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Copper-Catalyzed Oxidative Benzylic C(sp3)–H Amination. Direct Synthesis of Benzylic Carbamates.

Shuai Liu, Raphael Achou, Coline Boulanger, Govind Pawar, Nivesh Kumar, Jonathan Lusseau, Frédéric Robert and Yannick Landais*

University of Bordeaux, Institute of Molecular Sciences, UMR-CNRS 5255,
351 Cours de la Libération, 33405, Talence, France.

E-mail: yannick.landais@u-bordeaux.fr

SUPPORTING INFORMATION

Supporting Information

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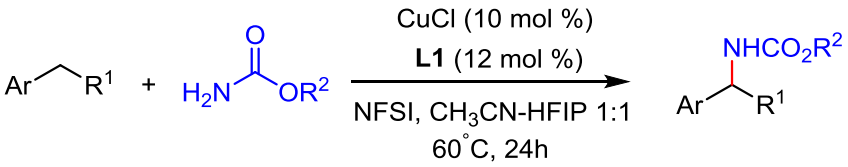
1. General Information

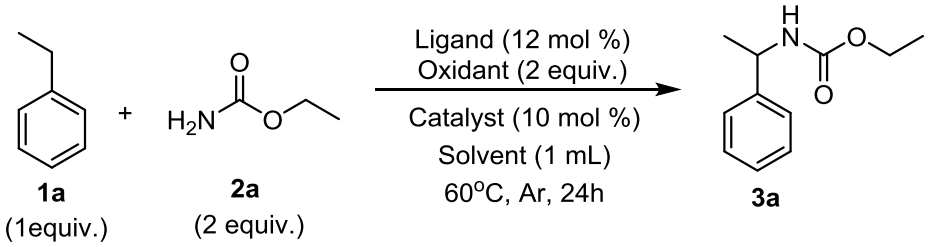
All reactions were carried out under an argon atmosphere. Solvents were dried over activated alumina columns on a M-BRAUN Solvent Purification System (SPS-800) unless otherwise noted. The calculated experimental yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous materials unless otherwise stated. All reagent-grade chemicals were obtained from commercial suppliers and were used as received unless otherwise stated. ^{1}H NMR and ^{13}C NMR were recorded at room temperature on various spectrometers: a Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and a Bruker Avance 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz respectively. The following abbreviations were used to explain the multiplicities: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, quint = quintuplet, hex = hexuplet, hept = heptuplet. Compounds were described as mixtures when it was not possible, in our hands, to separate both compounds. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 using a KBr pellet. High-resolution mass spectra (HRMS) were recorded with a Waters Q-TOF 2 spectrometer in the electrospray ionization (ESI) mode unless otherwise noted. Melting points were not corrected and determined by using a Stuart Scientific SMP3 apparatus. Analytical thin layer chromatography was performed using silica gel 60 F254 pre-coated plates (Merck) with visualization by ultraviolet light. Flash chromatography was performed on silica gel (0.043-0.063 mm) with ethyl acetate (EtOAc) and Petroleum ether (PE) as eluents unless otherwise indicated.

2. General Procedure



Synthesis of urethanes from benzylic hydrogens: In a glovebox under an argon atmosphere, the ligand L1 (0.03 mmol, 12 mol%), the CuCl (0.025 mmol, 10 mol%) in a 1:1 MeCN/HFIP mixture (1 mL) were placed in a dried sealed tube (10 mL). The resulting mixture was stirred at room temperature for 20 minutes. Then, NFSI (157 mg, 0.5 mmol, 2 equiv.), the carbamate (0.5 mmol, 2 equiv.) and the substrate (0.25 mmol, 1 equiv.) were added. The tube was sealed and the mixture was heated at 60°C for 24h. The mixture was then solubilized in DCM and evaporated under reduced pressure. The crude mixture was purified by column chromatography to afford the product.

3. Optimization Studies



Entry[a]	Substrate	Oxidant	Catalyst	Ligand	Solvent	Yield[b]
1	0.25 mmol	NFSI	CuCl	-	HFIP/CH_3CN (1:1)	48%
2	**0.25 mmol**	**NFSI**	**CuCl**	**L1**	**HFIP/CH_3CN (1:1)**	**72%**
3	0.25 mmol	Selectfluor	CuCl	L1	HFIP/CH_3CN (1:1)	5%
4	0.25 mmol	F-TEDA-PF_6	CuCl	L1	HFIP/CH_3CN (1:1)	53%
5	0.25 mmol	NFSI	Cu(OAC)	L1	HFIP/CH_3CN (1:1)	68%
6	0.2 5mmol	NFSI	$Fe(OAC)_2$	L1	HFIP/CH_3CN (1:1)	ND
7	0.25 mmol	NFSI	-	L1	HFIP/CH_3CN (1:1)	ND
8	0.25 mmol	NFSI	CuCl	L2	HFIP/CH_3CN (1:1)	ND
9	0.25 mmol	NFSI	CuCl	L3	HFIP/CH_3CN (1:1)	ND
10	0.25 mmol	NFSI	CuCl	L4	HFIP/CH_3CN (1:1)	ND
11	0.25 mmol	NFSI	CuCl	L5	HFIP/CH_3CN (1:1)	ND
12	0.25 mmol	NFSI	CuCl	L6	HFIP/CH_3CN (1:1)	ND
13	0.25 mmol	NFSI	CuCl	L7	HFIP/CH_3CN (1:1)	ND
14	0.2 5mmol	NFSI	CuCl	L8	HFIP/CH_3CN (1:1)	ND
15	0.25 mmol	NFSI	CuCl	L1	MeCN	33%
16	0.25 mmol	NFSI	CuCl	L1	MeCN/HFIP (99 :1)	37%
17	0.25 mmol	NFSI	CuCl	L1	MeCN/HFIP (98 :2)	40%
18	0.25 mmol	NFSI	CuCl	L1	MeCN/HFIP (95 :5)	27%
19	0.25 mmol	NFSI	CuCl	L1	MeCN/HFIP (9 :1)	27%
20	0.25 mmol	NFSI	CuCl	L1	MeCN/HFIP (7 :3)	54%
21	0.25 mmol	NFSI	CuCl	L1	MeCN/HFIP (6 :4)	56%
22	0.25 mmol	NFSI	CuCl	L1	HFIP	8%

[a] Reaction conditions: **1a** (0.25 mmol), Carbamate (0.5 mmol), NFSI (0.5 mmol), CuCl (0.025 mmol), Ligand (0.03 mmol) in a 1:1 MeCN/HFIP (1.0 mL) at 60℃ for 24 h. [b]Isolated yield.

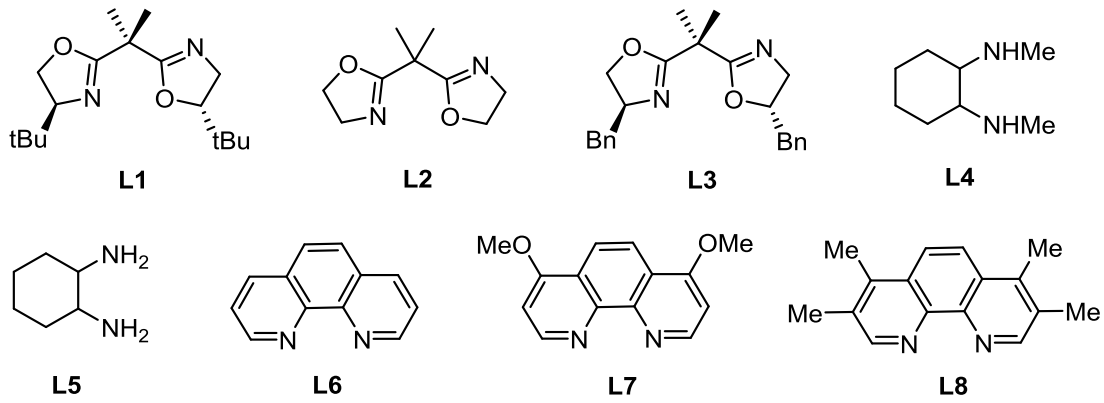


Figure S1. Ligands tested

Note 1

As observed in Table above, the role of the ligand in this reaction is critical. Several reasons may be invoked, such as the multiple ligation to copper which would lead to inactive metal catalyst.[i] Our best catalysts **L1** exhibits bulky *t*-Bu substituents which may prevent the formation for instance of an inactive dimer.

The redox potential of the Cu(II) complex **A** in Figure 2 may be modulated by the nature of the ligand and influence the thermodynamics of the oxidation of the benzylic radical into cation **F,**[ii] a key-intermediate in the radical-polar crossover pathway.

Note 2

An important difference in reactivity is observed between Selectfluor and its analogue having a PF_6 counter-anion (entry 3 *vs* 4). We have no satisfying explanation for this observation. Literature reveals a similar difference during fluorination of gycals using a triflate as a counter-anion which led to better results than Selectfluor due to its higher solubility.[iii] This cannot be applied here as both salts are insoluble at the start of the reaction.

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[i] E. R. Strieter, D. G. Blackmond, and S. L. Buchwald, *J. Am. Chem. Soc.* 2005, **127**, 4120.

[ii] S.-E. Suh, S.-J. Chen, M. Mandal, I. A. Guzei, C. J. Cramer, and S. S. Stahl, *J. Am. Chem. Soc.* 2020, **142**, 11388.

[iii] (a) P. T. Nyffeler, S. G. Duron, M. D. Burkart, S. P. Vincent, and C.-H. Wong, *Angew. Chem. Int. Ed.* 2005, **44**, 192; (b) S. P. Vincent, M. D. Burkart, C.-Y. Tsai, Z. Zhang, and C.-H. Wong, *J. Org. Chem.* 1999, **64**, 5264.

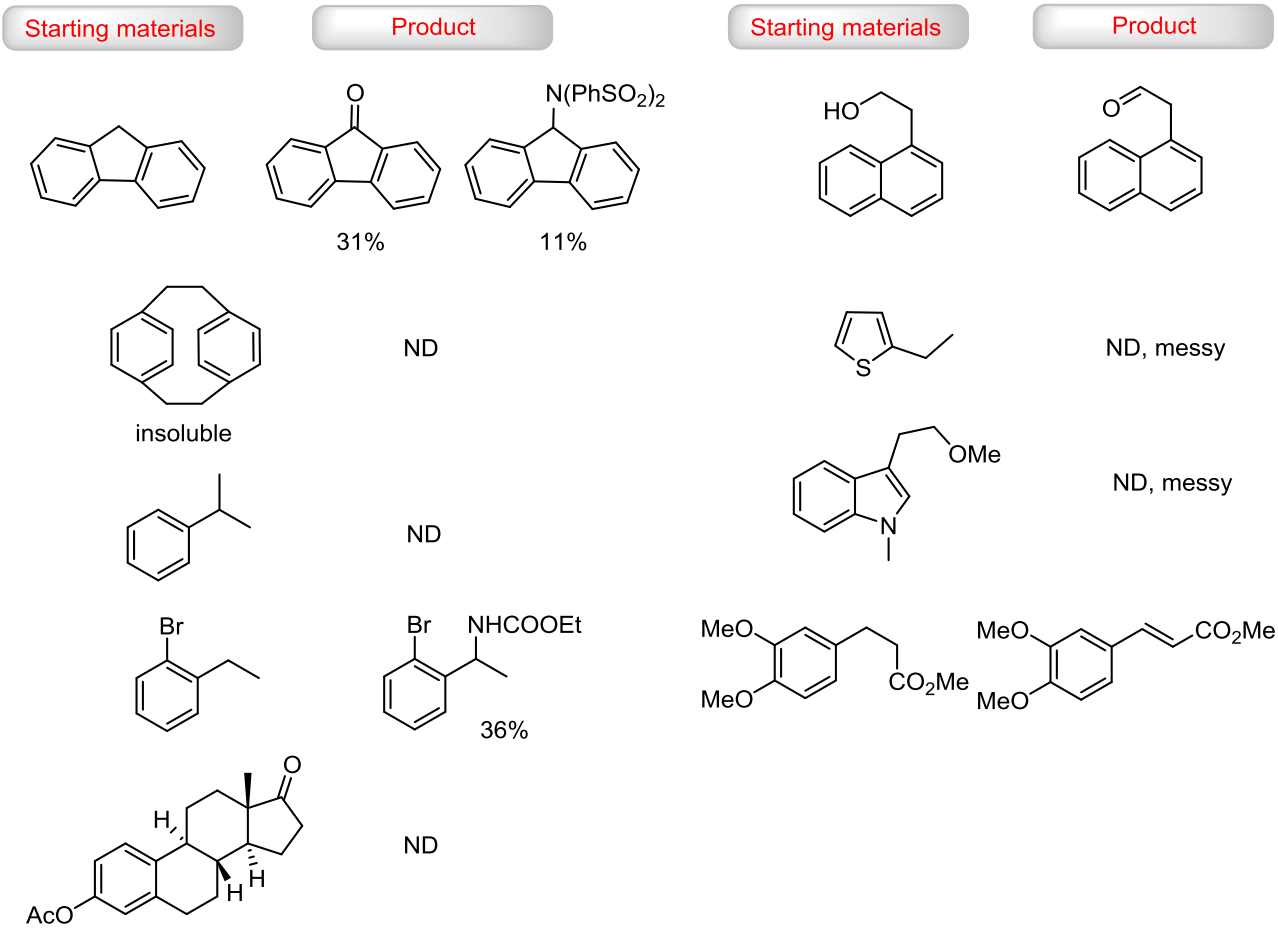
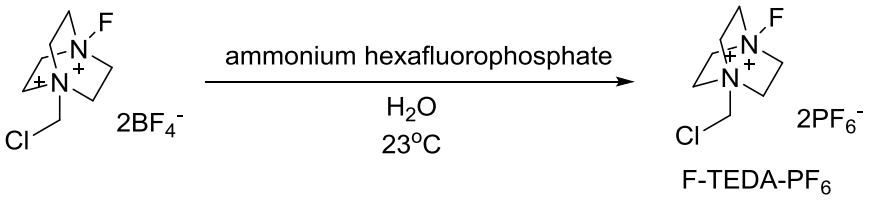


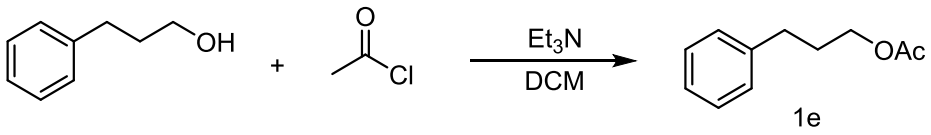
Figure S2. Substrates failing to provide the desired carbamates or leading to other products (oxidation)

4. Synthesis of Starting Materials



F-TEDA-PF6: (Compound above have been prepared following methods of a literature reference 1.) The ammonium hexafluorophosphate (2.93 g, 18 mmol, 6 equiv.) was added to Selectfluor (1.06 g, 3.0 mmol, 1 equiv.) in water (9.0 mL) at 23°C. The resulting mixture was stirred for 1 h, and then the suspension was filtered off and washed with water (5×5 mL) and Et_2O (10 mL). The solid was dried under vacuum at 40°C for 48h and the expected salt obtained as a white solid (1.14 g, 81%) used in the next step without further purification.

