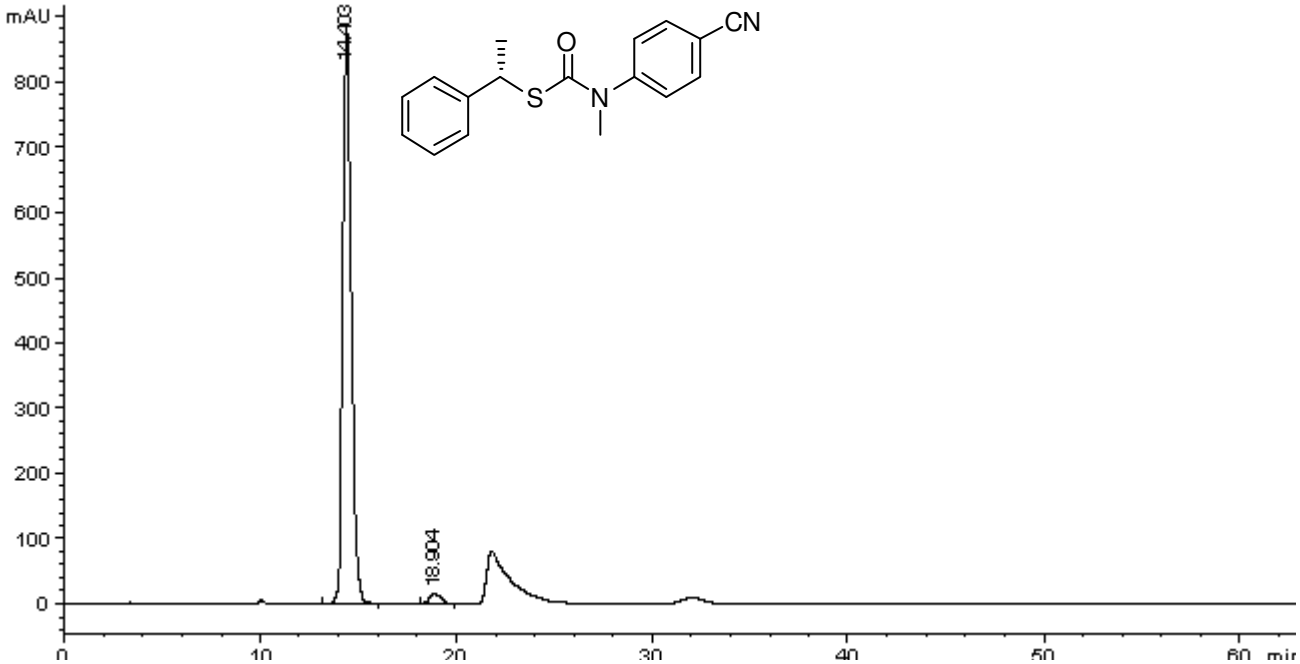
Racemic standard:



Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.764	VB	0.2680	1.49609e4	890.53448	48.6367
2	15.186	VV	0.3515	1.57996e4	699.50018	51.3633

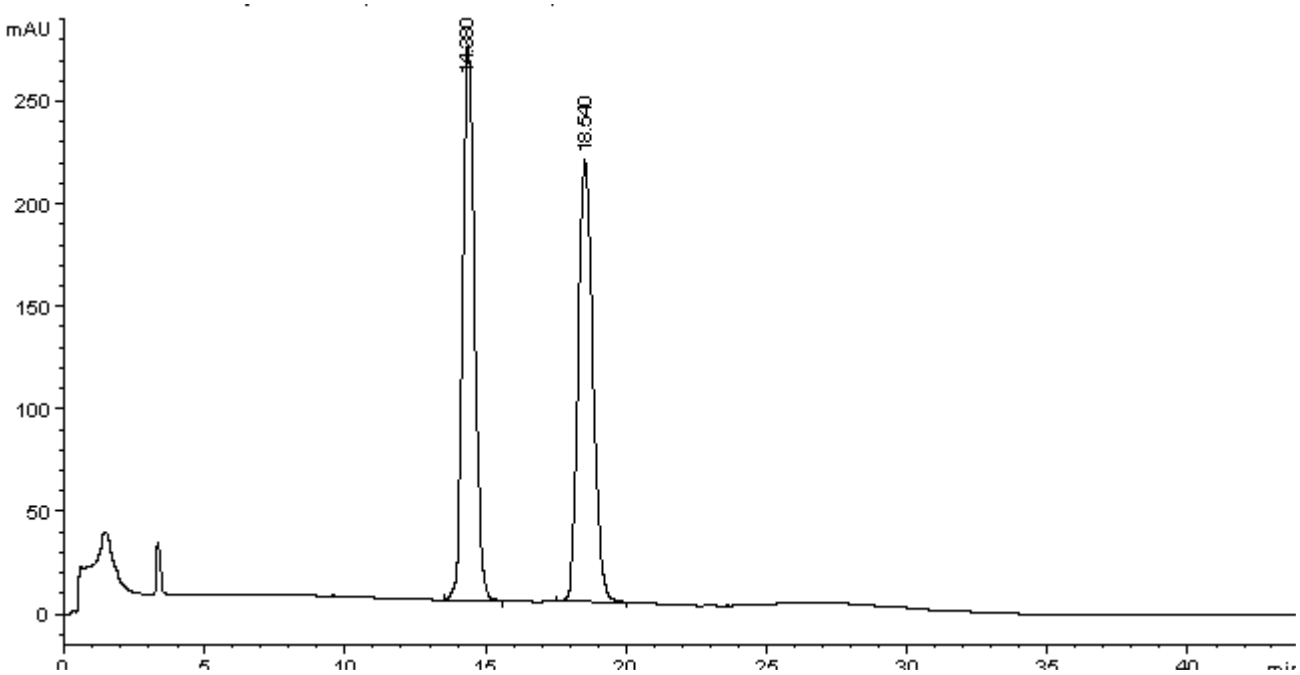
8f



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.403	BB	0.4536	2.68337e4	872.99139	98.0062
2	18.904	BB	0.4643	545.90295	15.00963	1.9938

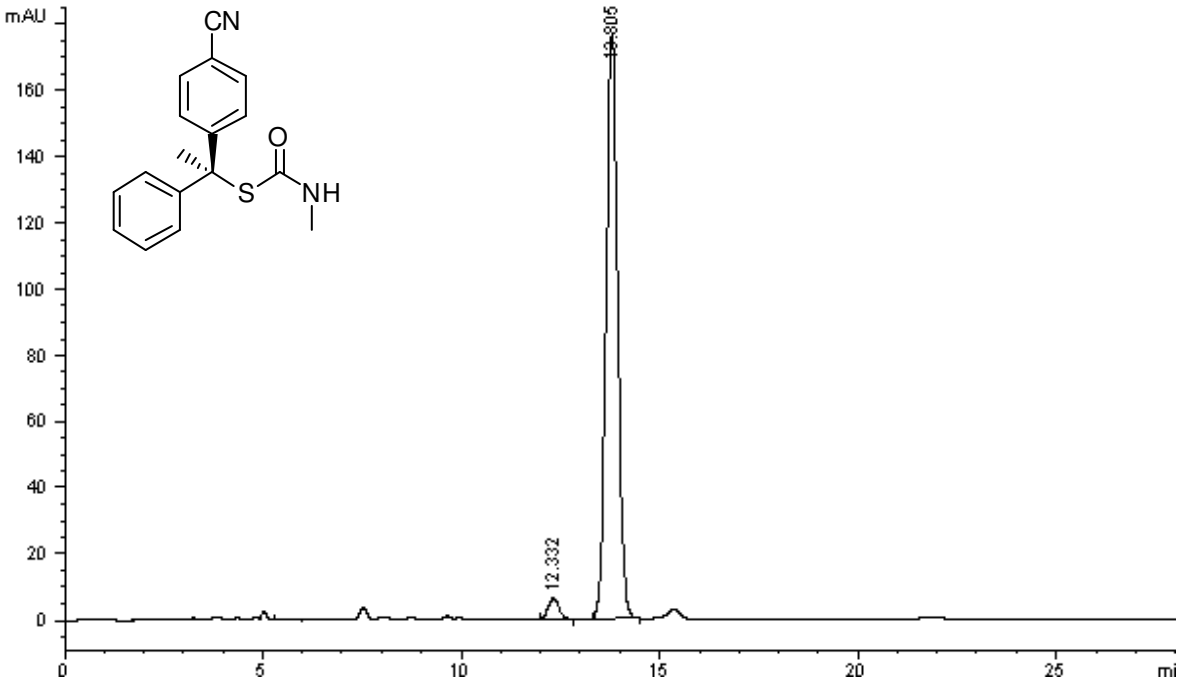
Racemic standard:



