

Supporting Information

Direct Amidation of *N*-Boc and *N*-Cbz Protected Amines via Rhodium-Catalyzed Coupling of Arylboroxines and Carbamates

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General Information

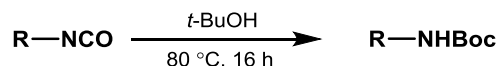
All anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. All other reagents were used as received, except where otherwise noted in the experimental text. Rhodium(I) complexes were purchased from Strem or Sigma-Aldrich and used as received. All reactions were carried out under an argon atmosphere unless otherwise stated.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F-254 silica gel plates with visualization by ultraviolet light (254 nm) and/or heating the plate after staining with a solution of 20% KMnO₄ w/v in H₂O. Flash column chromatography was carried out on Kieselgel 60 (0.040-0.063 mm) supplied by Merck under positive pressure.

Melting points (mp) were measured on a Büchi Melting Point B-540 apparatus. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) with the residual solvent peak of tetramethylsilane used as the internal standard at 0.00 ppm. ¹H NMR data are reported in the following order: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constants (*J*, Hz), integration and assignment. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF-QII spectrometer.

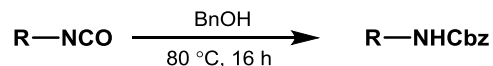
General Experimental Procedures

General procedure A: Preparation of *N*-Boc carbamates from isocyanates



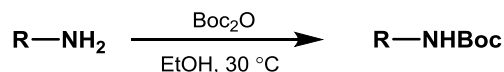
Isocyanate (3.0 mmol) and *tert*-butanol (3.3 mmol) were combined in a 20 mL headspace vial fitted with a suba seal cap and vented with a needle. The mixture was stirred at 80 °C over 16 h, then cooled to room temperature. The solids were dissolved in ethyl acetate (50 mL) and the solution was washed with H₂O (20 mL). The aqueous layer was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to afford the *N*-Boc carbamate which was used without further purification.

General procedure B: Preparation of *N*-Cbz carbamates from isocyanates



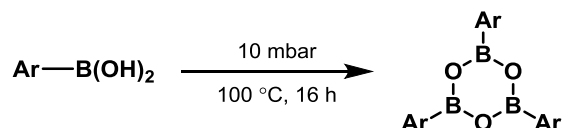
Isocyanate (3.0 mmol) and benzyl alcohol (3.3 mmol) were combined in a 20 mL headspace vial fitted with a suba seal cap and vented with a needle. The mixture was stirred at 80 °C over 16 h, then cooled to room temperature and purified by flash column chromatography (ethyl acetate/hexane) to afford the *N*-Cbz carbamate which was used without further purification.

General procedure C: Preparation of *N*-Boc carbamates from amines or anilines¹



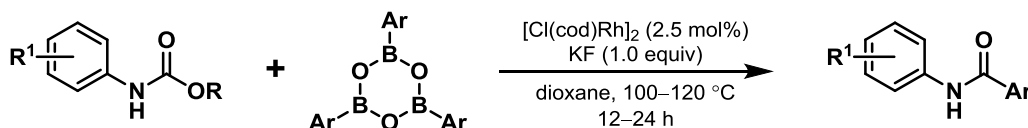
A 20 mL headspace vial was charged with a solution of amine (1.0 equiv) in absolute ethanol (2 mL/mmol). Di-*tert*-butyl dicarbonate (1.1 equiv) was added and the reaction mixture was stirred at 30 °C. The progress of the reaction was monitored by TLC. The crude reaction mixture was concentrated *in vacuo* and the residue was then purified by flash column chromatography (ethyl acetate/hexane) to afford the *N*-Boc carbamate which was used without further purification.

General procedure D: Preparation of trisarylboroxines from boronic acids



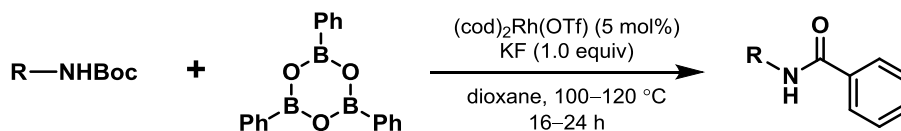
Commercially available boronic acids were weighed into a two-dram-vial which was covered with perforated aluminium foil. The vials were heated at 100 °C under reduced pressure (10 mbar) in a vacuum oven over 16 h. After cooling to room temperature, ¹H NMR spectroscopy was used to determine the extent of dehydration. Where the B-Ar ratio in the form of boronic acid to boroxine exceeded 0.15, the samples were resubmitted to a second round of dehydrating conditions in the vacuum oven for a further 16 h.

General procedure E: Amidation of *N*-Boc and *N*-Cbz protected anilines



N-Boc or *N*-Cbz protected aniline (0.50 mmol), KF (29 mg, 0.50 mmol) and [Cl(cod)Rh]₂ (6.2 mg, 13 μmol) were combined in a 20 mL headspace vial equipped with a magnetic stirrer bar. The vial was taken into a glovebox under Ar, where triarylboroxine (0.20 mmol) and 1,4-dioxane (1 mL) were added. The vial was sealed with a PTFE/silicon crimp-on septa and removed from the glovebox. The mixture was stirred at 100–120 °C over 12–24 h, then cooled to room temperature before it was diluted with CH₂Cl₂ (5 mL) and quenched with H₂O (5 mL). The aqueous layer was extracted with CH₂Cl₂ (2 x 5 mL) and the combined organic layers were dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford the corresponding amide product.

General procedure F: Amidation of *N*-Boc protected amines



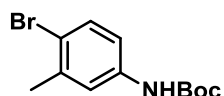
N-Boc protected amine (0.50 mmol), KF (29 mg, 0.50 mmol) and (cod)₂Rh(OTf) (12 mg, 25 μmol) were combined in a 20 mL headspace vial equipped with a magnetic stirrer bar. The vial was taken into a

glovebox under Ar, where triphenylboroxine (62 mg, 0.20 mmol) and 1,4-dioxane (1 mL) were added. The vial was sealed with a PTFE/silicon crimp-on septa and removed from the glovebox. The mixture was stirred at 100–120 °C over 16–24 h, then cooled to room temperature before it was diluted with ethyl acetate (5 mL) and quenched with H₂O (5 mL). The aqueous layer was extracted with ethyl acetate (2 x 5 mL) and the combined organic layers were dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford the corresponding amide product.

Preparation of *N*-Boc and *N*-Cbz Carbamate Substrates

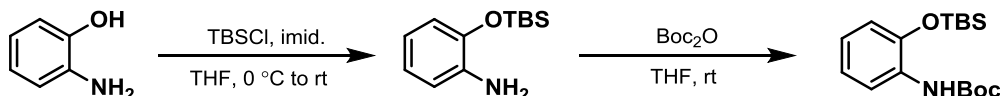
tert-Butyl carbamates of 3,5-dimethylaniline,² 4-methoxyaniline,³ 4-nitroaniline,³ 4-chloroaniline¹ and 2,6-dimethylaniline¹ were prepared from the corresponding isocyanate according to general procedure A and used without further purification. *tert*-Butyl carbamates of 7-amino-4-methylcoumarin⁴ and 2,6-diisopropylaniline¹ were prepared from the corresponding aniline according to general procedure C and used without further purification.

tert-Butyl (4-bromo-3-methylphenyl)carbamate



This compound was prepared according to general procedure A and isolated as a white solid (930 mg, quant). **mp** 121-123 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.5 Hz, 1H, ArH), 7.33 (s, 1H, ArH), 7.02 (dd, *J* = 8.5, 2.5 Hz, 1H, ArH), 6.47 (s, 1H, NH), 2.36 (s, 3H, CH₃), 1.51 (s, 9H, OC(CH₃)₃); **¹³C NMR** (101 MHz, CDCl₃) δ 152.6, 138.4, 137.5, 132.5, 120.6, 118.0, 117.4, 80.7, 28.3, 23.0; **HRMS** (ESI+) calc. for C₁₂H₁₆BrNO₂ [M+Na]⁺ 308.0257; found 308.0256.

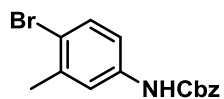
tert-Butyl [2-(*tert*-butyldimethylsilyloxy)phenyl]carbamate



To a solution of 2-aminophenol (344 mg, 3.15 mmol) and imidazole (422 mg, 6.20 mmol) in THF (6 mL) at 0 °C was added TBSCl (1.0M in THF, 3 mL, 3.00 mmol). The reaction mixture was allowed to warm to room temperature over 16 h, then diluted with ether (10 mL) and filtered through a cotton plug. The filtrate was washed with 1M aq. NaOH (2 x 5 mL), and the aqueous layers extracted with ether (2 x 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to afford an orange oil. The crude silyl ether was dissolved in absolute ethanol (5 mL), to which di-*tert*-butyl dicarbonate (740 μL, 3.22 mmol) was added. The reaction mixture was stirred at room temperature over 16 h, then concentrated and purified by flash column chromatography (0→10% ether/hexane) to afford the title *N*-Boc carbamate as an orange oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (br d, *J* = 7.5 Hz, 1H, ArH), 6.96-6.92 (m, ArH + NH), 6.87 (td, *J* = 8.0, 1.5 Hz, 1H, ArH), 6.79 (dd, *J* = 8.0, 1.5 Hz, 1H, ArH), 1.51 (s, 9H, OC(CH₃)₃), 1.02 (s, 9H, SiC(CH₃)₃), 0.24 (s, 6H, Si(CH₃)₂); **¹³C NMR** (101 MHz, CDCl₃) δ 152.7, 143.6, 130.1, 122.3, 121.8, 118.7, 117.8, 80.1, 28.3, 25.7, 18.2, -4.4; **HRMS** (ESI+) calc. for C₁₇H₂₉NO₃Si [M+Na]⁺ 346.1809; found 346.1825.

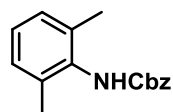
Benzyl carbamates of 3,5-dimethylaniline,² 4-methoxyaniline,² and 4-nitroaniline² were prepared from the corresponding isocyanate according to general procedure B and used without further purification.

Benzyl (4-bromo-3-methylphenyl)carbamate



This compound was prepared according to general procedure B and isolated by flash column chromatography (10→20% ethyl acetate/hexane) as a white solid (919 mg, 96%). **mp** 98-100 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.42-7.29 (m, 6H, ArH), 7.07 (dd, *J* = 8.5, 2.0 Hz, 1H, ArH), 6.70 (br s, 1H, NH), 5.18 (s, 2H, OCH₂), 2.35 (s, 3H, CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 153.1, 138.6, 136.9, 135.8, 132.6, 128.6, 128.4, 128.3, 120.8, 118.6, 117.6, 67.1, 23.0; **HRMS** (ESI+) calc. for C₁₅H₁₄NBrO₂ [M+Na]⁺ 342.0100; found 342.0106.

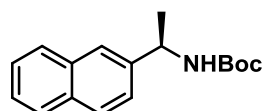
Benzyl (2,6-Dimethylphenyl)carbamate



This compound was prepared according to general procedure B and isolated by flash column chromatography (10→20% ethyl acetate/hexane) as a white solid (651 mg, 85%). **mp** 130-132 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41-7.22 (m, 5H, ArH), 7.12-7.05 (m, 3H, ArH), 6.15-5.98 (m, 1H, NH), 5.19 (br s, 2H, OCH_2), 2.25 (s, 6H, 2 x CH_3); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.2, 136.3, 135.8, 133.4, 128.5, 128.2, 128.1, 127.8, 127.3, 67.1, 18.3; **HRMS** (ESI+) calc. for $\text{C}_{16}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 278.1151; found 278.1160.

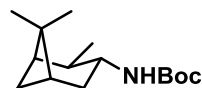
tert-Butyl carbamates of benzylamine,³ 1-adamantylamine² and cyclohexylamine⁵ were prepared from the corresponding amine according to general procedure C and used without further purification.

tert-Butyl (*R*)-(1-(naphthalen-2-yl)ethyl)carbamate



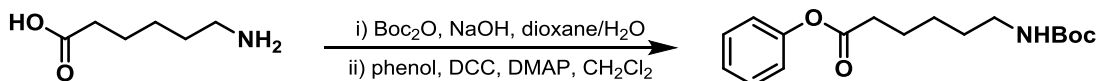
This compound was prepared according to general procedure C on a 2.0 mmol scale and isolated by flash column chromatography (10→20% ethyl acetate/hexane) as a pale yellow solid (512 mg, 94%). **mp** 112-114 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.28-7.80 (m, 3H, ArH), 7.73 (s, 1H, ArH), 7.49-7.42 (m, 3H, ArH), 5.04-4.71 (m, 2H, CH + NH), 1.54 (s, 3H, CH_3), 1.43 (s, 9H, $\text{OC}(\text{CH}_3)_3$); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.1, 141.4, 133.3, 132.6, 128.3, 127.8, 127.6, 126.1, 125.7, 124.5, 124.2, 79.5, 50.2, 28.4, 22.6; **HRMS** (ESI+) calc. for $\text{C}_{17}\text{H}_{21}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 294.1465; found 294.1476.

tert-Butyl ((1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)carbamate



This compound was prepared according to general procedure C on a 3.0 mmol scale and isolated by flash column chromatography (0→20% ethyl acetate/hexane) as an off-white solid (775 mg, quant). **mp** 84-86 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.47-4.45 (m, 1H, NH), 3.99-3.91 (m, 1H, NCH), 2.62-2.56 (m, 1H), 2.41-2.35 (m, 1H), 1.96-1.91 (m, 1H), 1.82-1.78 (m, 1H), 1.76-1.68 (m, 1H), 1.56-1.46 (m, 10H, CH + $\text{OC}(\text{CH}_3)_3$), 1.21 (s, 3H, CH_3), 1.12 (d, J = 7.0 Hz, 3H, CH_3), 1.02 (s, 3H, CH_3), 0.81 (d, J = 10.0 Hz, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.7, 79.0, 49.2, 47.7, 46.5, 41.6, 38.4, 37.6, 35.4, 28.4, 28.0, 23.2, 20.7; **HRMS** (ESI+) calc. for $\text{C}_{15}\text{H}_{27}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 276.1934; found 276.1940.

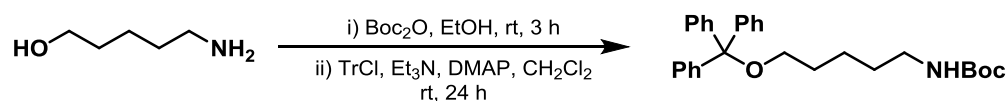
Phenyl 6-[(*tert*-butoxycarbonyl)amino]hexanoate



To a mixture of 6-aminohexanoic acid (525 mg, 4.0 mmol) and NaOH (160 mg, 4.0 mmol) in dioxane (10 mL) and H_2O (5 mL) at 0 °C was added di-*tert*-butyl dicarbonate (101 μL , 4.4 mmol) in three portions. The reaction mixture was warmed to room temperature over 3 h, then diluted with H_2O (25 mL) and washed with ethyl acetate (2 x 25 mL). The aqueous layer was acidified with 1M aqueous HCl to pH 1 and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford crude *N*-Boc 6-aminohexanoic acid. The crude acid intermediate, phenol (1.1 g, 12 mmol) and DMAP (611 mg, 5.0 mmol) were combined in a 50-mL round-bottomed flask. The flask was evacuated and flushed with Ar thrice, charged with CH_2Cl_2 (5 mL) and cooled to 0 °C. DCC (751 mg, 3.6 mmol) was added in one portion and the reaction mixture warmed to room temperature over 16 h. The cloudy mixture was filtered through a cotton plug and rinsed with ethyl

acetate (20 mL), and the filtrate was washed sequentially with 0.5M aqueous HCl (2 x 25 mL) and saturated aqueous NaHCO₃ (20 mL), then dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate/hexane) to afford an oil comprising a mixture of *N*-Boc carbamate and phenol. The mixture was dissolved in ethyl acetate (20 mL) and washed with 1M aqueous NaOH (3 x 10 mL). The aqueous layer was dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to afford the title *N*-Boc carbamate as a colourless solid (410 mg, 33% over 2 steps). **mp** 82-84 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.38 (t, *J* = 7.5 Hz, 2H, ArH), 7.23 (t, *J* = 7.5 Hz, 1H, ArH), 7.07 (d, *J* = 7.5 Hz, 2H, ArH), 4.57 (br s, 1H, NH), 3.17-3.12 (m, 2H, NCH₂), 2.57 (t, *J* = 7.5 Hz, 2H, OCH₂), 1.81-1.73 (m, 2H, CH₂), 1.58-1.51 (m, 2H, CH₂), 1.48-1.42 (m, 11H, CH₂ + OC(CH₃)₃); **¹³C NMR** (101 MHz, CDCl₃) δ 172.1, 156.0, 150.6, 129.4, 125.7, 121.5, 79.1, 40.3, 34.2, 29.7, 28.4, 26.2, 24.5; **HRMS** (ESI+) calc. for C₁₇H₂₅NO₄ [M+Na]⁺ 330.1676; found 330.1684.

tert-Butyl [5-(trityloxy)pentyl]carbamate

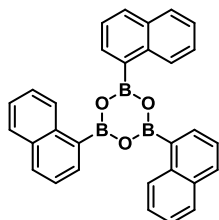


A 20 mL headspace vial was charged with a solution of 5-aminopentanol (870 μL, 8.0 mmol) in absolute ethanol (16 mL). Di-*tert*-butyl dicarbonate (2.0 mL, 8.8 mmol) was added and the reaction mixture was stirred at room temperature over 3 h. The crude reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (30→50% ethyl acetate/hexane) to afford the *N*-Boc carbamate as a colourless oil (1.04 g, 64%). To a solution of *N*-Boc carbamate (508 mg, 2.50 mmol) was added trityl chloride (767 mg, 2.75 mmol), followed by Et₃N (520 μL, 3.75 mmol) and DMAP (1 crystal). The reaction mixture was stirred at room temperature over 24 h, then quenched with H₂O (5 mL). The aqueous layer was extracted with ethyl acetate (3 x 5 mL) and the combined organic layers were dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. The resulting thick yellow oil was purified by flash column chromatography (0→10% ethyl acetate/hexane) to afford the title *N*-Boc carbamate as a sticky colourless gum (625 g, 65%). **¹H NMR** (400 MHz, CDCl₃) δ 7.43 (d, *J* = 7.5 Hz, 6H, ArH), 7.29 (t, *J* = 7.5 Hz, 6H, ArH), 7.22 (t, *J* = 7.5 Hz, 3H, ArH), 4.50 (br s, 1H, NH), 3.11-3.01 (m, 4H, NCH₂ + OCH₂), 1.66-1.59 (m, 2H, CH₂), 1.43-1.33 (m, 13H, OC(CH₃)₃ + 2 x CH₂); **¹³C NMR** (101 MHz, CDCl₃) δ 155.9, 144.4, 128.6, 127.7, 126.8, 86.3, 79.0, 63.3, 40.4, 29.8, 29.6, 28.4, 23.5; **HRMS** (ESI+) calc. for C₂₉H₃₅NO₃Si [M+Na]⁺ 468.2509; found 468.2520.

Preparation of Trisarylboroxine Substrates

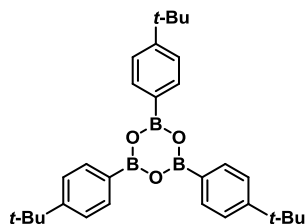
Tris(phenyl)boroxine,⁶ tris(*p*-tolyl)boroxine,⁷ tris(4-methoxyphenyl)boroxine,⁶ tris(4-chlorophenyl)boroxine,⁷ tris(4-bromophenyl)boroxine,⁸ tris(4-trifluoromethylphenyl)boroxine⁶ and tris(4-carbomethoxyphenyl)boroxine⁹ were prepared according to general procedure D and used without further purification.

Tris(1-naphthyl)boroxine



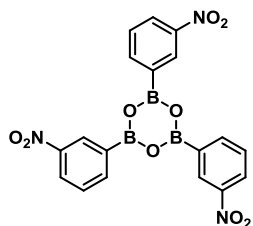
This compound was prepared according to general procedure D as a white powder and found to comprise 1.0:0.09 boroxine:boronic acid. ¹H NMR (400 MHz, CDCl₃) δ 9.29 (d, *J* = 8.5 Hz, 3H), 8.69 (dd, *J* = 7.0, 1.0 Hz, 3H), 8.13 (d, *J* = 8.0 Hz, 3H), 7.97 (d, *J* = 7.5 Hz, 3H), 7.70-7.66 (m, 6H), 7.60 (td, *J* = 7.5, 1.0 Hz, 3H).

Tris(4-*tert*-butylphenyl)boroxine



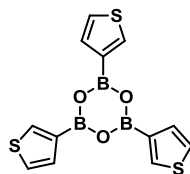
This compound was prepared according to general procedure D as a white powder and found to comprise 1.0:0.11 boroxine:boronic acid. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.0 Hz, 6H), 7.54 (d, *J* = 8.0 Hz, 6H), 1.38 (s, 27H, 3 x C(CH₃)₃).

Tris(3-nitrophenyl)boroxine



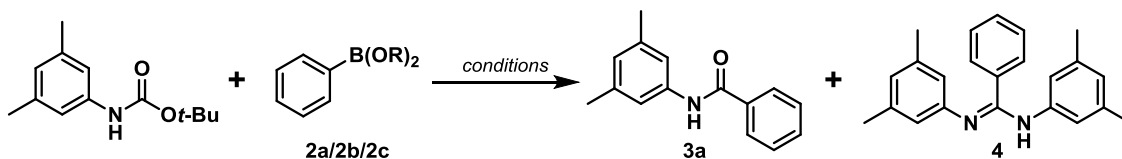
This compound was prepared according to general procedure D as yellow flakes which were insoluble in a variety of dry, deuterated NMR solvents. Reduction in mass before and after drying corresponded to the loss of 1 equivalent of H₂O, and the compound was used without further purification.

Tris(thiophen-3-yl)boroxine



This compound was prepared according to general procedure D as a sandy powder and found to comprise 1.0:0.13 boroxine:boronic acid. ¹H NMR (400 MHz, CDCl₃) δ 8.32 (dd, *J* = 2.5, 1.0 Hz, 3H), 7.69 (dd, *J* = 5.0, 1.0 Hz, 3H), 7.44 (dd, *J* = 5.0, 2.5 Hz, 3H).

Extended Optimization Tables for the Coupling of Boroxines and Carbamates



2a: phenylboronic acid 1,3-propanediol ester; **2b:** phenylboronic acid neopentylglycol ester; **2c:** trisphenylboroxine

Table S1: Optimizing rhodium(I)-catalyzed coupling of organoboron reagents and aromatic *tert*-butylcarbamate.

Entry	PhB(OR) ₂	Catalyst (mol%)	Base (equiv)	Solvent (T/°C)	Yield ^[a] /% (conv ^[b] /%)
1	2a	IPrCuCl (5.0)	NaOt-Bu (1.0)	DMF (140)	16 (100) ^[c]
2	2b	IPrCuCl (5.0)	NaOt-Bu (1.0)	DMF (140)	19 (100) ^[d]
3	2b	SIPrCuCl (5.0)	NaOt-Bu (1.0)	DMF (140)	21 (100)
4	2b	SIPrCuCl (5.0)	NaOt-Bu (0.5)	DMF (140)	30 (100)
5	2b	SIPrCuCl (5.0)	NaOt-Bu (0.2)	DMF (140)	28 (100)
6	2b	IMesCuCl (5.0)	NaOt-Bu (1.0)	DMF (140)	0 (100) ^[e]
7	2b	SIMesCuCl (5.0)	NaOt-Bu (1.0)	DMF (140)	<10 (95) ^[f]
8	2a/2b	[Cl(cod)Rh] ₂ (2.5)	NaOt-Bu (1.0)	dioxane (110)	– (0)
9	2c	[Cl(cod)Rh] ₂ (2.5)	NaOt-Bu (1.0)	dioxane (110)	37 (100)
10	2c	[Cl(nbd)Rh] ₂ (2.5)	NaOt-Bu (1.0)	dioxane (110)	25 (100)
11	2c	[Cl(cod)Rh] ₂ (2.5)	K ₂ CO ₃ (1.0)	dioxane (100)	– (0)
12	2c	[Cl(cod)Rh] ₂ (2.5)	KOH (1.0)	dioxane (100)	– (67) ^[g]
13	2c	[Cl(cod)Rh] ₂ (2.5)	Na ₂ B ₄ O ₇ (1.0)	dioxane (100)	– (0)
14	2c	[Cl(cod)Rh] ₂ (2.5)	B(OH) ₃ (1.0)	dioxane (100)	– (0)
15	2c	[Cl(cod)Rh] ₂ (2.5)	NaF (1.0)	dioxane (100)	14 (15)
16	2c	[Cl(cod)Rh] ₂ (2.5)	KF (1.0)	dioxane (100)	89 (100)
17	2c	[Cl(cod)Rh] ₂ (2.5)	CsF (1.0)	dioxane (100)	– (0)
18	2c	[Cl(cod)Rh] ₂ (2.5)	–	dioxane (100)	– (0)
19	2c	–	KF (1.0)	dioxane (100)	– (0)
20	2c ^[h]	[Cl(cod)Rh] ₂ (2.5)	KF (1.0)	dioxane (100)	88 (100)
21	2c ^[i]	[Cl(cod)Rh] ₂ (2.5)	KF (1.0)	dioxane (100)	86 (100)
22	2c ^[i]	[OH(cod)Rh] ₂ (2.5)	KF (1.0)	dioxane (100)	73 (100)
23	2c ^[i]	[Cl(cod)Rh] ₂ (2.5)	KF (1.0)	dioxane (80)	n.d. (28)
24	2c ^[i]	[Cl(cod)Rh] ₂ (2.5)	KF (1.0)	dioxane (90)	79 (100)

Standard reaction conditions: Carbamate (0.25 mmol), **2** (**2a/2b**: 0.50 mmol, **2c**: 0.17 mmol), base, solvent (0.5 mL), 16 h. [a] yield of isolated product. [b] determined by analysis of ¹H NMR spectrum of crude reaction mixture. [c] 9% of **4**. [d] 20% of **4**. [e] complete conversion to 3,5-dimethylaniline. [f] 22% of **4**. [g] 33% conversion to 3,5-dimethylaniline. [h] 0.13 mmol of **2c**. [i] 0.10 mmol of **2c**. n.d. = not determined.

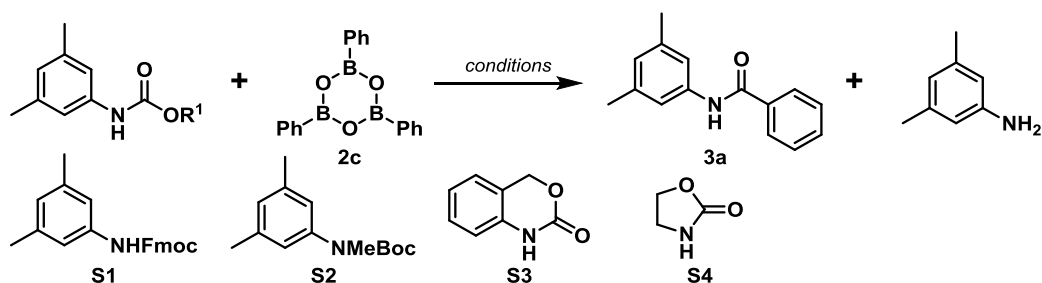


Table S2: Varying *O*-substitution on carbamate.

Entry	R ¹	Catalyst (mol%)	Base	Solvent (T/°C)	Yield ^[a] /% (conv ^[b] /%)
1	Me	[Cl(cod)Rh] ₂ (2.5)	KF	dioxane (100)	– (0)
2		[Cl(cod)Rh] ₂ (2.5)	NaOt-Bu	dioxane (100)	32 (100)
3		[Cl(cod)Rh] ₂ (2.5)	NaOMe	dioxane (100)	21 (100)
4	allyl	[Cl(cod)Rh] ₂ (2.5)	KF	dioxane (100)	0 (100) ^[c]
5	Bn	[Cl(cod)Rh] ₂ (2.5)	KF	dioxane (100)	n.d. (77)
6 ^[d]		[Cl(cod)Rh] ₂ (2.5)	KF	dioxane (100)	100 (100)
7	S1	[Cl(cod)Rh] ₂ (2.5)	KF	dioxane (100)	0 (95)
8	S2	[Cl(cod)Rh] ₂ (2.5)	KF	dioxane (100)	0 (13) ^[e]
9	S3	[Cl(cod)Rh] ₂ (2.5)	KF	dioxane (100)	0 (64)
10	S4	[Cl(cod)Rh] ₂ (2.5)	KF	dioxane (100)	– (0)

Standard reaction conditions: Carbamate (0.25 mmol), **2c** (0.10 mmol), base (0.25 mmol), solvent (0.5 mL), 16 h. [a] yield of isolated product. [b] determined by analysis of ¹H NMR spectrum of crude reaction mixture. [c] complete conversion to 3,5-dimethylaniline. [d] 24 h reaction time. [e] conversion to *N*-methyl-3,5-dimethylaniline. n.d. = not determined.

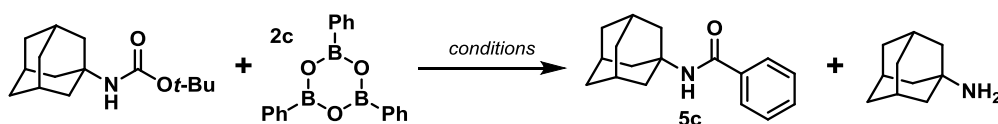


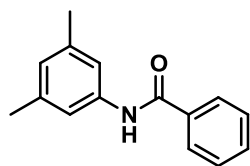
Table S3: Optimizing rhodium(I)-catalyzed coupling of trisarylboroxine and aliphatic *tert*-butylcarbamate.

Entry	Catalyst (mol%)	Solvent (T/°C)	Yield ^[a] /% (conv ^[b] /%)
1	[Cl(cod)Rh] ₂ (2.5)	dioxane (100)	8 (9)
2	[Cl(cod)Rh] ₂ (2.5)	diglyme (160)	58 (100) ^[c]
3 ^[d]	[Cl(cod)Rh] ₂ (2.5)	PhMe (120)	n.d. (6)
4 ^[d]	[Cl(cod)Rh] ₂ (2.5)	DMF (120)	– (0)
5	[Cl(nbd)Rh] ₂ (2.5)	dioxane (120)	n.d. (<10)
6	(cod) ₂ Rh(OTf) (5.0)	dioxane (120)	78 (91)
7	(cod) ₂ Rh(OTf) (5.0)	dioxane (100)	92 (95)

Standard reaction conditions: Carbamate (0.50 mmol), **2c** (0.20 mmol), KF (0.50 mmol), solvent (1 mL), 16 h. [a] yield of isolated product. [b] determined by analysis of ¹H NMR spectrum of crude reaction mixture. [c] 8% conversion to 1-adamantylamine. [d] 24 h reaction time. n.d. = not determined.

Rhodium-Catalyzed Amidation of *N*-Boc and *N*-Cbz Protected Amines

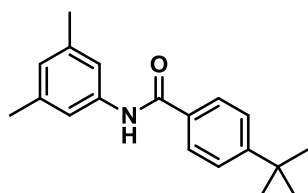
N-(3,5-Dimethylphenyl)benzamide (3a)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and *N*-Cbz aniline (100 °C, 24 h) and isolated by flash column chromatography (0→30% ether/hexane) to give the product as a white solid (*N*-Boc 94 mg, 83%; *N*-Cbz 116 mg, quant). **mp** 141-143 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (br s, 1H, NH), 7.83 (d, *J* = 7.5 Hz, 2H, ArH), 7.49 (t, *J* = 7.5 Hz, 1H, ArH), 7.41 (t, *J* = 7.5 Hz, 2H, ArH), 7.27 (s, 2H, ArH), 6.76 (s, 1H, ArH), 2.27 (s, 6H, 2 x CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 166.0, 138.8, 137.9, 135.1, 131.8, 128.7, 127.1, 126.4, 118.2, 21.5.

The spectroscopic data was found to be in agreement with that reported by Kelly and co-workers.¹⁰

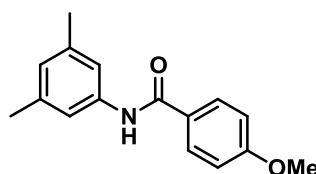
N-(3,5-Dimethylphenyl)-4-*tert*-butylbenzamide (3b)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and isolated by flash column chromatography (0→20% ether/hexane) to give the product as a white foam (131 mg, 93%). **mp** 118-120 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.5 Hz, 2H, ArH), 7.73 (br s, 1H, NH), 7.50 (d, *J* = 8.5 Hz, 2H, ArH), 7.29 (s, 2H, ArH), 6.80 (s, 1H, ArH), 2.33 (s, 6H, 2 x CH₃), 1.35 (s, 9H, C(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 165.5, 155.3, 138.8, 137.8, 132.2, 126.8, 126.2, 125.7, 117.8, 35.0, 31.1, 21.4.

The spectroscopic data was found to be in agreement with that reported by Zhang and co-workers.¹¹

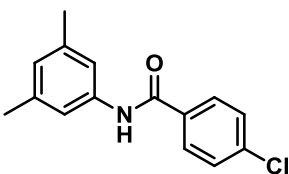
N-(3,5-Dimethylphenyl)-4-methoxybenzamide (3c)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and isolated by flash column chromatography (0→40% ether/hexane) to give the product as a white solid (104 mg, 81%). **mp** 124-125 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 9.0 Hz, 2H, ArH), 7.69 (br s, 1H, NH), 7.27 (s, 2H, ArH), 6.97 (d, *J* = 9.0 Hz, 2H, ArH), 6.79 (s, 1H, ArH), 3.87 (s, 3H, OCH₃), 2.32 (s, 6H, 2 x CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 165.1, 162.4, 138.8, 137.9, 128.8, 127.2, 126.1, 117.8, 113.9, 55.5, 21.4.

The spectroscopic data was found to be in agreement with that reported by Zhang and co-workers.¹¹

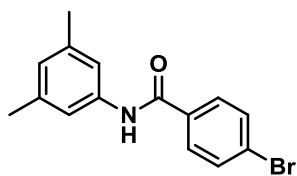
N-(3,5-Dimethylphenyl)-4-chlorobenzamide (3d)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and isolated by flash column chromatography (30% ether/hexane) to give the product as a beige solid (122 mg, 89%). **mp** 141-144 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.5 Hz, 2H, ArH), 7.69 (br s, 1H, NH), 7.46 (d, *J* = 8.5 Hz, 2H, ArH), 7.26 (s, 2H, ArH), 6.82 (s, 1H, ArH), 2.33 (s, 6H, 2 x CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 164.6, 138.9, 138.0, 137.4, 133.4, 129.0, 128.4, 126.6, 118.0, 21.4.