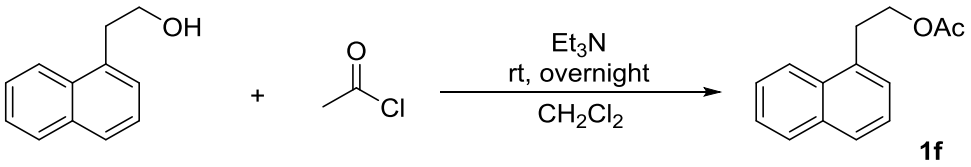
^{1}H NMR (300 MHz, CD_3CN) δ 5.29 (s, 2H), 4.71 (q, J = 7.4 Hz, 6H), 4.34 – 4.19 (m, 6H). ^{13}C NMR (76 MHz, CD_3CN) δ 69.67 (d, J = 2.7 Hz), 57.78 (d, J = 15.2 Hz), 54.26 (dt, J = 5.9, 2.6 Hz).
NMR spectroscopic data were identical to those previously reported.[1]



Benzenepropanol, 1-acetate (1e): A solution of 3-phenylpropan-1-ol (0.68 mg, 5.0 mmol, 1 equiv.) in DCM (20 mL) was added triethylamine (0.84 mL, 6 mmol, 1.2 equiv.), followed by the dropwise addition of acetyl chloride (0.43 mL, 6 mmol, 1.2 equiv.). The resulting mixture was stirred overnight at room temperature, then diluted with DCM (20 mL) and quenched with water (20 mL). After extraction with CH_2Cl_2 (3×25 mL), the solvent was dried over magnesium sulfate and removed in vacuo. The crude residue was purified by flash column chromatography on silica gel (PE/EA = 20:1) to afford the target compound **1e** (0.76 g, 76%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 4.11 (t, *J* = 6.6 Hz, 2H), 2.71 (dd, *J* = 8.7, 6.7 Hz, 2H), 2.07 (s, 3H), 2.04 – 1.92 (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.0, 141.2, 128.4, 128.4, 126.0, 63.8, 32.2, 30.2, 20.9.

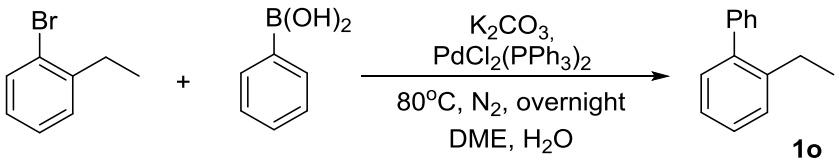
NMR spectroscopic data were identical to those previously reported.[2]



1-Naphthaleneethanol, 1-acetate (1f): A solution of 2-(1-naphthyl)ethanol (1.00 g, 6.32 mmol, 1 equiv.) in CH_2Cl_2 (20 mL) was placed under inert atmosphere and at 0℃ in an ice water bath. Triethylamine (1.06 mL, 7.59 mmol, 1.2 equiv.) was added at 0℃, followed by the dropwise addition of acetyl chloride (0.54 mL, 7.59 mmol, 1.2 equiv.). The resulting mixture was stirred overnight at room temperature, then diluted with dichloromethane (20 mL) and quenched with water (40 mL). The organic phase was separated and phases were washed with brine (2×20 mL) and eventually dried over magnesium sulfate. Solvent was removed in vacuo. The crude residue was purified by flash column chromatography on silica gel (PE/EA-10:1) to afford the target compound (1.10 g, 81%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.95 – 7.86 (m, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.35 (m, 4H), 4.44 (t, *J* = 7.4 Hz, 2H), 3.44 (t, *J* = 7.4 Hz, 2H), 2.08 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.2, 134.0, 133.8, 132.2, 128.9, 127.6, 127.1, 126.3, 125.8, 125.6, 123.71 64.6, 32.4, 21.2.

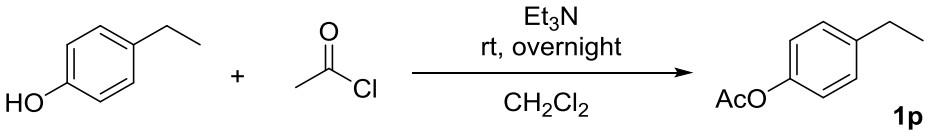
NMR spectroscopic data were identical to those previously reported.[3]



2-ethyl-1,1'-biphenyl (1o): In a 50 mL two-neck round bottom flask, 1-bromo-2-ethylbenzene (1 equiv. 5 mmol, 920 mg), phenylboronic acid (1.2 equiv. 6 mmol, 732 mg), K_2CO_3 aqueous solution (2M, 12 mL) and DME were added under N_2 atmosphere. The mixture was then stirred at room temperature for 30 minutes. Then, the $PdCl_2(PPh_3)_2$ (2 mol %, 0.1 mmol, 70 mg) was added and the reaction mixture was stirred at 80°C overnight under N_2 atmosphere. The mixture was extracted with EtOAc (3×20 mL), dried over Na_2SO_4. Solvent was removed in vacuo. The crude residue was purified by flash column chromatography on silica gel (PE/EA = 50:1) to afford the target compound (874 mg, 96%) as colorless oil.

^{1}H NMR (300 MHz, CDCl3) δ 7.53 – 7.25 (m, 9H), 2.69 (q, *J* = 7.5 Hz, 2H), 1.18 (td, *J* = 7.5, 0.8 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 142.1, 141.7, 130.1, 129.3, 128.7, 128.1, 127.6, 126.9, 125.7, 26.3, 15.8.

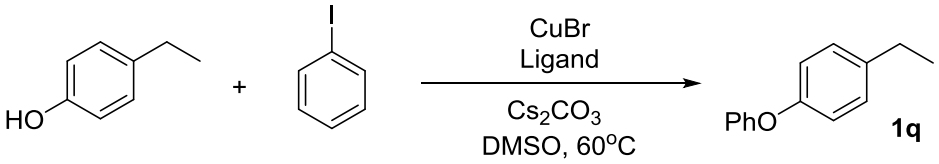
NMR spectroscopic data were identical to those previously reported.[4]



4-ethylphenyl acetate (1p): The product was obtained following the same procedure as **1f**. Colorless oil (0.77g, 94%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 6.99 (dd, *J* = 8.5, 2.2 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 1.24 (td, *J* = 7.6, 2.0 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 169.8, 148.7, 141.9, 128.9, 121.4, 28.4, 21.3, 15.7.

NMR spectroscopic data were identical to those previously reported.[5]

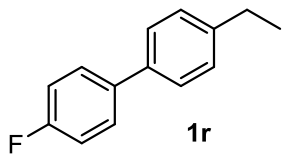


1-ethyl-4-phenoxybenzene (1q): In a three-necked reaction vessel equipped with a magnetic stirring bar, CuBr (144 mg, 1 mmol, 0.1 equiv.), Cs_2CO_3 (6.84 g, 21 mmol, 2.1 equiv.) and ethyl 2-oxocyclohexanecarboxylate (340 mg, 2 mmol, 0.2 equiv.) were dissolved in DMSO (10 mL) under a N_2 atmosphere. Then iodobenzene (2.04 g, 10 mmol, 1 equiv.) and 3-ethylphenol (1.47 g, 12 mmol, 1.2 equiv.) were added, and the mixture was heated to 60°C. After the reaction was completed, the crude solution was filtered through a pad of silica gel. The filtrate was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel (PE/EtOAc-50:1) to afford the target compound (1.7 g, 86%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 2H), 7.24 – 7.17 (m, 2H), 7.15 – 7.08 (m, 1H), 7.07 – 6.94 (m, 4H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.9, 155.0, 139.4, 130.0, 129.8, 129.8, 129.1, 122.9, 119.2, 118.5, 28.3, 15.9.

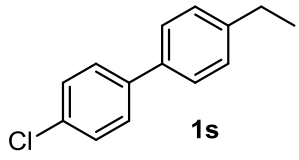
NMR spectroscopic data were identical to those previously reported.[6]

4-ethyl-4'-fluoro-1,1'-biphenyl (1r): The product was obtained following the same procedure as **1o**.



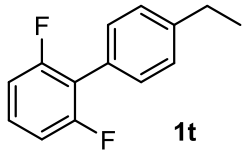
White solid (950 mg, 95%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.52 – 7.47 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.11 (m, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.8 Hz), 143.5, 137.8, 137.4 (d, *J* = 3.3 Hz), 128.6 (d, *J* = 8.0 Hz), 128.5, 127.1, 115.7 (d, *J* = 21.4 Hz), 28.6, 15.7.
NMR spectroscopic data were identical to those previously reported.[7]

4-chloro-4'-ethyl-1,1'-biphenyl (1s): The product was obtained following the same procedure as **1o**.



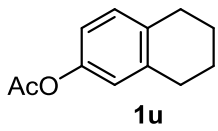
White solid (946 mg, 88%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 4H), 7.43 – 7.37 (m, 2H), 7.32 – 7.27 (m, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 143.9, 139.7, 137.5, 133.2, 129.0, 128.5, 128.3, 127.0, 28.7, 15.7.

4'-ethyl-2,6-difluoro-1,1'-biphenyl (1t): The product was obtained following the same procedure as **1o**. White solid (1.0 g, 93%).

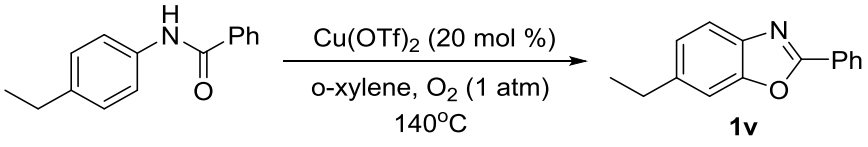


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H), 7.39 – 7.26 (m, 3H), 7.09 – 6.95 (m, 2H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 160.3 (dd, *J* = 248.2, 7.2 Hz), 144.4, 130.3 (t, *J* = 1.8 Hz), 128.7 (t, *J* = 10.4 Hz), 127.9, 126.5, 118.6 (t, *J* = 18.7 Hz), 113.9 – 108.3 (m), 28.8, 15.5.

5,6,7,8-tetrahydronaphthalen-2-yl acetate (1u): The product was obtained following the same procedure as **1p**. Colorless oil (1.56 g, 82%).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 – 7.04 (m, 1H), 6.90 – 6.77 (m, 2H), 2.91 – 2.72 (m, 4H), 2.31 (s, 3H), 1.84 (h, *J* = 3.4, 2.9 Hz, 4H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 169.6, 148.2, 138.3, 134.6, 129.8, 121. 6, 118.5, 29.4, 28.8, 23.1, 22.8, 21.0.
NMR spectroscopic data were identical to those previously reported.[8]

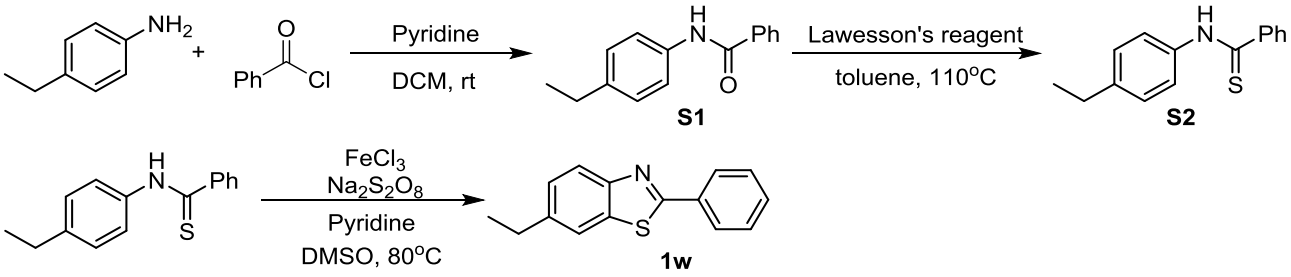


6-ethyl-2-phenylbenzo[d]oxazole (1v): (Compound above has been prepared following a reported method[11]). To a dried Schlenk tube was added the N-(4-ethylphenyl)benzamide (1.13 g, 5 mmol, 1 equiv.) and $Cu(OTf)_2$ (362 mg, 1 mmol, 0.2 equiv.). The tube and its contents were then purged under oxygen and *o*-xylene (10 ml) was added via syringe. The reaction mixture was then heated with stirring at 140°C for 48h under oxygen (balloon) atmosphere. The mixture was then concentrated

under reduced pressure. The residue was diluted with EtOAc and water, the combined organic phase washed with brine, dried ($MgSO_4$) and concentrated in vacuum. The residue was purified by silica gel chromatography to afford the target compound **1v** (360 mg, 32%) as yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 – 8.17 (m, 2H), 7.67 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.52 (ddd, *J* = 3.5, 2.4, 1.3 Hz, 3H), 7.41 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.20 (dd, *J* = 8.1, 1.6 Hz, 1H), 2.80 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 162.8, 151.2, 142.3, 140.2, 131.4, 129.0, 127.6, 127.5, 124.9, 119.6, 109.7, 29.3, 16.1.