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.380	BB	0.4510	8011.61523	270.93512	50.1447
2	18.540	BP	0.5657	7965.37988	215.78847	49.8553

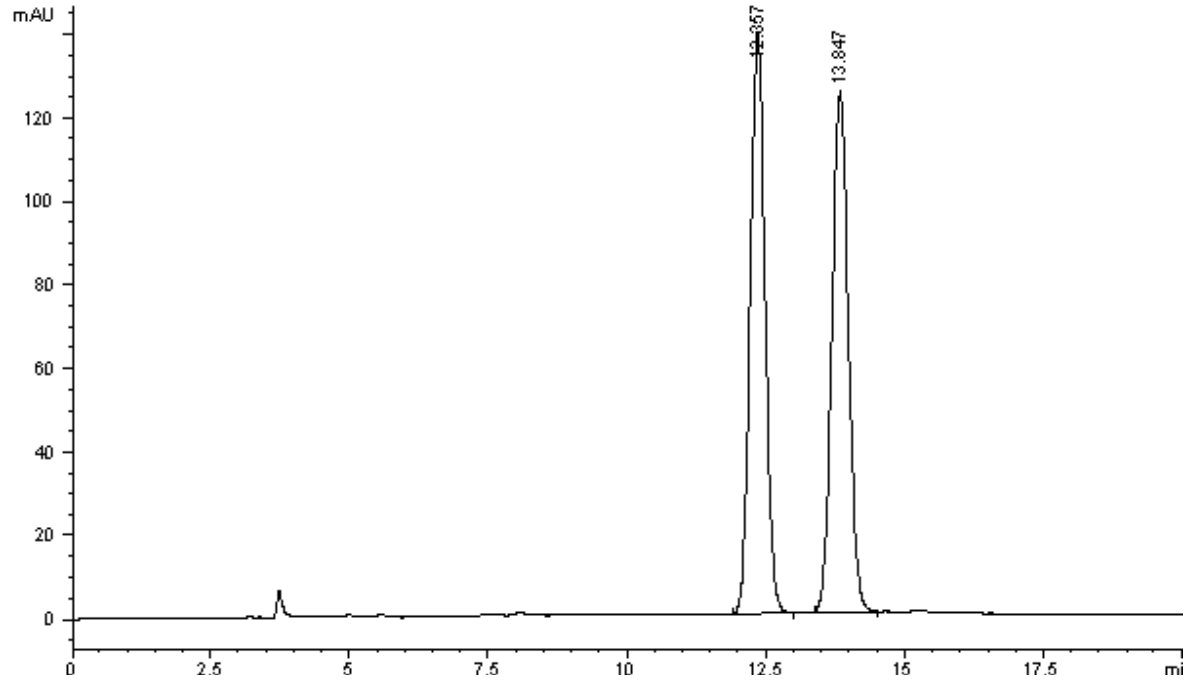
9f



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.332	PP	0.2790	115.12305	6.36524	3.1031
2	13.805	BP	0.3174	3594.84668	176.64243	96.8969

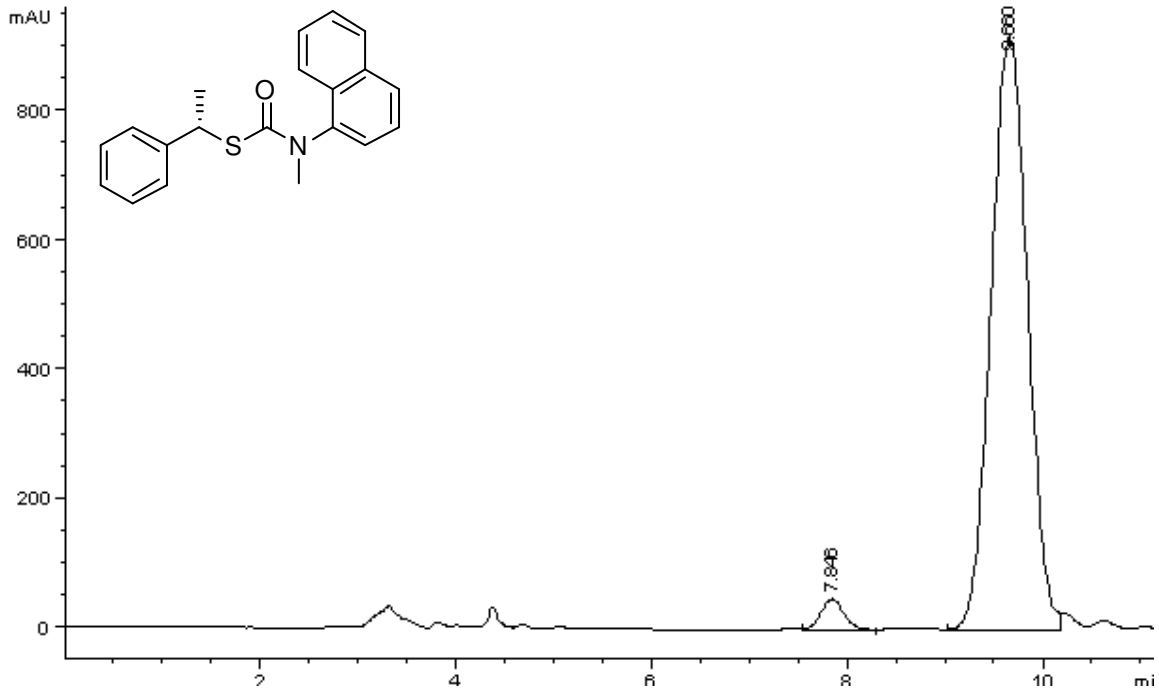
Racemic standard:



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.357	BB	0.2885	2580.01416	139.00005	50.0543
2	13.847	BB	0.3204	2574.41284	124.95570	49.9457

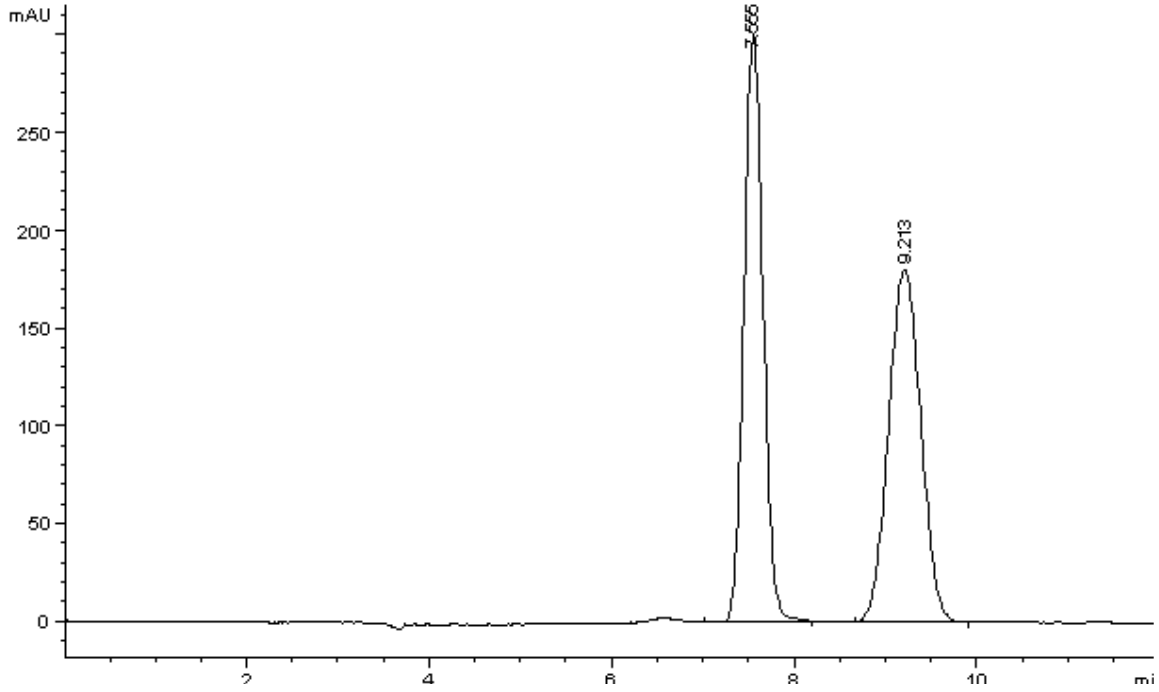
8h



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.846	VB	0.2426	736.47388	47.06042	3.0124
2	9.660	BV	0.4092	2.37117e4	918.59930	96.9876