The spectroscopic data was found to be in agreement with that reported by Zhang and co-workers.¹¹

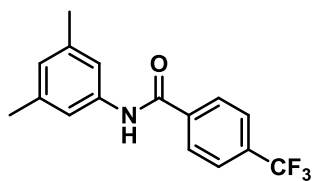
***N*-(3,5-Dimethylphenyl)-4-bromobenzamide (3e)**



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and isolated by flash column chromatography (30% ether/hexane) to give the product as a beige solid (128 mg, 84%). **mp** 149-151 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.76 (br s, 1H, NH), 7.72 (d, *J* = 8.5 Hz, 2H, ArH), 7.60 (d, *J* = 8.5 Hz, 2H, ArH), 7.26 (s, 2H, ArH), 6.81 (s, 1H, ArH), 2.32 (s, 6H, 2 x CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 164.7, 138.9, 137.4, 133.9, 132.0, 128.6, 126.6, 126.5, 118.0, 21.4.

The spectroscopic data was found to be in agreement with that reported by Zhang and co-workers.¹¹

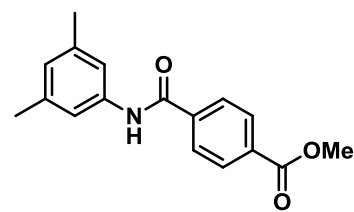
***N*-(3,5-Dimethylphenyl)-4-trifluoromethyl-benzamide (3f)**



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and isolated by flash column chromatography (10→20% ether/hexane) to give the product as a beige solid (123 mg, 84%). **mp** 149-152 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.0 Hz, 2H, ArH), 7.85 (br s, 1H, NH), 7.72 (d, *J* = 8.0 Hz, 2H, ArH), 7.27 (s, 2H, ArH), 6.83 (s, 1H, ArH), 2.32 (s, 6H, 2 x CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 164.4, 138.9, 138.4, 137.3, 133.4 (q, *J* = 33 Hz), 127.5, 126.8, 125.8 (q, *J* = 4 Hz), 123.6 (q, *J* = 272 Hz), 118.1, 21.4.

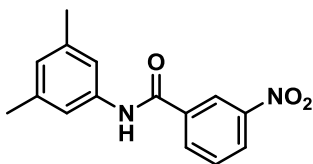
The spectroscopic data was found to be in agreement with that reported by Zhang and co-workers.¹¹

Methyl 4-[(3,5-Dimethylphenyl)carbamoyl]benzoate (3g)



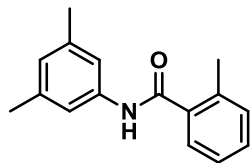
This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 12 h) and isolated by flash column chromatography (0→30% ethyl acetate/hexane) to give the product as a white solid (126 mg, 89%). **mp** 141-144 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.5 Hz, 2H, ArH), 7.92 (d, *J* = 8.5 Hz, 2H, ArH), 7.81 (br s, 1H, NH), 7.29 (s, 2H, ArH), 6.83 (s, 1H, ArH), 3.97 (s, 3H, CO₂CH₃), 2.34 (s, 6H, 2 x CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 166.3, 164.8, 139.1, 139.0, 137.5, 133.0, 130.1, 127.1, 126.8, 118.1, 52.6, 21.5; **HRMS** (ESI⁺) calc. for C₁₇H₁₇NO₃ [M+Na]⁺ 306.1101; found 306.1108.

***N*-(3,5-Dimethylphenyl)-3-nitrobenzamide (3h)**



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 24 h) and *N*-Cbz aniline (100 °C, 24 h) and isolated by flash column chromatography (10→30% ethyl acetate/hexane) to give the product as a bright yellow solid (*N*-Boc 72 mg, 53%; *N*-Cbz 121 mg, 90%). **mp** 179-181 °C (lit.¹² 177-179 °C); **¹H NMR** (400 MHz, CDCl₃) δ 8.67 (s, 1H, ArH), 8.39 (d, *J* = 8.0 Hz, 1H, ArH), 8.24 (d, *J* = 8.0 Hz, 1H, ArH), 7.95 (br s, 1H, NH), 7.69 (t, *J* = 8.0 Hz, 1H, ArH), 7.28 (s, 2H, ArH), 6.83 (s, 1H, ArH), 2.32 (s, 6H, 2 x CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 163.2, 148.2, 139.0, 137.0, 136.6, 133.3, 130.1, 127.0, 126.3, 121.7, 118.2, 21.4; **HRMS** (ESI⁺) calc. for C₁₅H₁₄N₂O₃ [M+Na]⁺ 293.0897; found 293.0904.

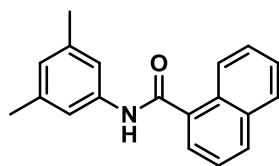
***N*-(3,5-Dimethylphenyl)-2-methylbenzamide (3i)**



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and isolated by flash column chromatography (0→20% ether/hexane) to give the product as a tan powder (106 mg, 89%). **mp** 181-182 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.47 (d, *J* = 7.5 Hz, 1H, ArH), 7.40-7.35 (m, 2H, ArH + NH), 7.29-7.24 (m, 4H, ArH), 6.82 (s, 1H, ArH), 2.52 (s, 3H, CH₃), 2.34 (s, 6H, 2 x CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 168.1, 138.9, 137.8, 136.6, 136.5, 131.3, 130.2, 126.6, 126.3, 125.9, 117.6, 21.4, 19.9.

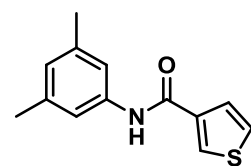
The spectroscopic data was found to be in agreement with that reported by Zhang and co-workers.¹¹

***N*-(3,5-Dimethylphenyl)-1-naphthamide (3j)**



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and *N*-Cbz aniline (100 °C, 24 h) and isolated by flash column chromatography (10→30% ether/hexane) to give the product as a sandy solid (*N*-Boc 113 mg, 82%; *N*-Cbz 115 mg, 84%). **mp** 171-173 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.33-8.31 (m, 1H, ArH), 7.92-7.87 (m, 2H, ArH), 7.82 (br s, 1H, NH), 7.64 (d, *J* = 7.0 Hz, 1H, ArH), 7.55-7.52 (m, 2H, ArH), 7.42 (t, *J* = 7.5 Hz, 1H, ArH), 7.33 (s, 2H, ArH), 6.84 (s, 1H, ArH), 2.35 (s, 6H, 2 x CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 167.6, 138.9, 137.9, 134.6, 133.7, 130.9, 130.1, 128.4, 127.3, 126.6, 126.4, 125.3, 125.1, 124.7, 117.8, 21.5; **HRMS** (ESI+) calc. for C₁₉H₁₇NO [M+Na]⁺ 298.1202; found 298.1211.

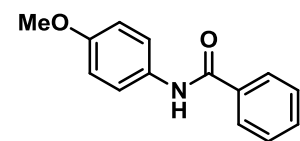
***N*-(3,5-Dimethylphenyl)-3-thiophenecarboxamide (3k)**



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and boroxine (3.0 equiv), and isolated by flash column chromatography (0→40% ether/hexane) to give the product as a beige solid (123 mg, 84%). **mp** 165-167 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.25 (br s, 1H, NH), 7.97 (dd, *J* = 3.0, 1.5 Hz, 1H, ArH), 7.49 (dd, *J* = 5.0, 1.5 Hz, 1H, ArH), 7.27 (dd, *J* = 5.0, 3.0 Hz, 1H, ArH), 7.22 (s, 2H, ArH), 6.73 (s, 1H, ArH), 2.21 (s, 6H, 2 x CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 161.5, 138.5, 137.7, 137.5, 128.7, 126.4, 126.2, 118.4, 21.2.

The spectroscopic data was found to be in agreement with that reported by Zhang and co-workers.¹¹

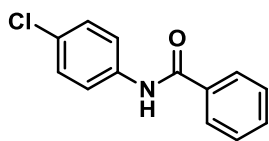
***N*-(4-Methoxyphenyl)benzamide (3l)**



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 24 h) and *N*-Cbz aniline (100 °C, 16 h) and isolated by flash column chromatography (10→20% acetone/hexane) to give the product as a white solid (*N*-Boc 93 mg, 82%; *N*-Cbz 99 mg, 87%). **mp** 161-163 °C (lit.¹³ 162-163 °C); **¹H NMR** (400 MHz, CDCl₃) δ 7.87 (d, *J* = 7.0 Hz, 2H, ArH), 7.76 (br s, 1H, NH), 7.57-7.53 (m, 3H, ArH), 7.48 (t, *J* = 7.5 Hz, 2H, ArH), 6.91 (d, *J* = 9.0 Hz, 2H, ArH), 3.82 (s, 3H, OCH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 165.6, 156.6, 135.0, 131.7, 130.9, 128.8, 126.9, 122.0, 114.2, 55.5.

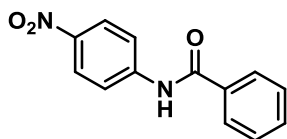
The spectroscopic data was found to be in agreement with that reported by Joullié and co-worker.¹⁴

N-(4-Chlorophenyl)benzamide (3m)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and isolated by flash column chromatography (10→40% ethyl acetate/hexane) to give the product as tan crystals (91 mg, 79%). **mp** 194-197 °C (lit.¹⁵ 199-200 °C); **¹H NMR** (400 MHz, CDCl₃) δ 7.87-7.83 (m, 3H, ArH + NH), 7.61 (d, *J* = 9.0 Hz, 2H, ArH), 7.57 (t, *J* = 7.5 Hz, 1H, ArH), 7.50 (t, *J* = 7.5 Hz, 2H, ArH), 7.34 (d, *J* = 9.0 Hz, 2H, ArH); **¹³C NMR** (101 MHz, CDCl₃) δ 165.7, 136.5, 134.6, 132.1, 129.6, 129.1, 128.9, 127.0, 121.4; **HRMS** (ESI+) calc. for C₁₃H₁₀ClNO [M+Na]⁺ 254.0343; found 254.0348.

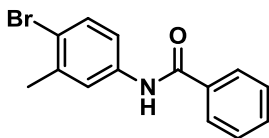
N-(4-Nitrophenyl)benzamide (3n)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 24 h) and *N*-Cbz aniline (100 °C, 16 h) and isolated by flash column chromatography (0→1% MeOH/CHCl₃) to give the product as a yellow solid (*N*-Boc 55 mg, 45% + 26% recovered carbamate; *N*-Cbz 76 mg, 63% + 9% recovered carbamate). **mp** 162-164 °C (lit.¹⁶ 160-162 °C); **¹H NMR** (400 MHz, *d*₆-DMSO) δ 10.85 (br s, 1H, NH), 8.28 (d, *J* = 9.5 Hz, 2H, ArH), 8.09 (d, *J* = 9.5 Hz, 2H, ArH), 8.00 (d, *J* = 7.5 Hz, 2H, ArH), 7.66 (t, *J* = 7.5 Hz, 1H, ArH), 7.58 (t, *J* = 7.5 Hz, 2H, ArH); **¹³C NMR** (101 MHz, *d*₆-DMSO) δ 166.4, 145.6, 142.5, 134.3, 132.3, 128.6, 128.0, 124.8, 119.9.

The spectroscopic data was found to be in agreement with that reported by Wang and co-workers.¹⁷

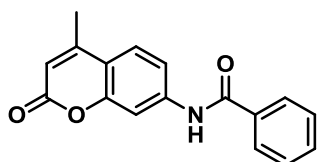
N-(4-Bromo-3-methylphenyl)benzamide (3o)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and *N*-Cbz aniline (100 °C, 16 h) and isolated by flash column chromatography (0→30% ether/hexane) to give the product as a beige solid (*N*-Boc 77 mg, 53%; *N*-Cbz 135 mg, 93%). **mp** 98-100 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.83 (br s, 1H, NH), 7.82 (d, *J* = 7.5 Hz, 2H, ArH), 7.54 (d, *J* = 2.5 Hz, 1H, ArH), 7.51 (t, *J* = 7.5 Hz, 1H, ArH), 7.43-7.38 (m, 3H, ArH), 7.32 (dd, *J* = 8.5, 2.5 Hz, 1H, ArH), 2.31 (s, 3H, CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 166.2, 138.5, 137.1, 134.6, 132.6, 131.9, 128.7, 127.1, 122.8, 119.8, 119.5, 23.0.

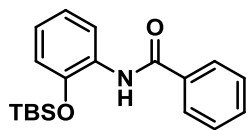
The spectroscopic data was found to be in agreement with that reported by Zhang and co-workers.¹¹

N-(4-Methyl-2-oxo-2H-chromen-7-yl)benzamide (3p)



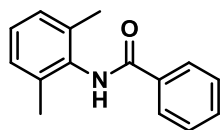
This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 24 h) and isolated by flash column chromatography (0→2% MeOH/CHCl₃) to give the product as an off-white solid (77 mg, 55% + 12% recovered carbamate). **mp** 240-242 °C (lit.¹⁸ 246-248 °C); **¹H NMR** (400 MHz, *d*₆-DMSO) δ 10.65 (br s, 1H, NH), 7.98-7.93 (m, 3H, ArH), 7.75 (s, 2H, ArH), 7.63-7.61 (m, 1H, ArH), 7.57-7.54 (m, 2H, ArH), 6.28 (s, 1H, ArH), 2.41 (s, 3H, CH₃); **¹³C NMR** (101 MHz, *d*₆-DMSO) δ 166.3, 160.2, 153.6, 153.3, 142.7, 134.5, 132.1, 128.6, 127.9, 125.9, 116.2, 115.4, 112.5, 106.7, 18.1; **HRMS** (ESI+) calc. for C₁₇H₁₃NO₃ [M+Na]⁺ 302.0788; found 302.0796.

N-[2-(*tert*-Butyldimethylsilyl)oxyphenyl]benzamide (3q)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (120 °C, 16 h) and isolated by flash column chromatography (0→10% ether/hexane) to give the product as an orange oil (129 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 8.54-8.52 (m, 2H, ArH + NH), 7.89 (d, *J* = 7.0 Hz, 2H, ArH), 7.55 (t, *J* = 7.5 Hz, 1H, ArH), 7.49 (t, *J* = 7.5 Hz, 2H, ArH), 7.05-6.97 (m, 2H, ArH), 6.88 (dd, *J* = 7.5, 2.0 Hz, 1H, ArH), 1.01 (s, 9H, SiC(CH₃)₃), 0.29 (s, 6H, Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 165.1, 144.2, 135.2, 131.7, 129.8, 128.7, 126.9, 123.7, 121.8, 120.1, 117.4, 25.8, 18.2, -4.3; HRMS (ESI+) calc. for C₁₉H₂₅NO₂Si [M+Na]⁺ 350.1547; found 350.1556.

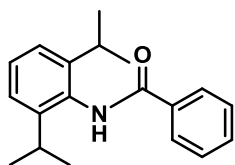
N-(2,6-Dimethylphenyl)benzamide (3r)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and *N*-Cbz aniline (100 °C, 16 h) and isolated by flash column chromatography (0→30% ether/hexane) to give the product as a white solid (*N*-Boc 66 mg, 59%; *N*-Cbz 83 mg, 74%). mp 159-161 °C (lit.¹⁹ 162-164 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.5 Hz, 2H, ArH), 7.58 (t, *J* = 7.5 Hz, 1H, ArH), 7.51 (t, *J* = 7.5 Hz, 2H, ArH), 7.39 (br s, 1H, NH), 7.18-7.11 (m, 3H, ArH), 2.29 (s, 6H, 2 x CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 165.9, 135.6, 134.5, 133.8, 131.9, 128.8, 128.3, 127.5, 127.2, 18.5.

The spectroscopic data was found to be in agreement with that reported by Jiang and co-workers.¹⁹

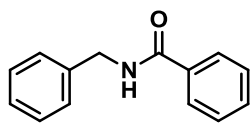
N-(2,6-Diisopropylphenyl)benzamide (3s)



This compound was prepared according to general procedure E from the corresponding *N*-Boc aniline (100 °C, 16 h) and isolated by flash column chromatography (5→10% ether/hexane) to give the product as a white solid (50 mg, 36%). mp 266-268 °C (lit.²⁰ 260-261 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.5 Hz, 2H, ArH), 7.55 (t, *J* = 7.5 Hz, 1H, ArH), 7.48-7.44 (m, 3H, ArH + NH), 7.34 (t, *J* = 7.5 Hz, 1H, ArH), 7.23 (t, *J* = 7.5 Hz, 2H, ArH), 3.13 (quint, *J* = 7.0 Hz, 2H, 2 x CH), 1.20 (d, *J* = 7.0 Hz, 12H, 2 x CH(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 146.4, 134.5, 131.7, 131.2, 128.8, 128.5, 127.2, 123.5, 28.9, 23.6.

The spectroscopic data was found to be in agreement with that reported by Wang and co-workers.²¹

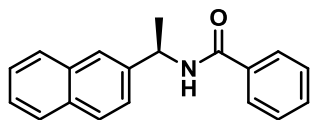
N-Benzylbenzamide (3t)



This compound was prepared according to general procedure F from the corresponding *N*-Boc amine (100 °C, 16 h) and isolated by flash column chromatography (10→30% ethyl acetate/hexane) to give the product as a white solid (84 mg, 80%). mp 108-109 °C (lit.²² 104 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 7.5 Hz, 2H, ArH), 7.47 (t, *J* = 7.5 Hz, 1H, ArH), 7.38 (t, *J* = 7.5 Hz, 2H, ArH), 7.32-7.25 (m, 5H, ArH), 6.75 (br s, 1H, NH), 4.59 (d, *J* = 6.0 Hz, 2H, CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 167.5, 138.3, 134.3, 131.5, 128.7, 128.6, 127.9, 127.6, 127.0, 44.1.

The spectroscopic data was found to be in agreement with that reported by Yamamoto and co-workers.²²

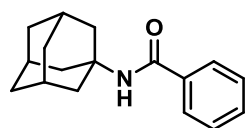
(*R*)-*N*-[1-(Naphthalen-2-yl)ethyl]benzamide (3u)



This compound was prepared according to general procedure F from the corresponding *N*-Boc amine (100 °C, 16 h) and isolated by flash column chromatography (0.5% MeOH/CHCl₃) to give the product as a white solid (117 mg, 85%). **mp** 163-165 °C (lit.²³ 143-145 °C); **¹H NMR** (400 MHz, CDCl₃) δ 7.80-7.76 (m, 6H, ArH), 7.48-7.42 (m, 4H, ArH), 7.35 (t, *J* = 7.5 Hz, 2H, ArH), 6.72 (d, *J* = 7.0 Hz, 1H, NH), 5.45 (quint, *J* = 7.0 Hz, 1H, NCH), 1.63 (d, *J* = 7.0 Hz, 3H, CH₃); **¹³C NMR** (101 MHz, CDCl₃) δ 166.6, 140.5, 134.4, 133.2, 132.6, 131.4, 128.4, 128.4, 127.8, 127.5, 126.9, 126.1, 125.8, 124.7, 124.5, 49.2, 21.5.

The spectroscopic data was found to be in agreement with that reported by Seidel and co-workers.²³

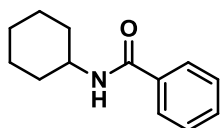
N-(Adamantan-1-yl)benzamide (3v)



This compound was prepared according to general procedure F from the corresponding *N*-Boc amine (100 °C, 16 h) and isolated by flash column chromatography (10→20% ethyl acetate/hexane) to give the product as a white solid (118 mg, 92%). **mp** 154-157 °C (lit.²⁴ 154-156 °C); **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.0 Hz, 2H, ArH), 7.45 (t, *J* = 8.0 Hz, 1H, ArH), 7.38 (t, *J* = 8.0 Hz, 2H, ArH), 5.89 (br s, 1H, NH), 2.12 (s, 9H, 3 x CH₂ + 3 x CH), 1.71 (s, 6H, 3 x CH₂); **¹³C NMR** (101 MHz, CDCl₃) δ 166.6, 136.0, 131.0, 128.4, 126.7, 52.2, 41.6, 36.3, 29.4.

The spectroscopic data was found to be in agreement with that reported by Zhang and co-workers.¹¹

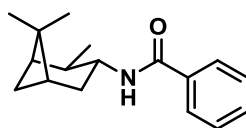
N-Cyclohexylbenzamide (3w)



This compound was prepared according to general procedure F from the corresponding *N*-Boc amine (100 °C, 16 h) and isolated by flash column chromatography (10→30% ethyl acetate/hexane) to give the product as a white solid (81 mg, 80%). **mp** 153-155 °C (lit.¹⁹ 152-154 °C); **¹H NMR** (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.5 Hz, 2H, ArH), 7.46 (t, *J* = 7.5 Hz, 1H, ArH), 7.38 (t, *J* = 7.5 Hz, 2H, ArH), 6.29 (br d, *J* = 7.0 Hz, 1H, NH), 4.00-3.91 (m, 1H, NCH), 2.02-1.98 (m, 2H), 1.76-1.71 (m, 2H), 1.67-1.60 (m, 1H), 1.44-1.33 (m, 2H), 1.29-1.22 (m, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 166.6, 134.9, 131.1, 128.3, 126.8, 48.6, 33.0, 25.4, 24.9.

The spectroscopic data was found to be in agreement with that reported by Jiang and co-workers.¹⁹

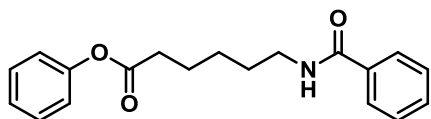
N-[(1*R*,2*R*,3*R*,5*S*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl]benzamide (3x)



This compound was prepared according to general procedure F from the corresponding *N*-Boc amine (100 °C, 16 h) and isolated by flash column chromatography (10→20% ethyl acetate/hexane) to give the product as a white solid (109 mg, 85%). **mp** 126-127 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (d, *J* = 7.5 Hz, 2H, ArH), 7.45 (t, *J* = 7.5 Hz, 1H, ArH), 7.37 (t, *J* = 7.5 Hz, 2H, ArH), 6.48 (br d, *J* = 8.5 Hz, 1H, NH), 4.53-4.45 (m, 1H, NCH), 2.69-2.62 (m, 1H), 2.43-2.37 (m, 1H), 1.98-1.91 (m, 2H), 1.85-1.82 (m, 1H), 1.64 (ddd, *J* = 14.0, 6.0, 2.5 Hz, 1H), 1.23 (s, 3H, CH₃), 1.14 (d, *J* = 7.0 Hz, 3H, CH₃), 1.06 (s, 3H,

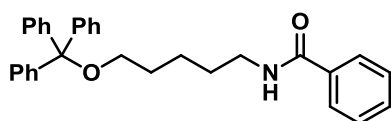
CH₃), 0.95 (d, *J* = 10.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 134.8, 131.0, 128.3, 126.8, 48.2, 47.6, 45.9, 41.4, 38.3, 37.0, 35.0, 27.9, 23.2, 20.7; HRMS (ESI+) calc. for C₁₇H₂₃NO [M+Na]⁺ 280.1672; found 280.1679.

Phenyl 6-benzamidohexanoate (3y)



This compound was prepared according to general procedure F from the corresponding *N*-Boc amine (120 °C, 16 h) and isolated by flash column chromatography (10→40% ethyl acetate/hexane) to give the product (8:1, amide:lactam) as an off-white solid (81 mg, 59%). mp 80-81 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.5 Hz, 2H, ArH), 7.46 (t, *J* = 7.5 Hz, 1H, ArH), 7.38-7.33 (m, 4H, ArH), 7.21 (t, *J* = 7.5 Hz, 1H, ArH), 7.05 (d, *J* = 7.5 Hz, 2H, ArH), 6.63 (br s, 1H, NH), 3.47-3.42 (m, 2H, NCH₂), 2.55 (t, *J* = 7.5 Hz, 2H, OCH₂), 1.81-1.73 (m, 2H, CH₂), 1.68-1.61 (m, 2H, CH₂), 1.51-1.43 (m, 2H, CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 172.1, 167.5, 150.5, 134.5, 131.2, 129.3, 128.4, 126.8, 125.7, 121.4, 39.6, 34.0, 29.1, 26.2, 24.3; HRMS (ESI+) calc. for C₁₉H₂₁NO₃ [M+Na]⁺ 334.1414; found 334.1422.

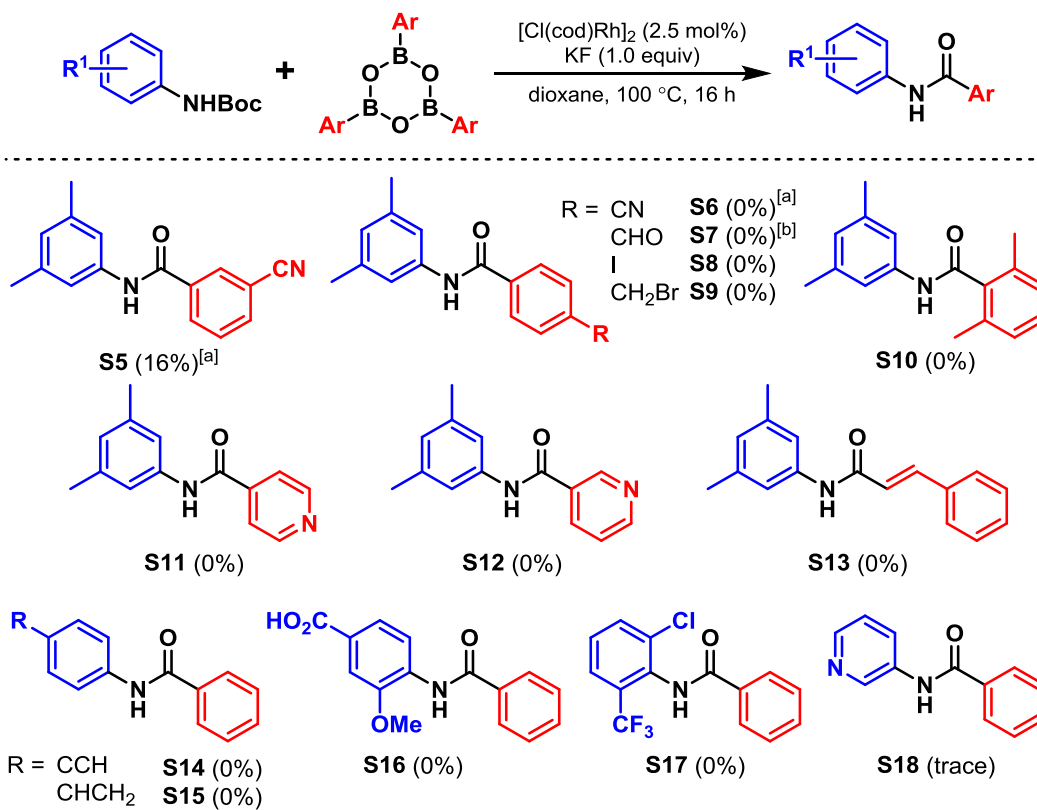
N-[5-(Trityloxy)pentyl]benzamide (3z)



This compound was prepared according to general procedure F from the corresponding *N*-Boc amine (120 °C, 16 h) and isolated by flash column chromatography (10→30% ethyl acetate/hexane) to give the product as a white solid (112 mg, 50%). mp 138-139 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.5 Hz, 2H, ArH), 7.48-7.36 (m, 9H, ArH), 7.29-7.25 (m, 6H, ArH), 7.23-7.19 (m, 3H, ArH), 6.23 (br s, 1H, NH), 3.43-3.38 (m, 2H, NCH₂), 3.06 (t, *J* = 6.5 Hz, 2H, OCH₂), 1.69-1.62 (m, 2H, CH₂), 1.60-1.52 (m, 2H, CH₂), 1.48-1.42 (m, 2H, CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 167.5, 144.3, 134.7, 131.2, 128.6, 128.5, 127.7, 126.8, 126.7, 86.3, 63.2, 39.9, 29.6, 29.4, 23.6; HRMS (ESI+) calc. for C₃₁H₃₁NO₂ [M+Na]⁺ 472.2247; found 472.2254.

Extended List of Boroxine and Carbamate Substrates

Scheme S1: Additional boroxine and carbamate substrates



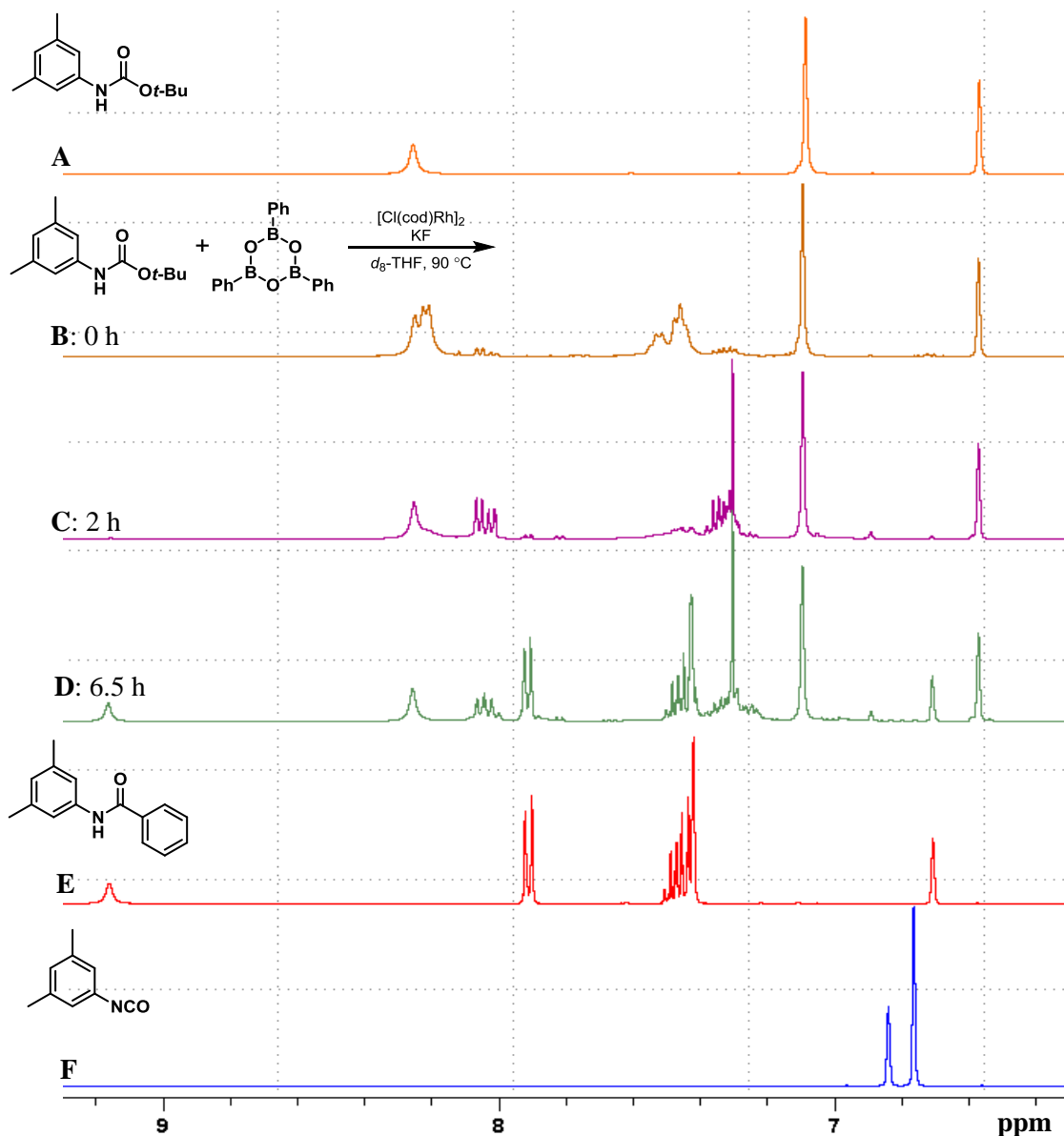
[a] recovered benzonitrile. [b] recovered benzoic acid.

Monitoring Reaction Intermediates by ^1H NMR Spectroscopy

Time-course reaction monitoring

The boroxine-carbamate coupling reaction was set up in a JY valve NMR tube (Norell S-5-400-JY-7) with anhydrous d_8 -THF as solvent under an argon atmosphere and heated in an oil bath at 90 °C. The reaction tube was removed from the oil bath, cooled to room temperature and analysed by ^1H NMR spectroscopy at the time points specified below. After 6.5 h, 33% carbamate conversion was achieved when measured against 1,3,5-trimethoxybenzene as internal standard (spectrum D, Figure 1). Peaks corresponding to 3,5-dimethylphenylisocyanate were not observed over the course of the reaction (reference spectrum F, Figure 1).