NMR spectroscopic data were identical to those previously reported.[9]

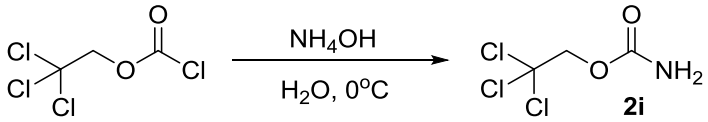


N-(4-ethylphenyl)benzamide (S1) : To a solution of 3-ethylaniline (2.42 g, 20 mmol, 1 equiv.) and pyridine (2.3 mL, 28 mmol, 1.4 equiv.) in DCM (40 mL) at 0 °C, benzoyl chloride (3.10 g, 22 mmol, 1.1 equiv.) was added dropwise. The reaction was gradually warmed to room temperature and stirred overnight. After being quenched with water, the mixture was extracted with DCM. The organic phase was washed with HCl(aq) (1M) and brine, dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude residue was recrystallized with PE/EtOAc to afford **S4** (4.3 g, 95%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 1H), 7.89 – 7.79 (m, 2H), 7.61 – 7.47 (m, 3H), 7.47 – 7.37 (m, 2H), 7.22 – 7.12 (m, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 166.0, 140.7, 135.7, 135.1, 131.7, 128.7, 128.4, 127.2, 120.7, 28.4, 15.8.

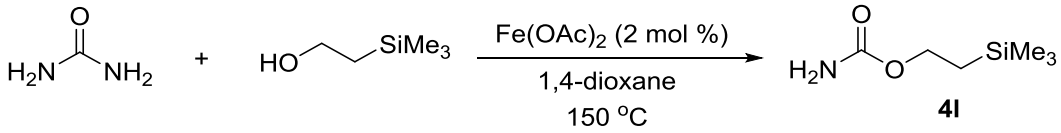
N-(4-ethylphenyl)benzothioamide (S2): To a three-necked vessel (50 mL) equipped with a stir bar, **S4** (2.25 g, 10 mmol, 1 equiv.) and Lawesson's reagent (2.12 g, 5.25 mmol, 0.52 equiv.) were dissolved in anhydrous toluene (15 mL) under a N_2 atmosphere. The resulting mixture was stirred at 110℃ for 3 h. After cooling to room temperature, the organic solvent was removed, and the residue purified by flash column chromatography on silica gel (PE/EtOAc-10:1) to afford **S5** (723 mg, 30%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.94 – 7.80 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.46 (dt, *J* = 14.7, 7.1 Hz, 3H), 7.29 (s, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 198.4, 143.4, 136.8, 131.4, 128.80, 128.6, 126.8, 123.9, 28.7, 15.5.

6-ethyl-2-phenylbenzo[d]thiazole (1w): (Compound above has been prepared following a reported method[12]). To a three-necked vessel (50 mL) equipped with a stir bar, $FeCl_3$ (10 mg, 0.06 mmol, 0.1 equiv.), **S5** (145 mg, 0.6 mmol, 1 equiv.) and $Na_2S_2O_8$ (286 mg, 1.2 mmol, 2 equiv) were dissolved in a solution of pyridine (95 mg, 1.2 mmol, 2 equiv.) in DMSO (2 mL) under a N_2 atmosphere. The mixture was stirred at 80℃ for 3h. After cooling to room temperature, the reaction mixture was quenched with water and extracted with EtOAc (2×5 mL). The organic layers were combined, dried over $MgSO_4$, concentrated under reduced pressure, and purified by silica gel chromatography

(PE/EtOAc-20:1) to yield the product (100 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 – 8.05 (m, 2H), 8.04 – 7.95 (m, 1H), 7.70 (dq, *J* = 1.4, 0.7 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.34 (dt, *J* = 8.5, 1.1 Hz, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 167.2, 152.5, 141.9, 135.4, 133.9, 130.8, 129.1, 127.5, 126.9, 122.9, 120.3, 29.1, 15.9.
NMR spectroscopic data were identical to those previously reported.[10]

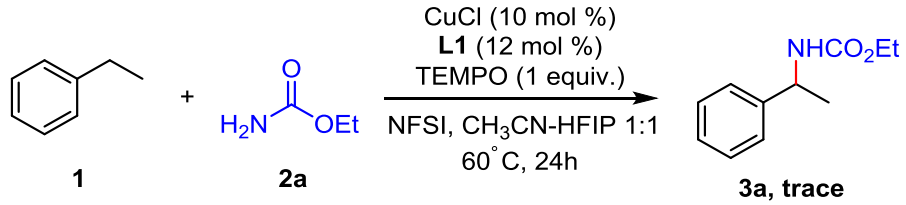


2,2,2-trichloroethyl carbamate: (Compound above has been prepared following a reported method[13]). Commercially available 2,2,2-trichloroethyl chloroformate was added dropwise to an excess of ammonium hydroxide with vigorous stirring at 0ºC. The white precipitated product was dissolved in methylene chloride, washed with water and brine, dried over $MgSO_4$, filtered, and the solvent removed. The product was isolated as a white solid in near quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.16 (s, 2H), 4.72 (s, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.2, 95.4, 74.8.
NMR spectroscopic data were identical to those previously reported.[13]



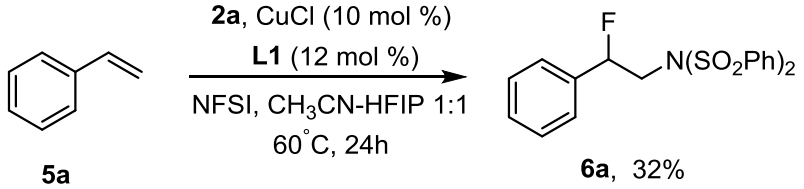
2-(trimethylsilyl)ethyl carbamate (4l): (Compound above has been prepared following a reported method[14]). In a glass pressure tube (25 mL) under an Ar atmosphere, $Fe(OAc)_2$ (17.4 mg, 0.1 mmol, 0.02 equiv.), urea (301 mg, 5 mmol, 1 equiv.) and alcohol (887 mg, 7.5 mmol, 1.5 equiv.) were dissolved in 1,4-dioxane (10 mL). Next the tube was closed and the resulting mixture stirred at 150ºC in an oil bath for 6h. After cooling down to room temperature, the crude mixture was directly purified by flash chromatography on silica gel to afford the corresponding product (115 mg, 14%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.62 (s, 2H), 4.23 – 4.08 (m, 2H), 1.08 – 0.80 (m, 2H), 0.04 (s, 9H).

5. Mechanistic Investigations



In a glovebox under an argon atmosphere, the ligand **L1** (8.9 mg, 0.03 mmol, 12 mol%), CuCl (2.5 mg, 0.025 mmol, 10 mol%) in a 1:1 MeCN/HFIP mixture (1 mL) were placed in a dried sealed tube (10 mL). The resulting mixture was stirred at room temperature for 20 minutes. Then, NFSI (157 mg, 0.5 mmol, 2 equiv.), ethyl carbamate **2a** (45 mg, 0.5 mmol, 2 equiv.), ethylbenzene (27 mg, 0.25 mmol, 1 equiv.) and TEMPO (39 mg, 0.25mmol, 1 equiv.) were added. The tube was sealed and the mixture was heated at 60°C for 24h. The crude mixture was filtered and evaporated under reduced

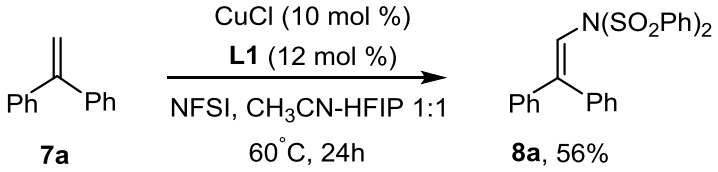
pressure, and the crude reaction mixture submitted to ^{1}H NMR.



In a glovebox under an argon atmosphere, the ligand **L1** (8.9 mg, 0.03 mmol, 12 mol%), CuCl (2.5 mg, 0.025 mmol, 10 mol%) in a 1:1 MeCN/HFIP mixture (1 mL) were placed in a dried sealed tube (10 mL). The resulting mixture was stirred at room temperature for 20 minutes. Then, NFSI (157 mg, 0.5 mmol, 2 equiv.), ethyl carbamate **2a** (45 mg, 0.5 mmol, 2 equiv.) and alkene (0.25 mmol, 1 equiv.) were added. The tube was sealed and the mixture was heated at 60°C for 24h. The mixture was then solubilized in DCM and evaporated under reduced pressure. The crude mixture was purified by column chromatography to afford the product **6a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 1H), 7.90 – 7.82 (m, 3H), 7.67 – 7.37 (m, 11H), 5.40 (t, *J* = 7.3 Hz, 1H), 4.36 – 4.25 (m, 1H), 4.16 – 4.05 (m, 1H). ^{13}C NMR (151 MHz, CDCl3) δ 138.9, 138.0, 134.1, 129.2, 129.1, 129.1, 129.0, 128.9, 128.8, 128.7, 128.3, 125.85 (d, *J* = 6.9 Hz), 60.5, 54.6.

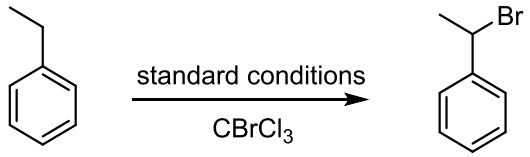
HRMS (ESI): $[M+Na]^+$ $C_{20}H_{18}O_4FNS_2Na^+$: calcd. 442.05535 found 442.05522.



In a glovebox under an argon atmosphere, the ligand **L1** (8.9 mg, 0.03 mmol, 12 mol%), CuCl (2.5 mg, 0.025 mmol, 10 mol%) in a 1:1 MeCN/HFIP mixture (1 mL) were placed in a dried sealed tube (10 mL). The resulting mixture was stirred at room temperature for 20 minutes. Then, NFSI (157 mg, 0.5 mmol, 2 equiv.), ethyl carbamate **2a** (45 mg, 0.5 mmol, 2 equiv.) and alkene (0.25 mmol, 1 equiv.) were added. The tube was sealed and the mixture was heated at 60°C for 24h. The mixture was then solubilized in DCM and evaporated under reduced pressure. The crude mixture was purified by column chromatography to afford the product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dq, *J* = 7.7, 1.1 Hz, 4H), 7.57 (tt, *J* = 7.2, 1.2 Hz, 2H), 7.40 (tt, *J* = 7.4, 1.0 Hz, 4H), 7.35 – 7.20 (m, 10H), 6.13 (s, 1H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 152.4, 139.9, 138.7, 136.9, 133.9, 130.0, 129.2, 128.9, 128.8, 128.8, 128.5, 128.4, 128.3, 116.4.

HRMS (ESI): $[M+Na]^+$ $C_{26}H_{21}NO_4S_2Na^+$: calcd. 498.08042 found 498.07968.