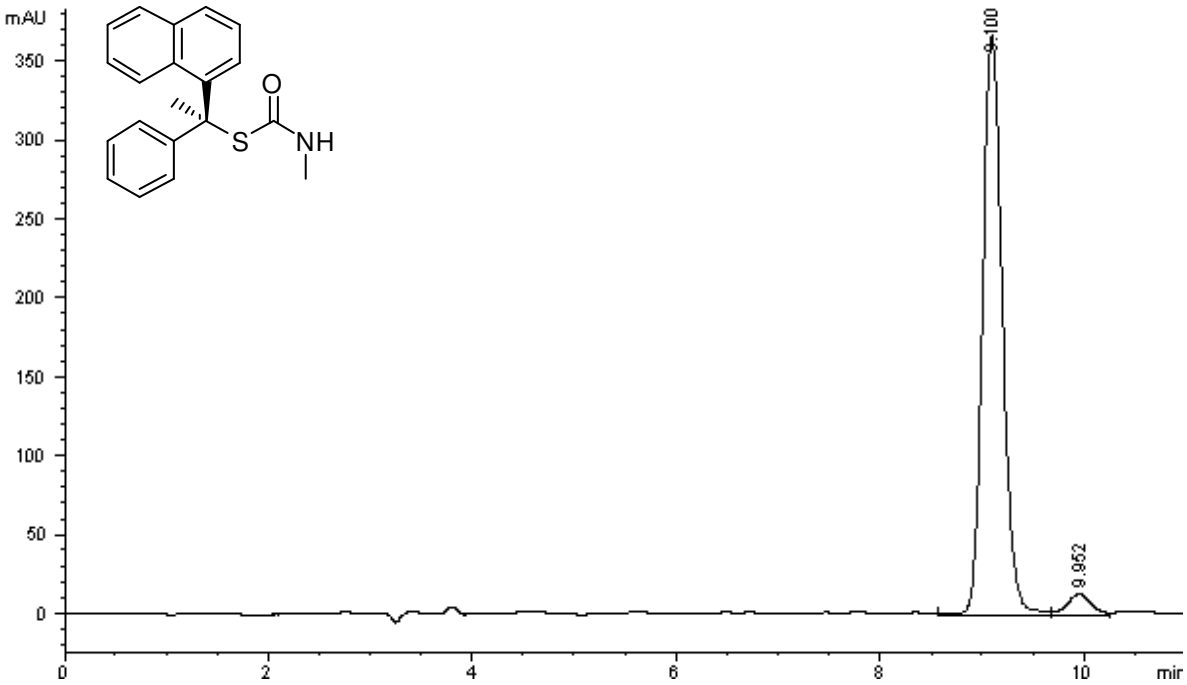
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.555	VB	0.2324	4445.96631	300.89343	50.2396
2	9.213	PP	0.3895	4403.55371	179.94400	49.7604

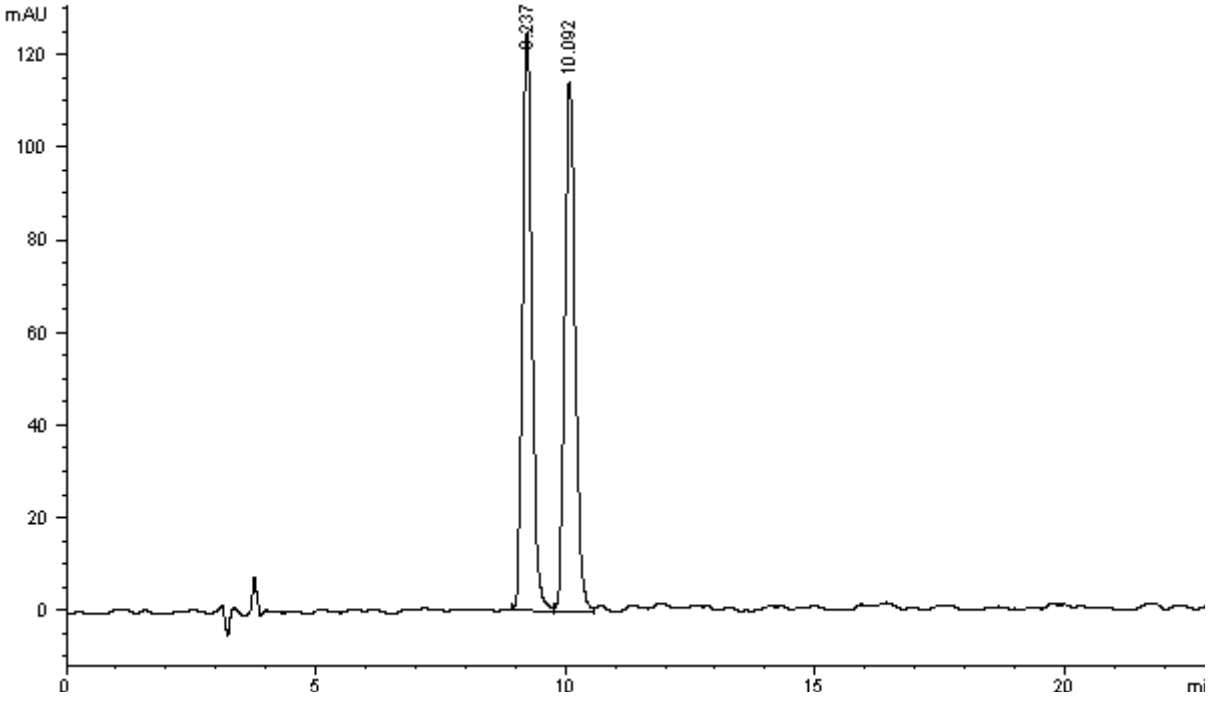
9h



Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.100	VV	0.2093	4950.50195	367.16678	95.9788
2	9.952	VV	0.2350	207.40828	13.22181	4.0212

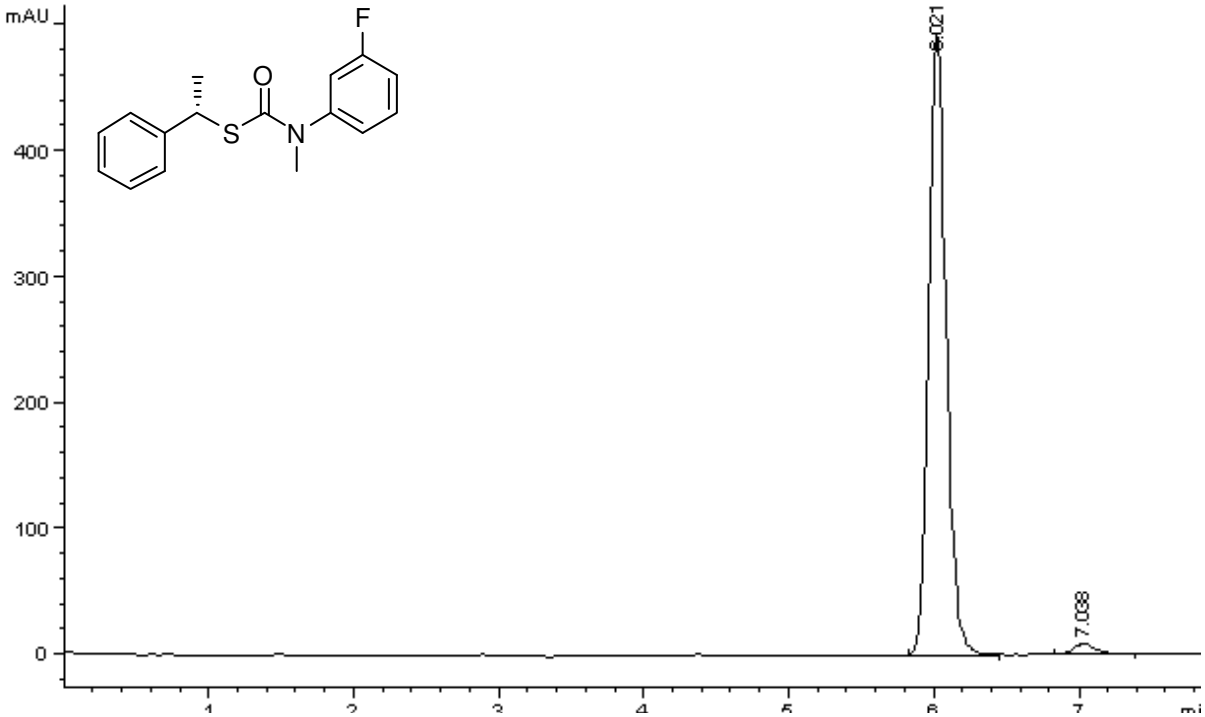
Racemic standard:



Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.237	BV	0.2038	1666.59631	124.76659	49.9382
2	10.092	VV	0.2262	1670.71814	114.49640	50.0618

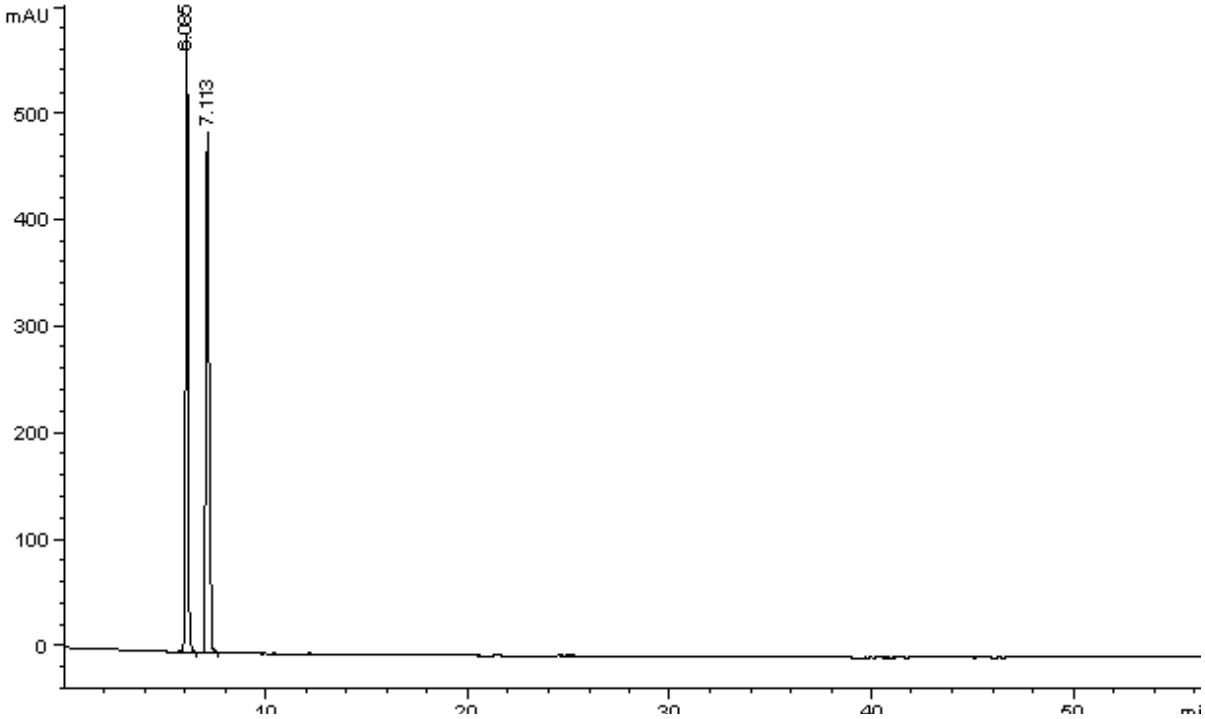
8i



Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.021	BB	0.1306	4190.14893	495.74854	97.7847
2	7.038	BB	0.1619	94.92882	8.79970	2.2153

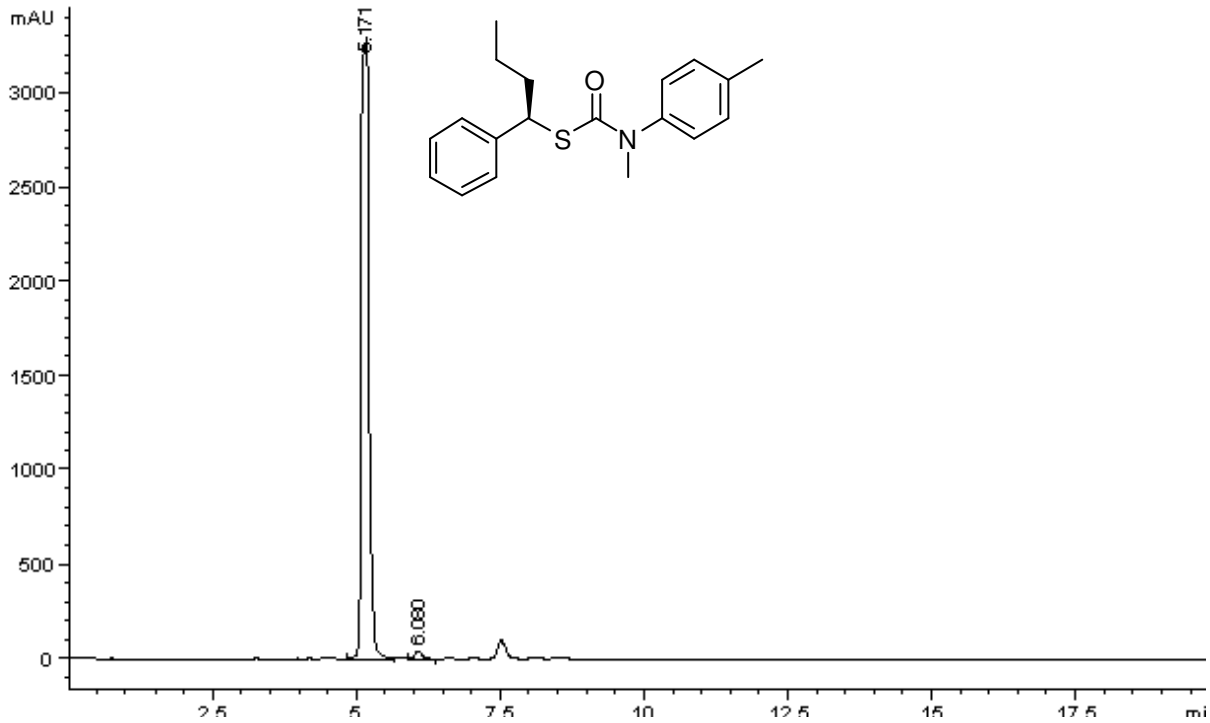
Racemic standard:



Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.085	BB	0.1323	4997.20215	581.43939	50.0015
2	7.113	BB	0.1594	4996.89600	488.42007	49.9985

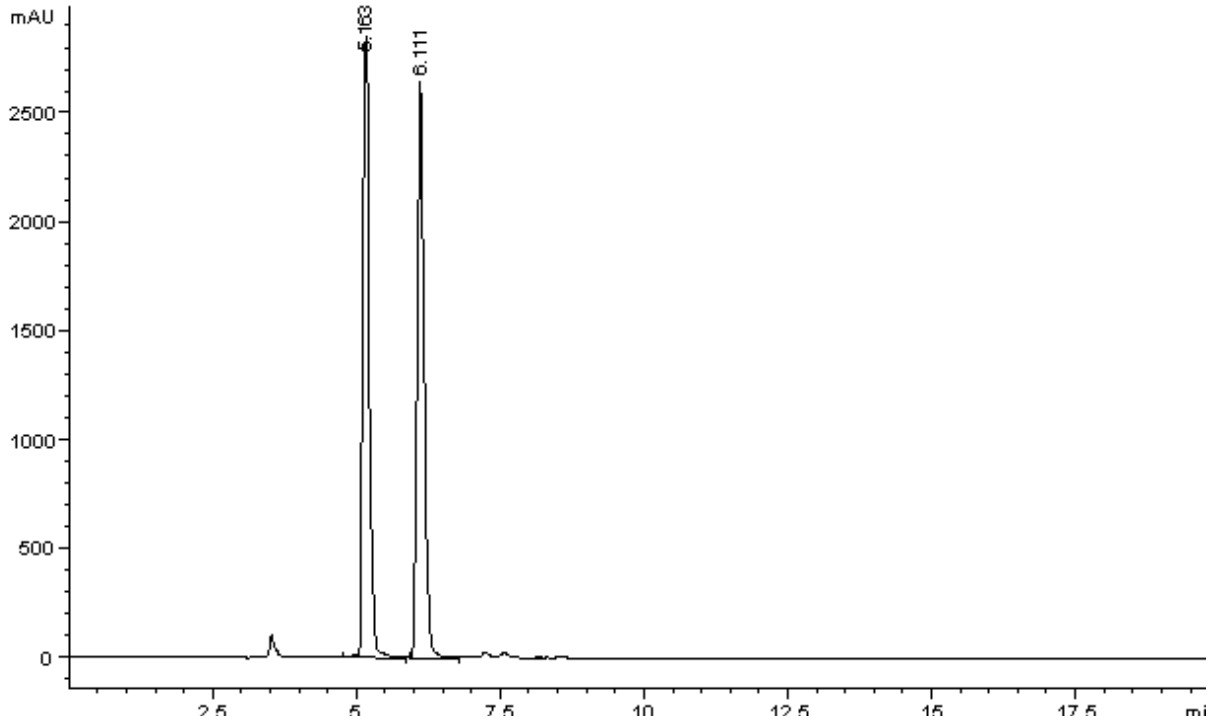
8j



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.171	BV	0.1432	3.03482e4	3302.40942	98.9402
2	6.080	VB	0.1280	325.06757	37.92142	1.0598