Figure S1: Time-course reaction monitoring by ^1H NMR spectroscopy (d_8 -THF, 400 MHz)



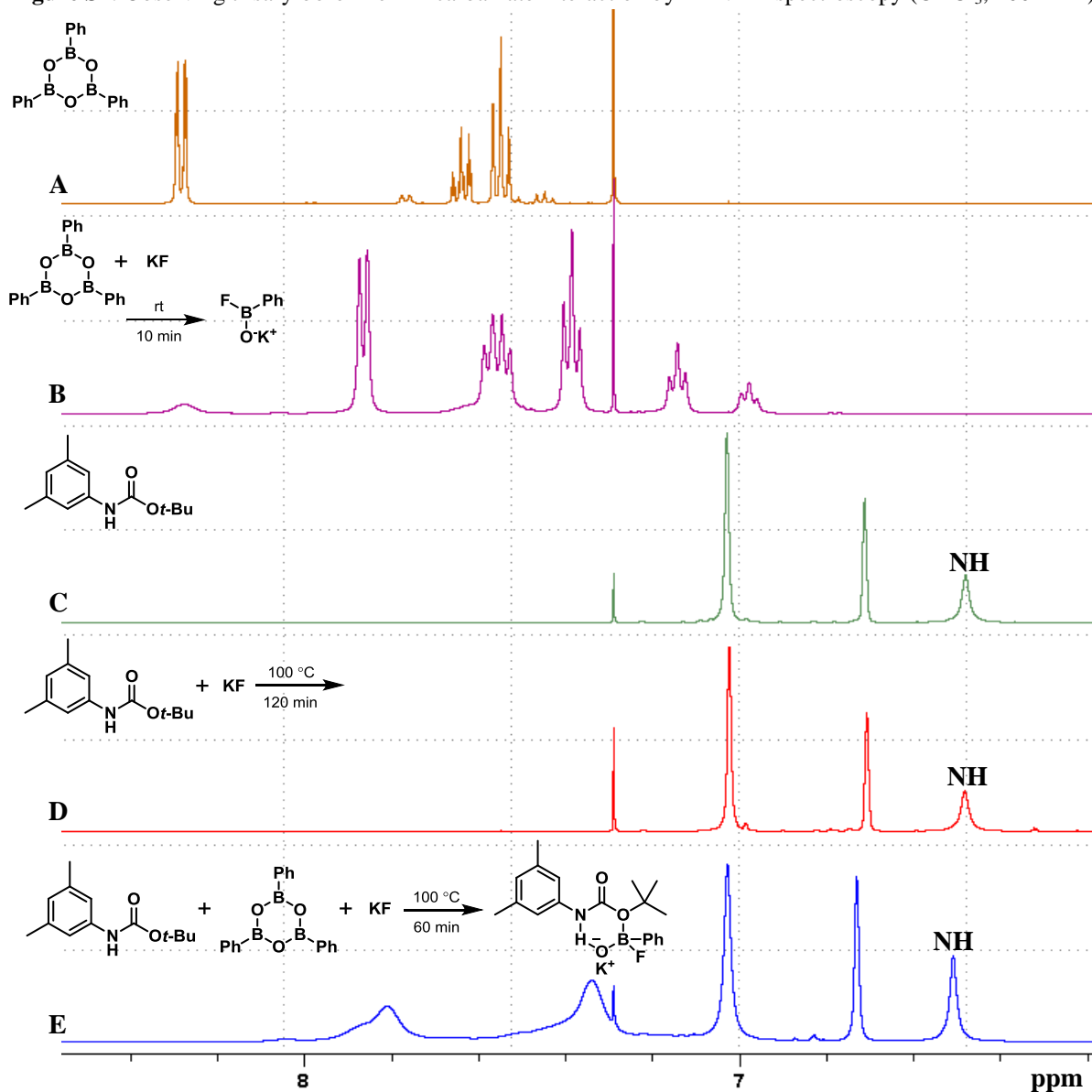
A: *tert*-butyl carbamate **1**. **B:** Carbamate **1** (0.10 mmol), trisphenylboroxine (0.04 mmol), KF (0.10 mmol), $[\text{Cl}(\text{cod})\text{Rh}]_2$ (5 μmol), d_8 -THF (0.6 mL), 90 °C, 0 h. **C:** Sample prepared in **B**, 2 h. **D:** Sample prepared in **B**, 6.5 h. **E:** *N*-(3,5-dimethylphenyl)benzamide. **F:** 3,5-dimethylphenylisocyanate.

Observing trisarylboroxine-KF-carbamate interaction

The reagents were mixed in a 3-mL headspace vial fitted with a stirrer bar under the conditions specified below, then transferred to an NMR tube for acquisition of ^1H NMR spectra at 298 K.

Mixing trisphenylboroxine and KF resulted in near-instantaneous conversion of boroxine to more than one new species (spectra A and B, Figure 2), with assignment of the major species as mixed borate PhBFO^-K^+ .²⁵ Mixing carbamate **1a** and KF showed no discernable change to the environment of the N–H bond (spectrum D), whereas mixing carbamate, boroxine and KF led to an upfield shift for both the N–H (+0.03 ppm) and $\text{C}_{\text{para}}\text{-H}$ (+0.02 ppm) peaks (spectrum E), which suggests hydrogen bonding interactions involving the carbamate moiety.

Figure S2: Observing trisarylboroxine-KF-carbamate interaction by ^1H NMR spectroscopy (CDCl_3 , 400 MHz)



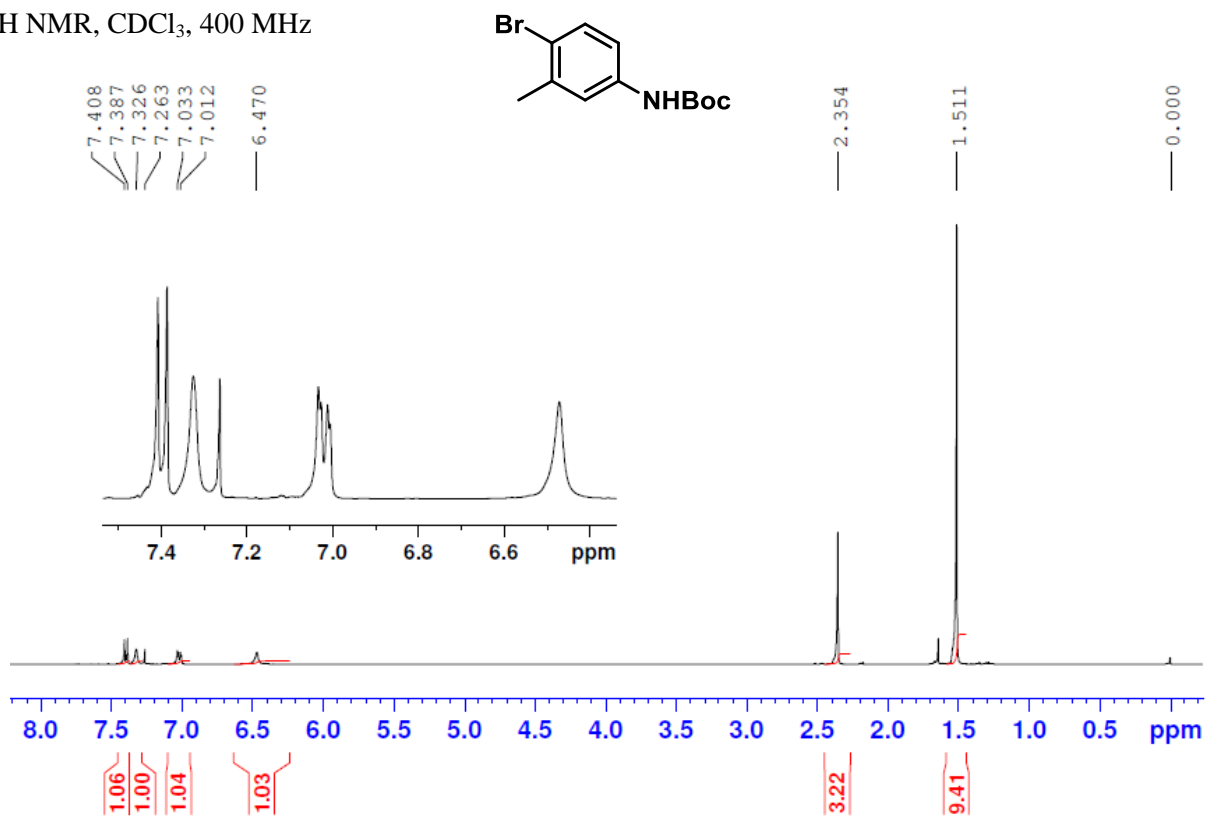
A: trisphenylboroxine. **B:** trisphenylboroxine (0.04 mmol), KF (0.1 mmol), CDCl_3 (0.6 mL), rt, 10 min. **C** *tert*-butyl carbamate **1** (0.20 mmol). **D:** *tert*-butyl carbamate **1** (0.1 mmol), KF (0.1 mmol), CDCl_3 (0.6 mL), 100 °C, 2 h. **E:** *tert*-butyl carbamate **1** (0.2 mmol), trisphenylboroxine (0.08 mmol), KF (0.2 mmol), CDCl_3 (0.6 mL), 100 °C, 1 h.

References

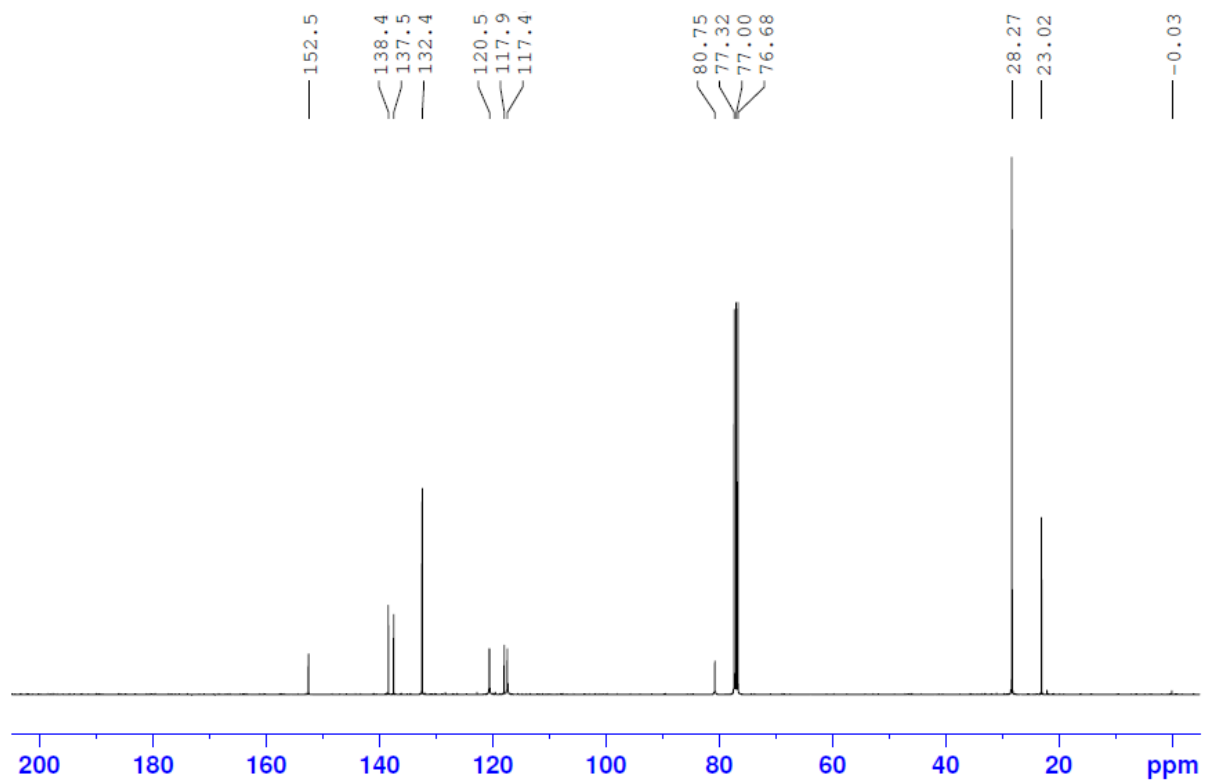
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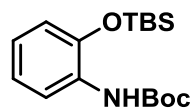
^1H and ^{13}C NMR Spectra of Novel *N*-Boc and *N*-Cbz Carbamates

^1H NMR, CDCl_3 , 400 MHz

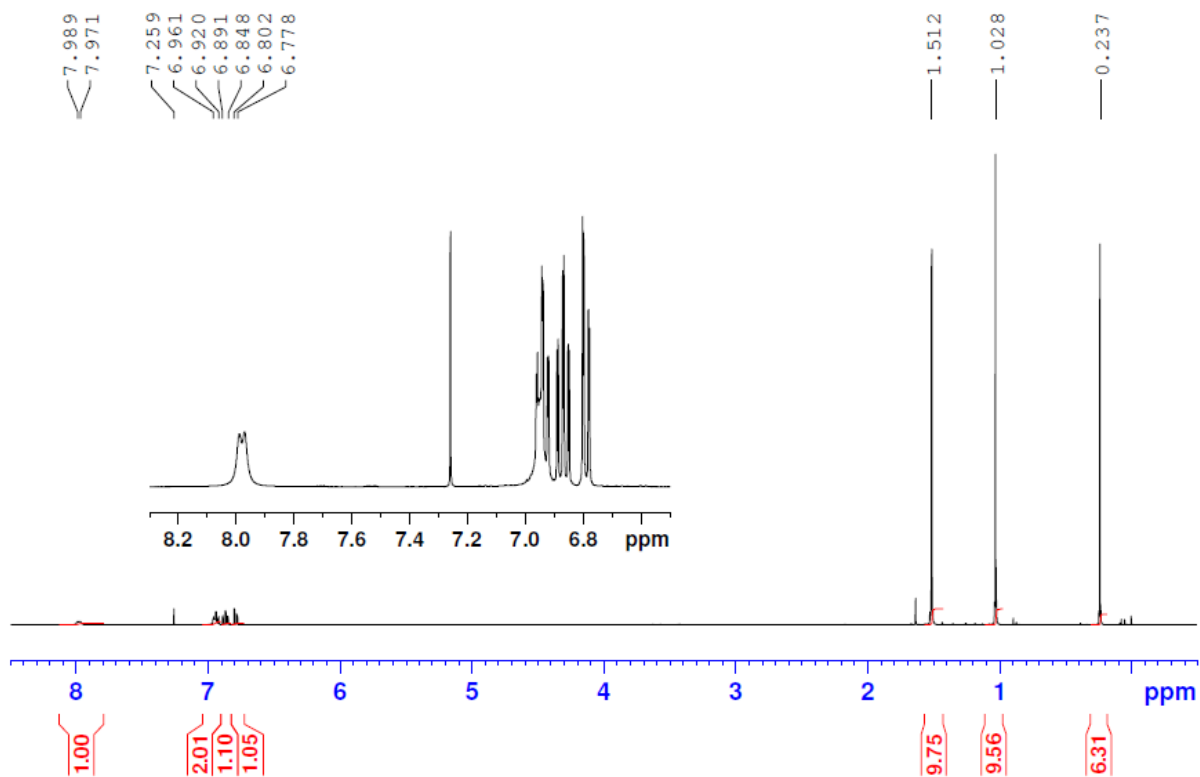


^{13}C NMR, CDCl_3 , 101 MHz

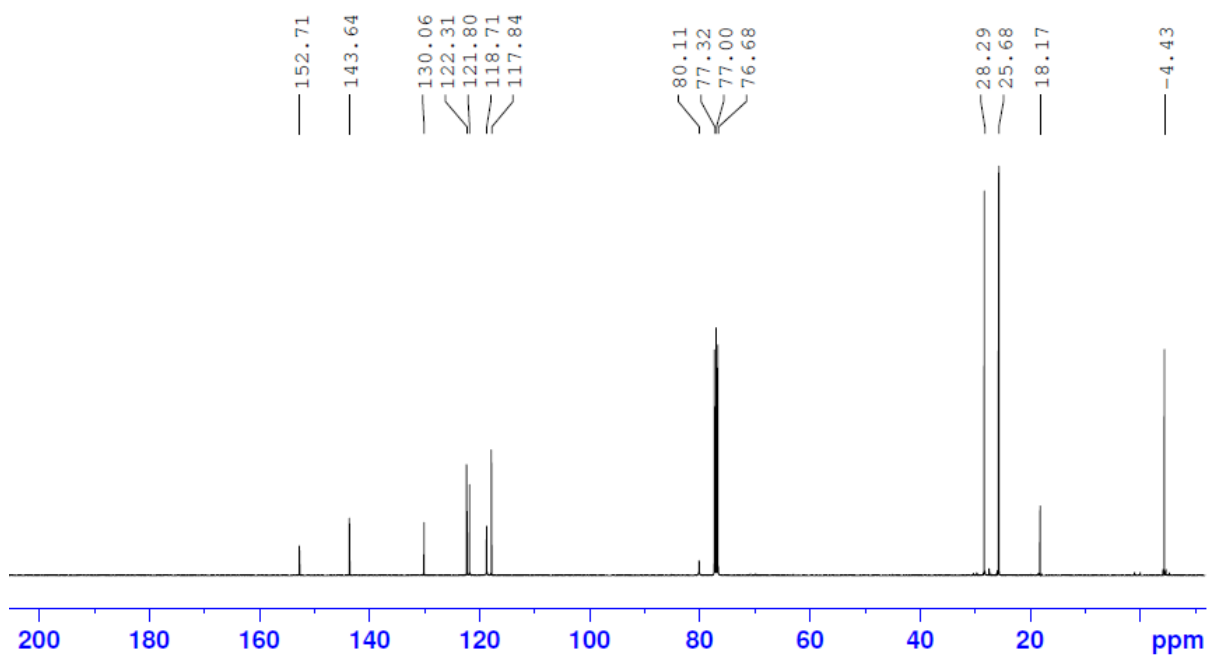




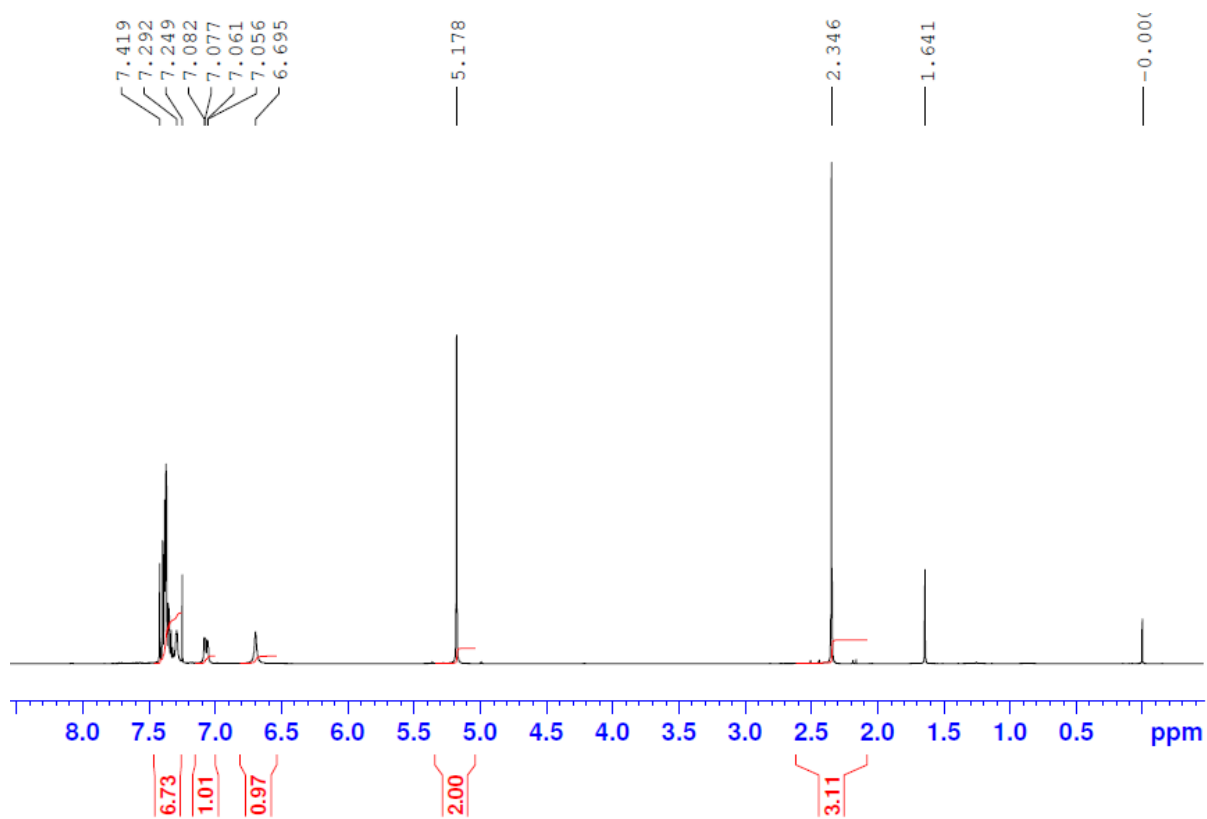
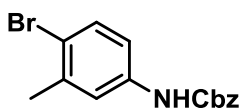
$^1\text{H NMR}$, CDCl_3 , 400 MHz



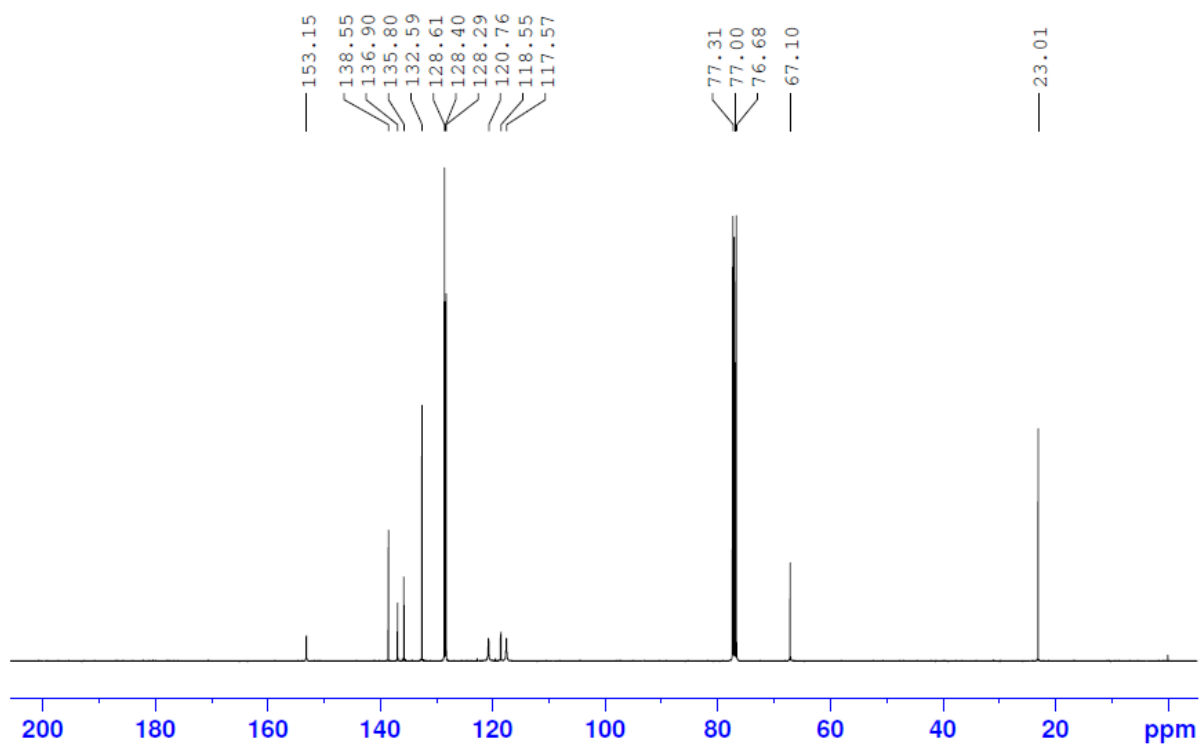
$^{13}\text{C NMR}$, CDCl_3 , 101 MHz



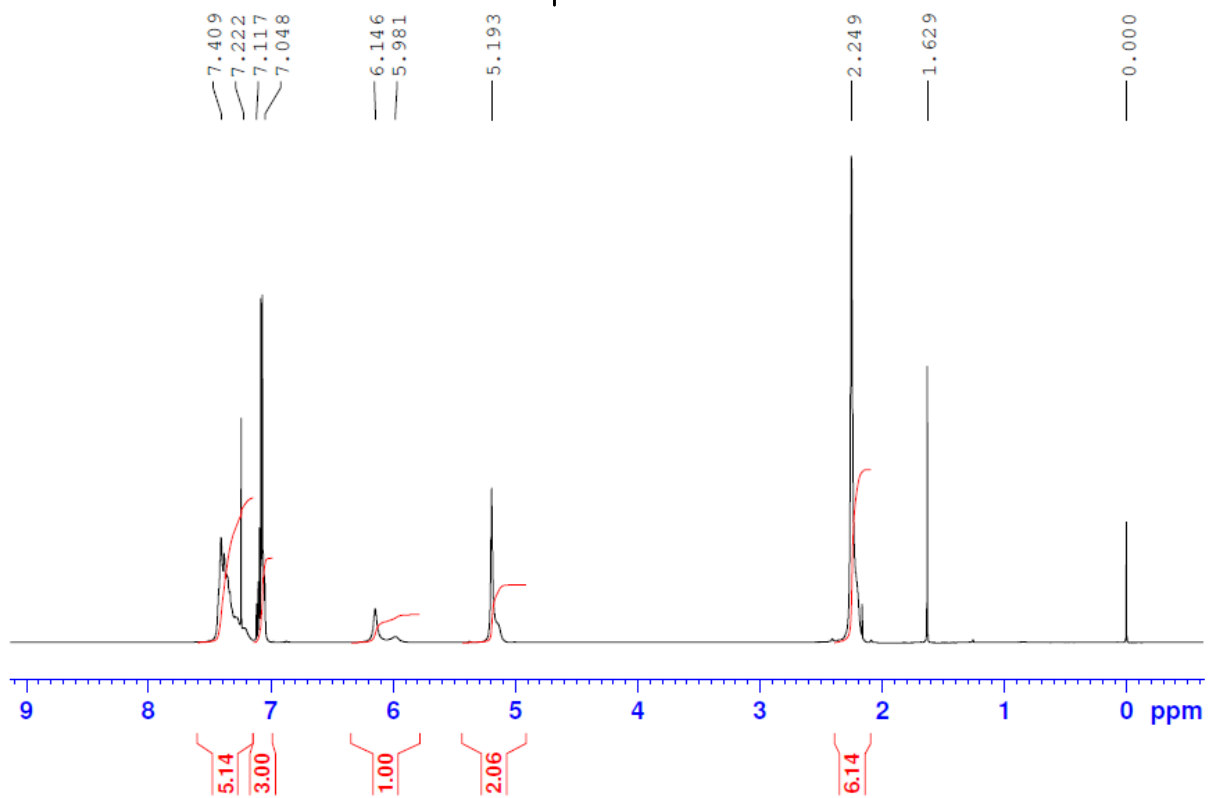
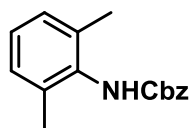
^1H NMR, CDCl_3 , 400 MHz