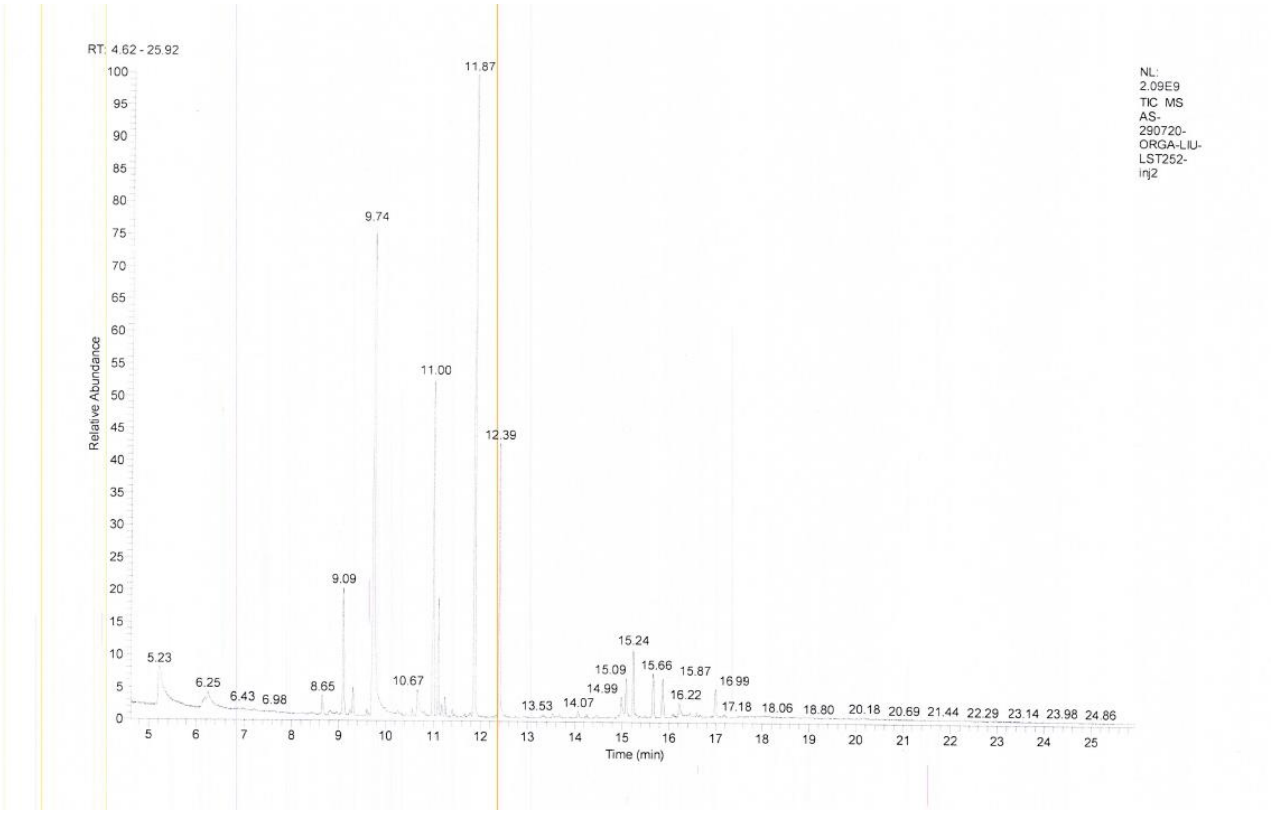


In a glovebox under an argon atmosphere, the ligand **L1** (8.9 mg, 0.03 mmol, 12 mol%), CuCl (2.5 mg, 0.025 mmol, 10 mol%) in a 1:1 MeCN/HFIP mixture (1 mL) were placed in a dried sealed tube

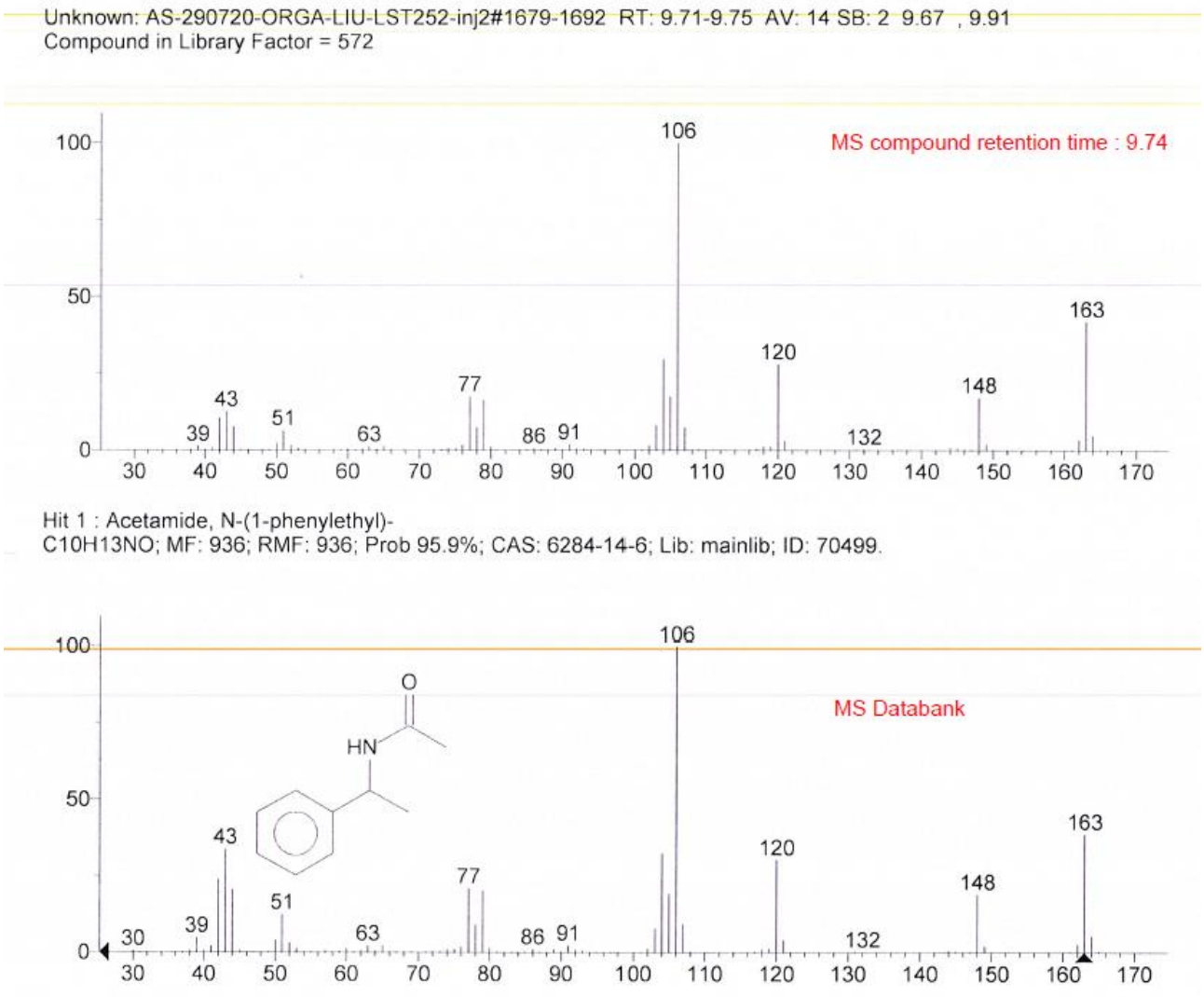
(10 mL). The resulting mixture was stirred at room temperature for 20 minutes. Then, NFSI (157 mg, 0.5 mmol, 2 equiv.), 1-ethylbenzene (26.5 mg, 0.25 mmol, 1 equiv.) and $CBrCl_3$ (98 mg, 0.5 mmol, 2 equiv.) were added. The tube was sealed and the mixture was heated at 60°C for 24h. The mixture was filtered and evaporated under reduced pressure, and the crude reaction mixture submitted to GC-MS studies.

Data below summarize

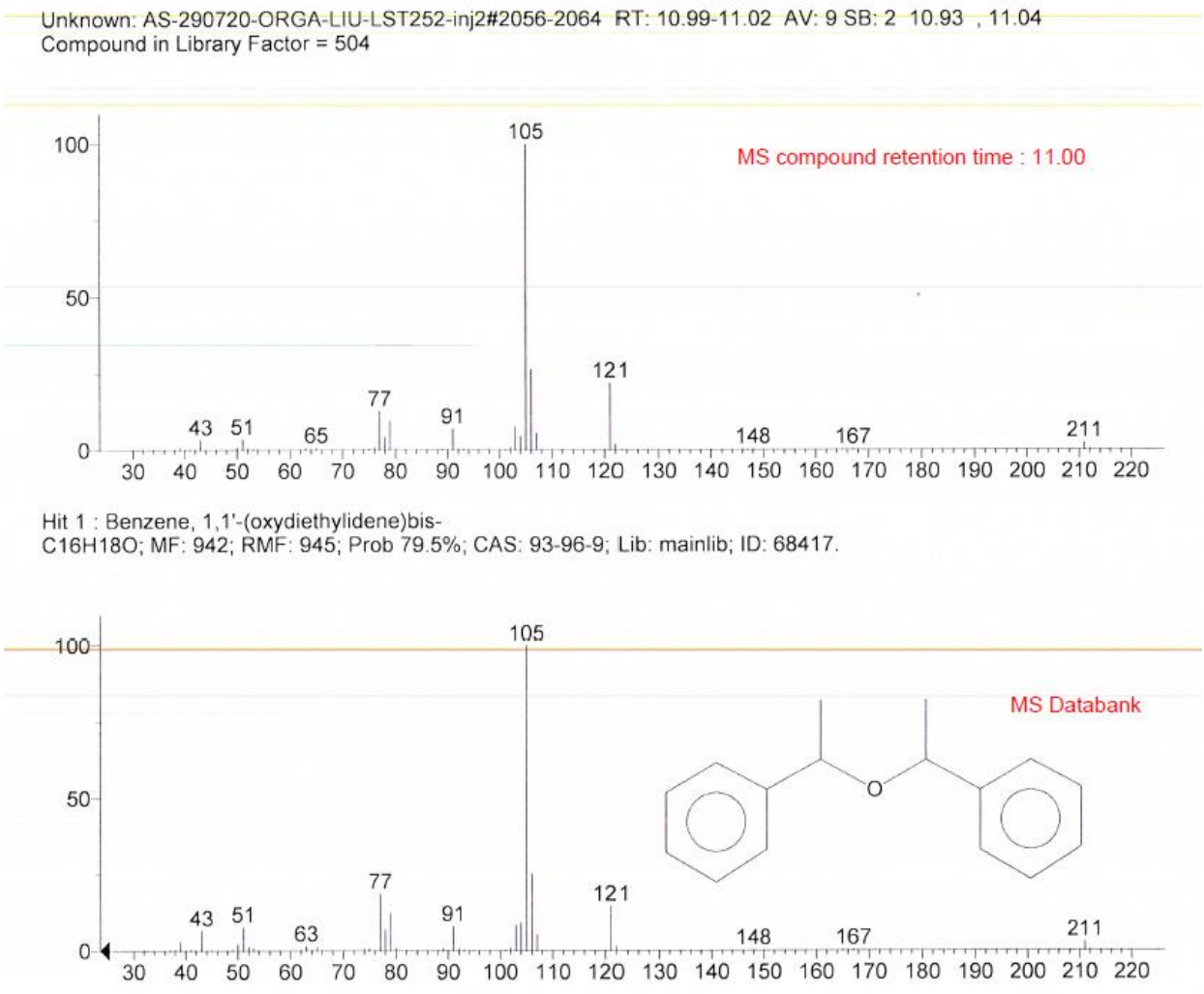
- GC of the crude reaction mixture
- MS of some representative compounds present in the reaction mixture (retention time indicated)
- Below each compound, known compound with match mass spectrometry