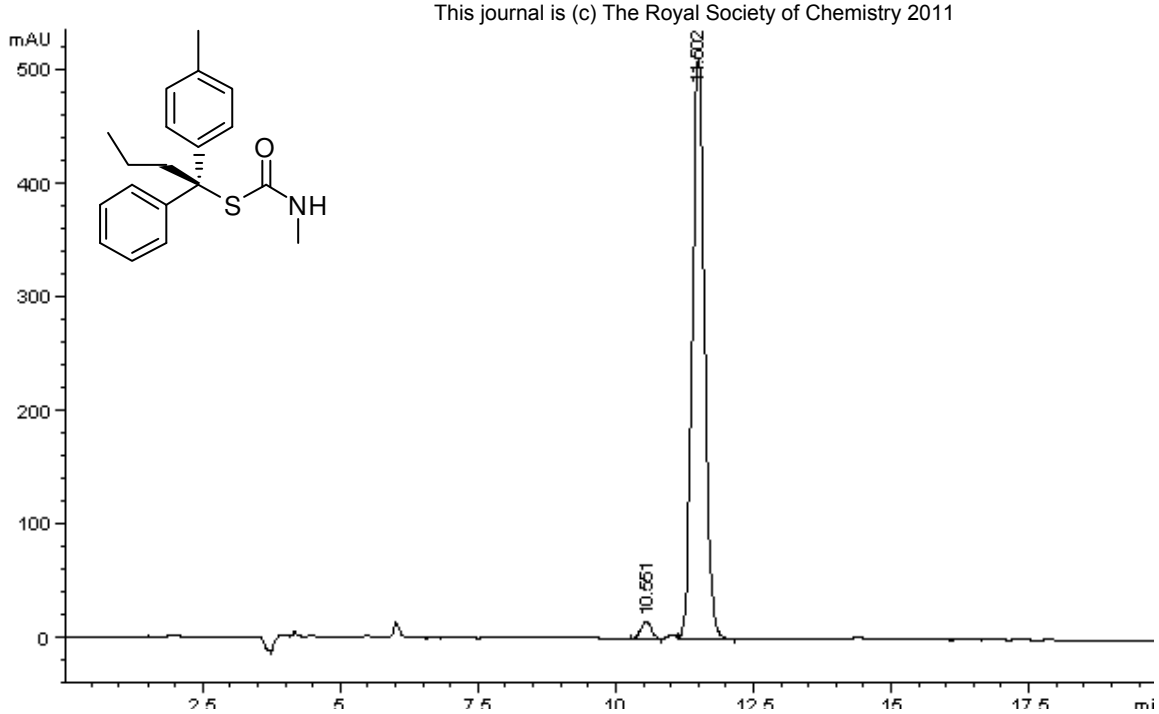
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.163	VB	0.1152	2.13529e4	2855.33984	49.3186
2	6.111	BV	0.1248	2.19429e4	2645.46411	50.6814

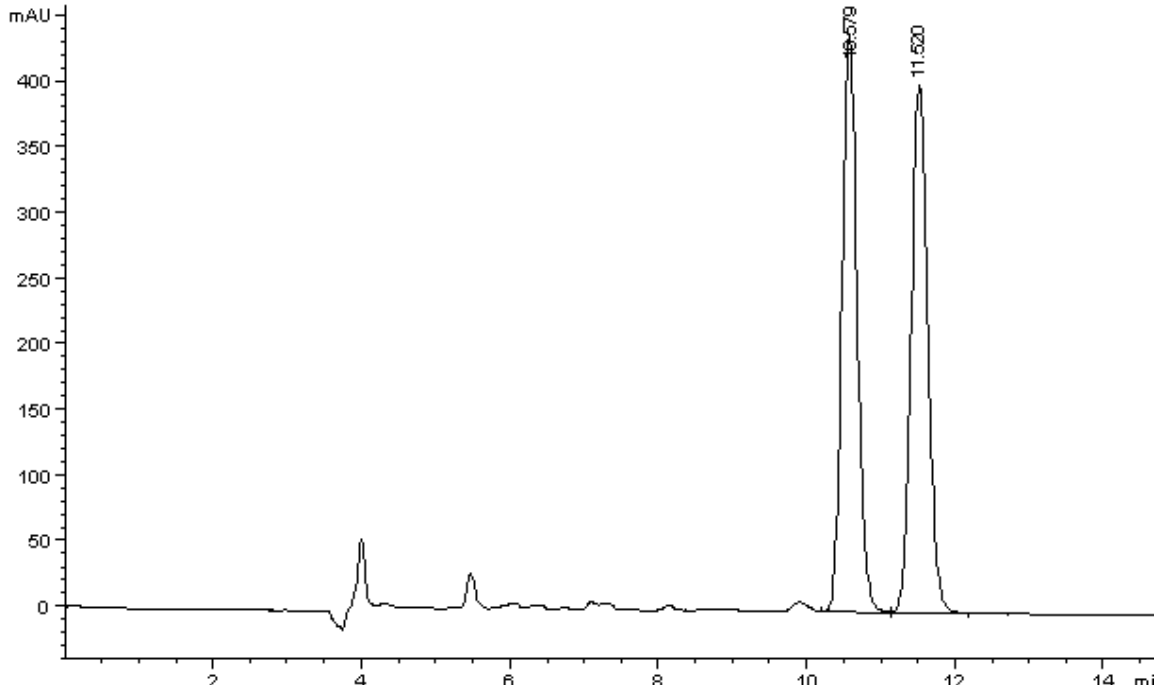
9j



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.551	PV	0.2092	208.94469	15.50872	2.5468
2	11.502	VB	0.2420	7995.26318	512.41595	97.4532

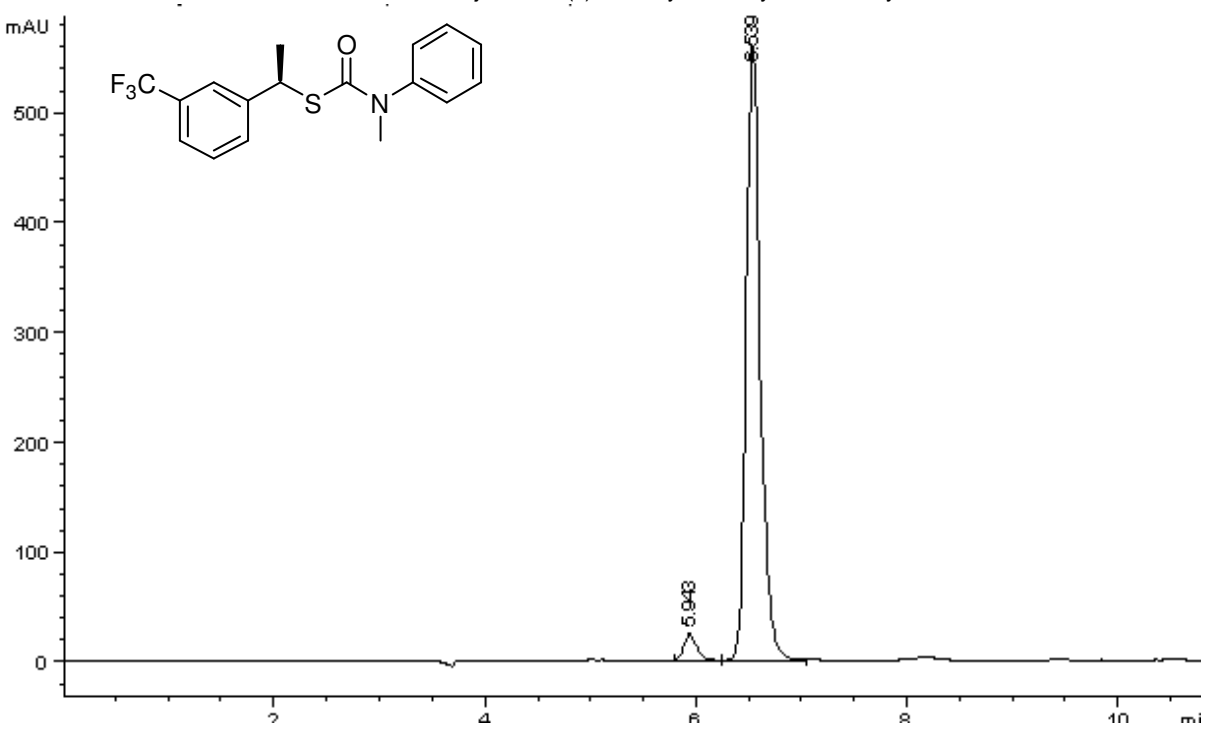
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.579	VV	0.2179	6279.26855	441.47629	49.9320
2	11.520	VB	0.2422	6296.37646	403.20587	50.0680