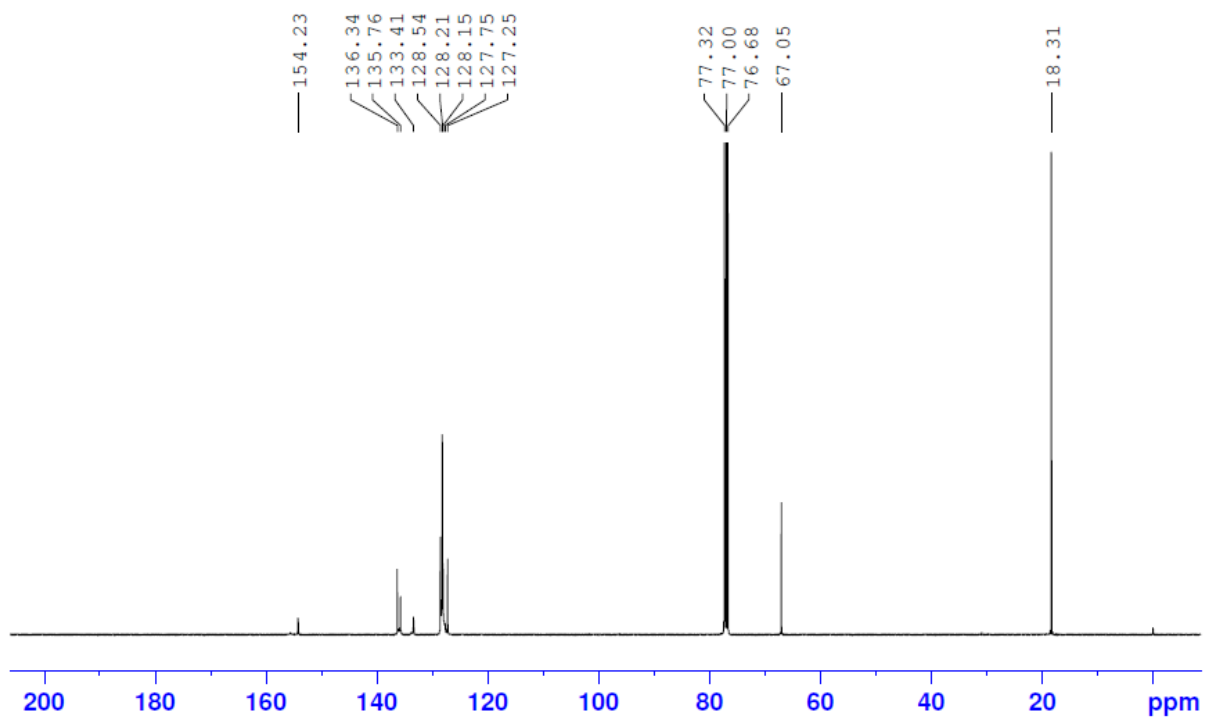
^{13}C NMR, CDCl_3 , 101 MHz

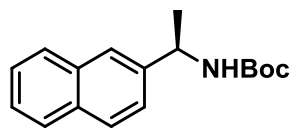


^1H NMR, CDCl_3 , 400 MHz

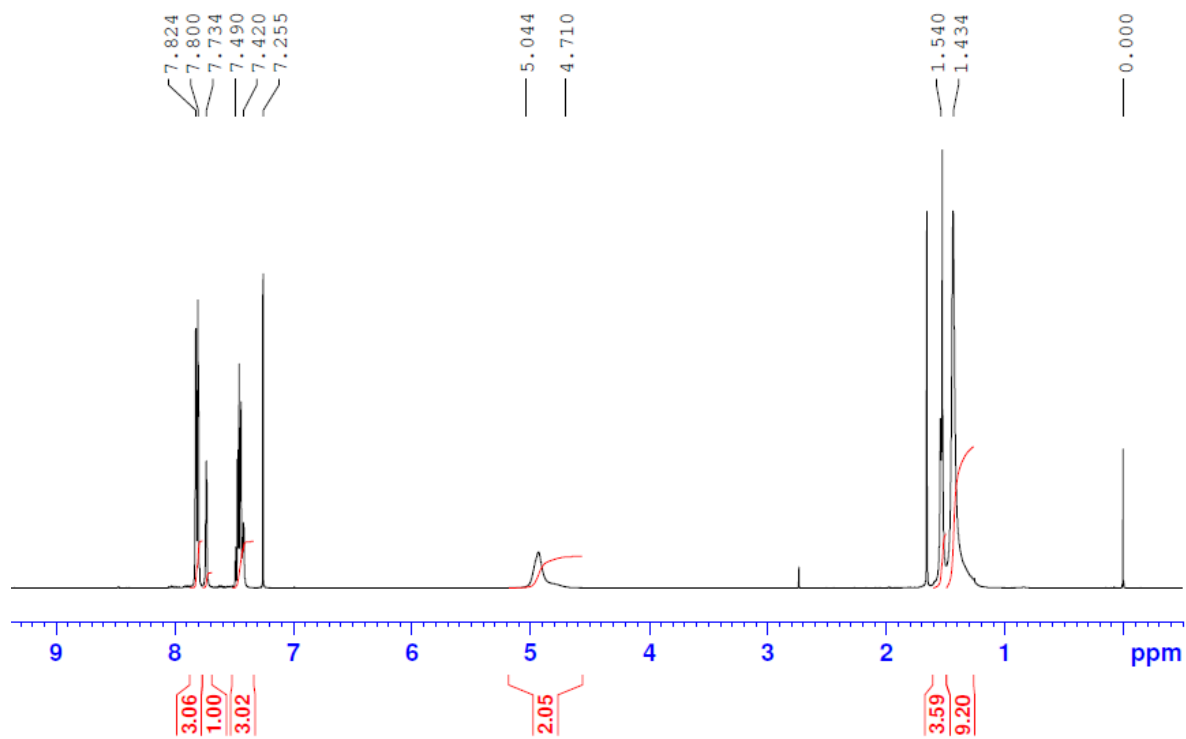


^{13}C NMR, CDCl_3 , 101 MHz

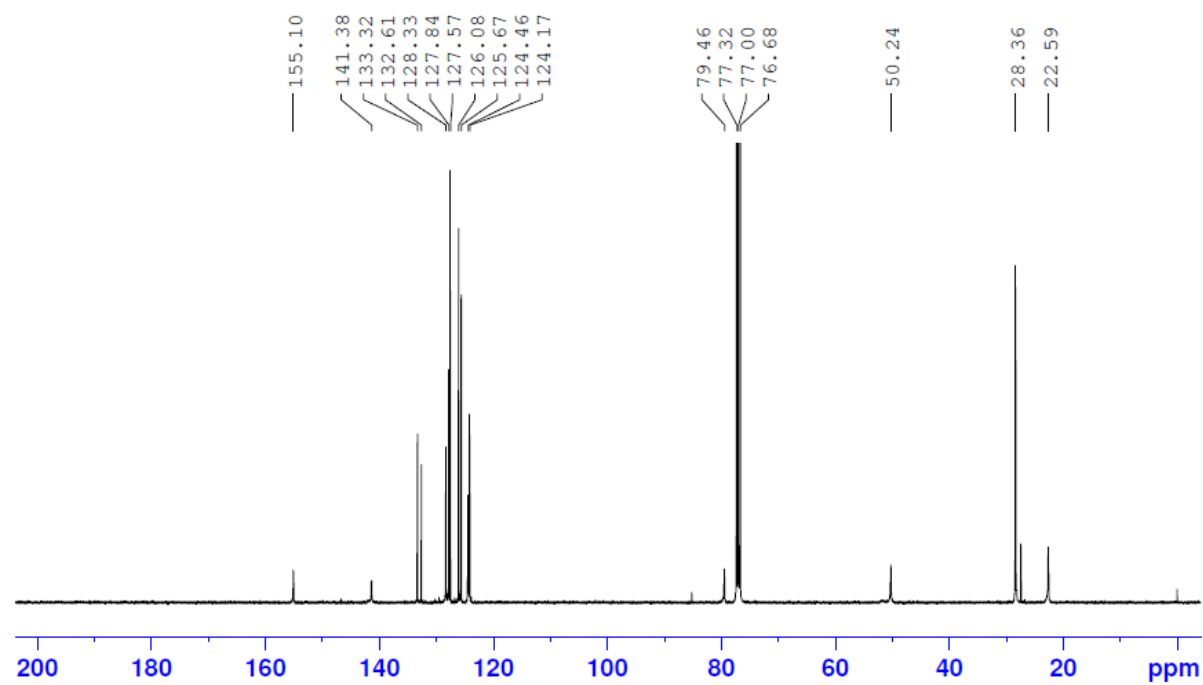


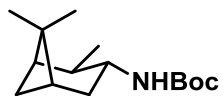


^1H NMR, CDCl_3 , 400 MHz

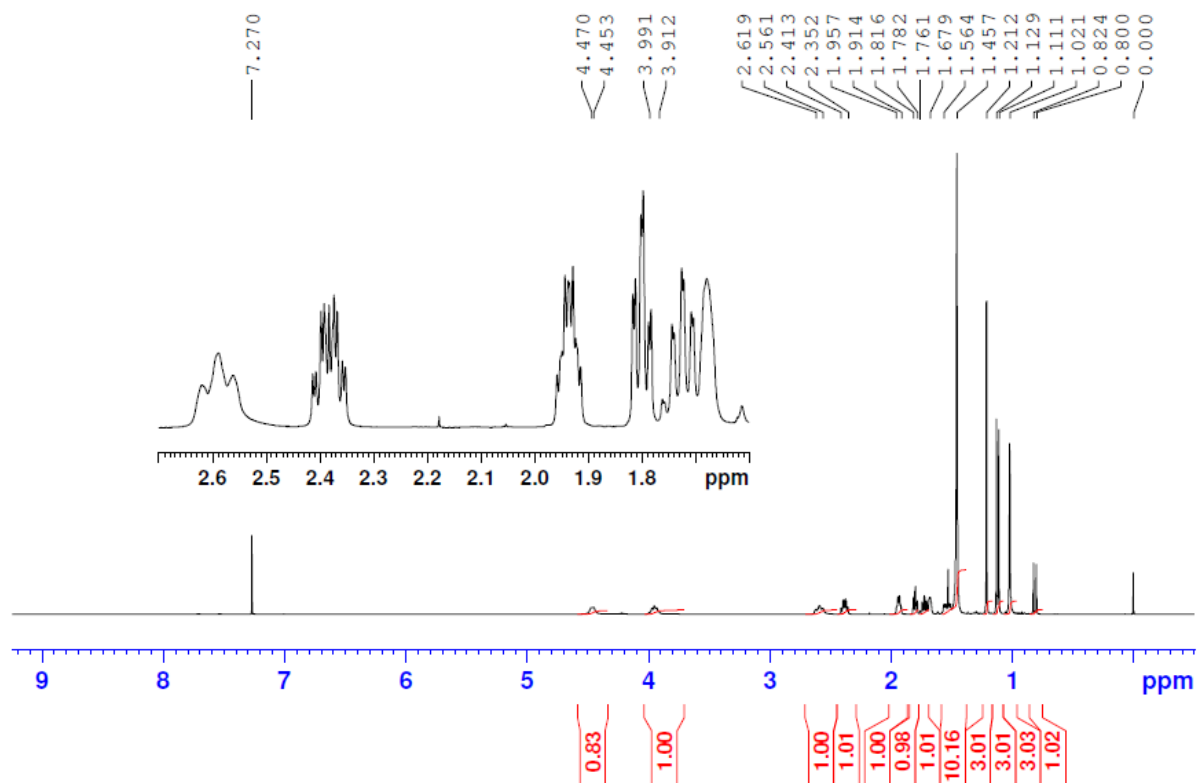


^{13}C NMR, CDCl_3 , 101 MHz

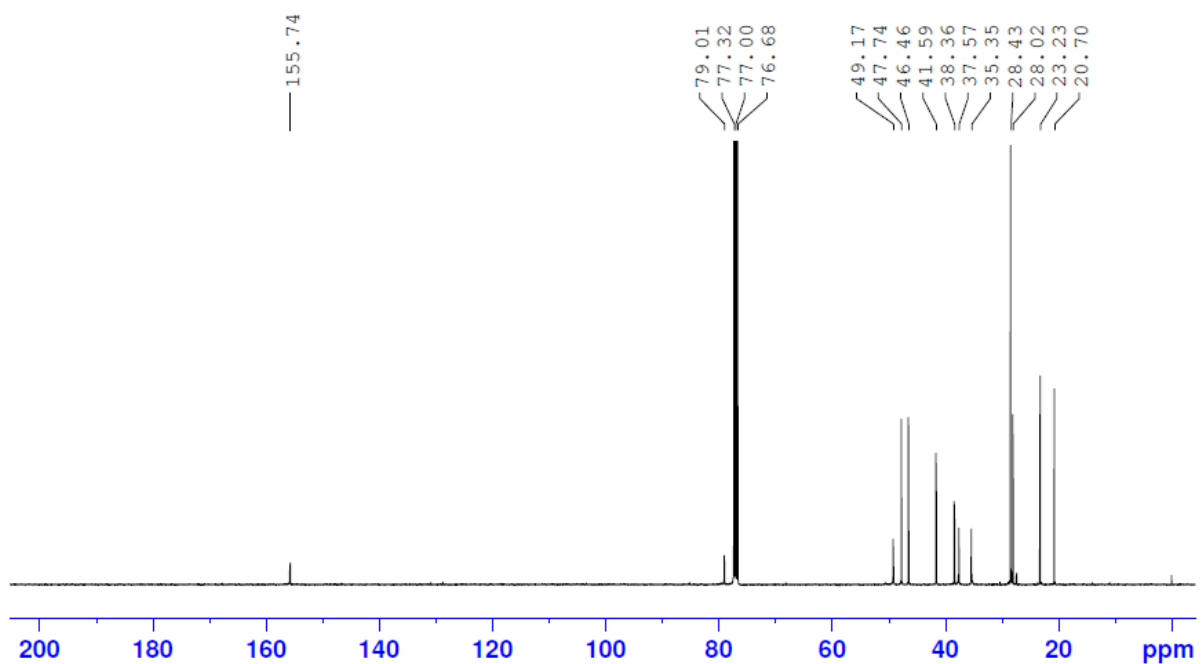


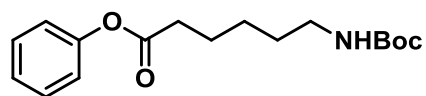


^1H NMR, CDCl_3 , 400 MHz

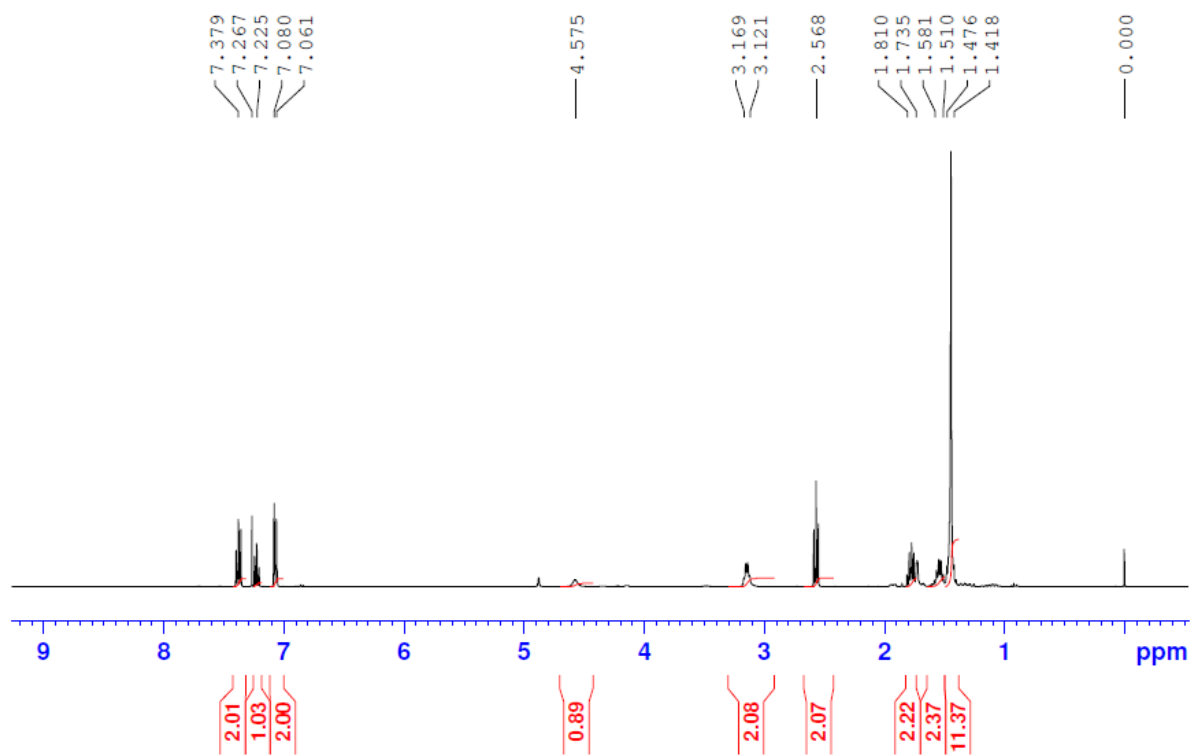


^{13}C NMR, CDCl_3 , 101 MHz

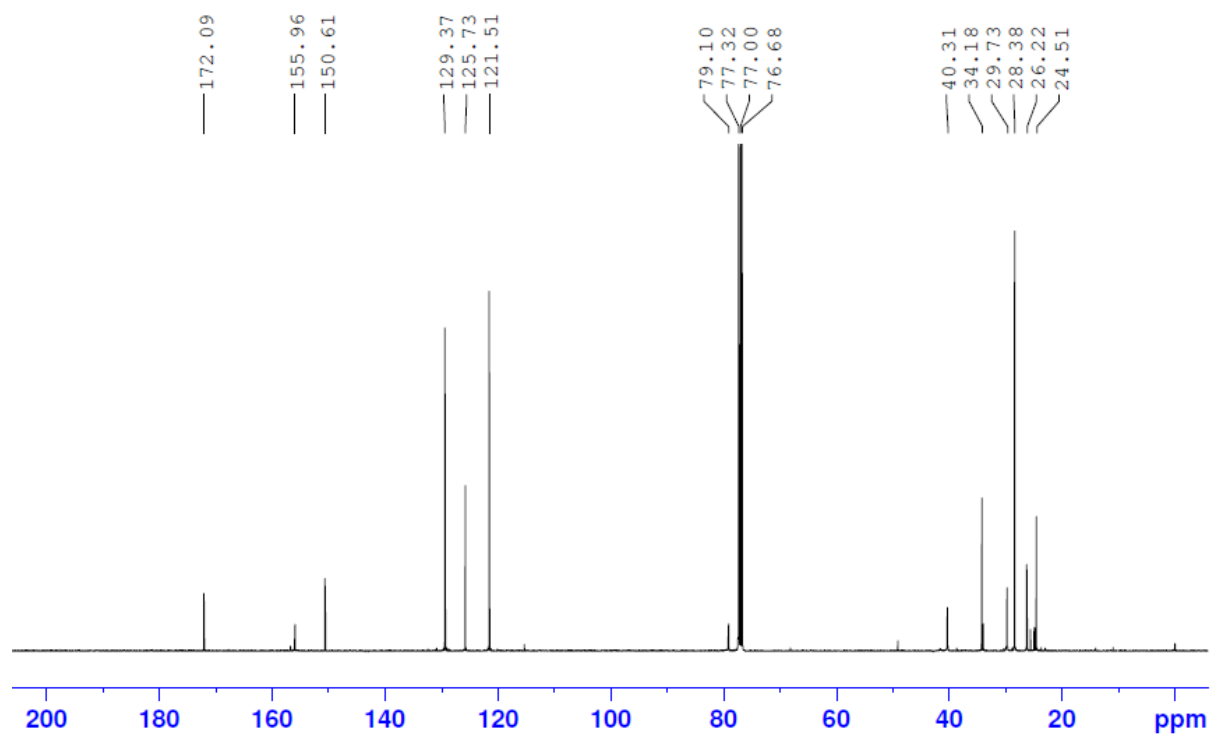


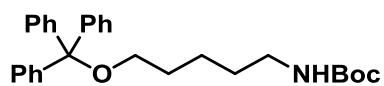


$^1\text{H NMR}$, CDCl_3 , 400 MHz

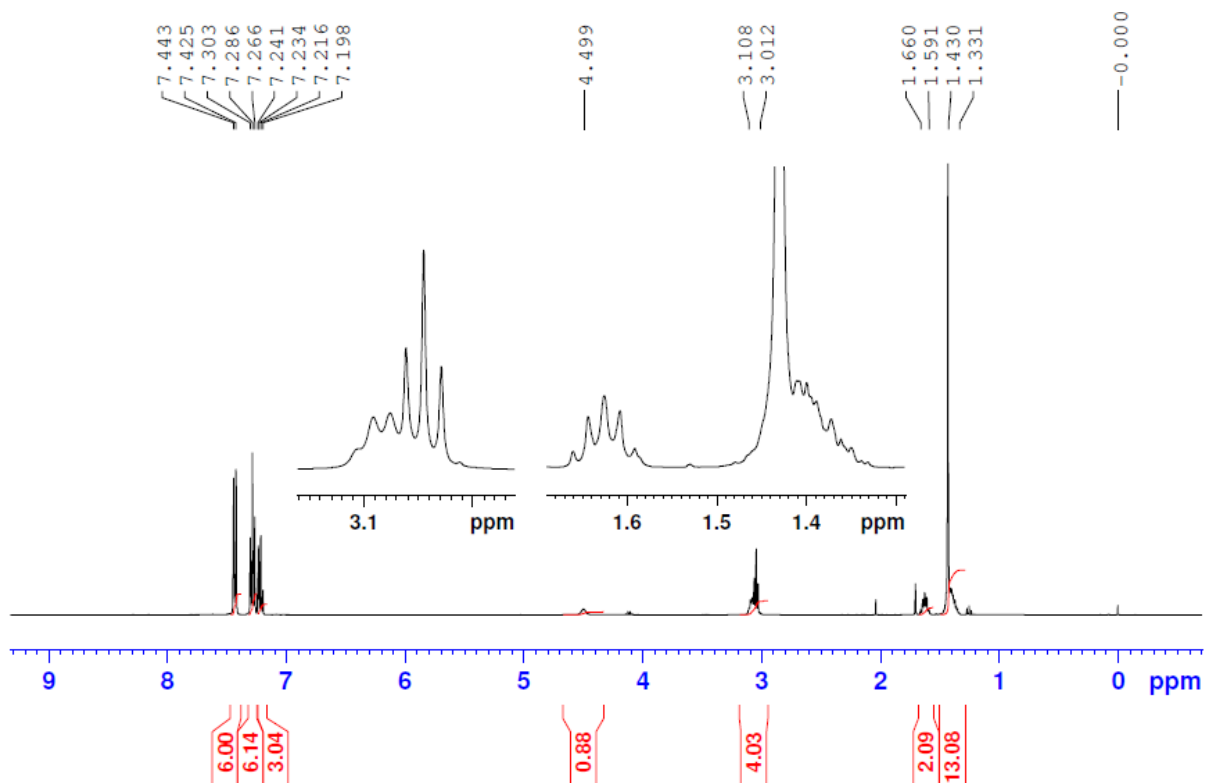


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

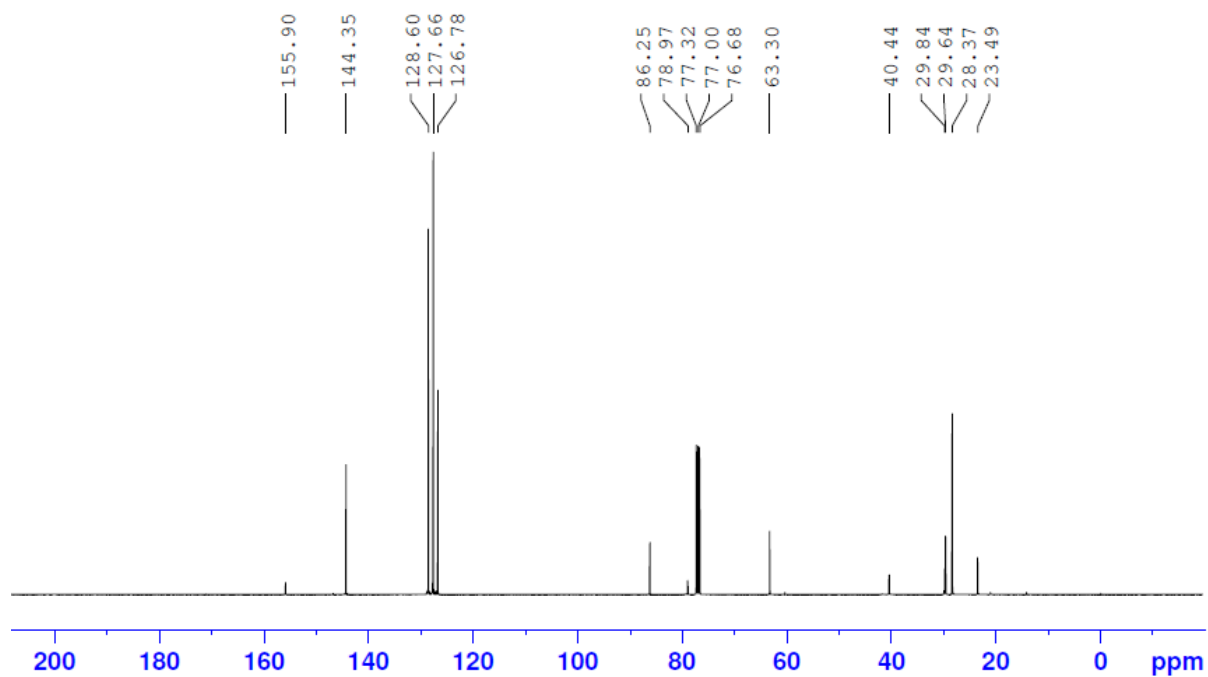




$^1\text{H NMR}$, CDCl_3 , 400 MHz

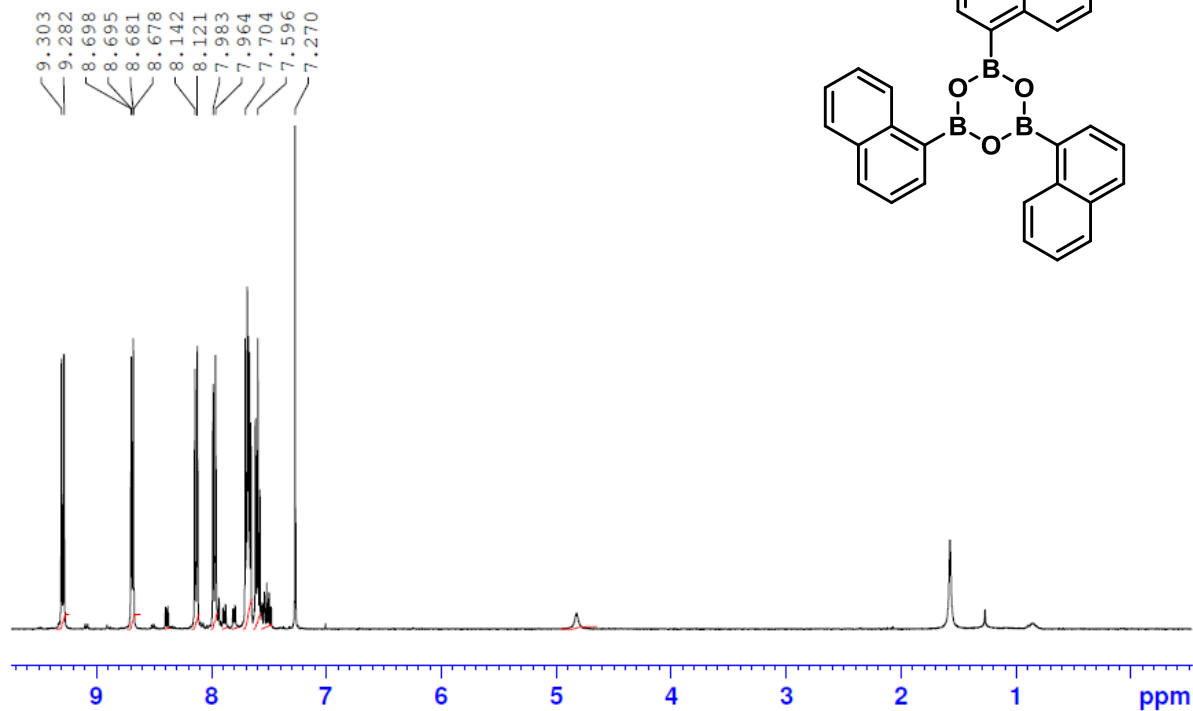


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

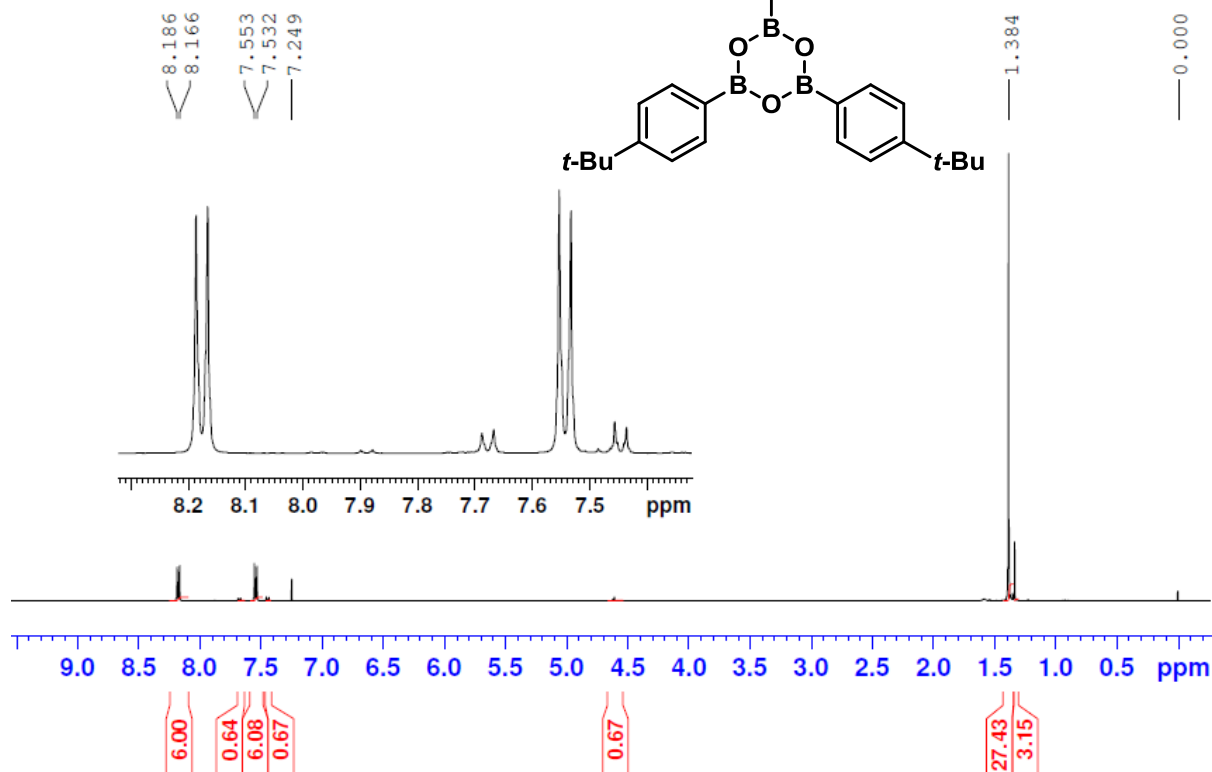


¹H NMR Spectra of Novel Trisarylboroxines

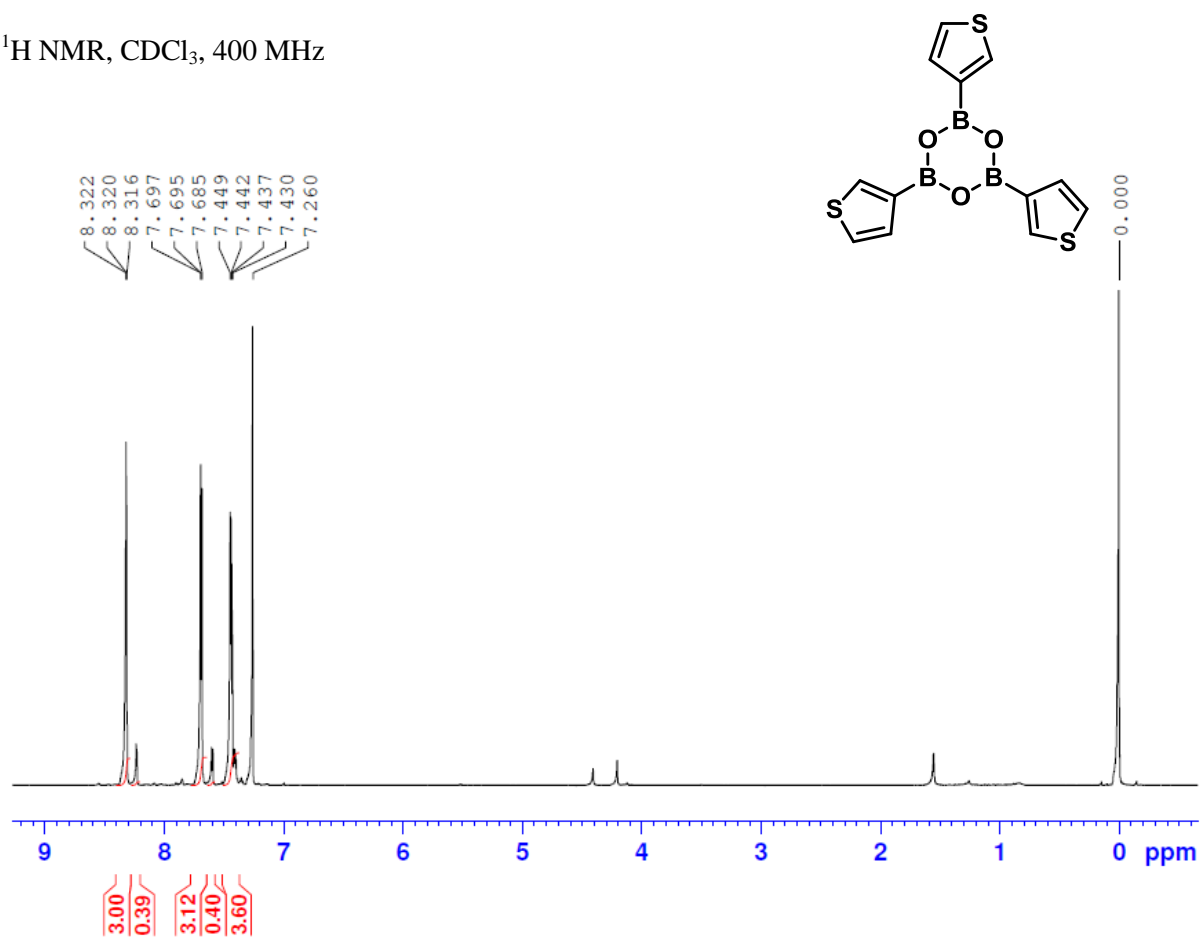
¹H NMR, CDCl₃, 400 MHz



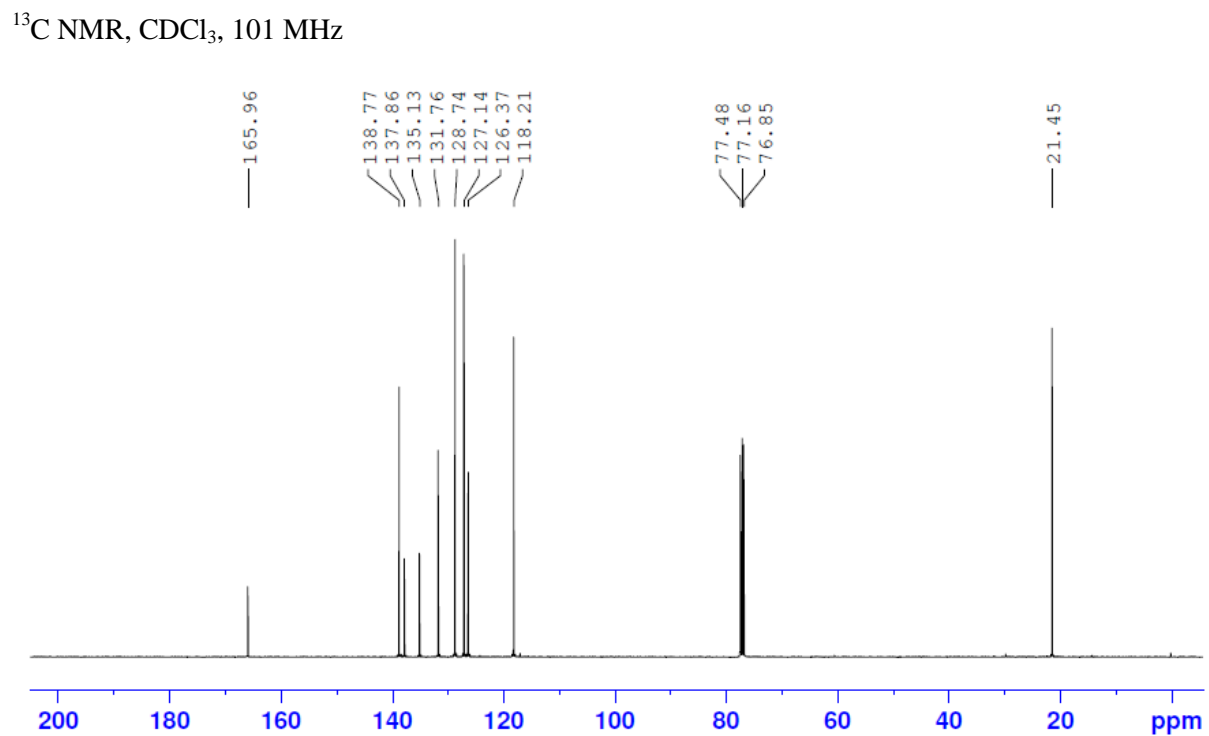
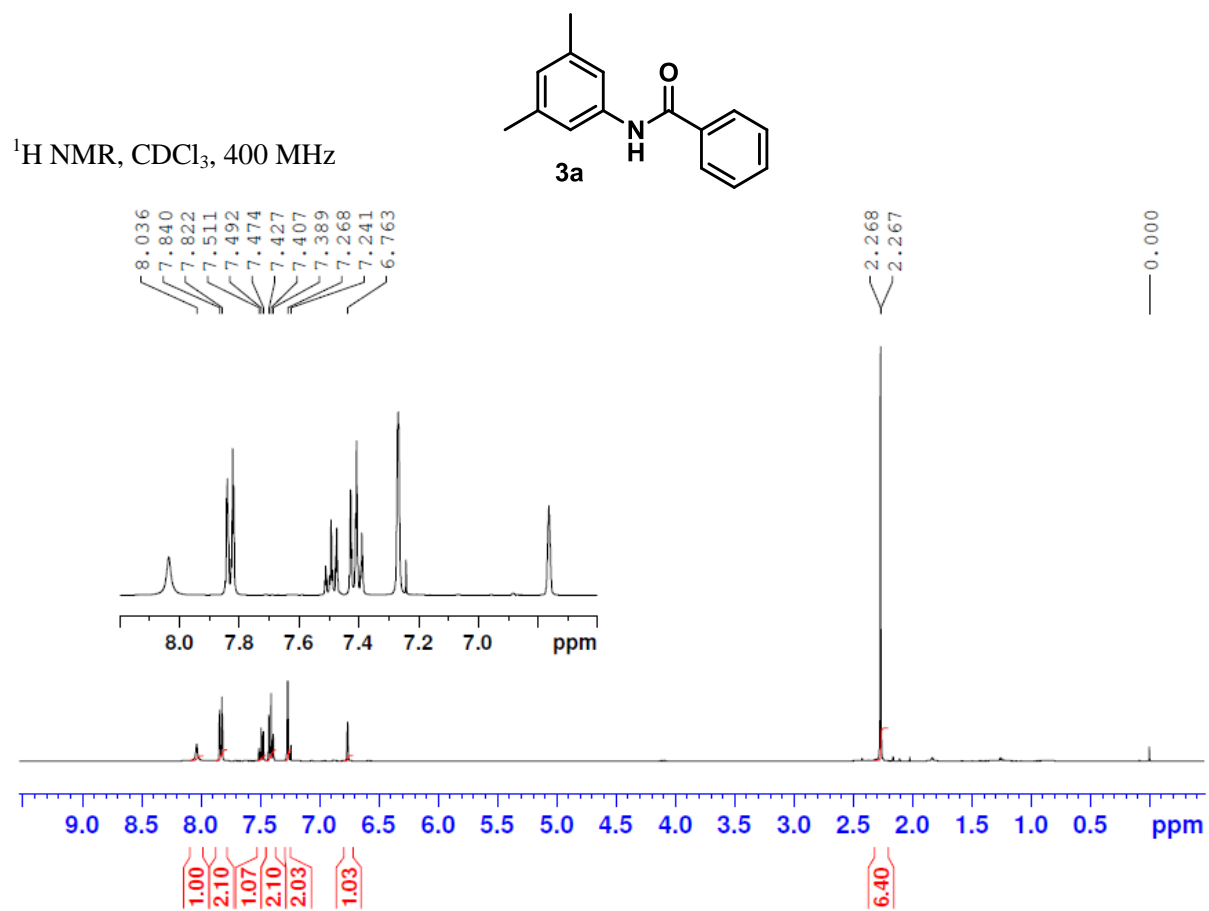
¹H NMR, CDCl₃, 400 MHz