GC-MS Reaction of **1a** with $CBrCl_3$

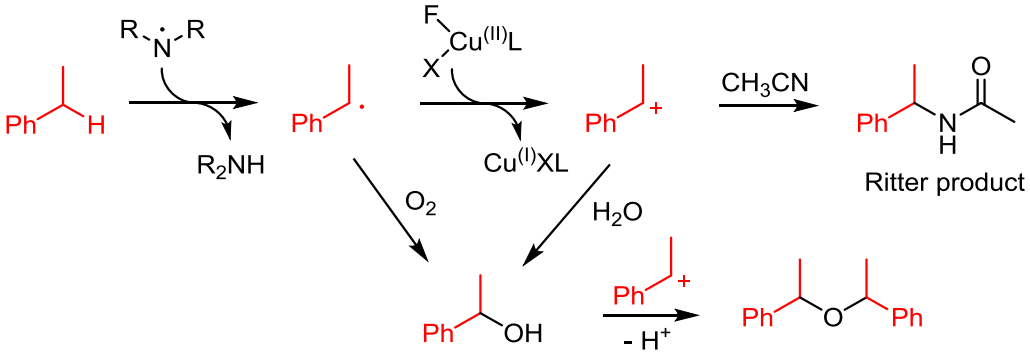


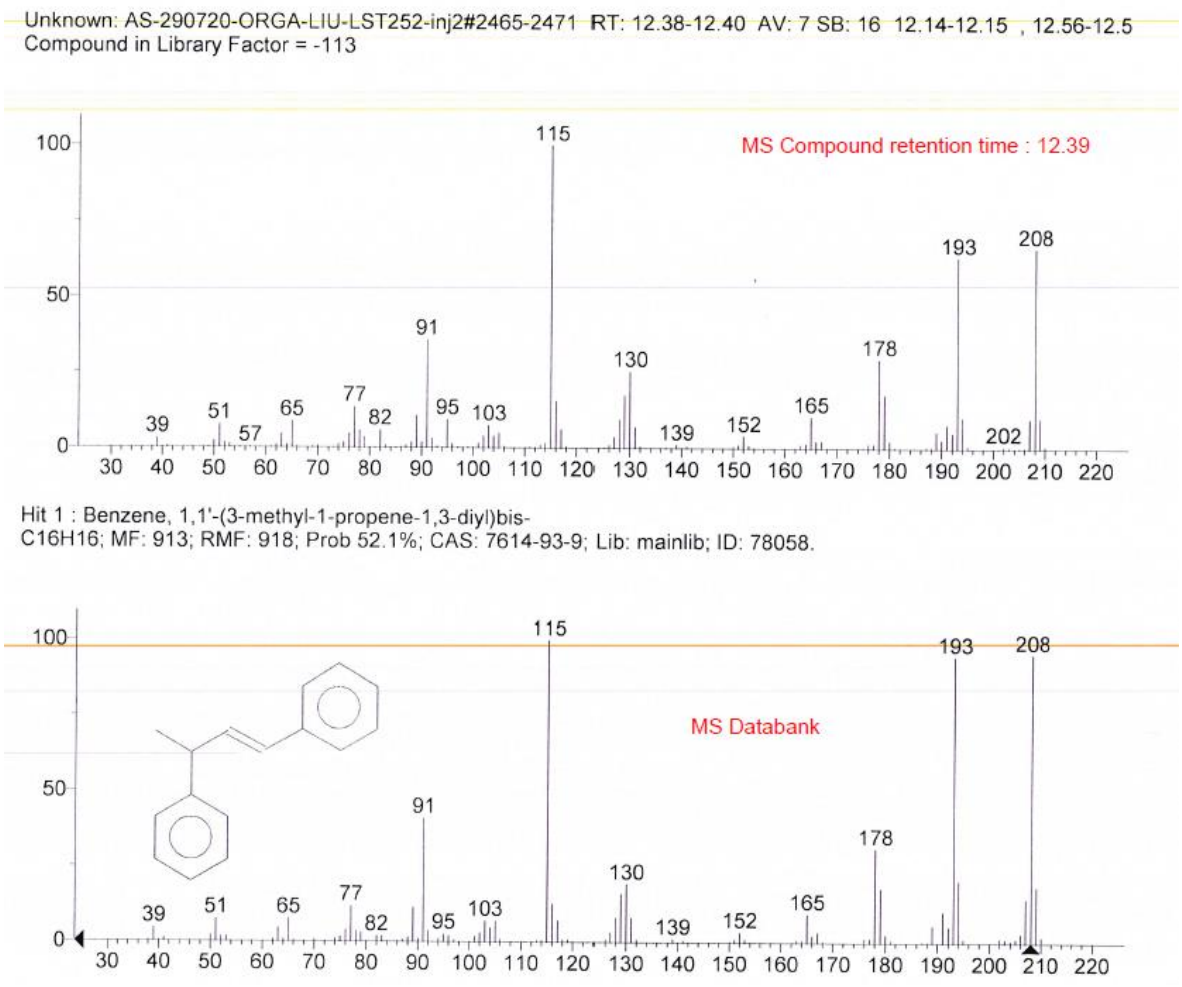
Mass spectra of Ritter product from ethylbenzene **1a**



Mass spectra of a benzyl ether product from ethylbenzene **1a**

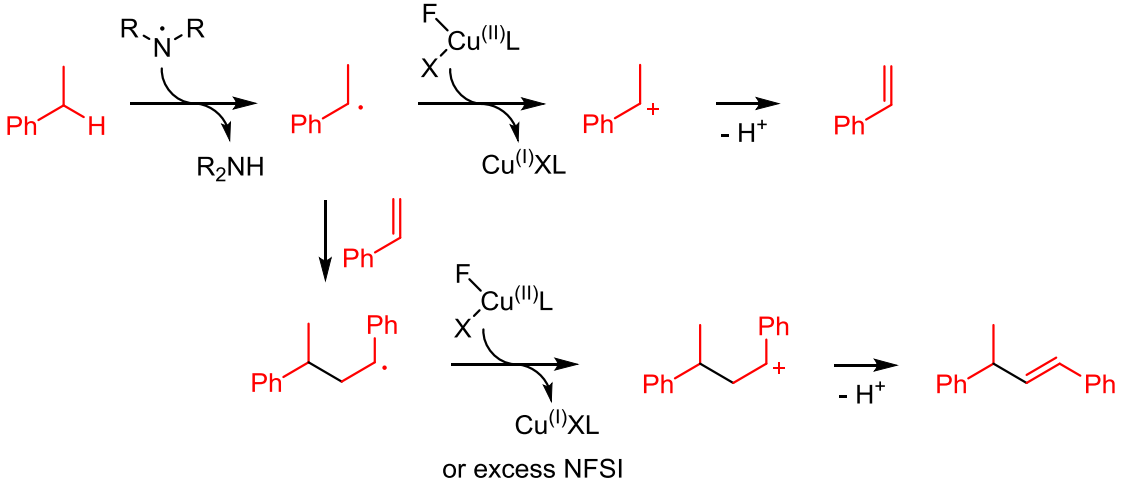
The presence of the Ritter product and that of the ether may be explained as shown below. Hydrogen abstraction by the sulfonamidyl radical provides a benzylic radical which may be oxidized further into a cation. The latter reacts with the solvent (CH_3CN) to provide the corresponding amide. The benzylic alcohol may be formed through reaction of the benzyl radical with oxygen traces or through reaction of the benzylic cation with traces of water. Ether is then generated through the reaction of the benzyl alcohol with the benzyl cation.

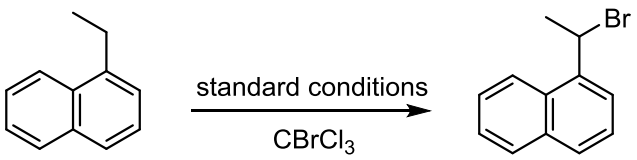




Mass spectra of a dimeric product generated from ethylbenzene **1a**

The dimeric product above is postulated to be generated as shown below. The benzylic cation formed as explained before loses a proton to form styrene. The benzylic radical may then add onto styrene to provide a stabilized benzylic radical that is oxidized into the corresponding cation (by Cu(II) or excess NFSI) affording the dimeric product with structure as shown.

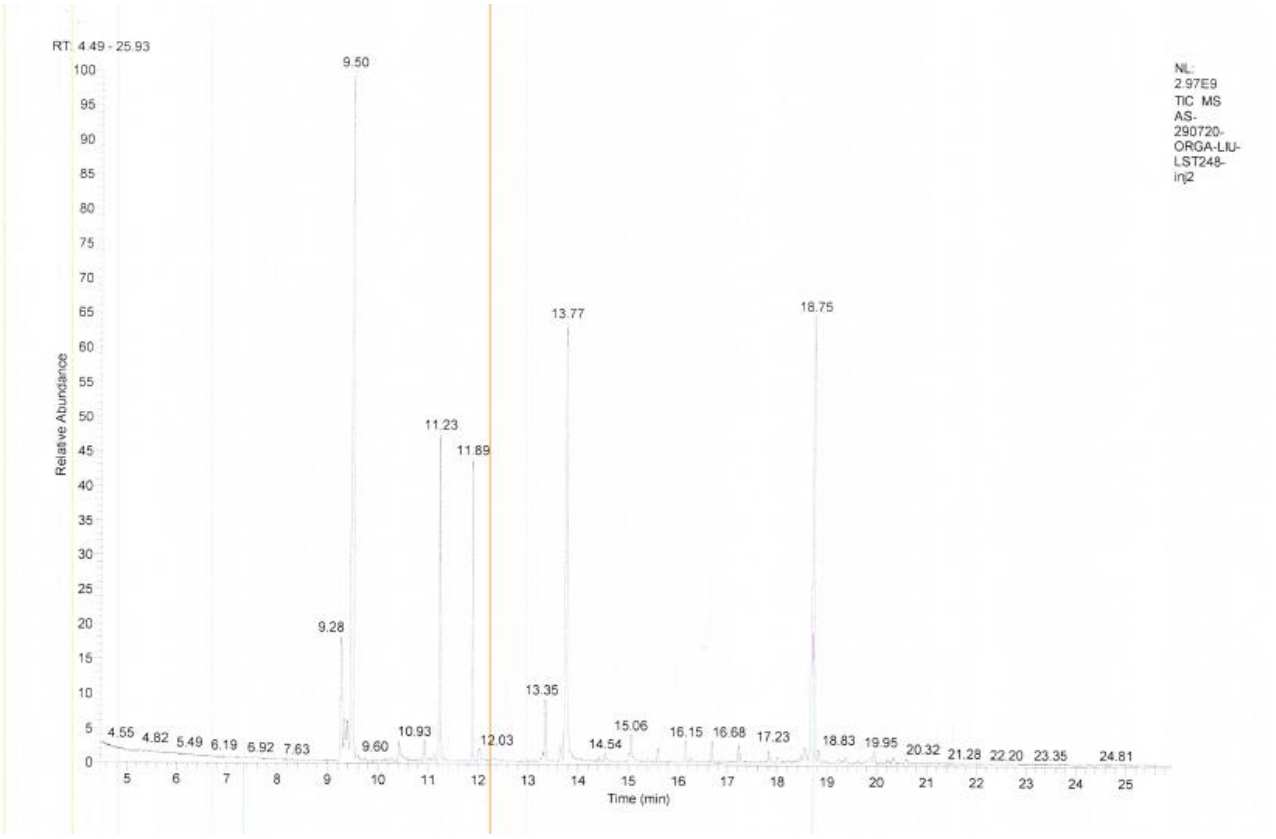




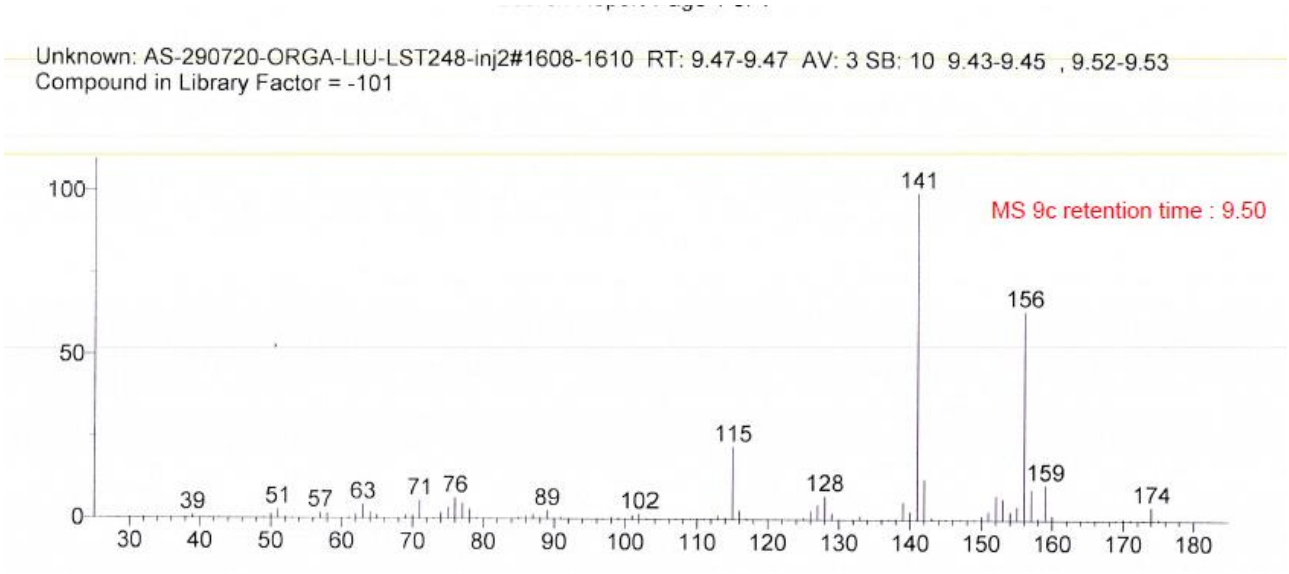
In a glovebox under an argon atmosphere, the ligand **L1** (8.9 mg, 0.03 mmol, 12 mol%), CuCl (2.5 mg, 0.025 mmol, 10 mol%) in a 1:1 MeCN/HFIP mixture (1 mL) were placed in a dried sealed tube (10 mL). The resulting mixture was stirred at room temperature for 20 minutes. Then, NFSI (157 mg, 0.5 mmol, 2 equiv.), 1-ethylnaphthalene (39 mg, 0.25 mmol, 1 equiv.) and $CBrCl_3$ (98 mg, 0.5 mmol, 2 equiv.) were added. The tube was sealed and the mixture was heated at 60°C for 24h. The mixture was filtered and evaporated under reduced pressure, and the crude reaction mixture submitted to GC-MS studies.