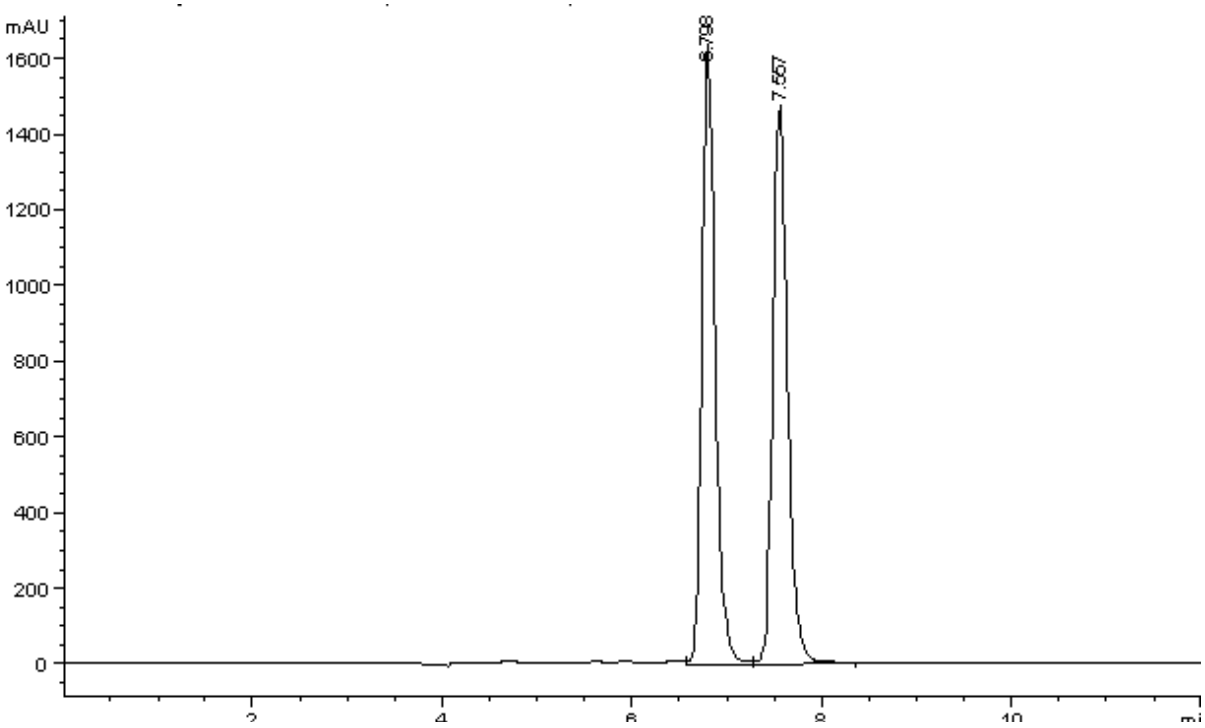
8k



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.943	BP	0.1258	195.42192	24.31819	3.6047
2	6.539	VB	0.1403	5225.90430	563.06769	96.3953

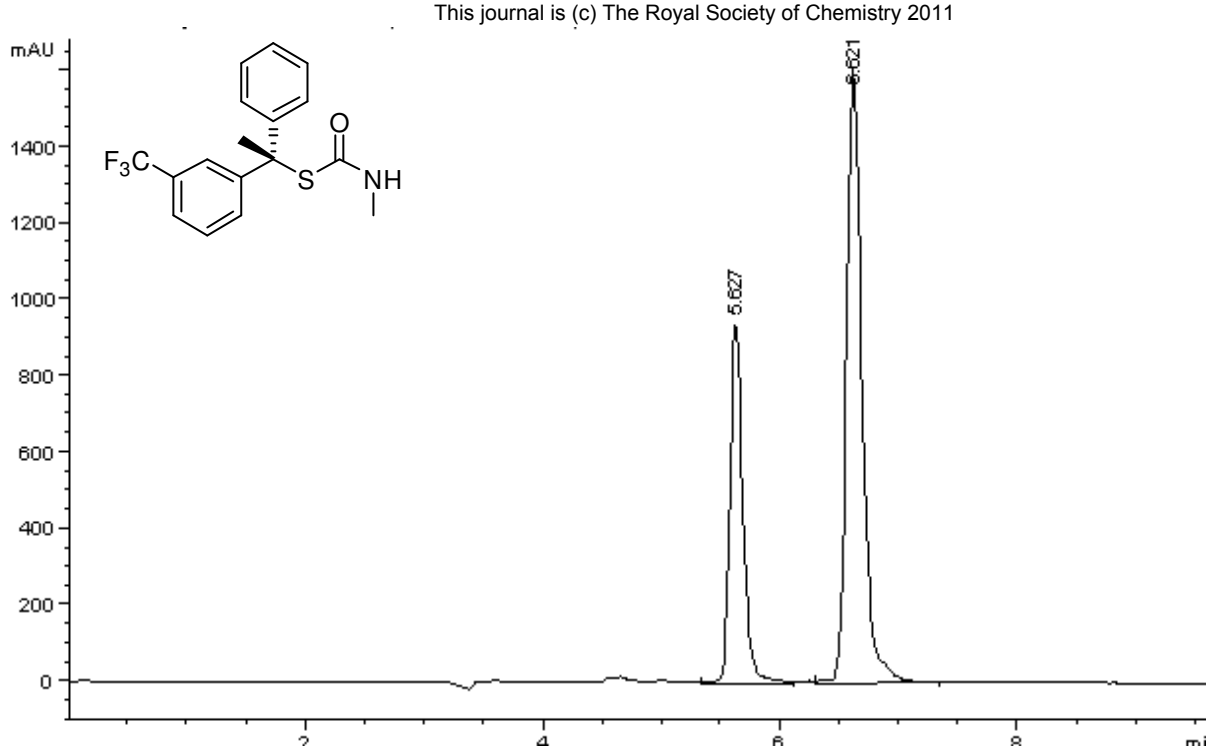
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.798	VV	0.1499	1.59813e4	1636.77844	49.8660
2	7.557	VV	0.1671	1.60672e4	1475.05676	50.1340