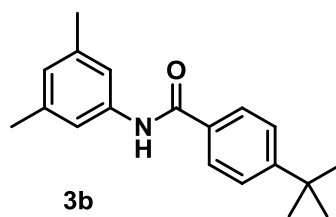


^1H NMR, CDCl_3 , 400 MHz

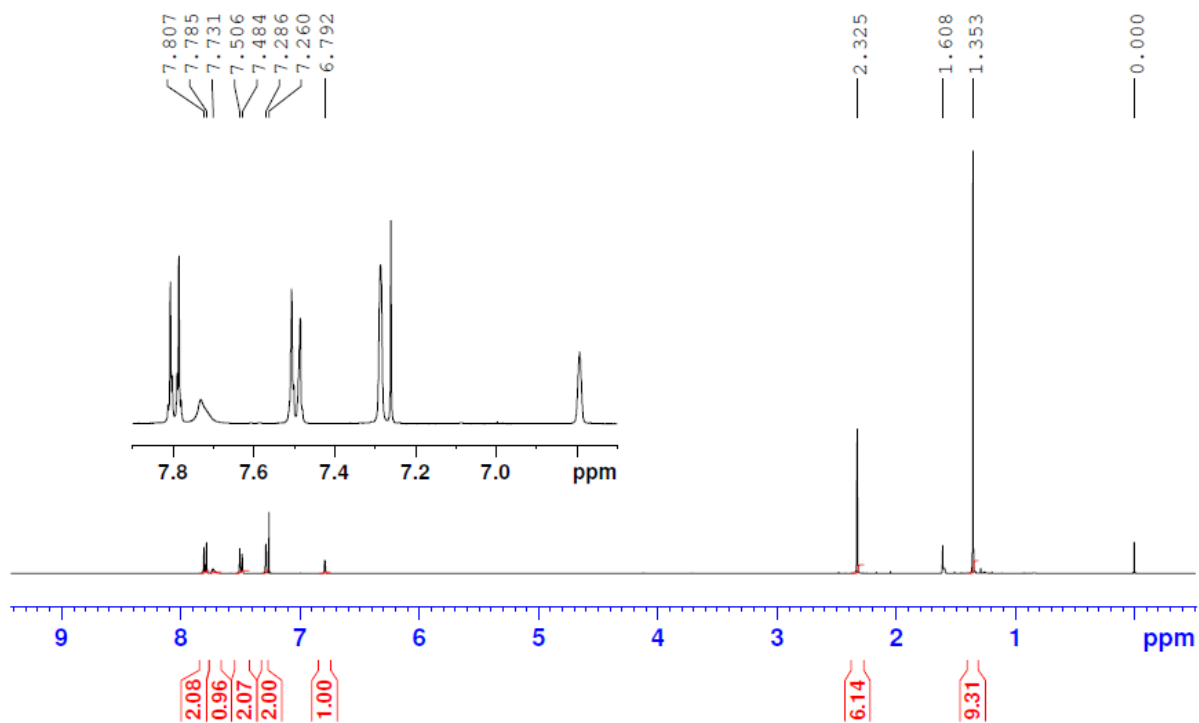


^1H and ^{13}C NMR Spectra of Amide Products

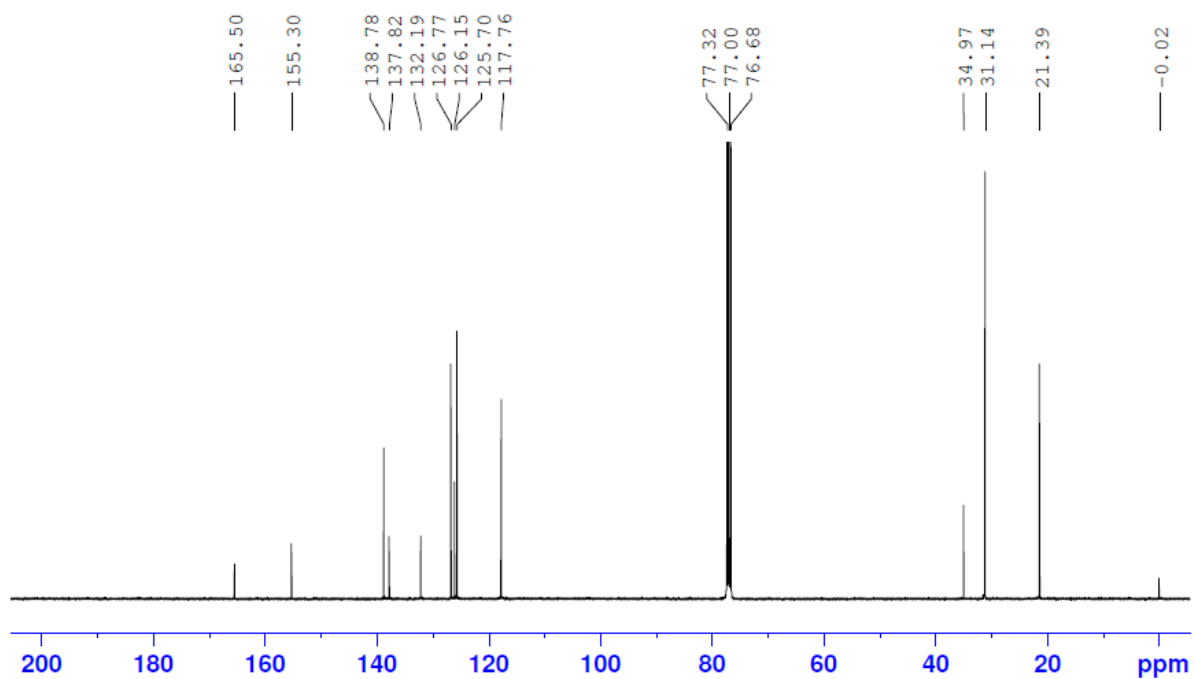


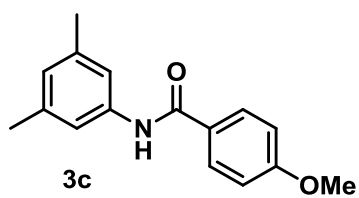


^1H NMR, CDCl_3 , 400 MHz

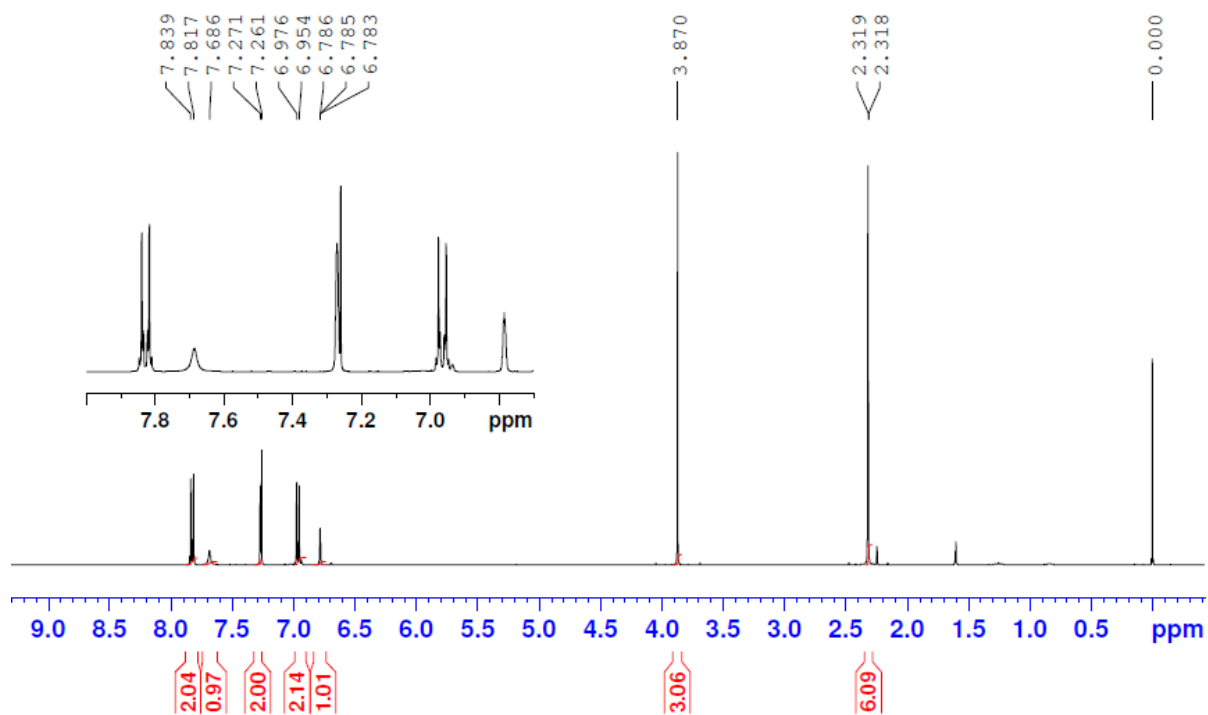


^{13}C NMR, CDCl_3 , 101 MHz

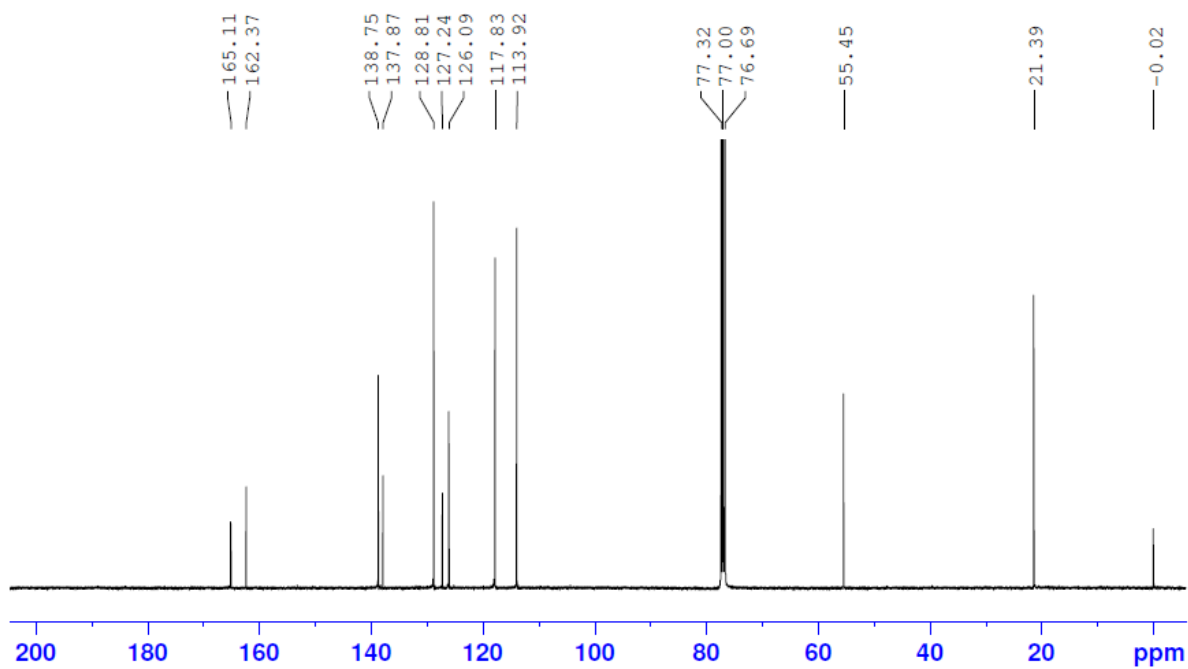


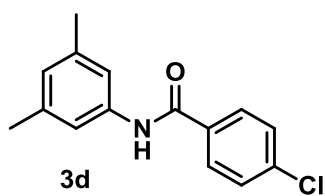


$^1\text{H NMR}$, CDCl_3 , 400 MHz

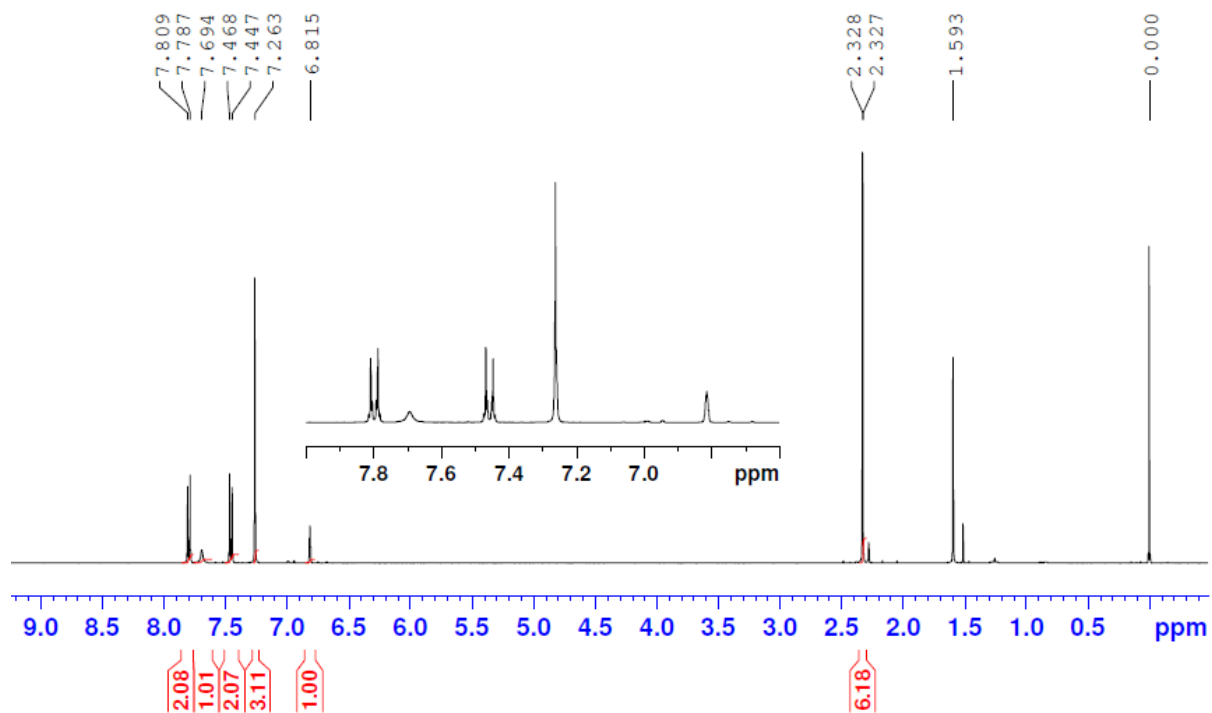


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

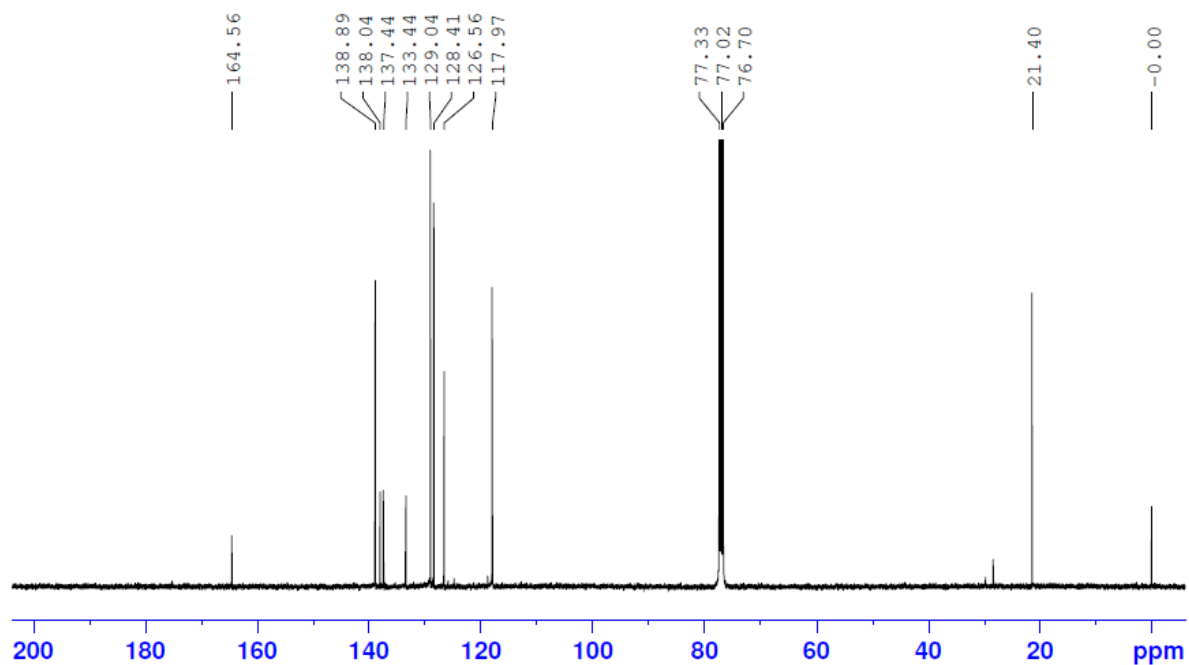


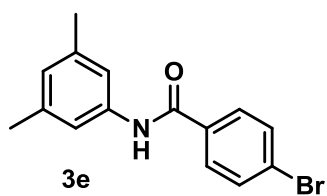


$^1\text{H NMR}$, CDCl_3 , 400 MHz

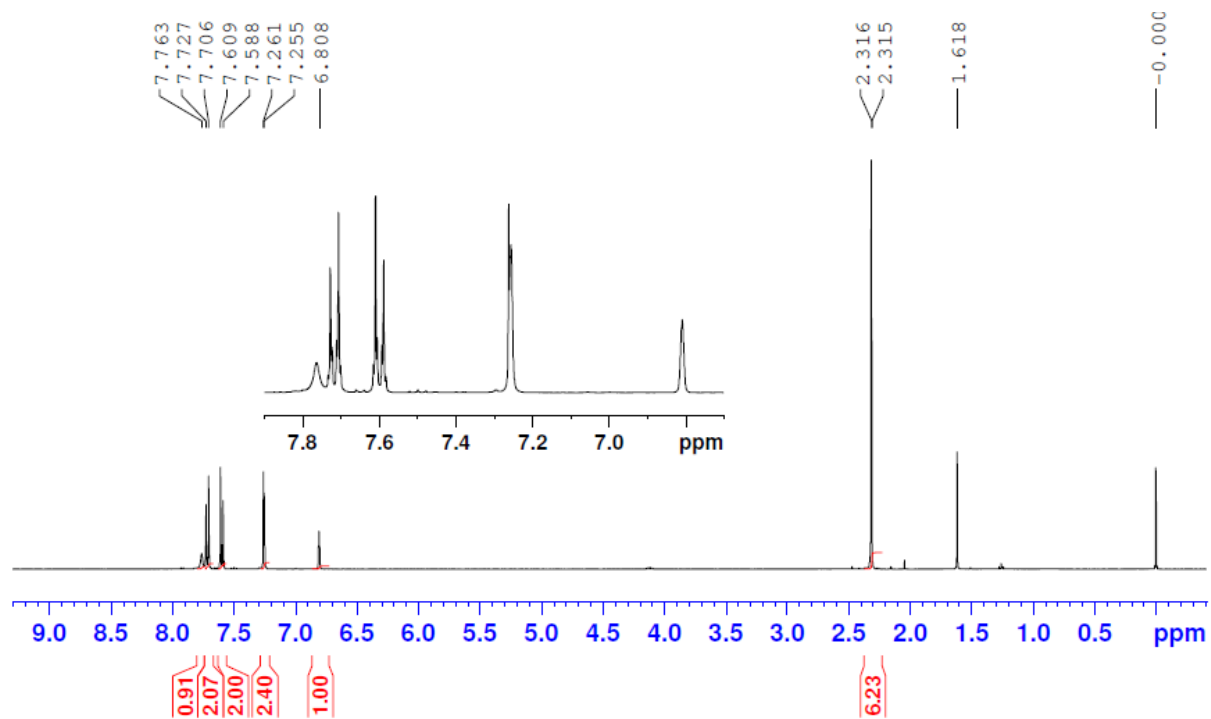


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

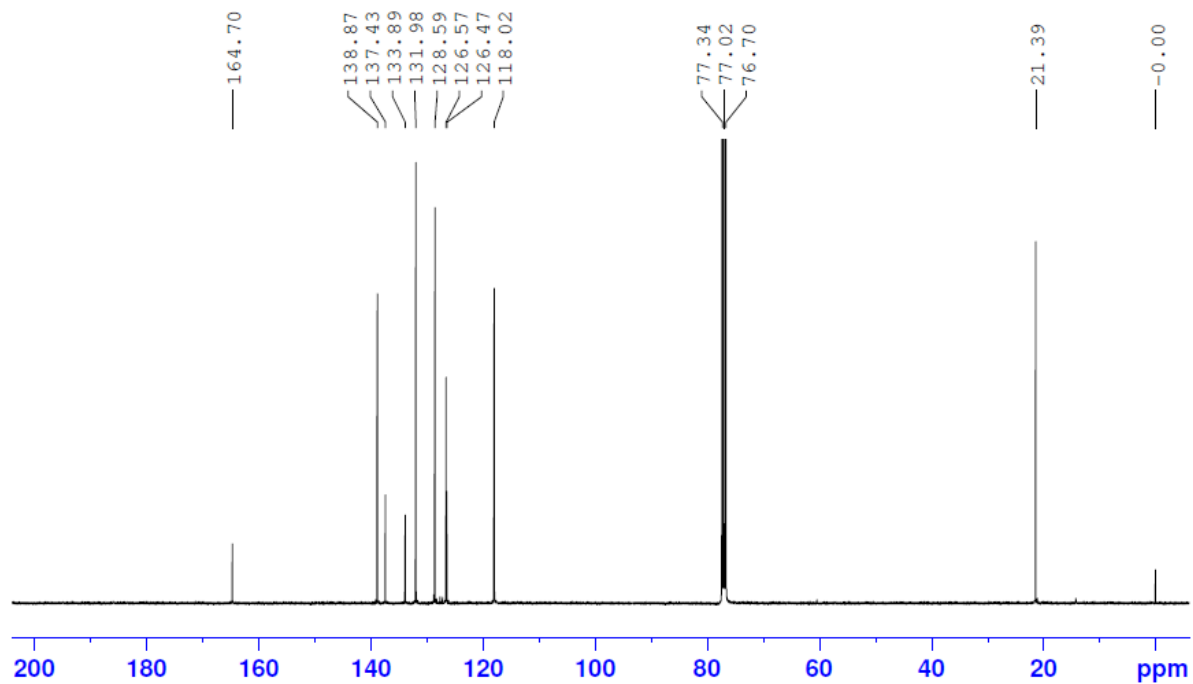


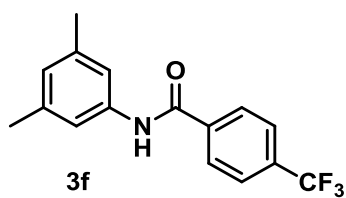


$^1\text{H NMR}$, CDCl_3 , 400 MHz

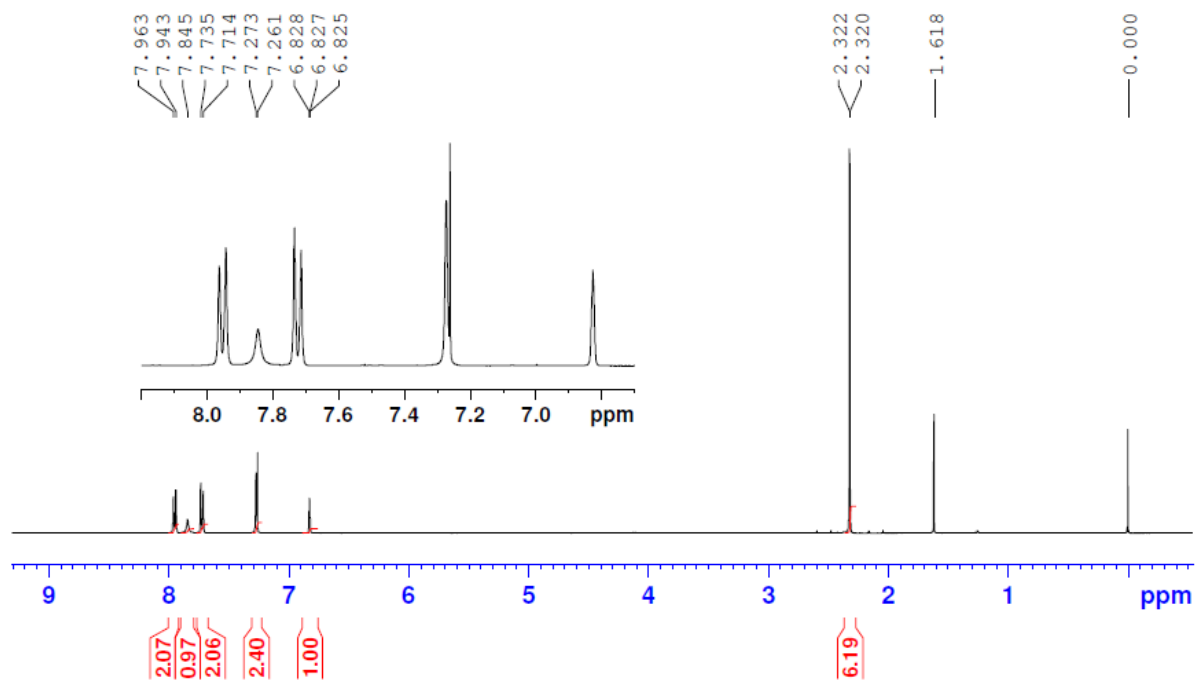


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

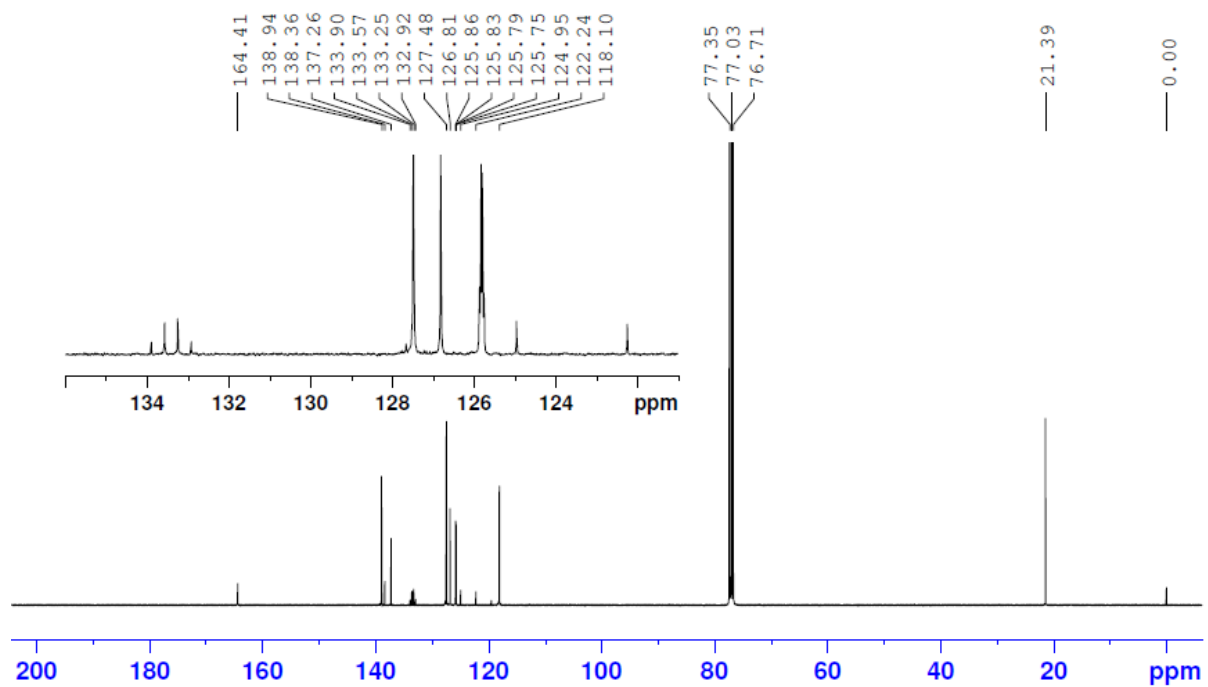