Data below summarize

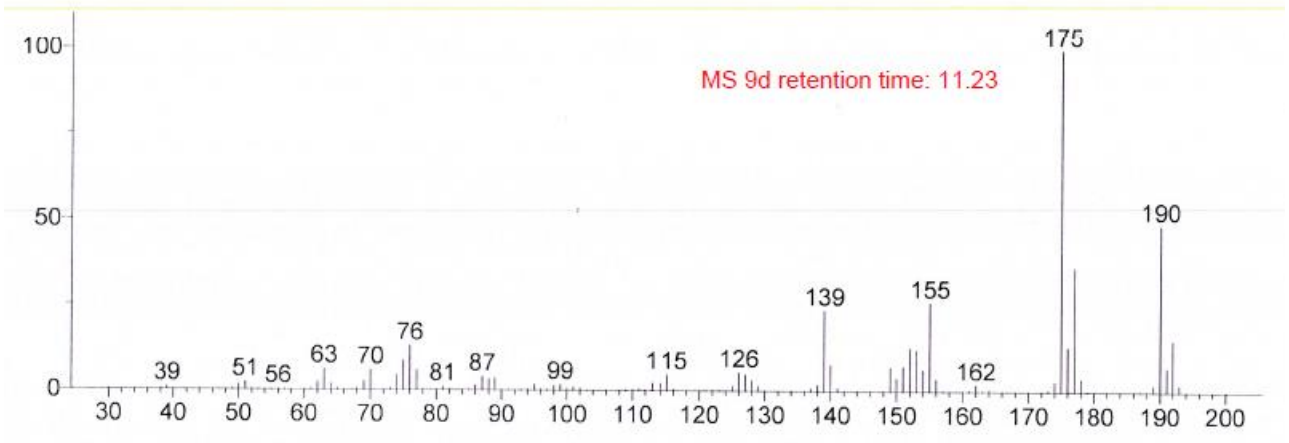
- GC of the crude reaction mixture
- MS of some representative compounds present in the reaction mixture (retention time indicated)
- Below each compound, known compound with match mass spectrometry



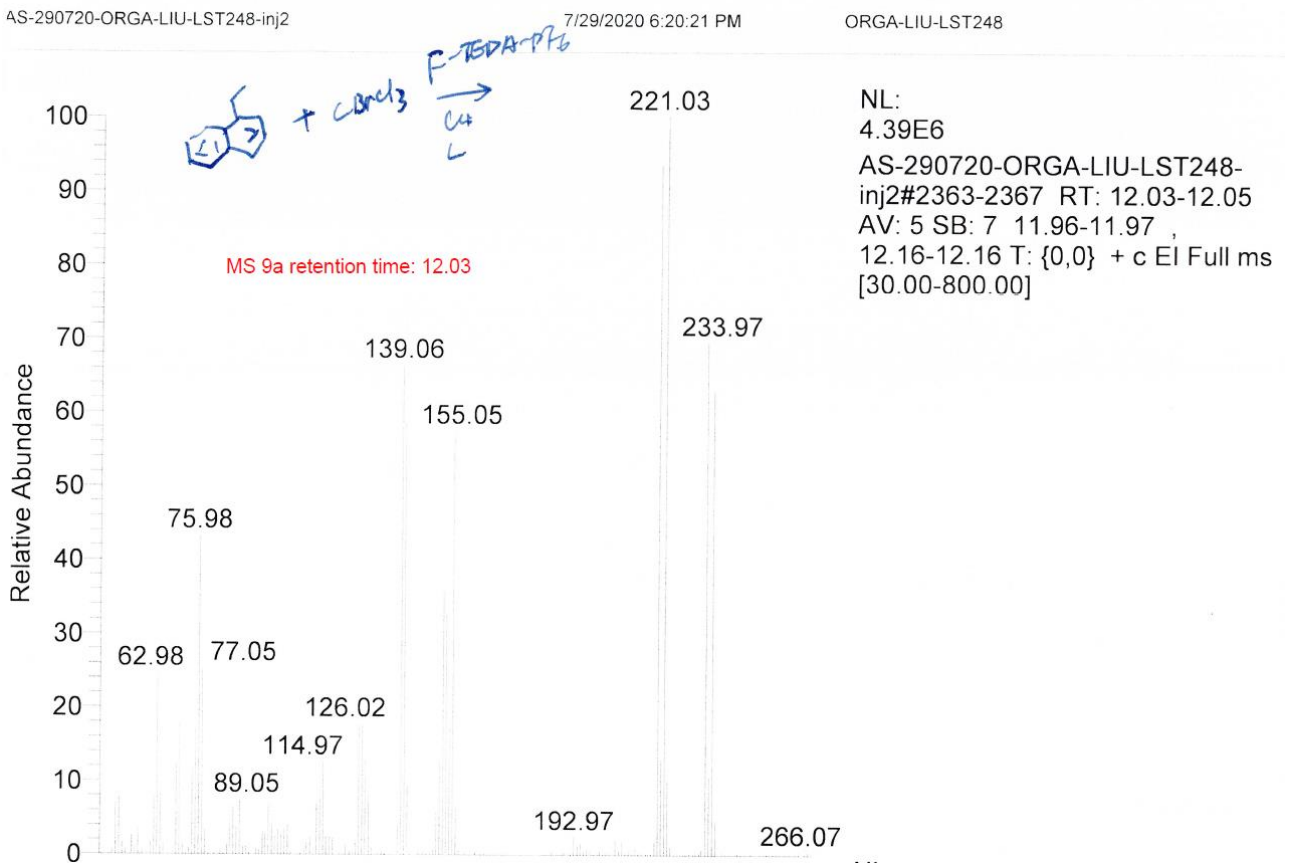
GC-MS Reaction **1b** with $CBrCl_3$



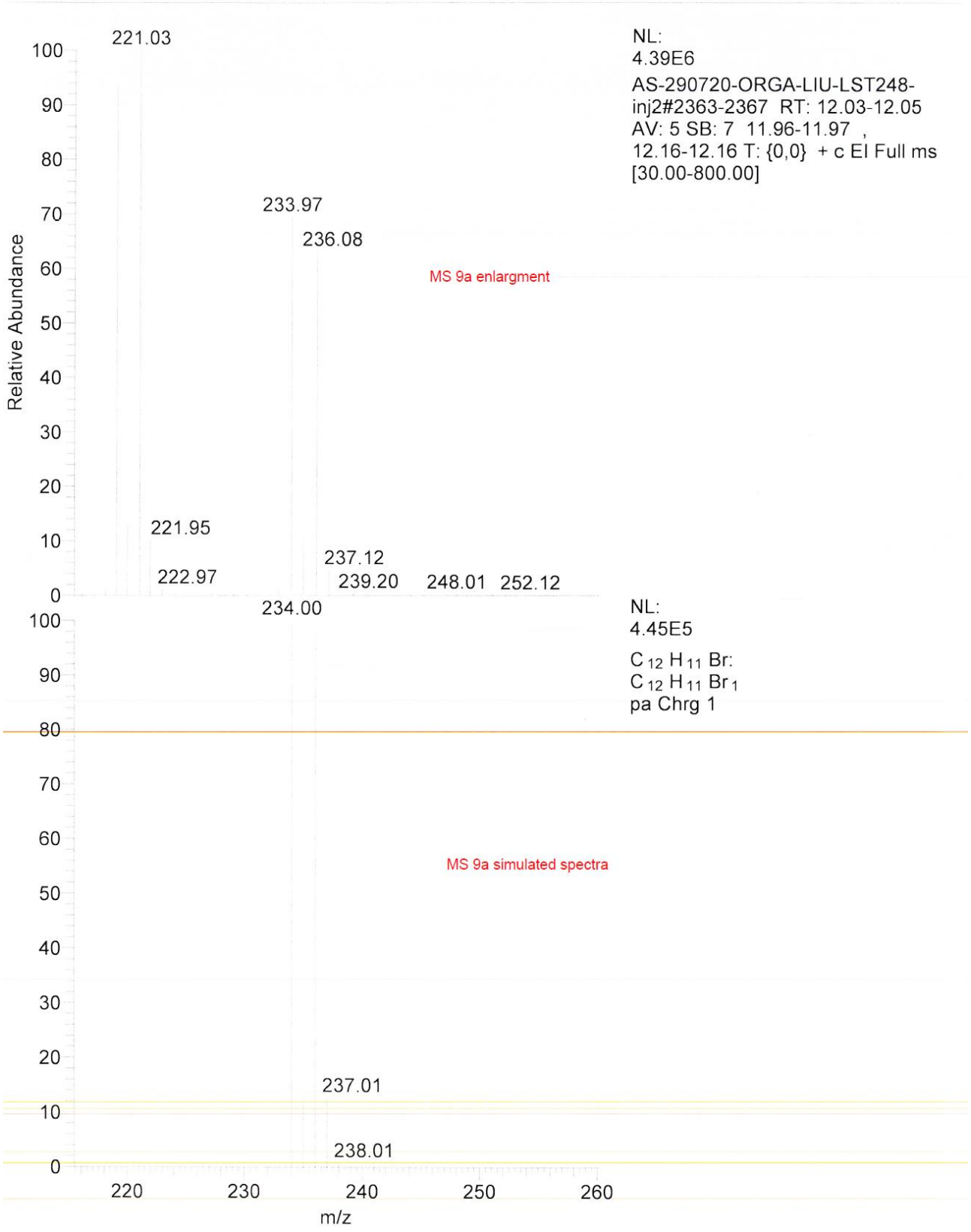
Mass spectra of fluoroethylnaphthalene **9c**



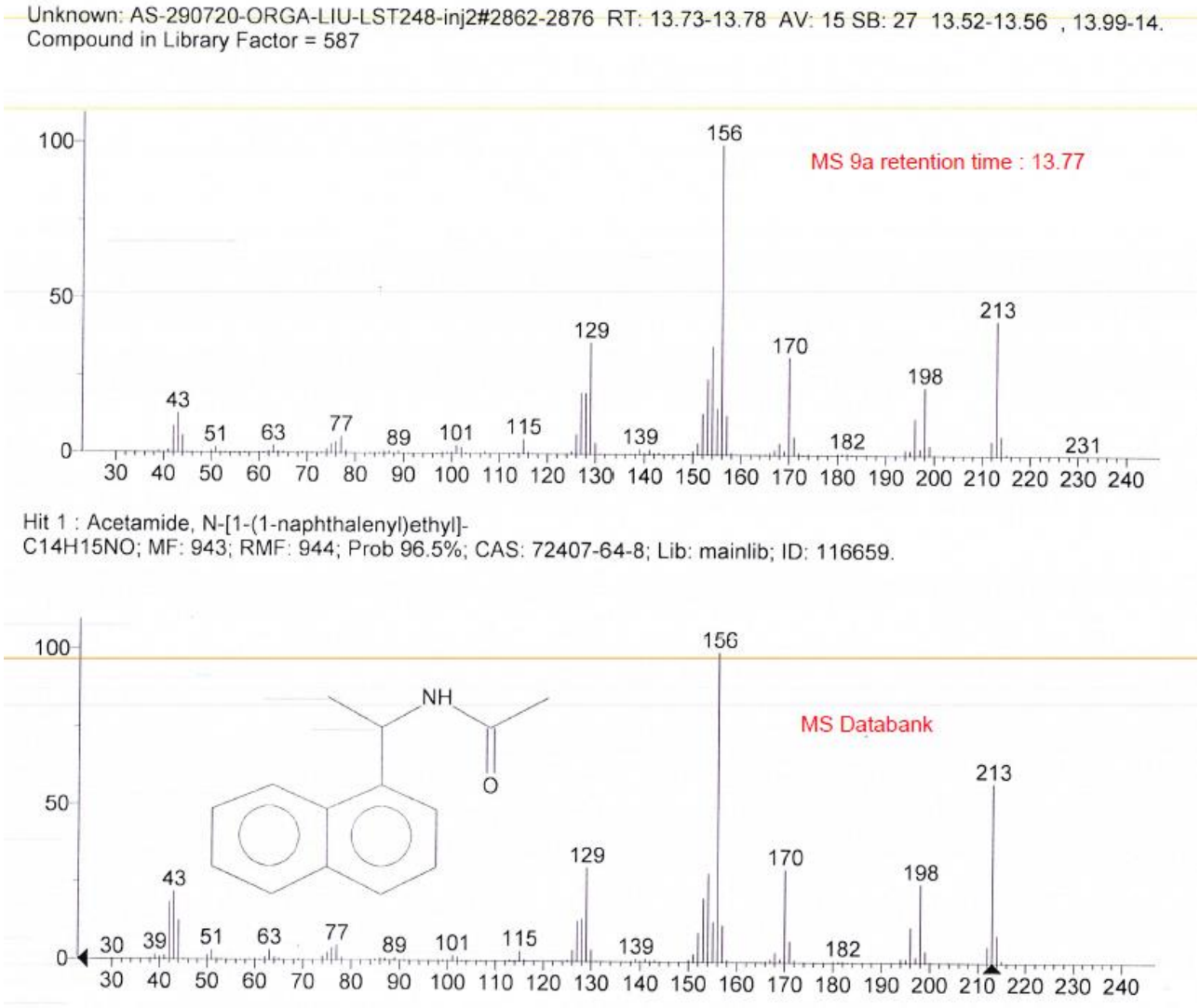
Mass spectra of chloroethylnaphthalene **9d**



Mass spectra of bromoethylnaphthalene **9a**

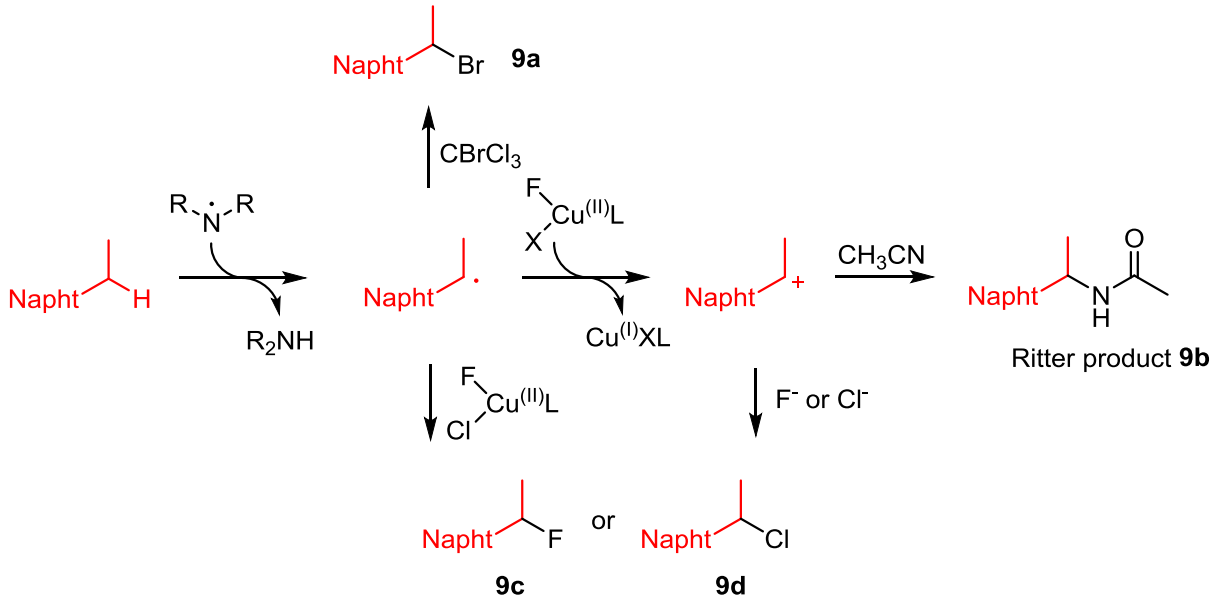


Mass spectra of bromoethylnaphthalene **9a** (enlargement)