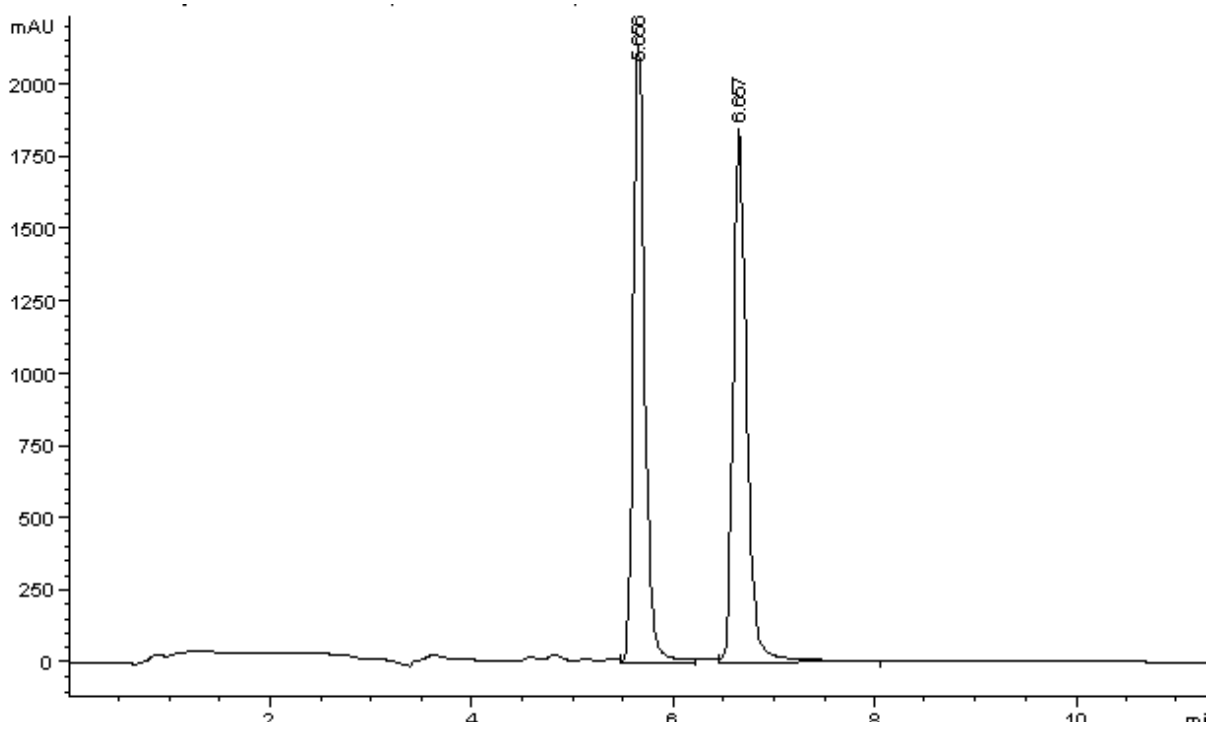
9k



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.627	VV	0.1141	7327.46387	948.82990	33.2815
2	6.621	VB	0.1425	1.46892e4	1609.44104	66.7185

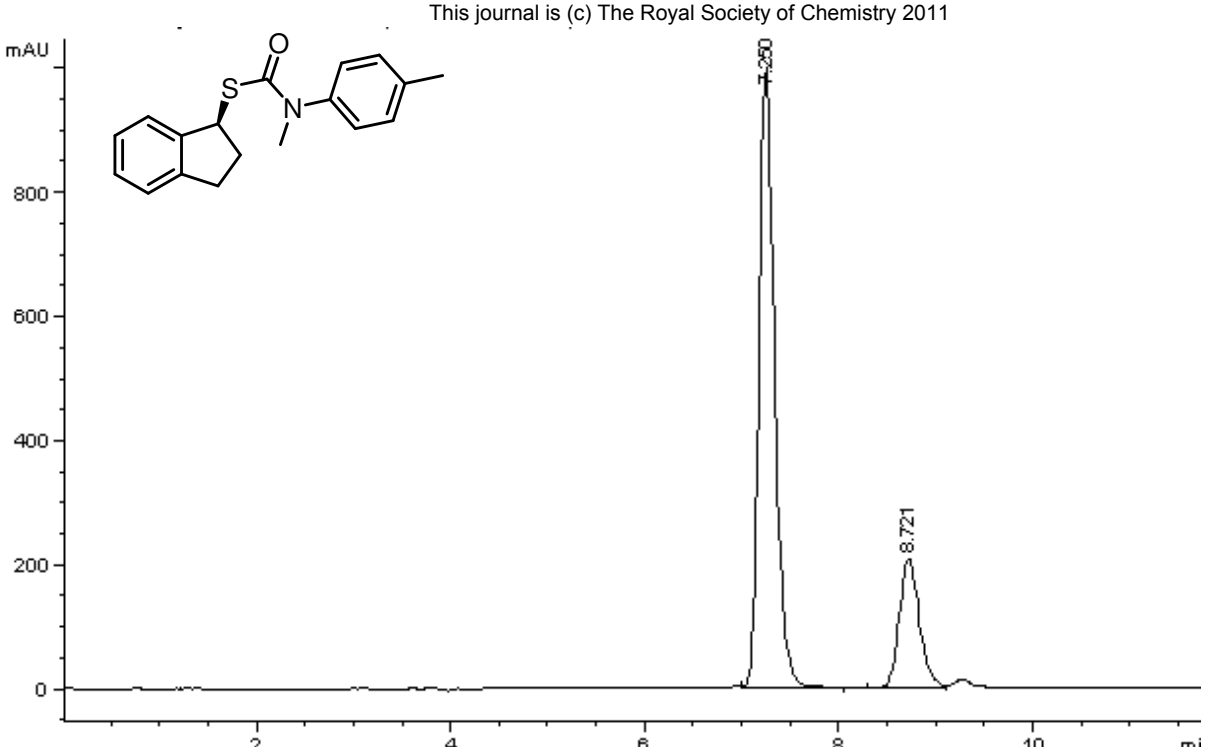
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.656	VV	0.1212	1.70870e4	2139.42187	49.1248
2	6.657	VB	0.1480	1.76959e4	1843.32483	50.8752

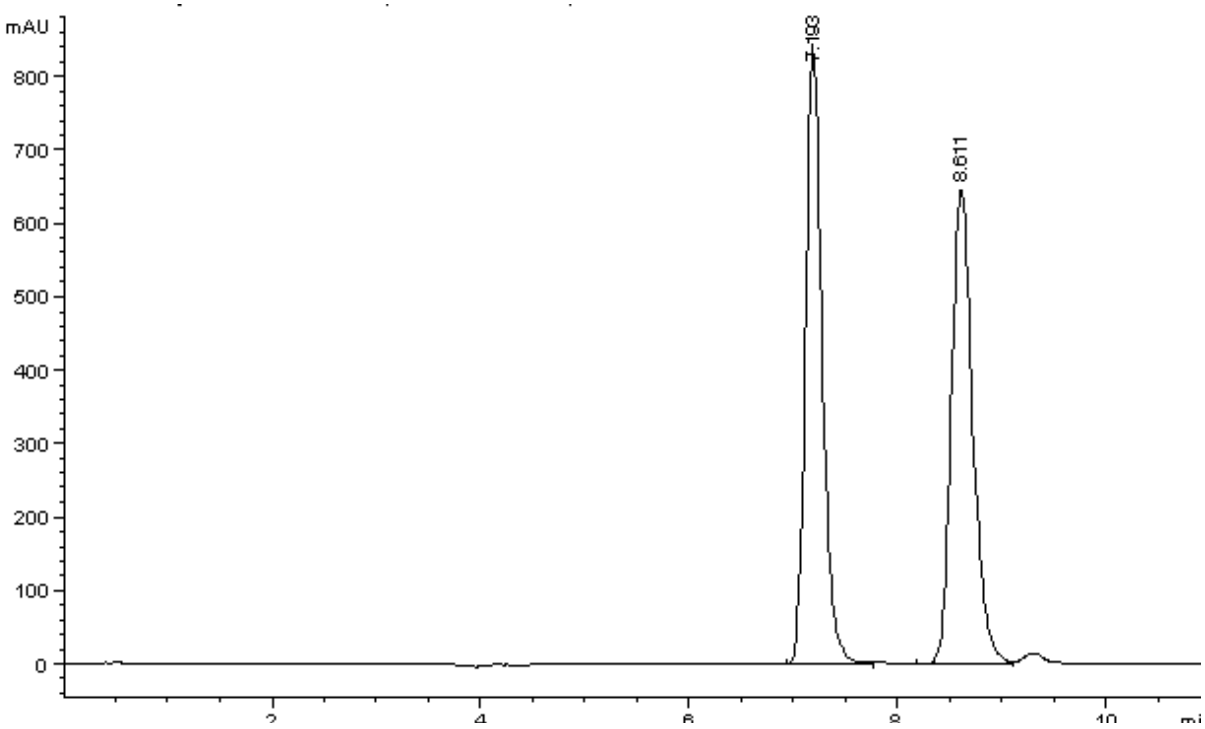
8m



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.250	VB	0.1706	1.11712e4	997.93323	78.7691
2	8.721	BV	0.2257	3011.00684	207.03917	21.2309

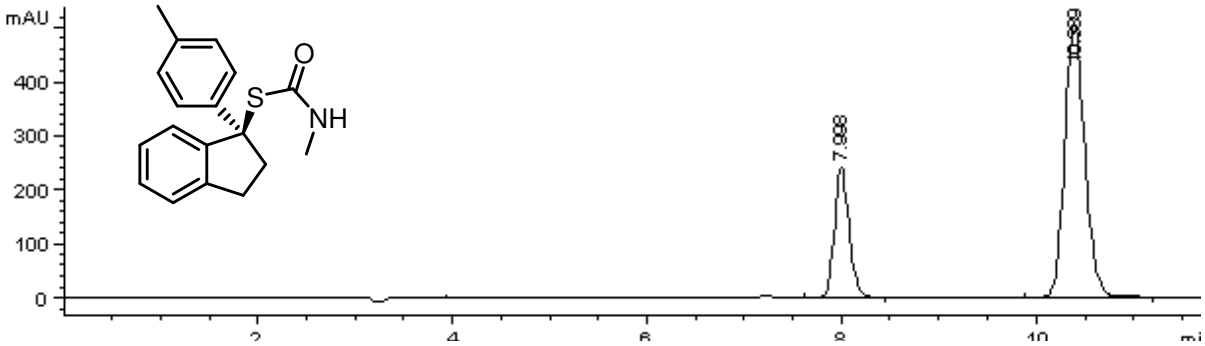
Racemic standard:



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

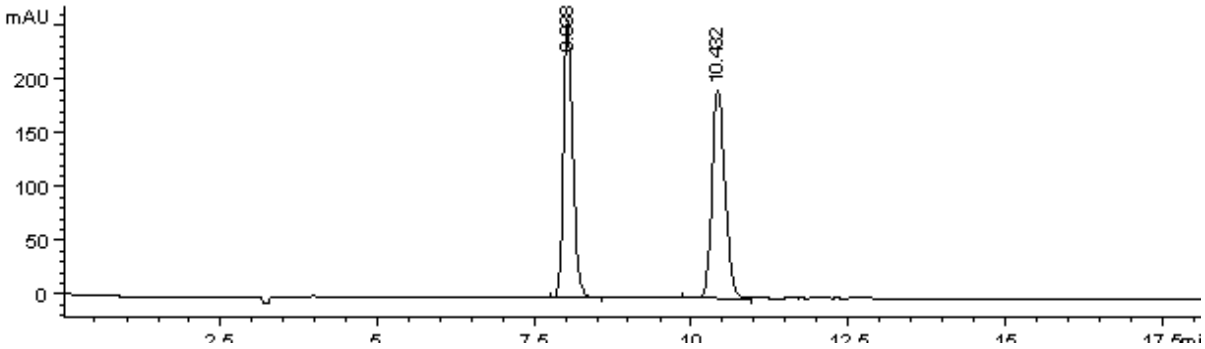
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.193	PB	0.1693	9327.82520	841.88147	50.1032
2	8.611	BV	0.2195	9289.38281	646.97845	49.8968

9m



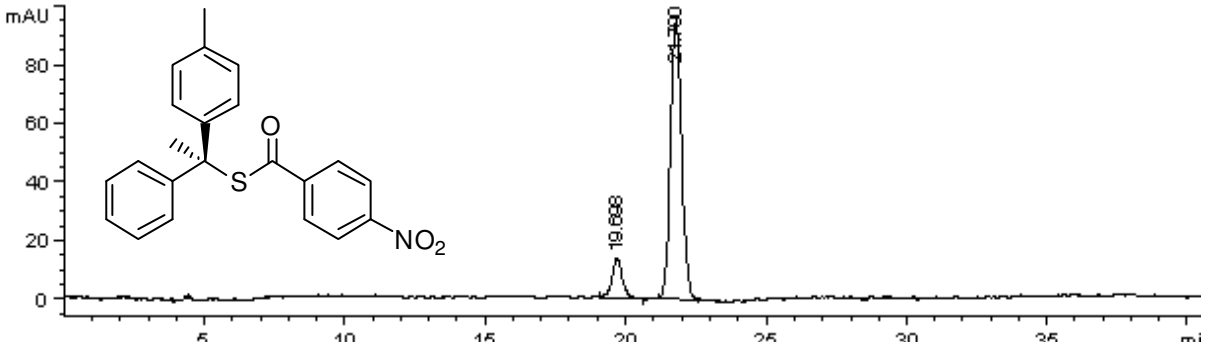
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.998	BB	0.1665	2616.29443	241.35350	25.8454
2	10.389	BB	0.2263	7506.57031	514.39606	74.1546

Racemic standard:



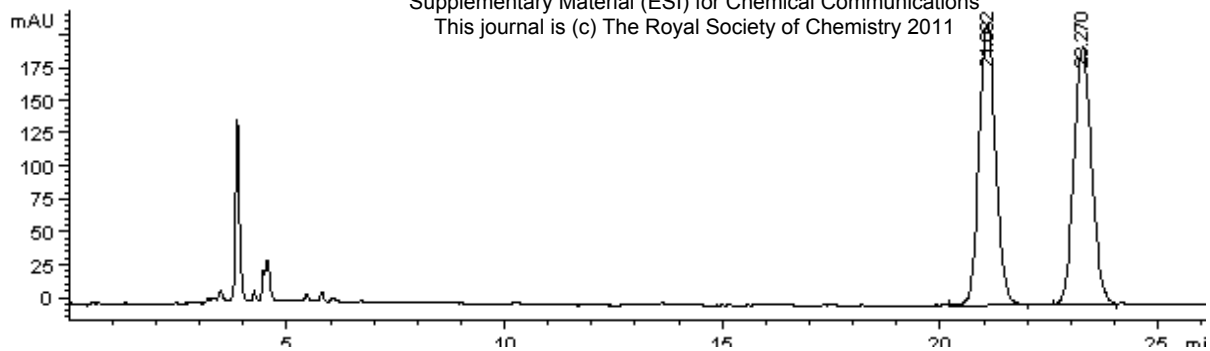
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.038	VB	0.1647	2766.22510	258.81976	49.7583
2	10.432	PV	0.2241	2793.09766	193.84222	50.2417

11



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.698	BP	0.3939	359.33282	13.52659	11.8369
2	21.790	BB	0.4225	2676.36719	95.64412	88.1631

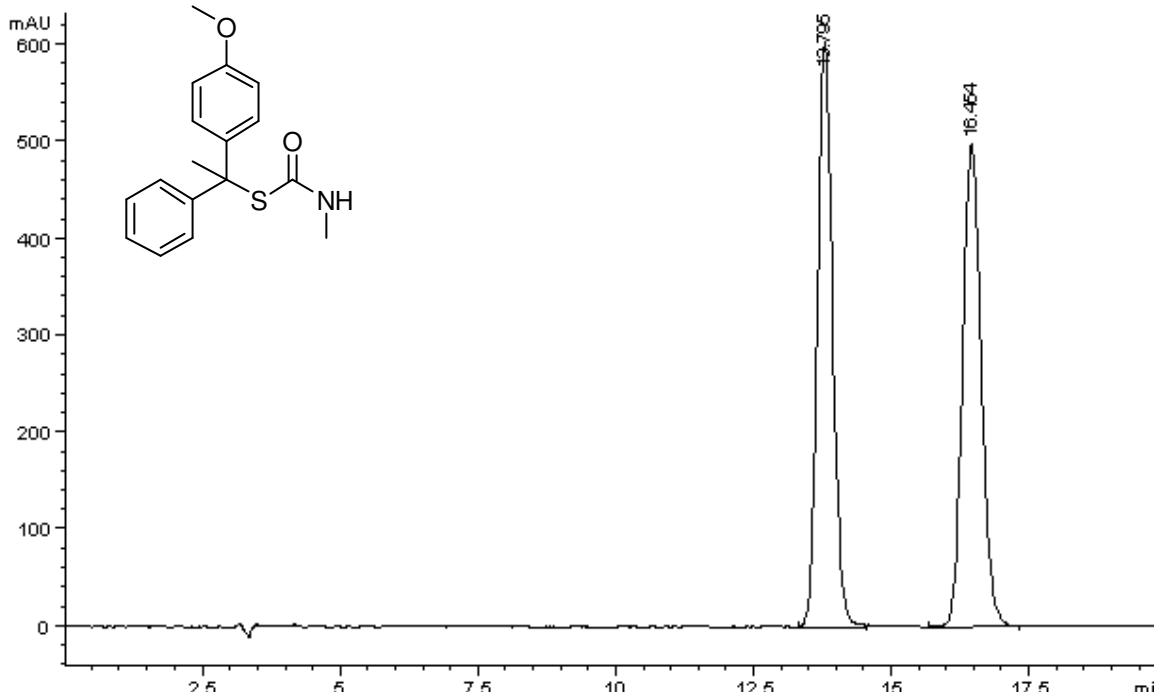
Racemic standard:



Signal 2: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.082	VP	0.4046	5660.93848	214.01173	50.3711
2	23.270	BV	0.4411	5577.53418	195.33821	49.6289

9b



Signal 1: DAD1 C, Sig=214,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.795	PV	0.2982	1.17253e4	604.75543	49.9900
2	16.454	PB	0.3665	1.17300e4	498.55902	50.0100