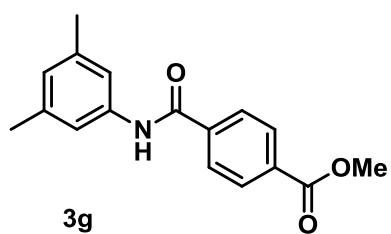


¹H NMR, CDCl₃, 400 MHz

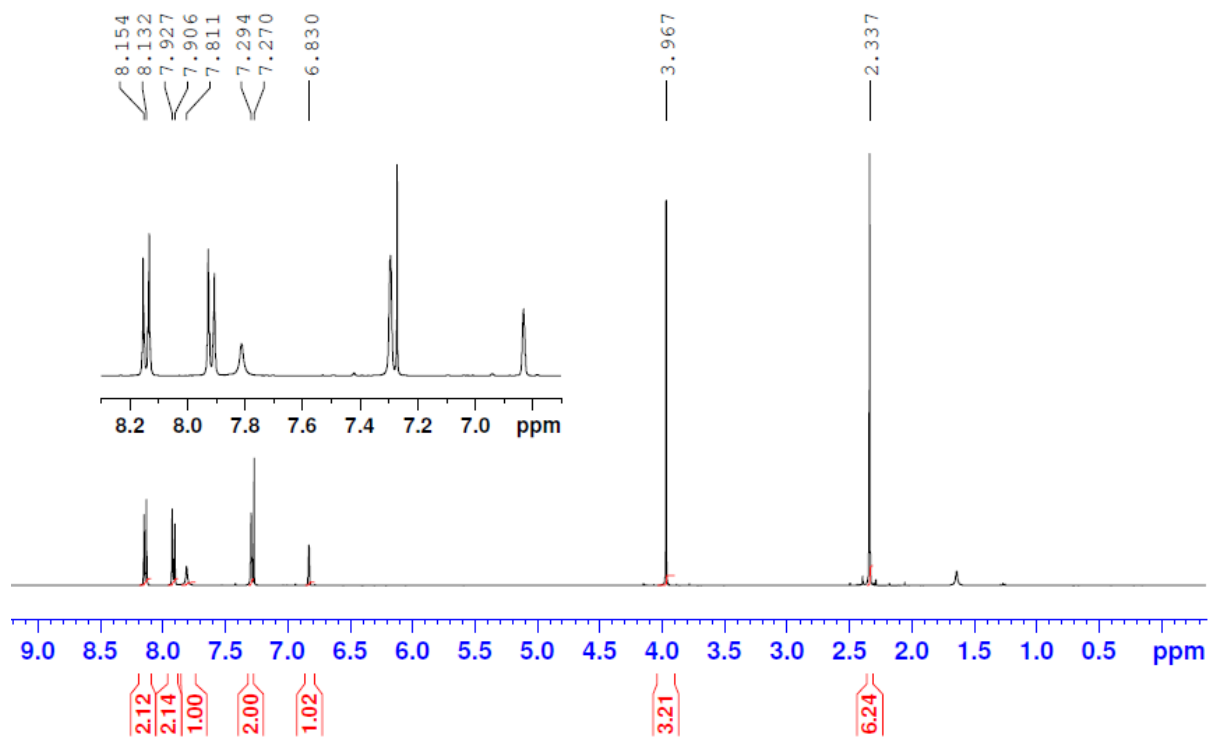


¹³C NMR, CDCl₃, 101 MHz

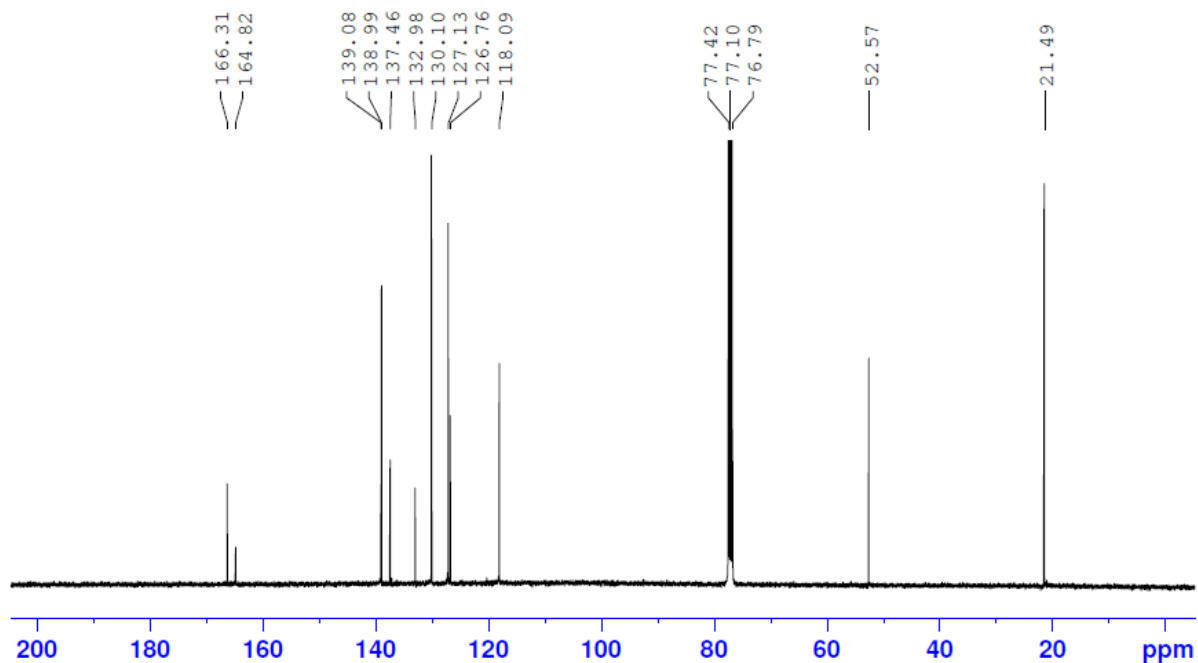


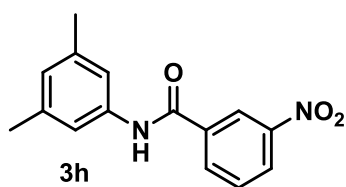


$^1\text{H NMR}$, CDCl_3 , 400 MHz

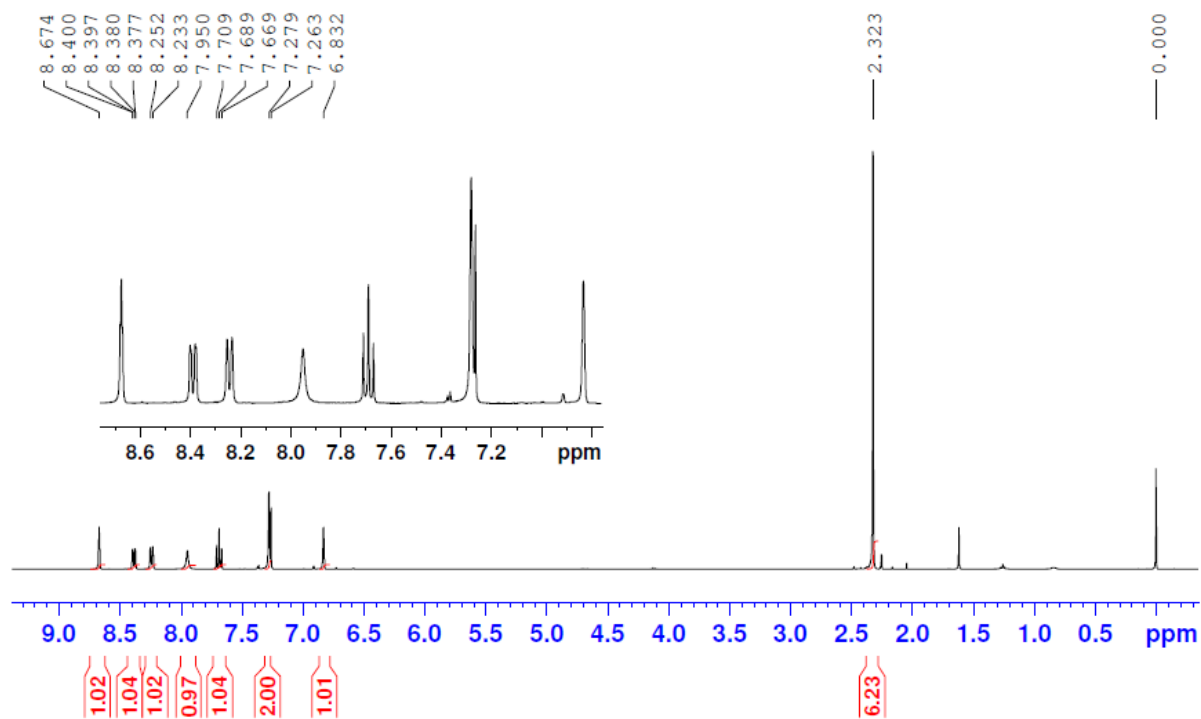


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

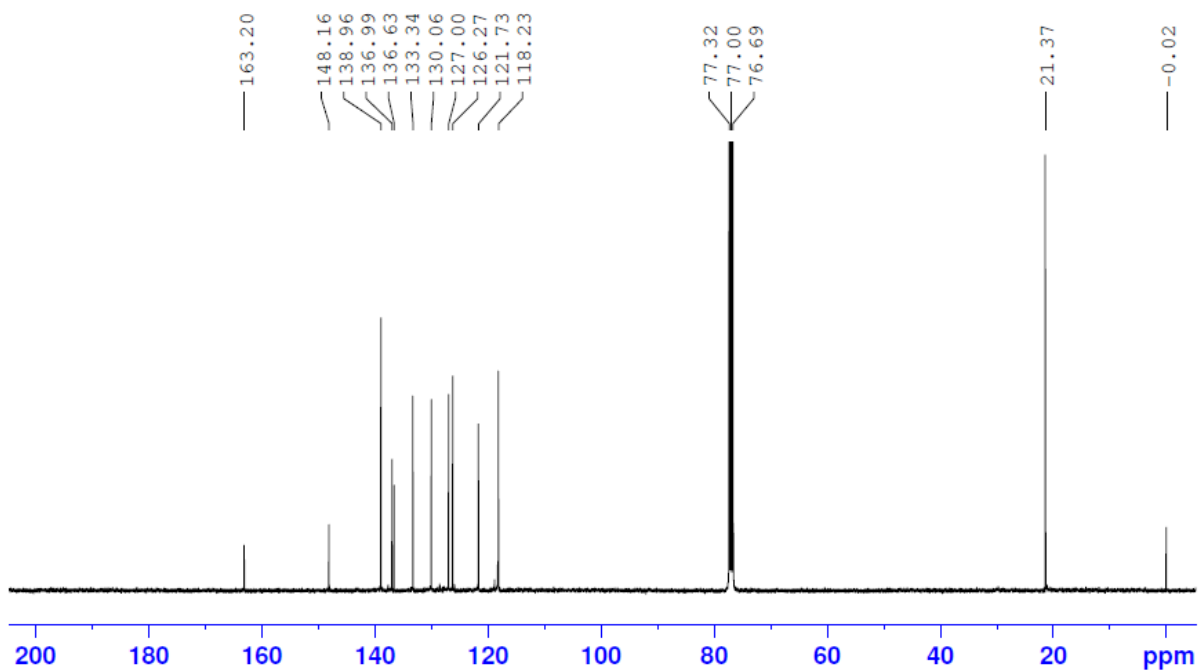


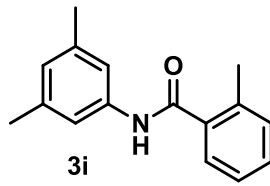


$^1\text{H NMR}$, CDCl_3 , 400 MHz

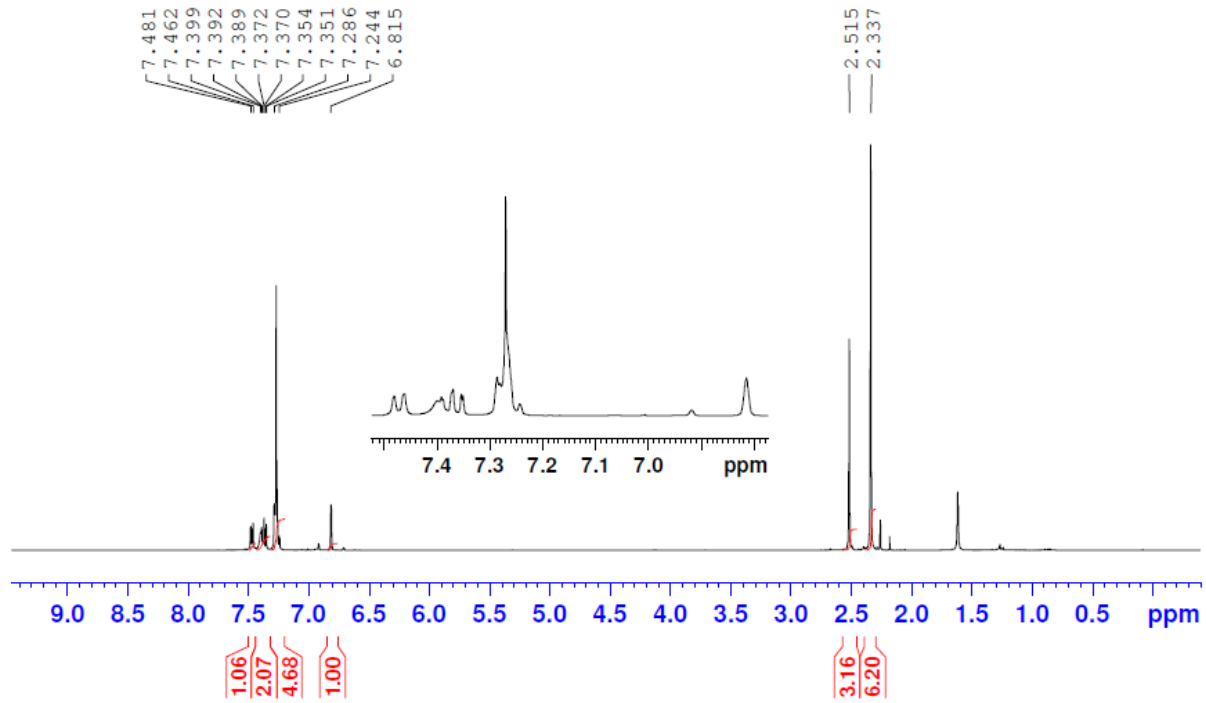


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

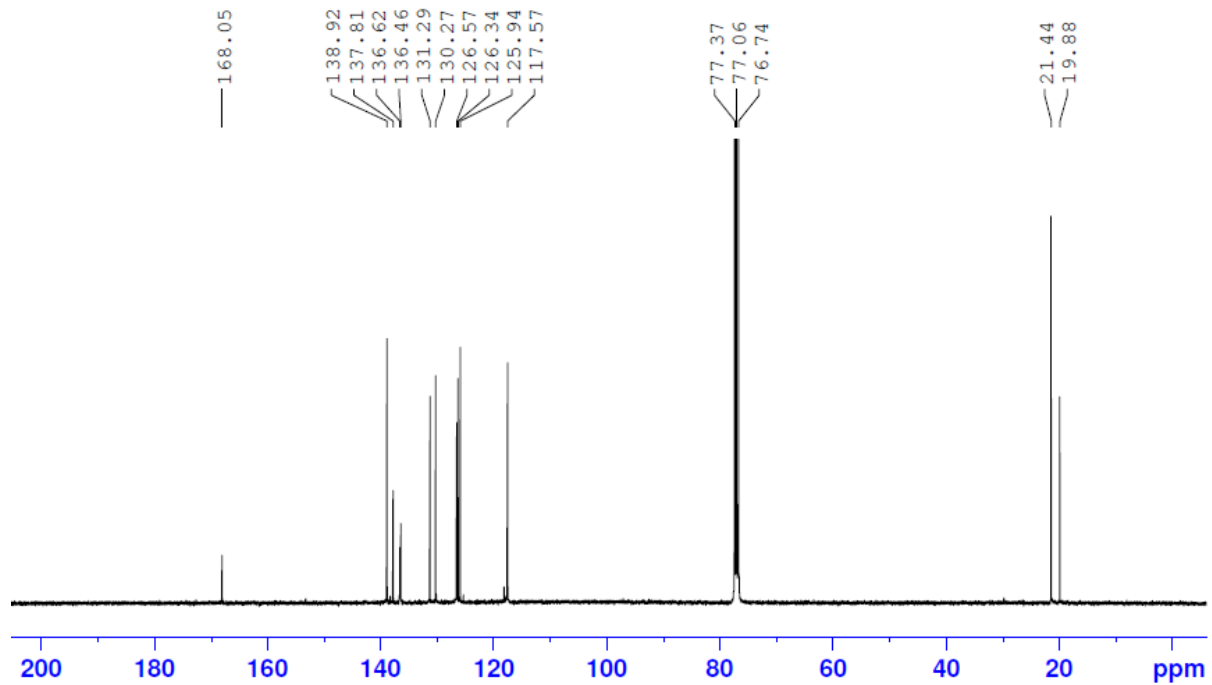


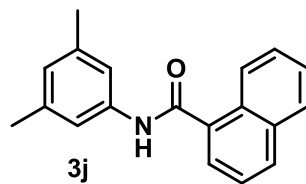


$^1\text{H NMR}$, CDCl_3 , 400 MHz

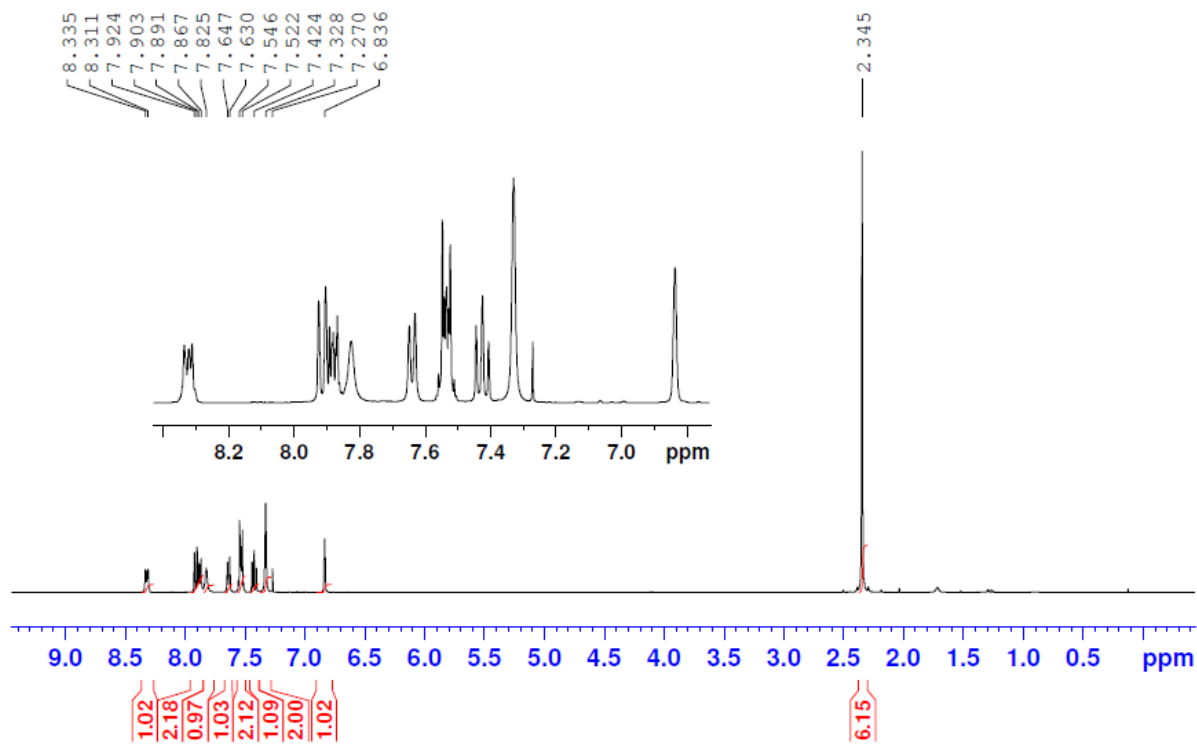


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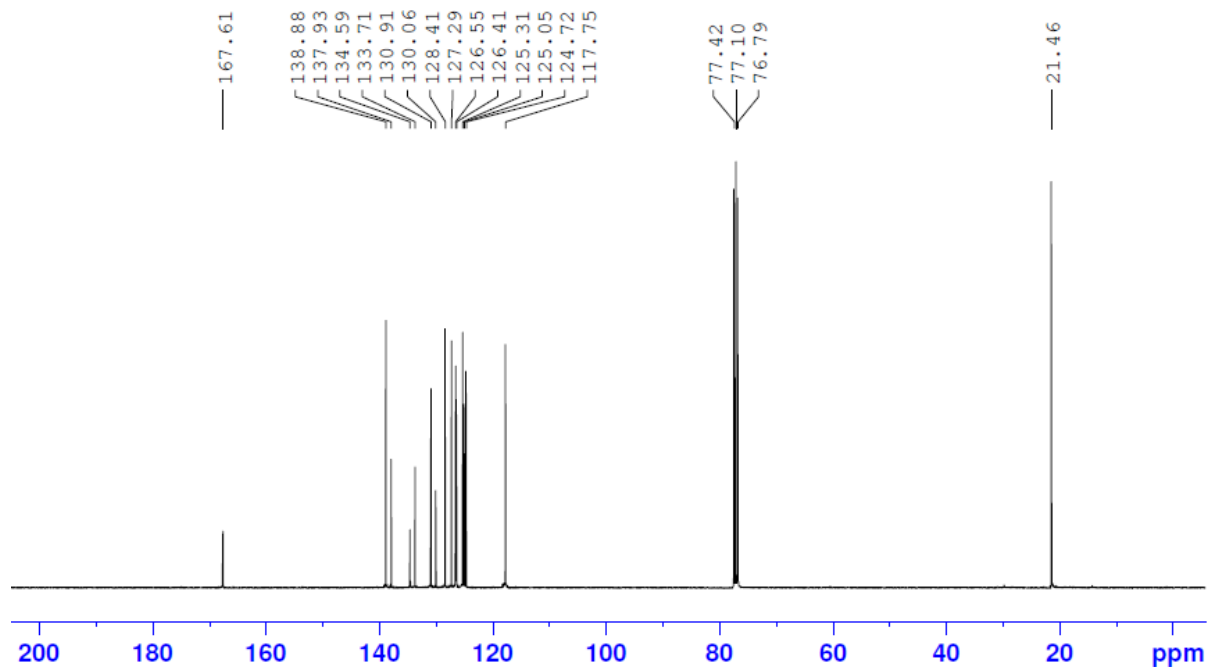


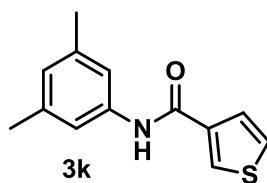


$^1\text{H NMR}$, CDCl_3 , 400 MHz

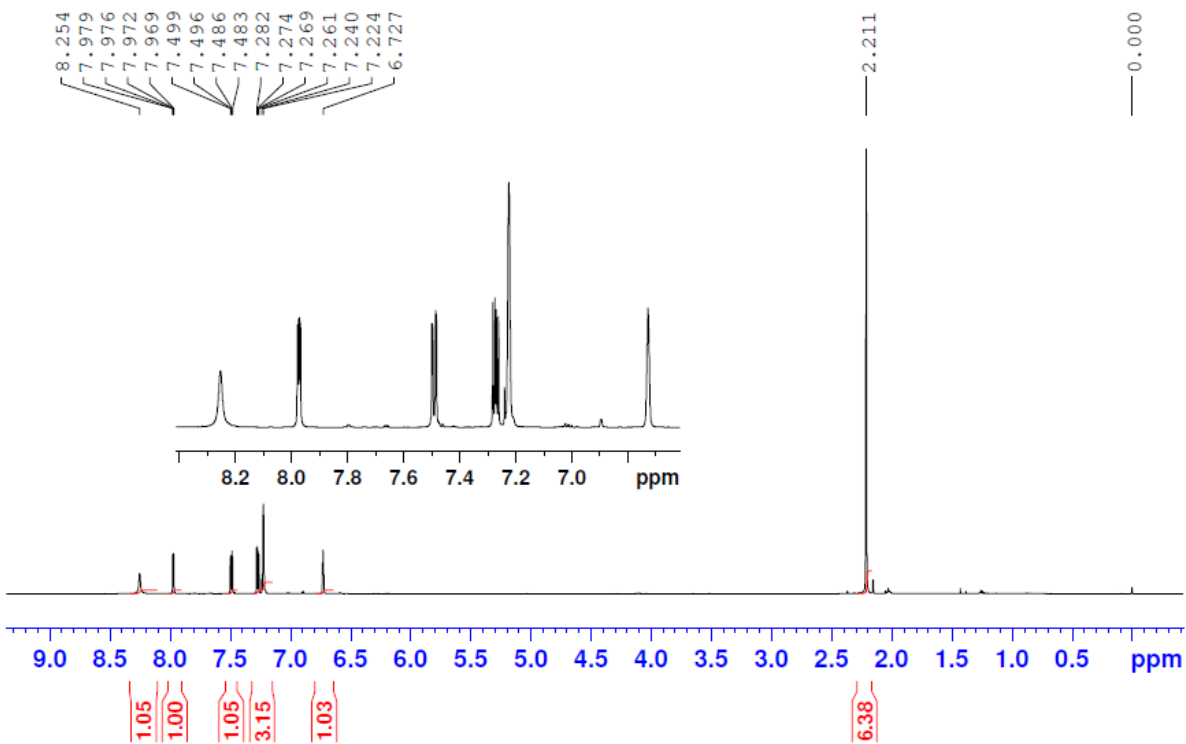


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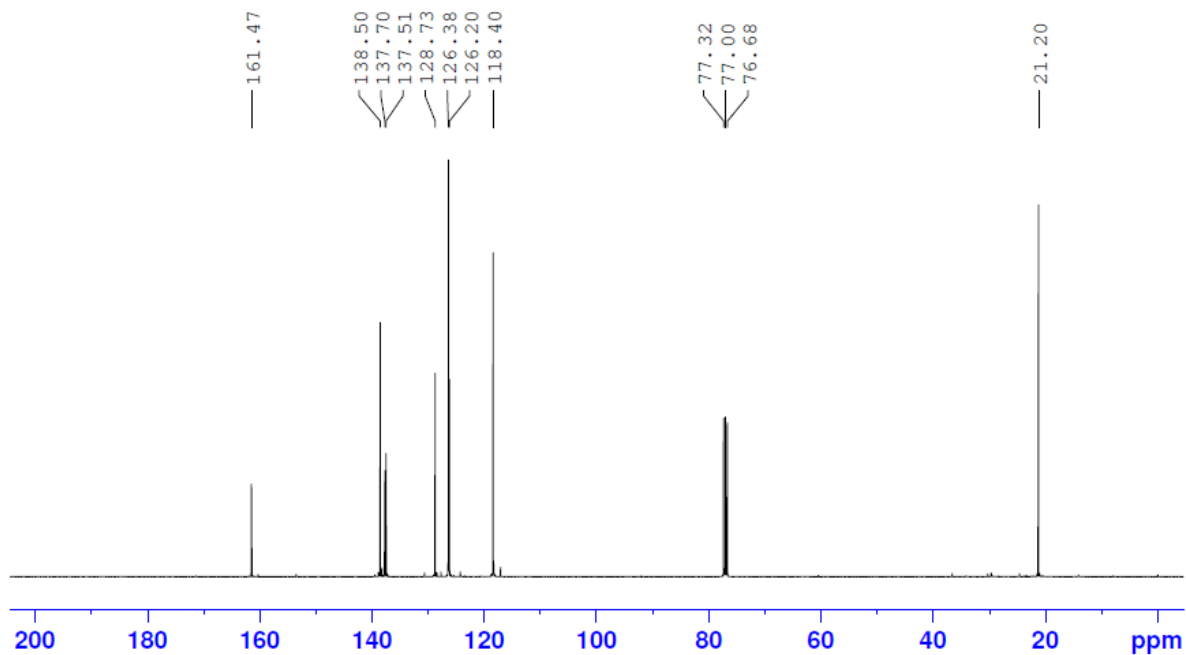