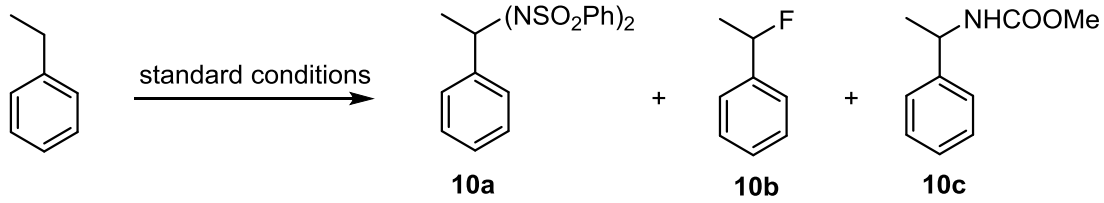


Mass spectra of Ritter product **9b**

The presence of the Ritter product **9b** as well as bromide **9a**, fluoride **9c**, and chloride **9d** may be explained as shown below. Hydrogen abstraction by the sulfonamidyl radical provides a benzylic radical which may be oxidized further into a cation. The latter reacts with the solvent (CH_3CN) to provide the corresponding amide **9b**. Bromide **9a** is generated through reaction of the benzylic radical with $CBrCl_3$. Fluoride **9c**, and chloride **9d** may be formed through two different pathway: (1) through reaction of the benzyl radical with Cu(II)FCl or the fluorosulfonylamide; (2) through reaction of the benzyl cation with fluoride or chloride anions present in the medium.

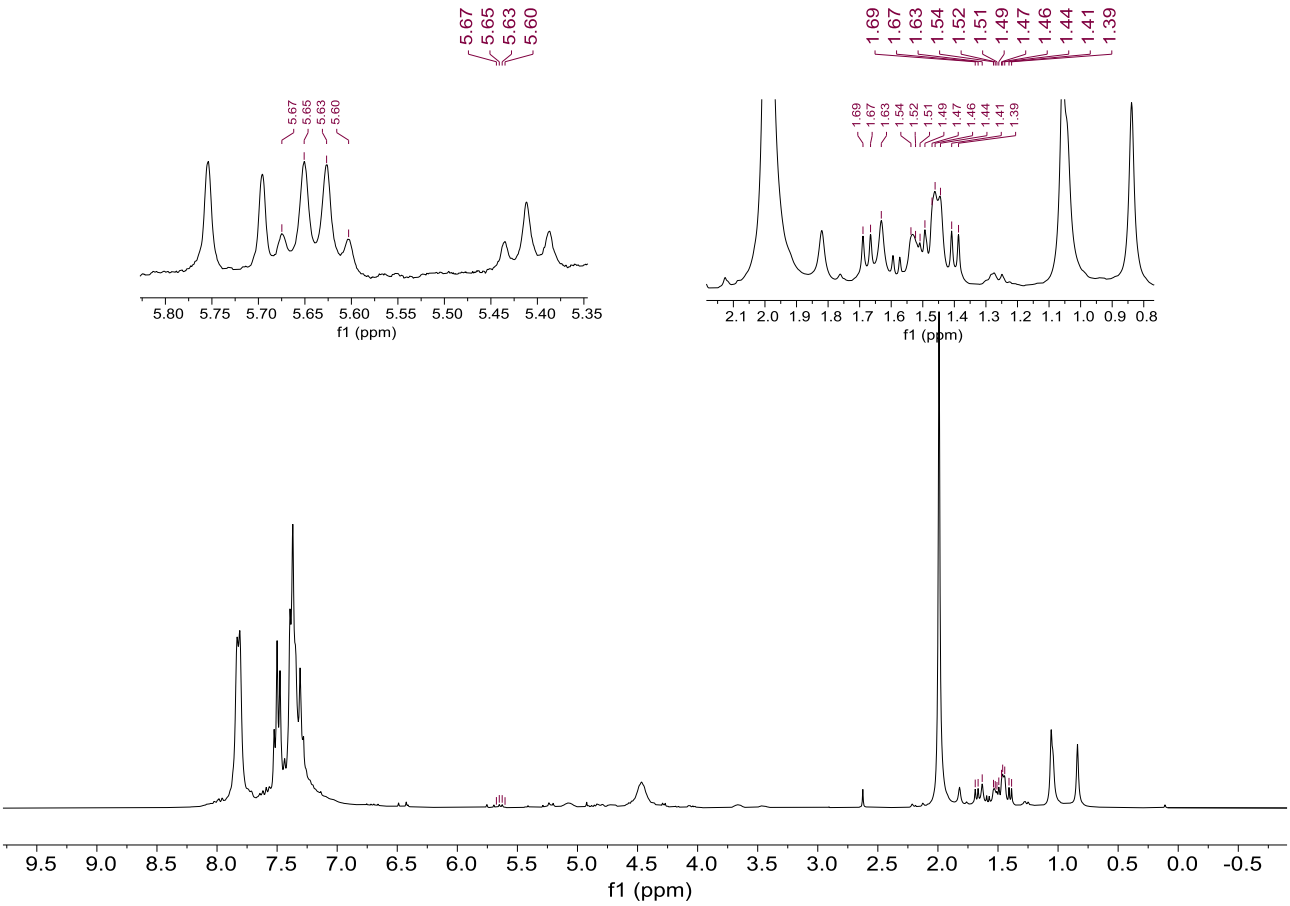


Reaction of **1a** with NFSI, but without **2a**



In a glovebox under an argon atmosphere, the ligand **L1** (8.9 mg, 0.03 mmol, 12 mol%), CuCl (2.5 mg, 0.025 mmol, 10 mol%) in a 1:1 MeCN/HFIP mixture (1 mL) were placed in a dried sealed tube (10 mL). The resulting mixture was stirred at room temperature for 20 minutes. Then, NFSI (157 mg, 0.5 mmol, 2 equiv.) and 1-ethylbenzene (26.5 mg, 0.25 mmol, 1 equiv.) were added. The tube was sealed and the mixture was heated at 60°C for 24h. After that, the solvent was removed by atmospheric distillation and $CDCl_3$ was added for crude NMR.

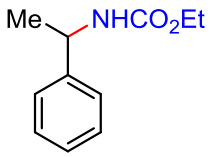
^{1}H NMR showed the presence of **10a** as one of the constituent of a complex mixture, where fluoride **10b** and Ritter product **10c** if present, were present in trace amounts. Therefore, a nucleophilic displacement of a benzylic fluoride by the carbamate H_2NCO_2Et seems unlikely in our case.



Crude NMR of reaction of **1a** with NFSI, without **2a**

6. Characterization Data

Ethyl (1-phenylethyl)carbamate (3a)



Rf = 0.25-0.3 (PE : EA = 5:1).

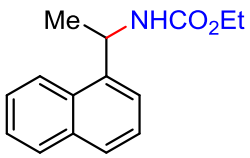
FT-IR **ν**max (cm^{-1}) = 3324, 2979, 1699, 1538, 1532, 1247, 1064, 700.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 5H), 5.08 – 4.70 (m, 2H), 4.10 (qd, *J* = 7.1, 1.7 Hz, 2H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (76 MHz, CDCl3) δ 155.9, 143.8, 128.7, 127.4, 126.0, 60.9, 50.7, 22.64 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{11}H_{15}O_2NNa^+$: calcd. 216.09950 found 216.09873.

Ethyl (1-(naphthalen-1-yl)ethyl)carbamate (3b)



Rf = 0.25-0.3 (PE : EA = 10:1).

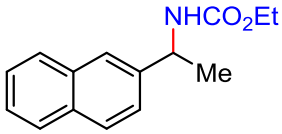
m.p. = 98-101°C

FT-IR **ν**max (cm^{-1}) = 3324, 2978, 1694, 1704, 1531, 1513, 1245, 1064, 777.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.73 (m, 2H), 7.60 – 7.40 (m, 4H), 5.65 (d, *J* = 7.3 Hz, 1H), 4.99 (s, 1H), 4.13 (qd, *J* = 7.1, 0.9 Hz, 2H), 1.65 (d, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.9, 139.1, 134.1, 131.0, 129.0, 128.3, 126.5, 125.9, 125.4, 123.4, 122.3, 61.0, 46.7, 21.9, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{15}H_{17}O_2NNa^+$: calcd. 266.11515 found 266.11470.

Ethyl (1-(naphthalen-2-yl)ethyl)carbamate (3c)



Rf = 0.25-0.3 (PE : EA = 10:1).

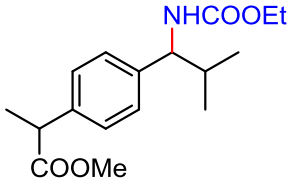
m.p. = 66-68°C

FT-IR **ν**max (cm^{-1}) = 3323, 2977, 1699, 1527, 1246, 1064.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.69 (m, 4H), 7.55 – 7.38 (m, 3H), 5.03 (s, 2H), 4.12 (qd, *J* = 7.1, 1.9 Hz, 2H), 1.57 (d, *J* = 6.4 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.0, 141.2, 133.5, 132.8, 128.6, 128.0, 127.7, 126.3, 125.9, 124.6, 124.4, 61.0, 50.8, 22.6, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{15}H_{17}O_2NNa^+$: calcd. 266.11515, found 266.11465.

Methyl 2-(4-(1-((ethoxycarbonyl)amino)-2-methylpropyl)phenyl)propanoate (3d)



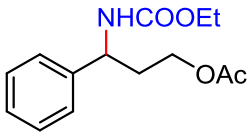
Rf = 0.25-0.3 (PE : EA = 5:1).

FT-IR **ν**max (cm^{-1}) = 3337, 2975, 2959, 1736, 1720, 1529, 1515, 1238, 1212, 1168, 1036.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 4.99 (d, *J* = 9.1 Hz, 1H), 4.43 (d, *J* = 8.7 Hz, 1H), 4.07 (qd, *J* = 7.1, 3.2 Hz, 2H), 3.75 – 3.67 (m, 1H), 3.65 (s, 3H), 1.98 (h, *J* = 6.8 Hz, 1H), 1.53 – 1.41 (m, 3H), 1.20 (d, *J* = 7.3 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 175.2, 175.1, 156.3, 141.0, 139.3, 127.6, 127.1, 61.0, 60.7, 52.2, 45.2, 33.8, 19.9, 18.7, 18.7, 18.6, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{17}H_{25}O_4NNa^+$: calcd. 330.16758 found 330.16681.

3-((ethoxycarbonyl)amino)-3-phenylpropyl acetate (3e)



Rf = 0.25-0.3 (PE : EA = 5:1).

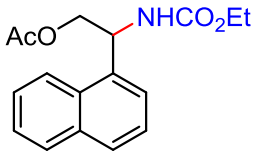
m.p. = 83-85°C

FT-IR **ν**max (cm^{-1}) = 3330, 2975, 1739, 1719, 1699, 1530, 1368, 1245, 1046, 701.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 5H), 5.06 (d, *J* = 8.3 Hz, 1H), 4.83 (d, *J* = 8.4 Hz, 1H), 4.13 – 4.02 (m, 4H), 2.13 (td, *J* = 6.5, 4.2 Hz, 2H), 2.03 (s, 3H), 1.24 – 1.15 (m, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.1, 156.0, 141.8, 128.9, 127.7, 126.4, 61.5, 61.1, 52.7 35.4, 21.0, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{14}H_{19}O_4NNa^+$: calcd. 288.12063 found 288.12035.

2-((ethoxycarbonyl)amino)-2-(naphthalen-1-yl)ethyl acetate (3f)



Rf = 0.2 (PE : EA = 5:1).

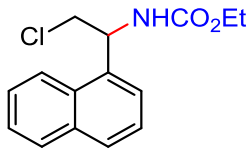
m.p. = 95-97°C

FT-IR **ν**max (cm^{-1}) = 3332, 2981, 1739, 1715, 1531, 1237, 1061, 1040, 778.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.85 (ddd, *J* = 19.2, 7.1, 2.4 Hz, 2H), 7.62 – 7.43 (m, 4H), 5.87 (s, 1H), 5.38 (d, *J* = 8.3 Hz, 1H), 4.56 – 4.32 (m, 2H), 4.12 (dt, *J* = 8.5, 6.5 Hz, 2H), 2.07 (s, 3H), 1.24 (d, *J* = 10.6 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 171.2, 156.1, 134.4, 134.0, 130.9, 129.1, 128.8, 126.9, 126.1, 125.3, 123.4, 122.9, 66.1, 61.3, 50.4, 21.0, 14.7.