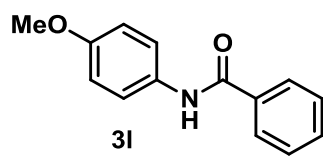


^1H NMR, CDCl_3 , 400 MHz

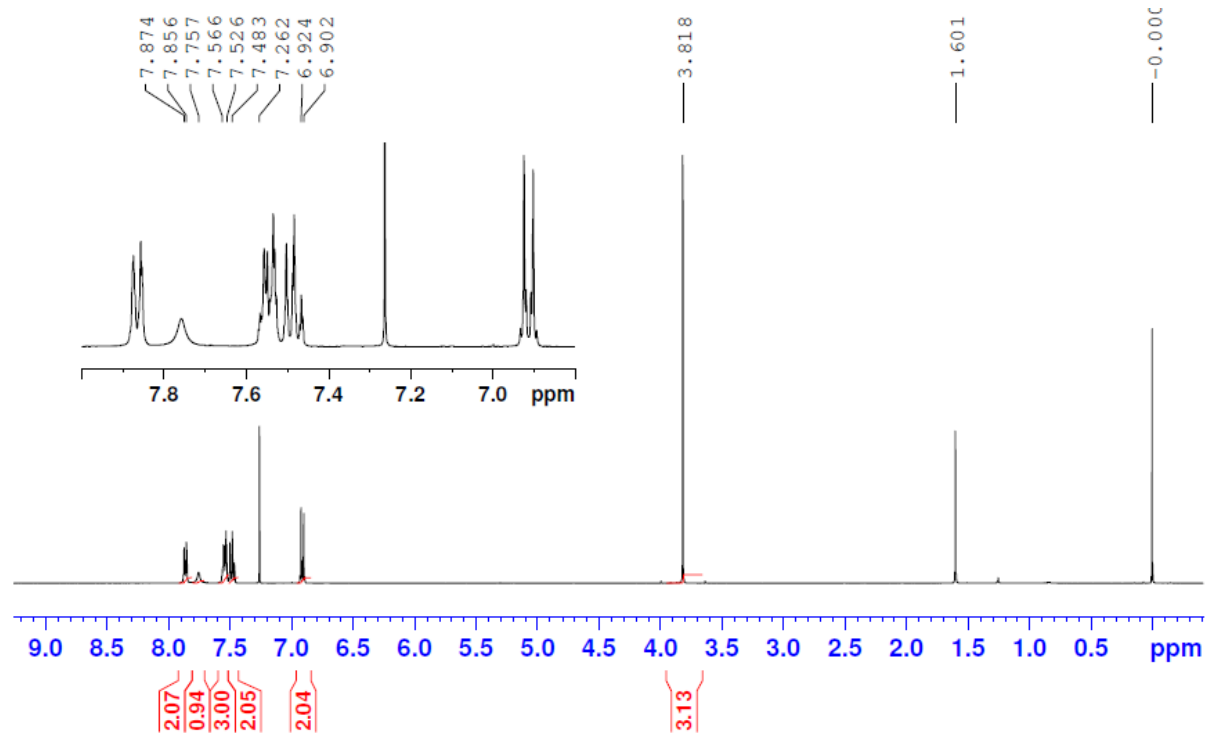


^{13}C NMR, CDCl_3 , 101 MHz

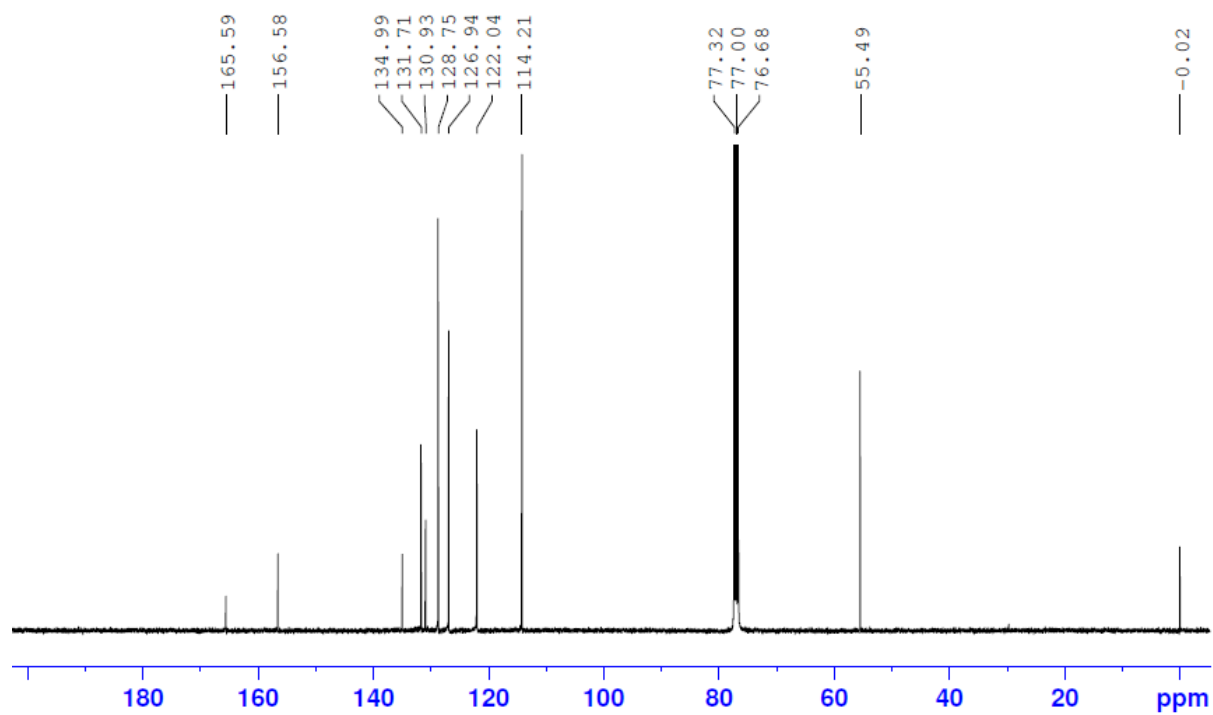


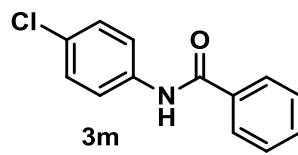


^1H NMR, CDCl_3 , 400 MHz

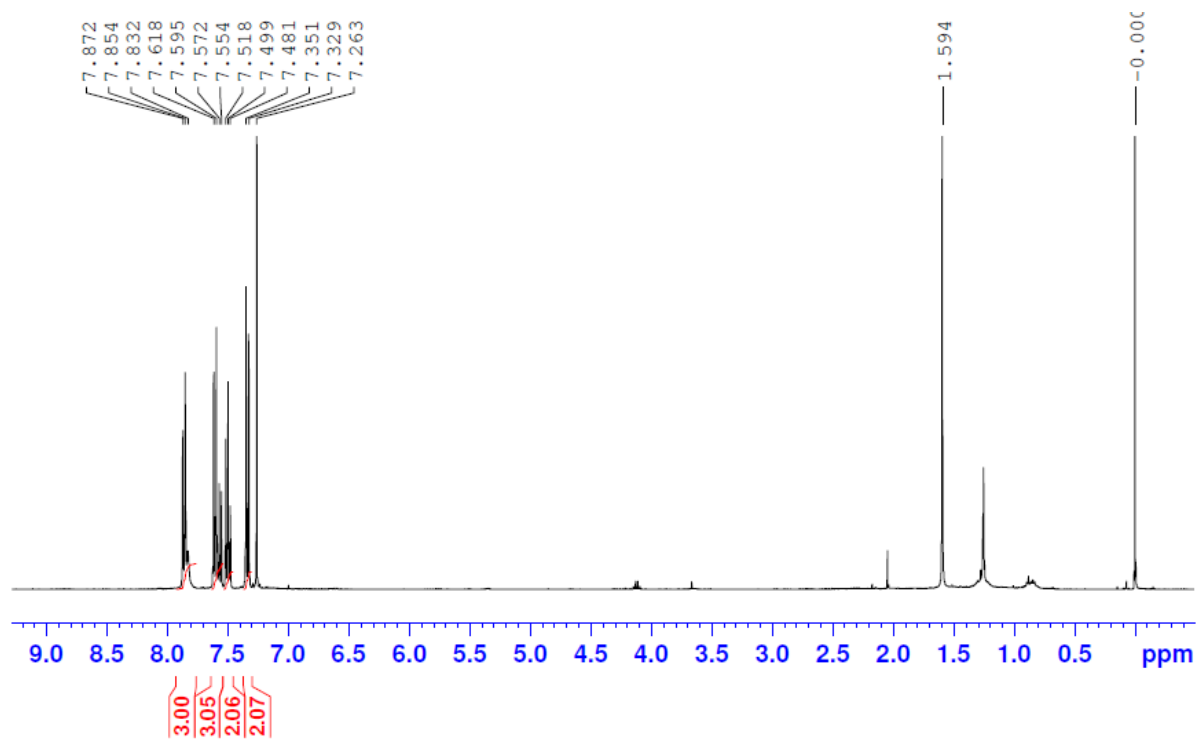


^{13}C NMR, CDCl_3 , 101 MHz

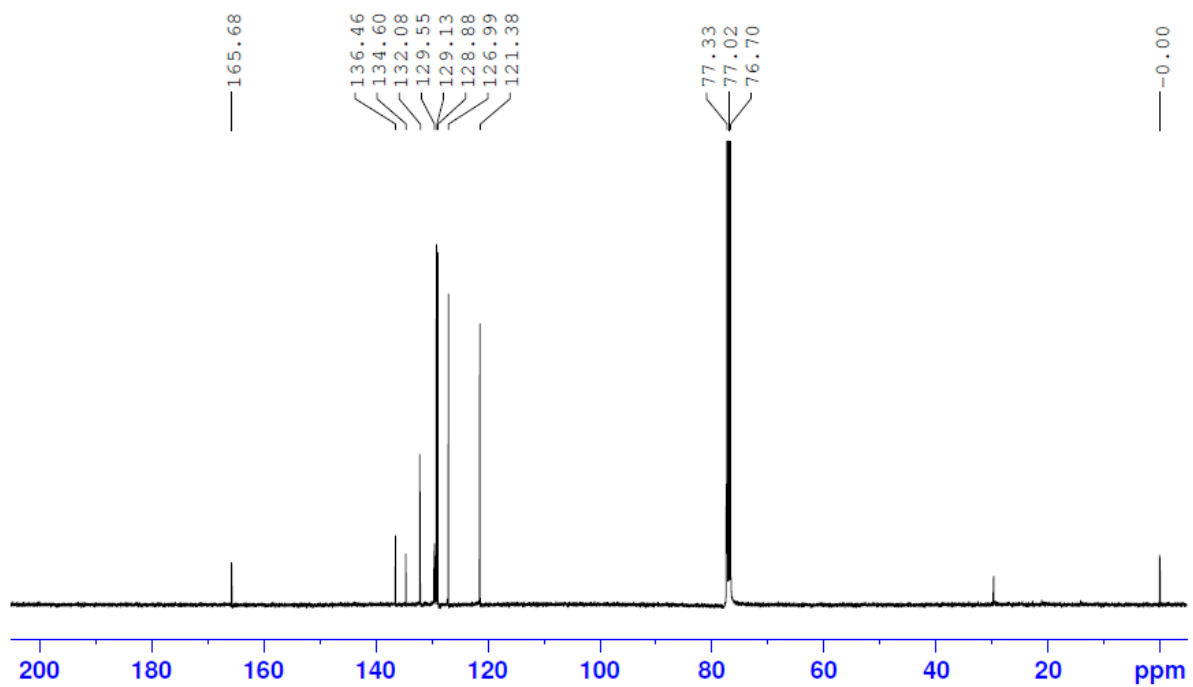


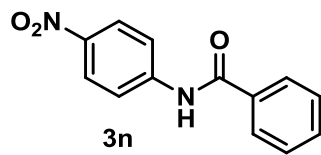


^1H NMR, CDCl_3 , 400 MHz

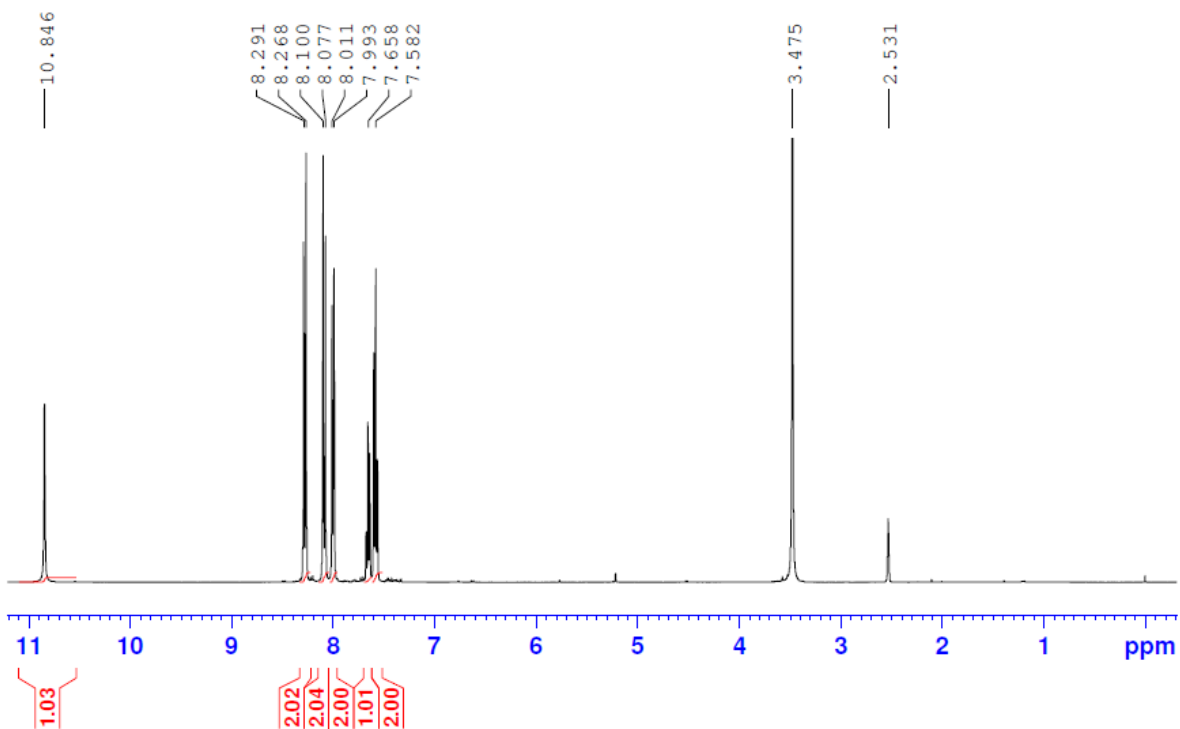


^{13}C NMR, CDCl_3 , 101 MHz

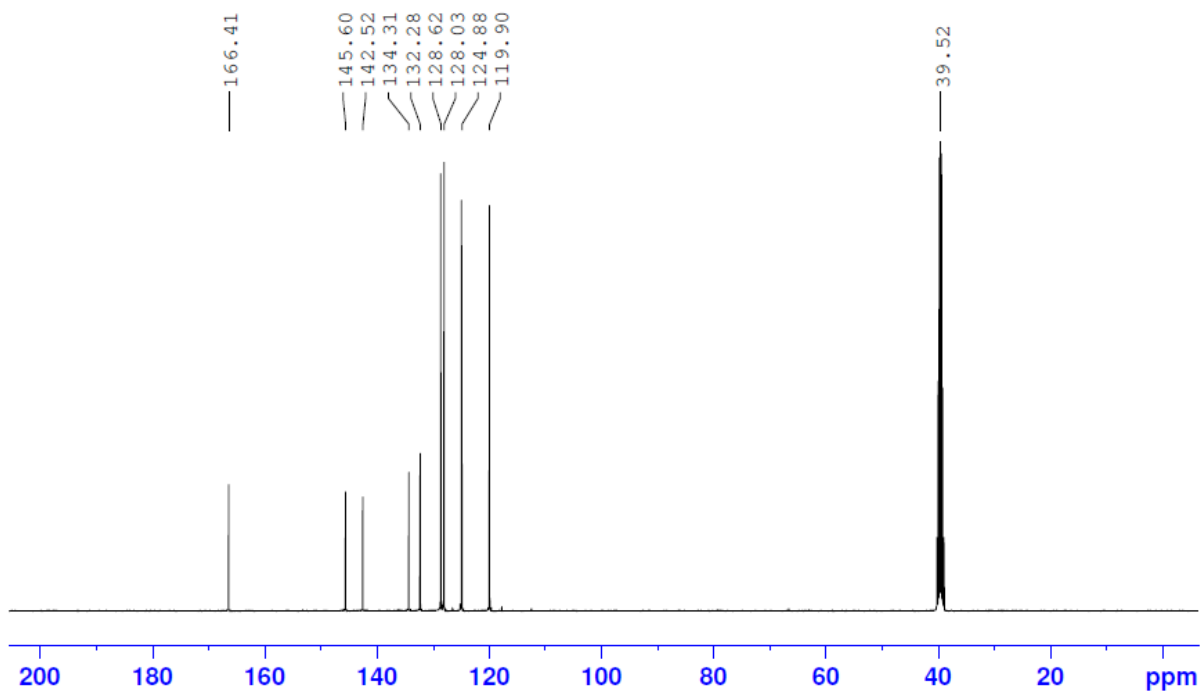


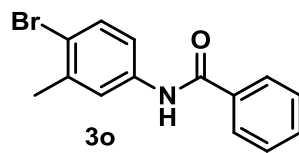


^1H NMR, d_6 -DMSO, 400 MHz

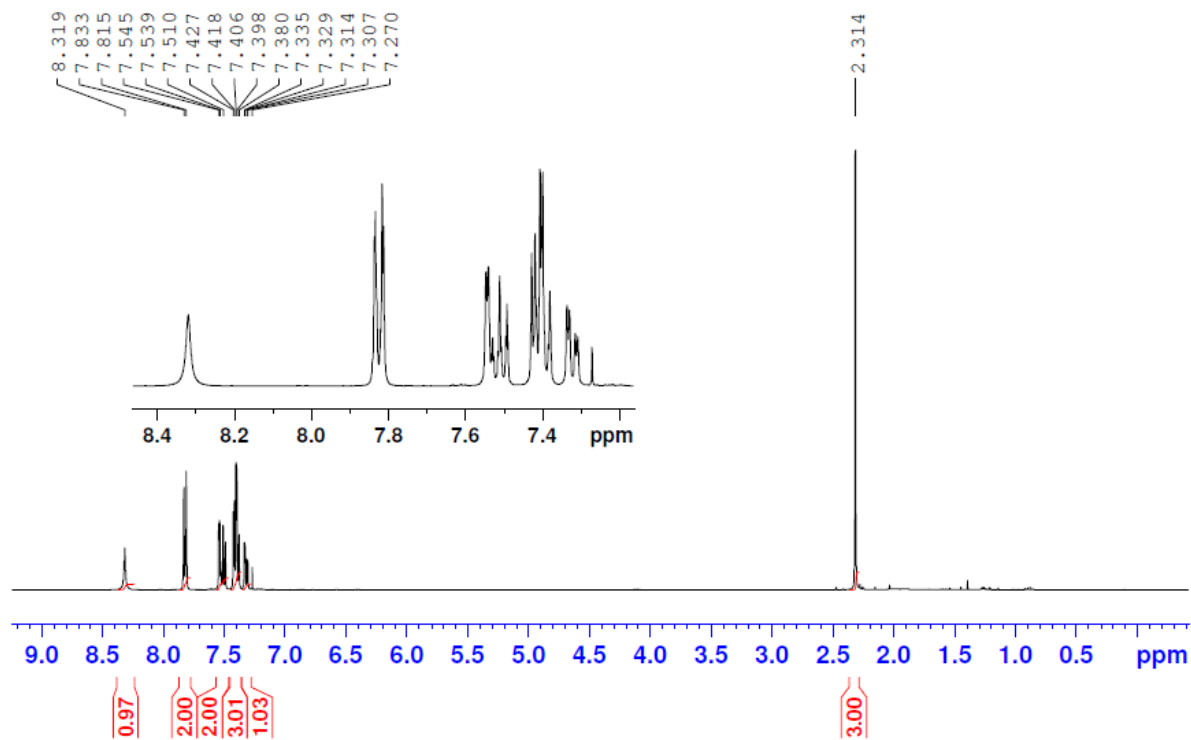


^{13}C NMR, d_6 -DMSO, 101 MHz

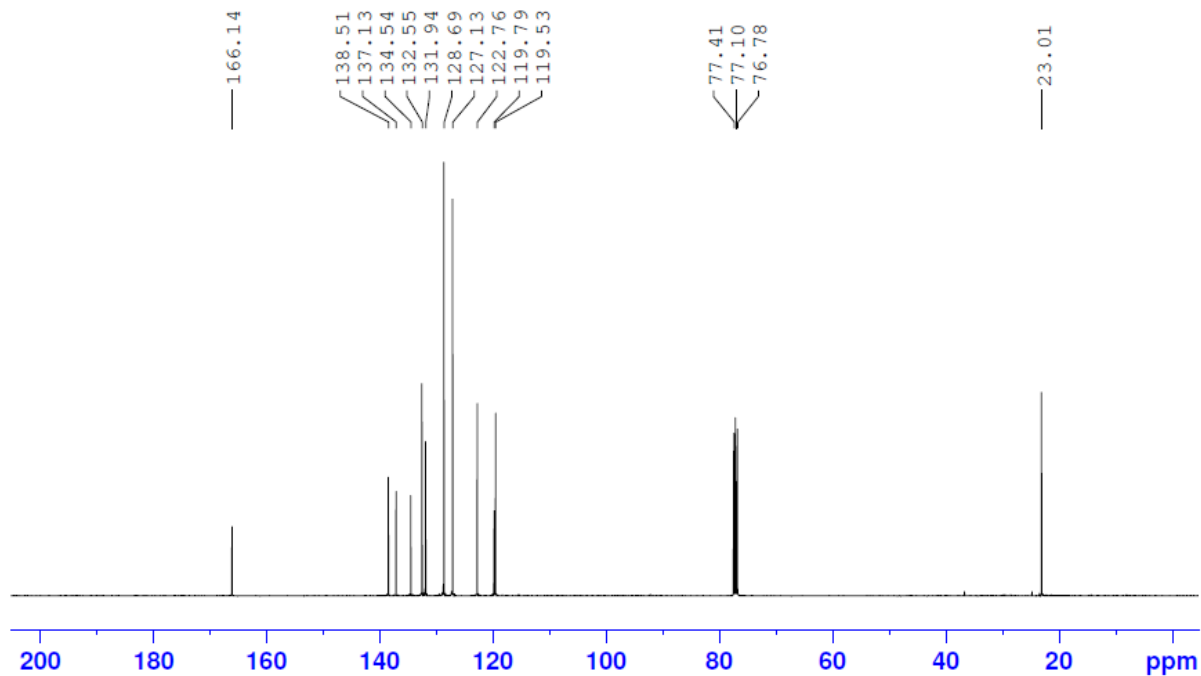


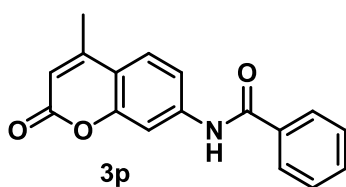


$^1\text{H NMR}$, CDCl_3 , 400 MHz

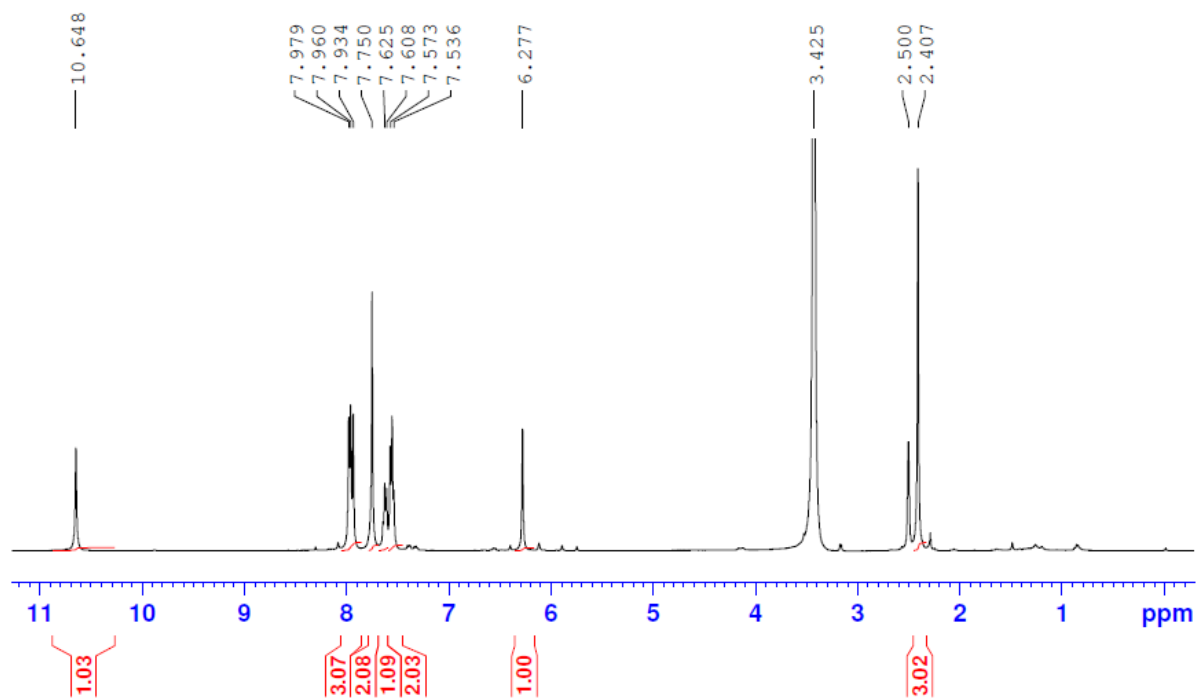


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

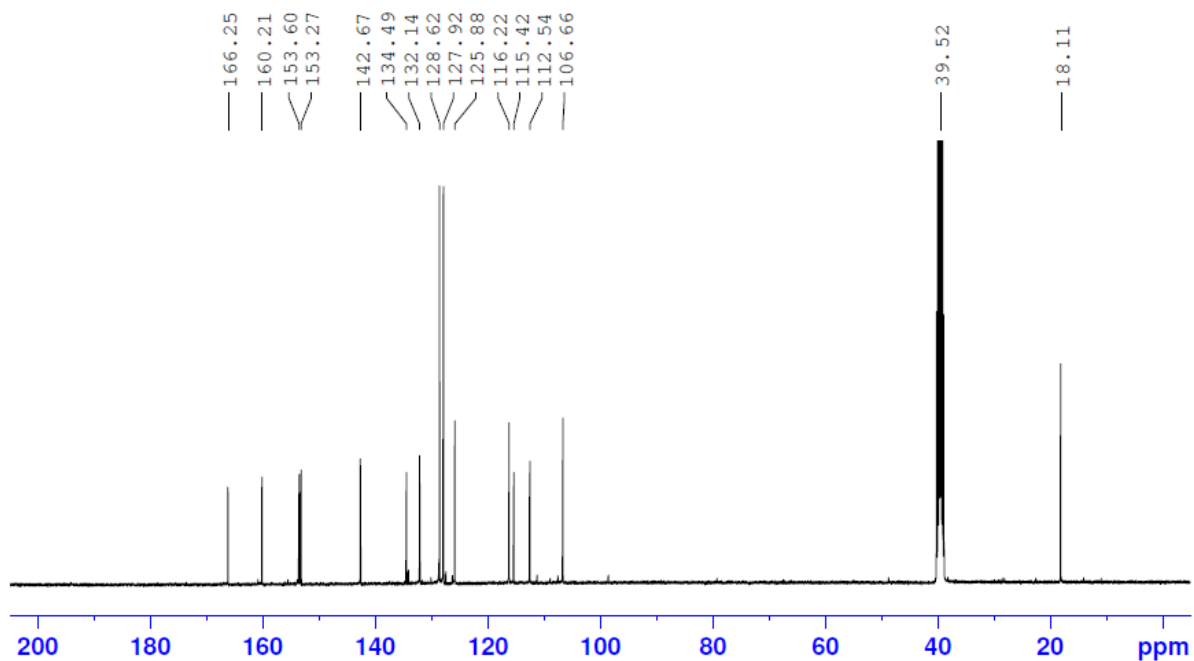


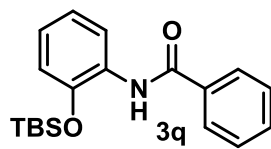


$^1\text{H NMR}$, d_6 -DMSO, 400 MHz

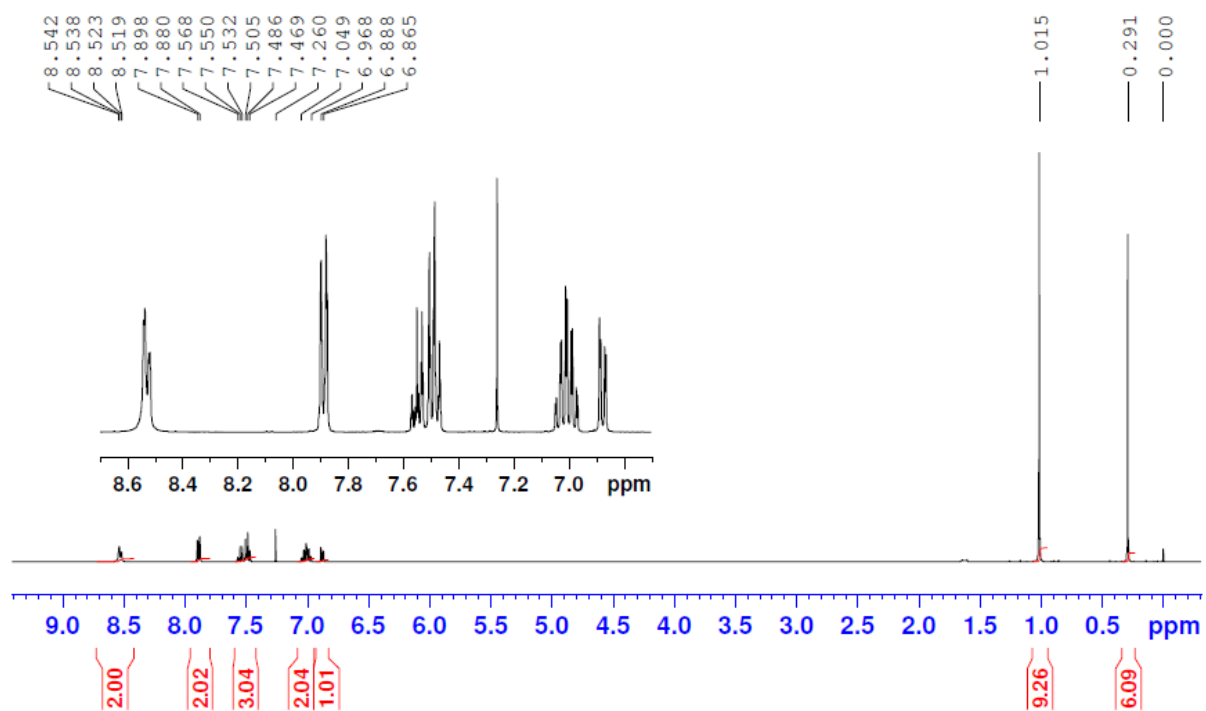


$^{13}\text{C NMR}$, d_6 -DMSO, 101 MHz

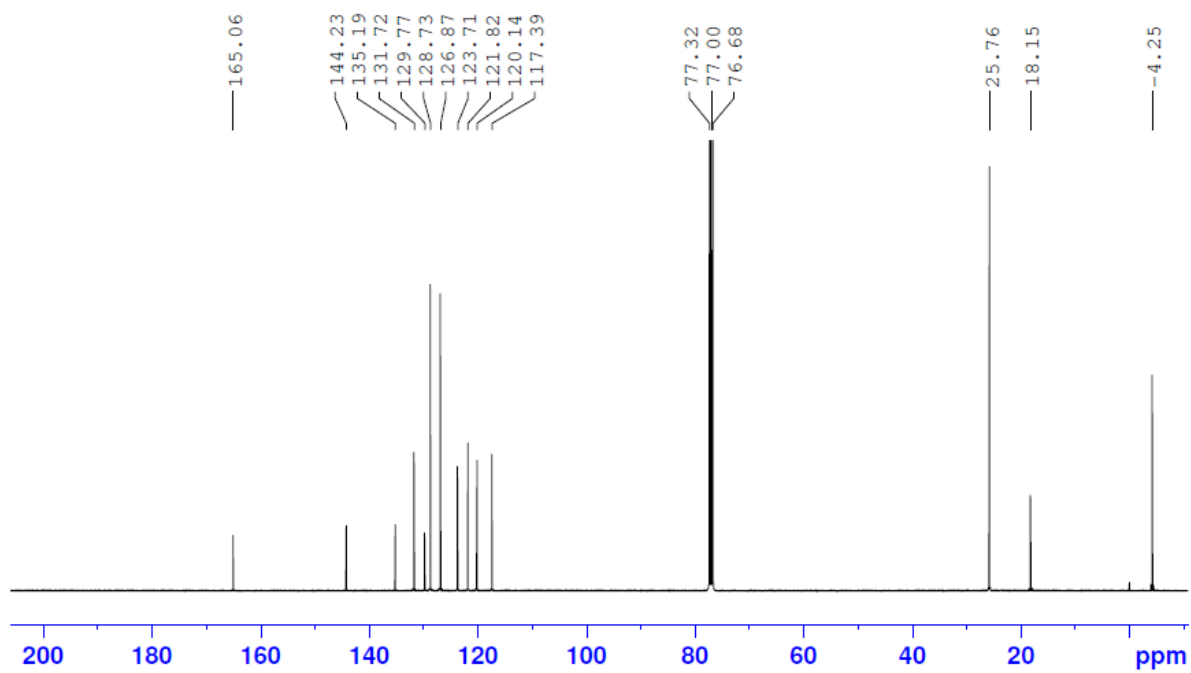


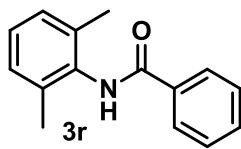


$^1\text{H NMR}$, CDCl_3 , 400 MHz

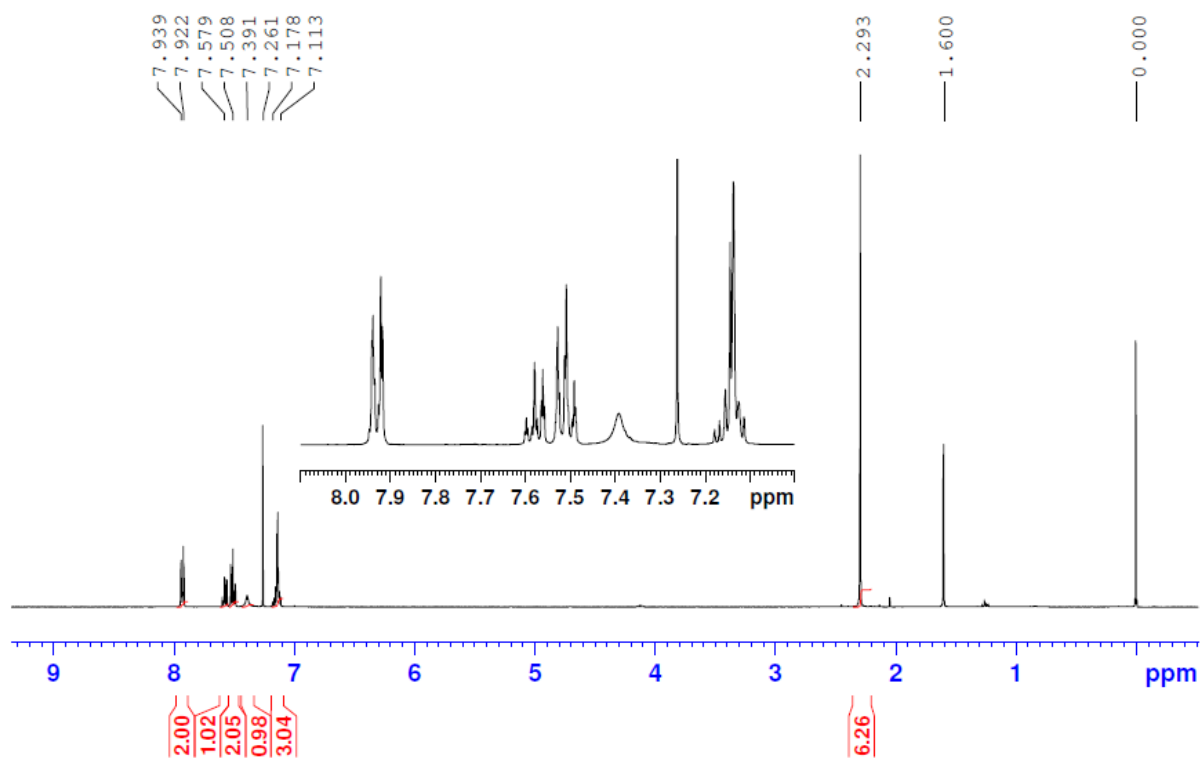


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

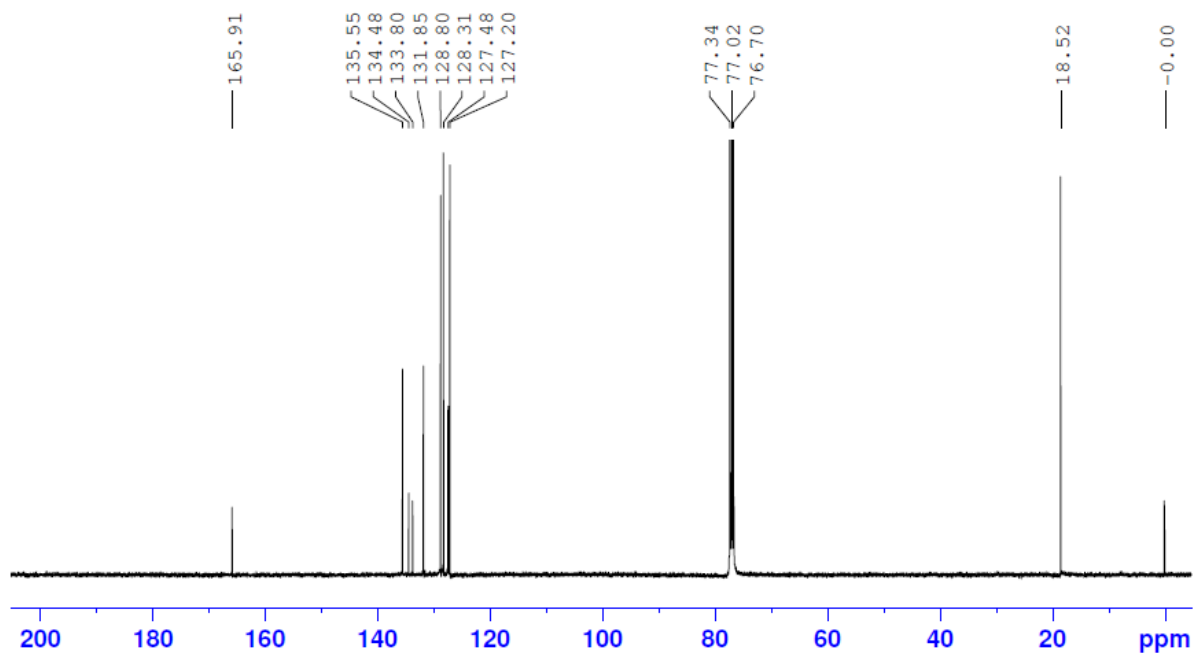


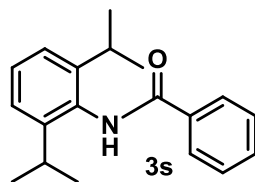


$^1\text{H NMR}$, CDCl_3 , 400 MHz

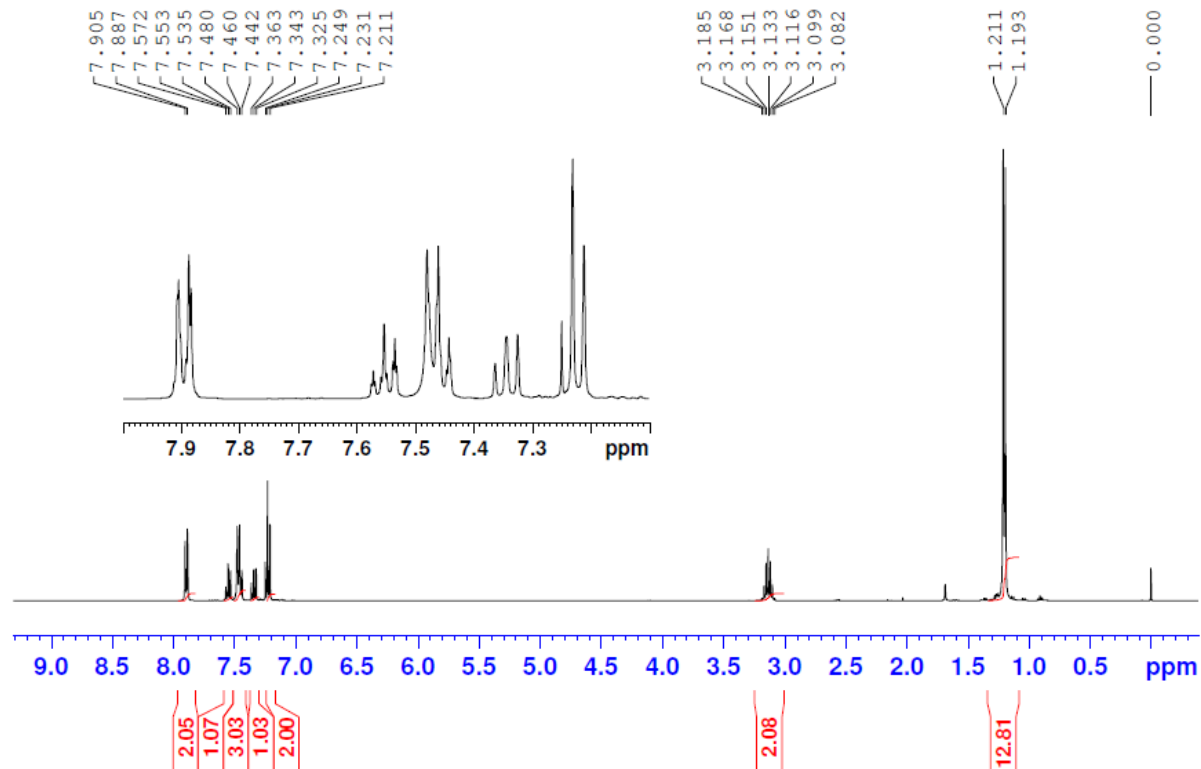


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

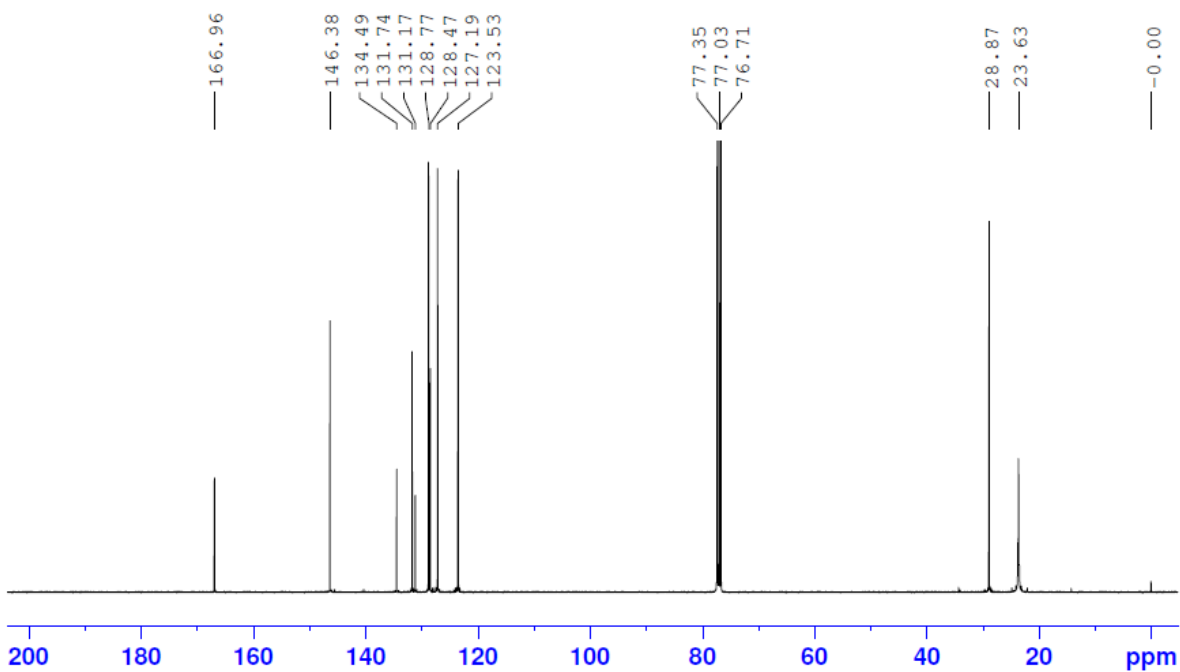


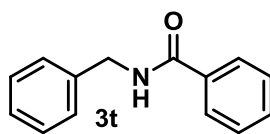


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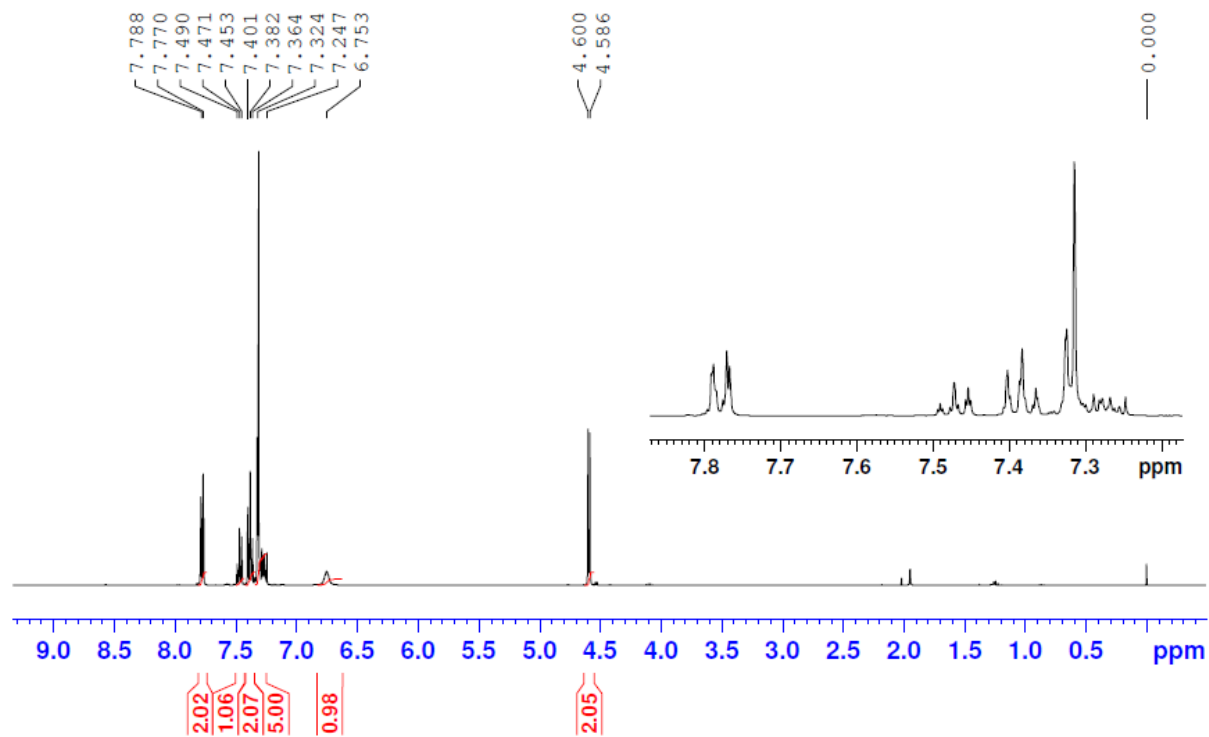


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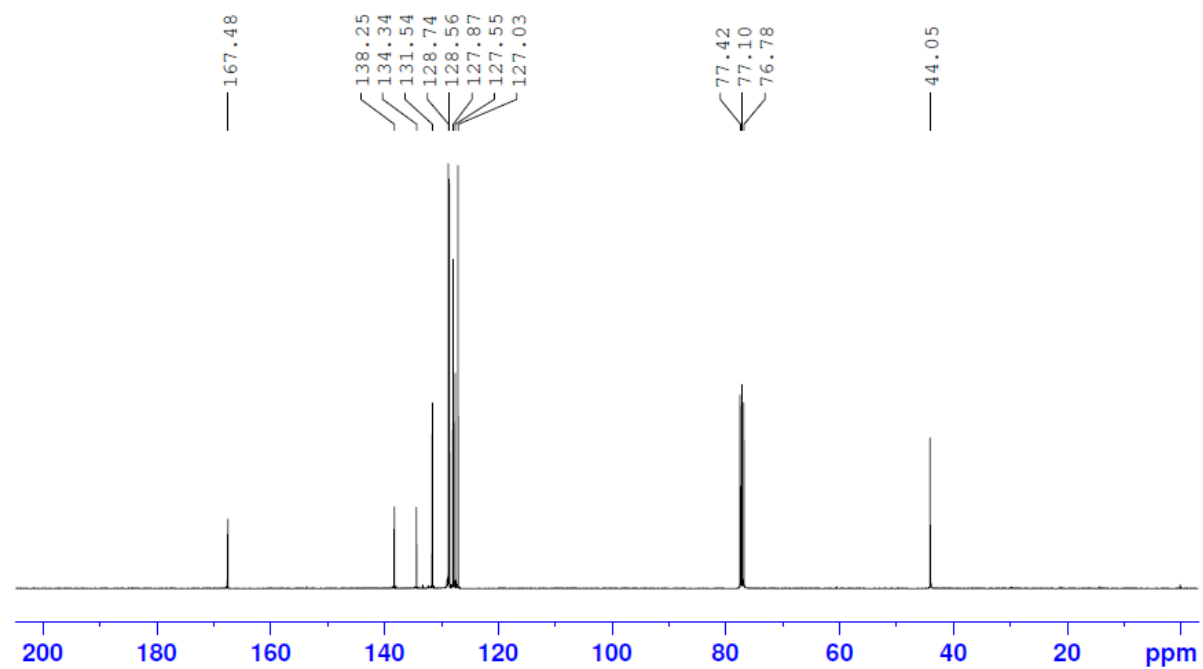


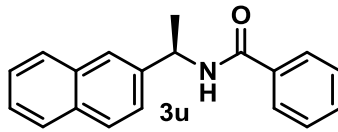


^1H NMR, CDCl_3 , 400 MHz

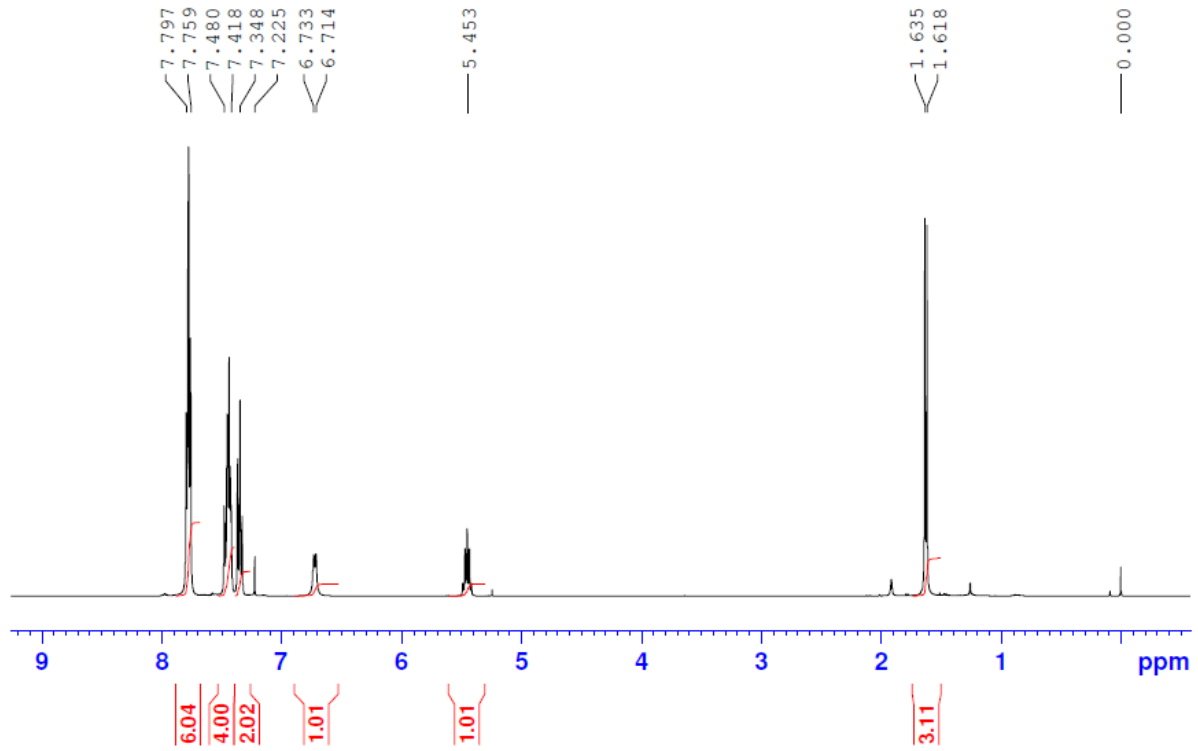


^{13}C NMR, CDCl_3 , 101 MHz

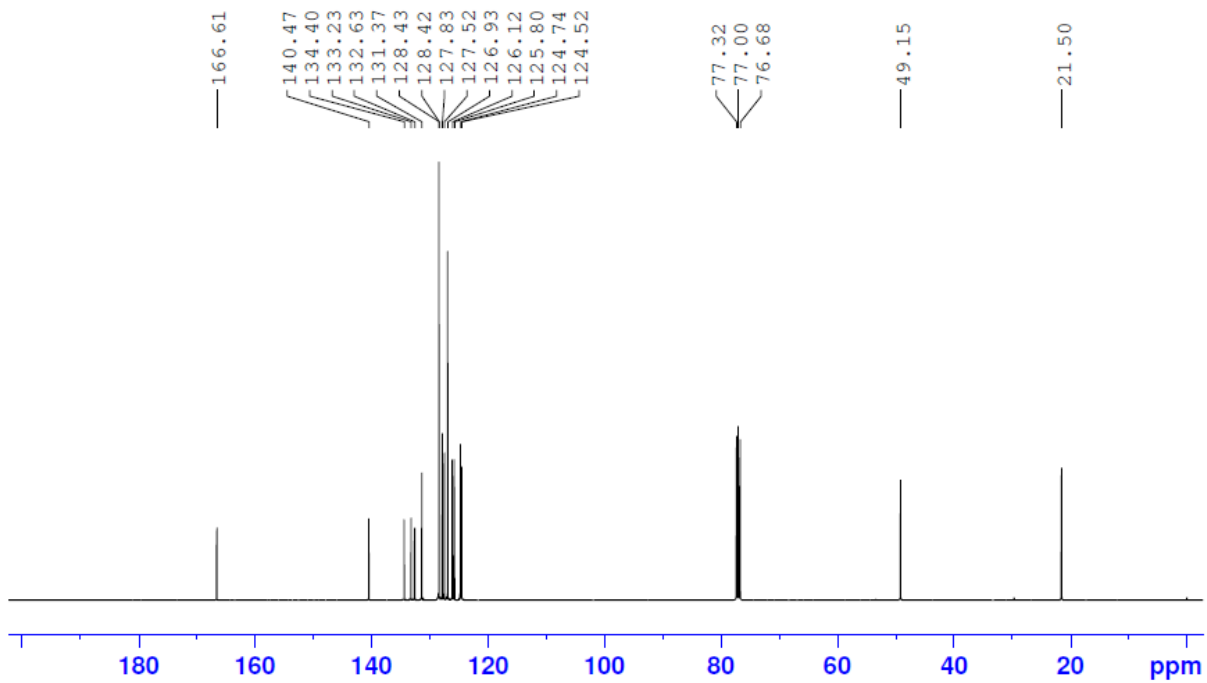


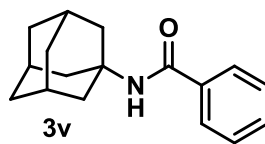


^1H NMR, CDCl_3 , 400 MHz

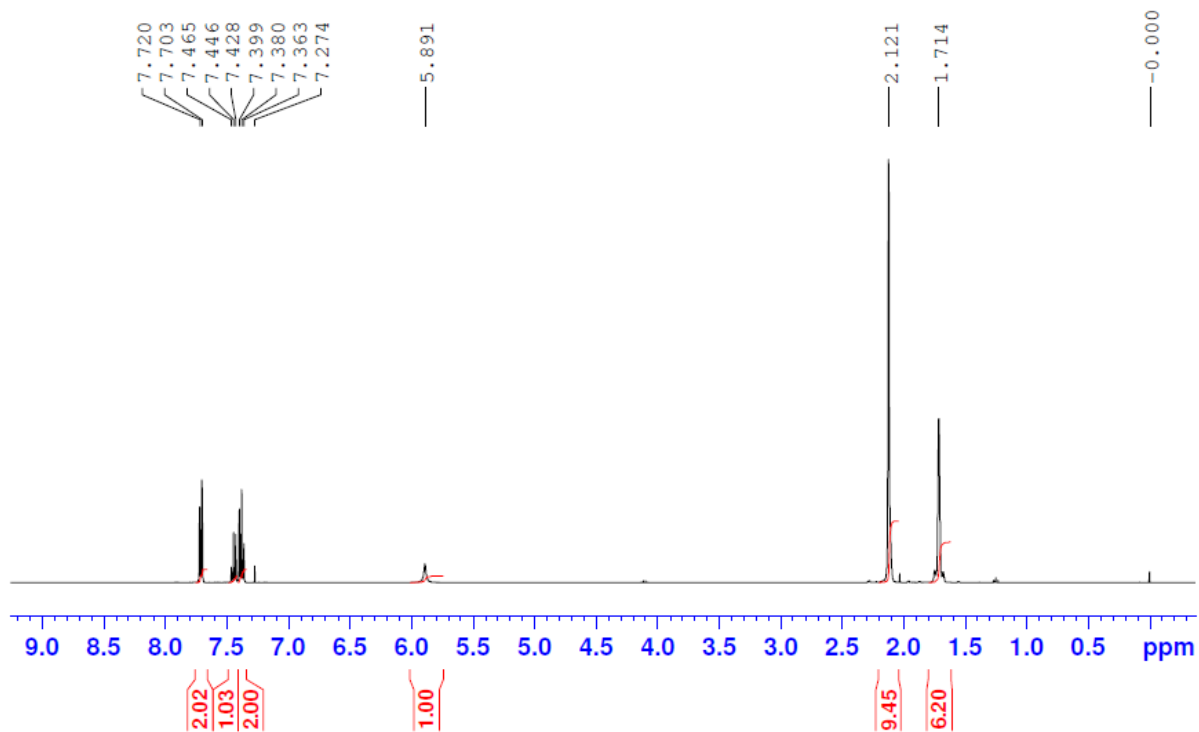


^{13}C NMR, CDCl_3 , 101 MHz

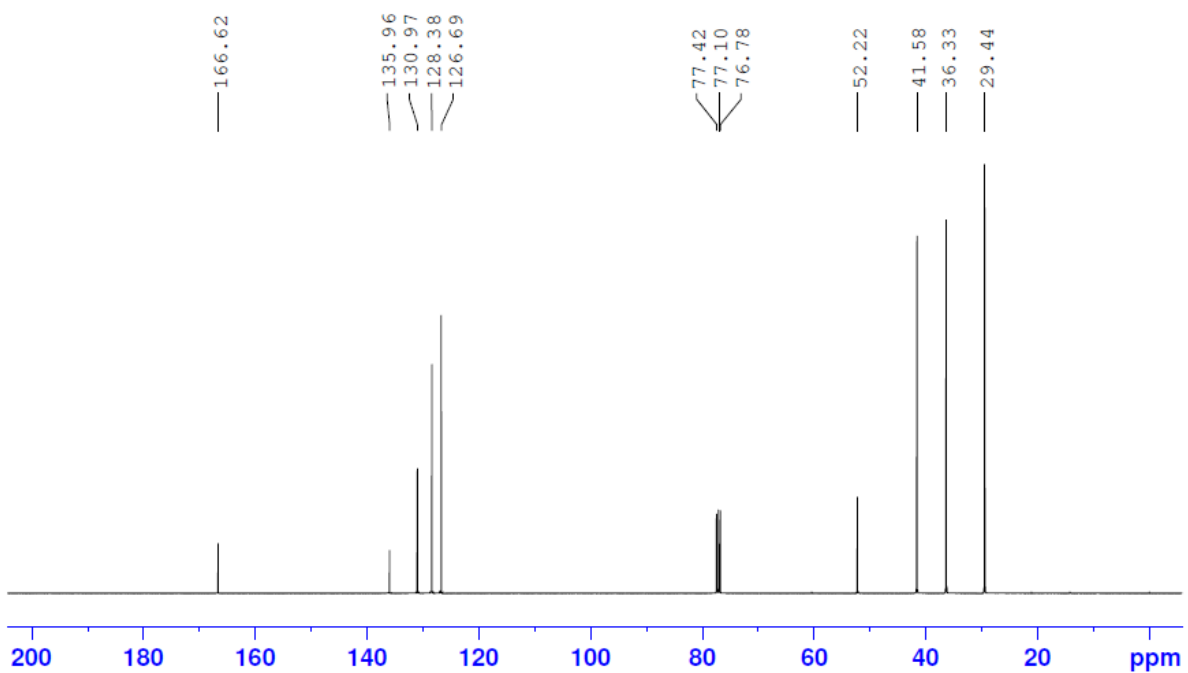


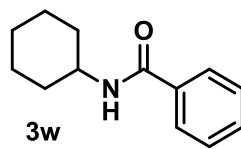


^1H NMR, CDCl_3 , 400 MHz

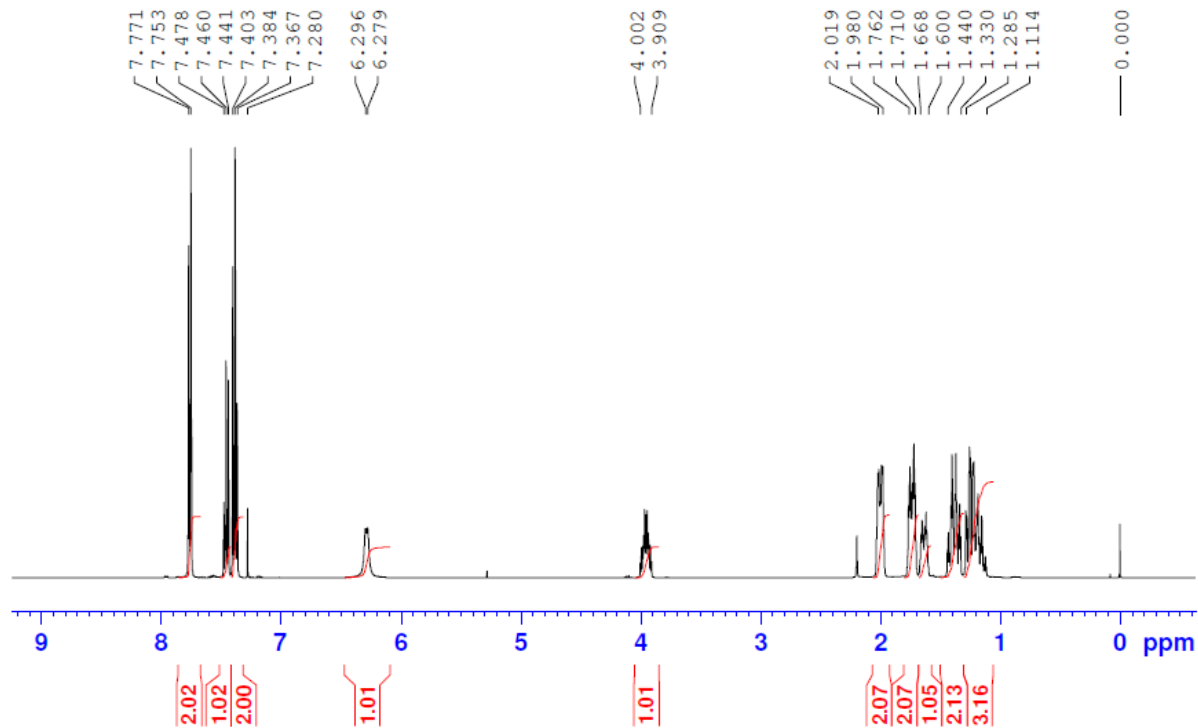


^{13}C NMR, CDCl_3 , 101 MHz

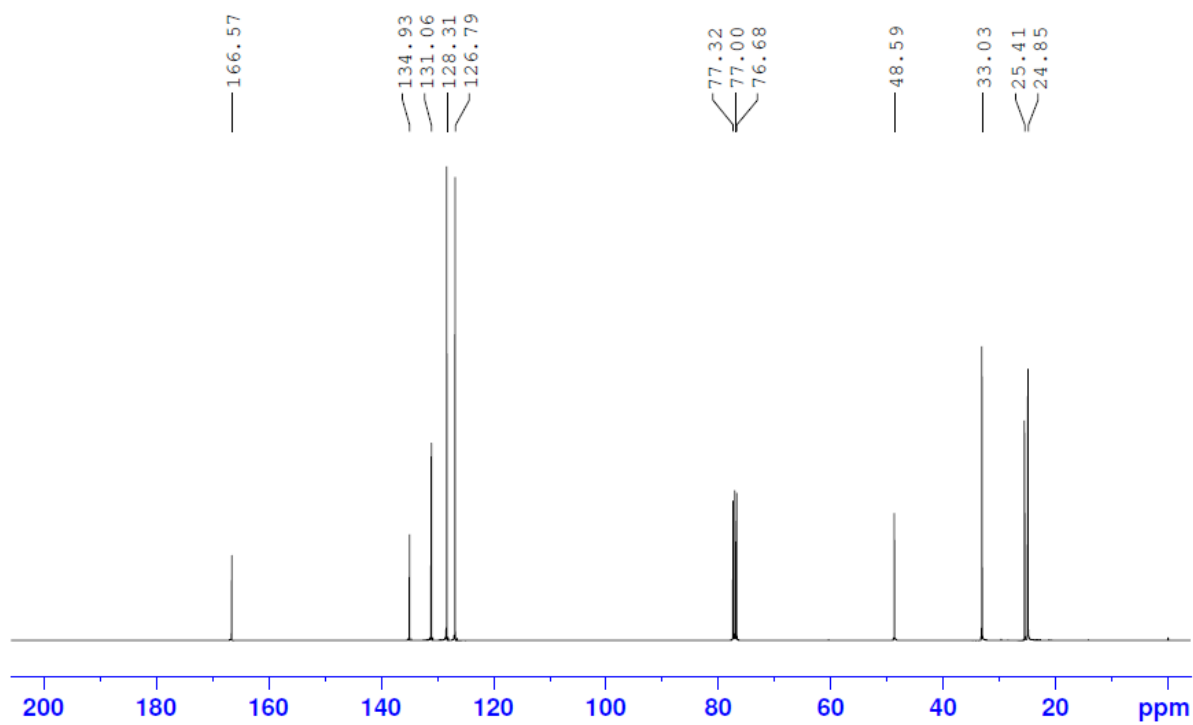


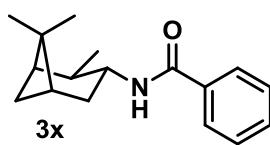


$^1\text{H NMR}$, CDCl_3 , 400 MHz

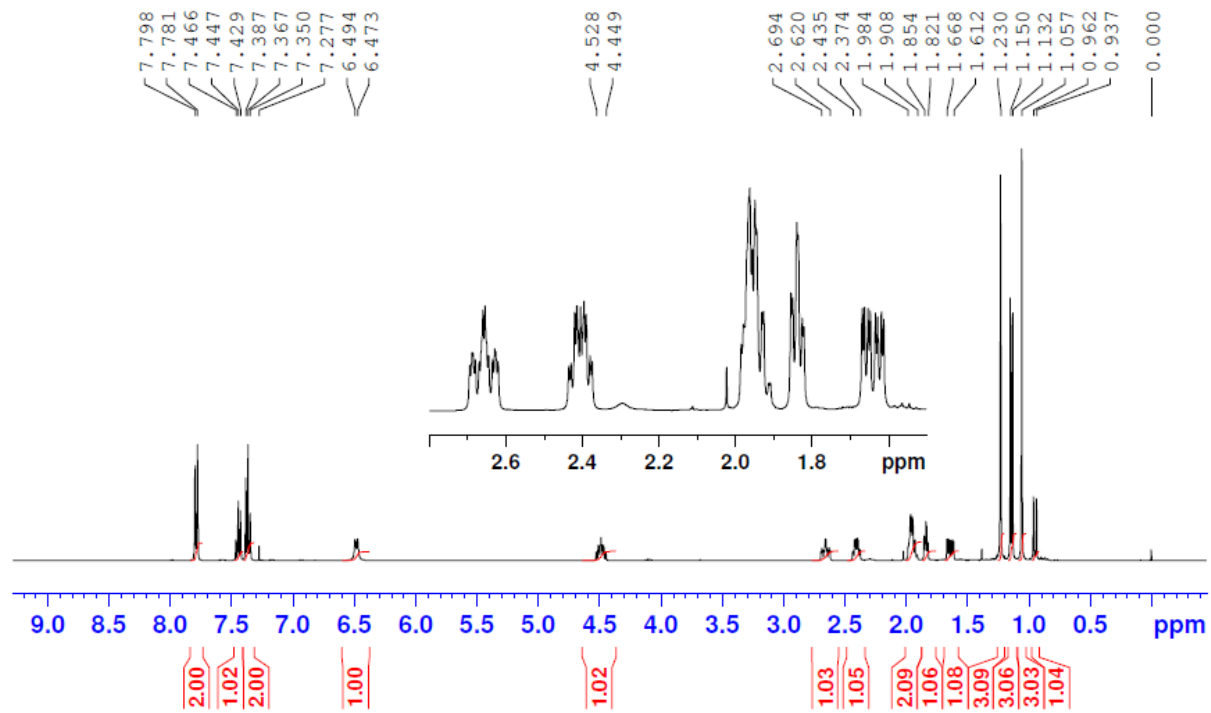


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

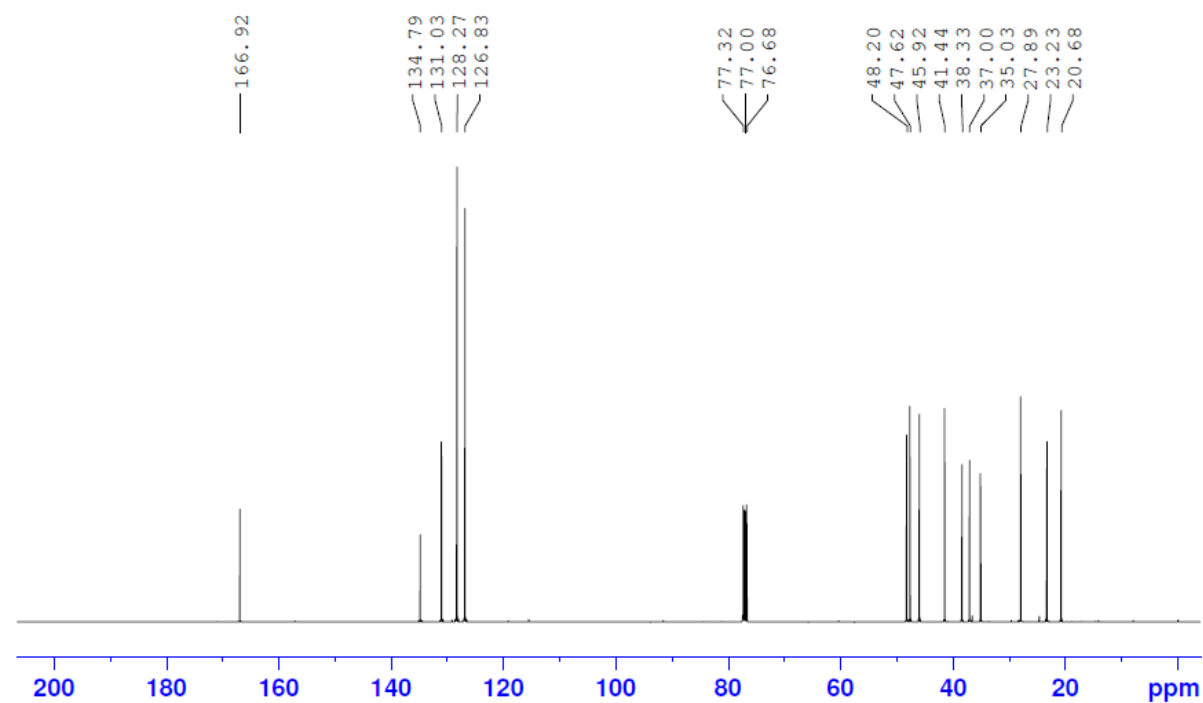


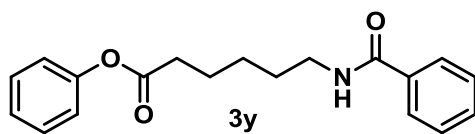


$^1\text{H NMR}$, CDCl_3 , 400 MHz

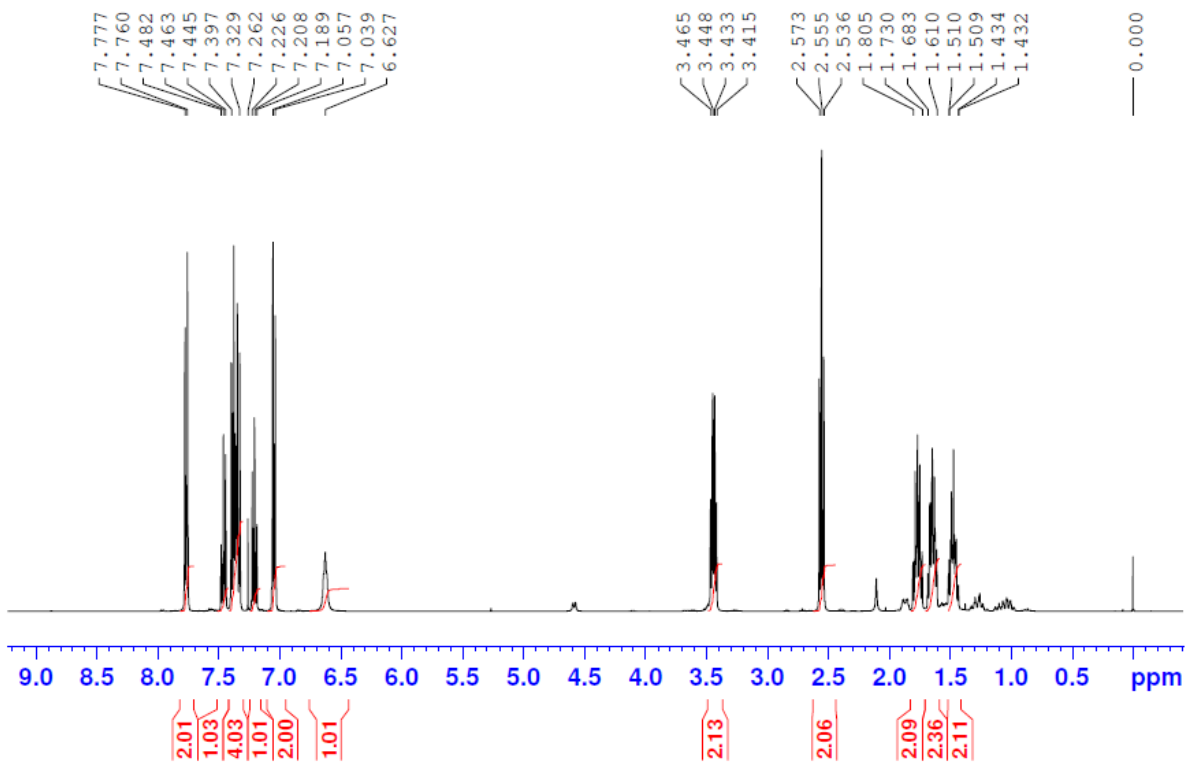


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz

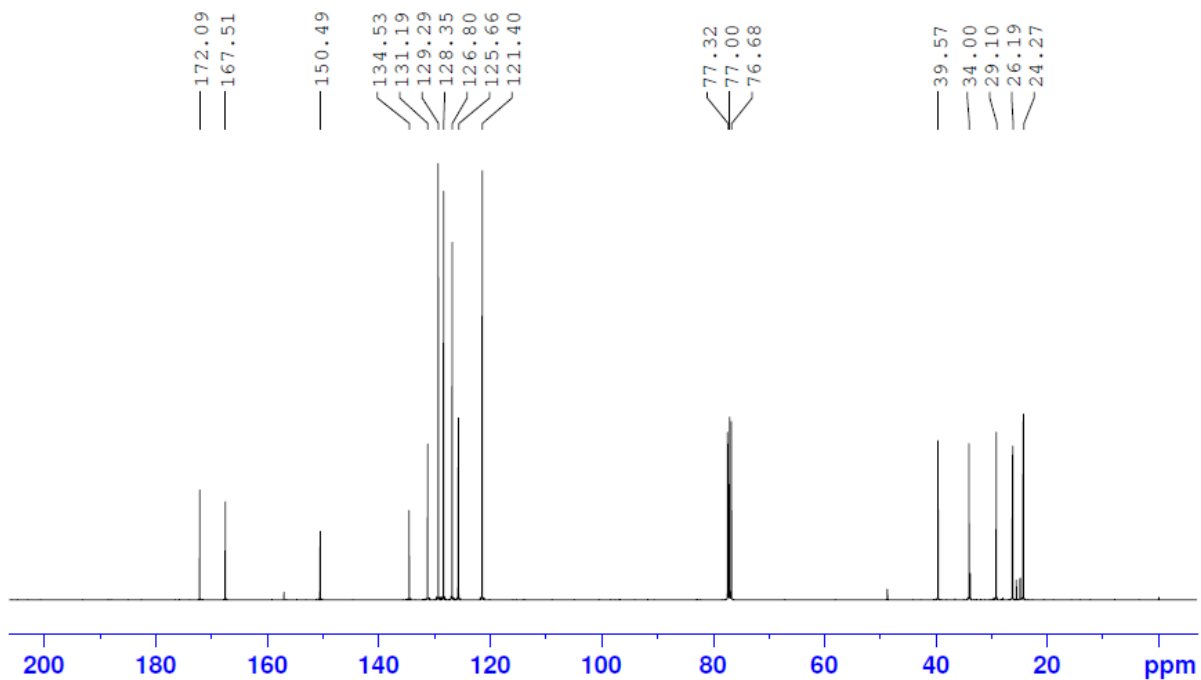


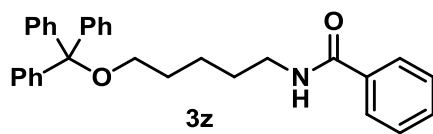


$^1\text{H NMR}$, CDCl_3 , 400 MHz

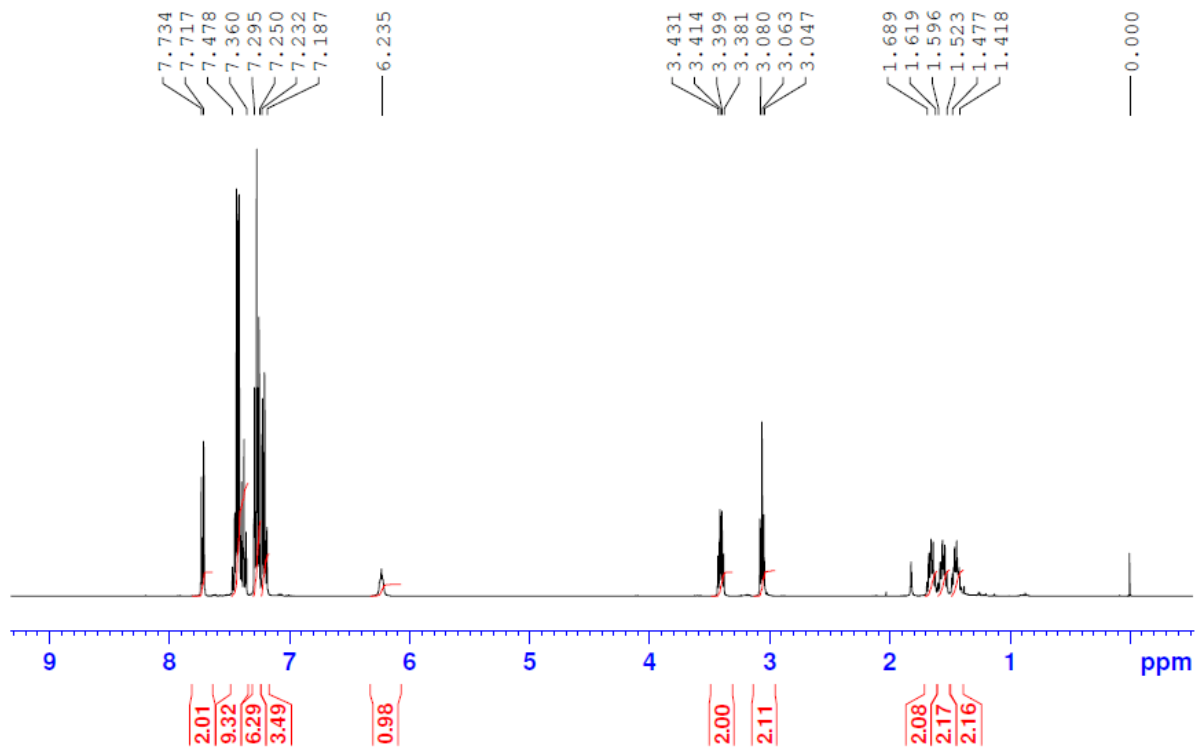


$^{13}\text{C NMR}$, CDCl_3 , 101 MHz





^1H NMR, CDCl_3 , 400 MHz



^{13}C NMR, CDCl_3 , 101 MHz