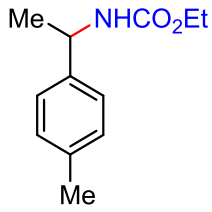
HRMS (ESI): $[M+Na]^+$ $C_{17}H_{19}O_4NNa^+$: calcd. 324.12063 found 324.12085.

Ethyl (2-chloro-1-(naphthalen-1-yl)ethyl)carbamate (3g)



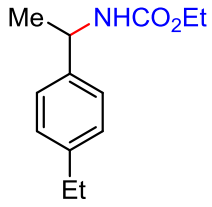
Rf = 0.3-0.4 (PE : EA = 5:1).
m.p. = 115-117°C
FT-IR **ν**max (cm^{-1}) = 3319, 3057, 2980, 1695, 1532, 1514, 1253, 1058, 779.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.86 (ddd, *J* = 18.2, 7.7, 1.8 Hz, 2H), 7.63 – 7.43 (m, 4H), 5.89 (d, *J* = 7.8 Hz, 1H), 5.39 (d, *J* = 8.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.04 (dd, *J* = 11.3, 5.4 Hz, 1H), 3.91 (dd, *J* = 10.9, 5.9 Hz, 1H), 1.26 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.0, 134.3, 134.1, 130.8, 129.3, 129.0, 126.9, 126.1, 125.3, 123.7, 122.5, 61.5, 51.9, 47.2, 14.7.
HRMS (ESI): $[M+Na]^+$ $C_{15}H_{16}O_2NClNa^+$: calcd. 300.07618 found 300.07637.

Ethyl (1-(p-tolyl)ethyl)carbamate (3h)



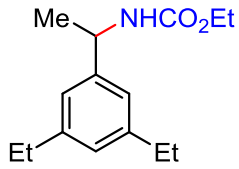
Rf = 0.25-0.3 (PE : EA = 5:1).
FT-IR **ν**max (cm^{-1}) = 3325, 2977, 2930, 1699,1529, 1515, 1245, 1064.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.09 (m, 4H), 5.10 – 4.59 (m, 2H), 4.10 (qd, *J* = 7.1, 1.4 Hz, 2H), 2.33 (s, 3H), 1.46 (d, *J* = 6.6 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.0, 140.8, 137.0, 129.4, 126.0, 60.9, 50.4, 31.1, 21.2, 14.7.
HRMS (ESI): $[M+Na]^+$ $C_{12}H_{17}O_2NNa^+$: calcd. 230.11515, found 230.11481.

Ethyl (1-(4-ethylphenyl)ethyl)carbamate (3i)



Rf = 0.25-0.3 (PE : EA = 10:1).
m.p. = 44-46°C
FT-IR **ν**max (cm^{-1}) = 3325, 3053, 2970, 2932, 2873, 1704, 1525.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.11 (m, 4H), 4.83 (dd, *J* = 15.5, 9.0 Hz, 2H), 4.10 (qd, *J* = 7.1, 1.3 Hz, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.22 (td, *J* = 7.4, 2.3 Hz, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.0, 143.4, 141.0, 128.2, 126.1, 60.9, 50.5, 28.6, 22.6, 15.6, 14.7.
HRMS (ESI): $[M+Na]^+$ $C_{13}H_{19}O_2NNa^+$: calcd. 244.13080 found 244.13049.

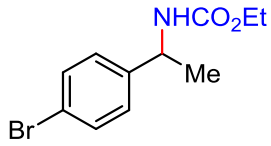
Ethyl (1-(3,5-diethylphenyl)ethyl)carbamate (3j)



Rf = 0.25-0.3 (PE : EA = 10:1).
m.p. = 60-63°C
FT-IR **ν**max (cm^{-1}) = 3325, 2967, 2933, 1700, 1532, 1246, 1062.
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (s, 3H), 4.86 (d, *J* = 34.5 Hz, 2H), 4.11 (qd, *J* = 7.1, 1.2 Hz, 2H), 2.72 – 2.54 (m, 4H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.23 (td, *J* = 7.4, 1.6 Hz, 9H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.9, 144.7, 143.7, 126.6, 123.0, 60.9, 50.8, 29.0, 22.8, 15.7, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{15}H_{23}O_2NNa^+$: calcd. 272.16210, found 272.16149.

Ethyl (1-(4-bromophenyl)ethyl)carbamate (3k)



Rf = 0.25 (PE : EA = 10:1).

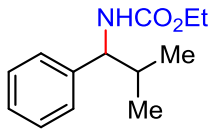
m.p. = 57-59°C

FT-IR **ν**max (cm^{-1}) = 3319, 2978, 1695, 1529, 1247, 1064.

^1H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.40 (m, 2H), 7.24 – 7.11 (m, 2H), 5.03 – 4.62 (m, 2H), 4.09 (qd, *J* = 7.1, 2.0 Hz, 2H), 1.44 (d, *J* = 6.9 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.9, 143.0, 131.8, 127.8, 121.1, 61.1, 50.2, 22.6, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{11}H_{14}O_2NBrNa^+$: calcd. 294.01001 found 294.01014.

Ethyl (2-methyl-1-phenylpropyl)carbamate (3l)



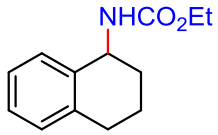
Rf = 0.25-0.3 (PE : EA = 10:1).

FT-IR **ν**max (cm^{-1}) = 3323, 2959, 1694, 1533, 1239, 1035, 701.

^1H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.28 – 7.19 (m, 3H), 5.02 (s, 1H), 4.47 (s, 1H), 4.10 (qd, *J* = 6.9, 2.7 Hz, 2H), 2.00 (dq, *J* = 13.0, 6.5 Hz, 1H), 1.23 (q, *J* = 7.6 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.4, 142.1, 128.5, 127.2, 126.9, 61.1, 61.0, 33.9, 19.9, 18.7, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{13}H_{19}O_2NNa^+$: calcd. 244.13080, found 244.13045.

Ethyl (1,2,3,4-tetrahydronaphthalen-1-yl)carbamate (3m)



Rf = 0.25-0.3 (PE : EA = 10:1).

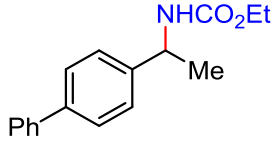
m.p. = 65-68°C

FT-IR **ν**max (cm^{-1}) = 3313, 3060, 3019, 2978, 2933, 2863, 1694, 1528.

^1H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 1H), 7.21 – 7.13 (m, 2H), 7.13 – 7.04 (m, 1H), 4.89 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.77 (q, *J* = 6.8 Hz, 2H), 2.05 (td, *J* = 9.6, 6.5 Hz, 1H), 1.94 – 1.73 (m, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.3, 137.6, 137.0, 129.2, 128.8, 127.4, 126.3, 60.9, 49.2, 30.6, 29.3, 20.0, 14.8.

HRMS (ESI): $[M+Na]^+$ $C_{13}H_{17}O_2NNa^+$: calcd. 242.11515 found 242.11484.

Ethyl (1-([1,1'-biphenyl]-4-yl)ethyl)carbamate (3n)



m.p. = 125-128°C

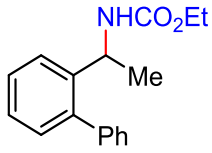
Rf = 0.25-0.3 (PE : EA = 10:1).

FT-IR **ν**max (cm^{-1}) = 3304, 2980, 1689, 1542, 1254, 1066.

^1H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.51 (m, 4H), 7.50 – 7.30 (m, 5H), 5.20 – 4.66 (m, 2H), 4.14 (qd, *J* = 7.1, 1.9 Hz, 2H), 1.52 (d, *J* = 6.8 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.0, 142.9, 140.9, 140.3, 128.8, 127.4, 127.3, 127.2, 126.5, 60.9, 50.4, 22.6, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{17}H_{19}O_2NNa^+$: calcd. 292.13080, found 292.13088.

Ethyl (1-([1,1'-biphenyl]-2-yl)ethyl)carbamate (3o)



Rf = 0.25-0.3 (PE : EA = 10:1)

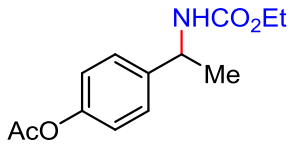
m.p. = 125-129°C

FT-IR **ν**max (cm^{-1}) = 3332, 2975, 1704, 1520, 1250, 1066.

^1H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.26 (m, 8H), 7.20 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.93 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 1.32 – 1.04 (m, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.58, 141.90, 141.05, 130.47, 129.40, 128.33, 128.04, 127.23, 126.97, 124.84, 60.82, 47.72, 23.40, 14.75.

HRMS (ESI): $[M+Na]^+$ $C_{17}H_{19}O_2NNa^+$: calcd. 292.13080 found 292.13115.

4-(1-((ethoxycarbonyl)amino)ethyl)phenyl acetate (3p)



Rf = 0.25-0.3 (PE : EA = 5:1).

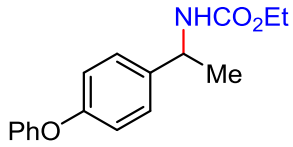
m.p. = 107-109°C

FT-IR **ν**max (cm^{-1}) = 3328, 2979, 1761, 1702, 1526, 1508, 1370, 1218, 1064.

^1H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.11 – 6.97 (m, 2H), 4.89 (d, *J* = 33.7 Hz, 2H), 4.09 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.28 (s, 3H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 169.6, 155.9, 149.8, 141.4 127.2, 121.7, 77.6, 77.2, 76.7, 61.0, 50.1, 22.5, 21.2, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{13}H_{17}O_4NNa^+$: calcd. 274.10498 found 274.10521.

Ethyl (1-(4-phenoxyphenyl)ethyl)carbamate (3q)



Rf = 0.25-0.3 (PE : EA = 10:1)

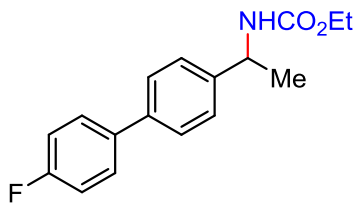
m.p. = 50-52°C

FT-IR **ν**max (cm^{-1}) = 3324, 2978, 1700, 1590, 1506, 1489, 1238, 1064.

^1H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 4H), 7.14 – 7.06 (m, 1H), 7.05 – 6.90 (m, 4H), 5.13 – 4.61 (m, 2H), 4.11 (qd, *J* = 7.1, 2.2 Hz, 2H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.3, 156.5, 155.9, 138.7, 130.1, 129.9, 129.8, 127.4, 123.4, 119.0, 60.9, 50.1, 22.6, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{17}H_{19}O_3NNa^+$: calcd. 308.12571 found 308.12619.

Ethyl (1-(4'-fluoro-[1,1'-biphenyl]-4-yl)ethyl)carbamate (3r)



Rf = 0.25 (PE : EA = 10:1).

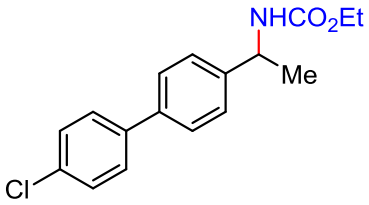
m.p. = 155-158°C

FT-IR **ν**max (cm^{-1}) = 3292, 2987, 1686, 1547, 1255, 1065, 822, 520.

^1H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 4H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.02 (m, 2H), 4.90 (dd, *J* = 20.1, 13.0 Hz, 2H), 4.12 (qd, *J* = 7.1, 1.8 Hz, 2H), 1.51 (d, *J* = 6.7 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.3 Hz), 156.0 , 143.0 , 139.4 , 137.1 (d, *J* = 3.2 Hz), 128.7 (d, *J* = 8.0 Hz), 127.4 , 126.5 , 115.7 (d, *J* = 21.4 Hz), 61.0 , 50.4 , 22.7 , 14.7 .

HRMS (ESI): $[M+Na]^+$ $C_{17}H_{18}O_2NFNa^+$: calcd. 310.12138 found 310.12014.

Ethyl (1-(4'-chloro-[1,1'-biphenyl]-4-yl)ethyl)carbamate (3s)



Rf = 0.25 (PE : EA = 10:1).

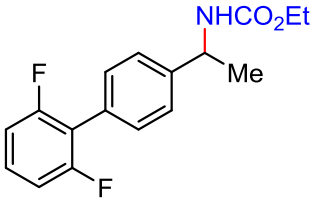
m.p. = 154-157°C

FT-IR **ν**max (cm^{-1}) = 3289, 2982, 1686, 1542, 1251, 1062, 817, 513.

^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (tt, *J* = 7.7, 2.2 Hz, 4H), 7.43 – 7.34 (m, 4H), 5.10 – 4.77 (m, 2H), 4.12 (qd, *J* = 7.1, 1.9 Hz, 2H), 1.51 (d, *J* = 6.8 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.0, 143.4, 139.4, 139.1, 133.5, 129.0, 128.4, 127.3, 126.6, 61.0, 50.4, 22.7, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{17}H_{18}O_2NClNa^+$: calcd. 326.09183 found 326.09073.

Ethyl (1-(2',6'-difluoro-[1,1'-biphenyl]-4-yl)ethyl)carbamate (3t)



Rf = 0.25 (PE : EA = 10:1).

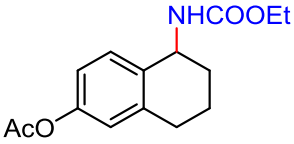
m.p. = 135-137°C

FT-IR **ν**max (cm^{-1}) = 3354, 2981, 1688, 1521, 1464, 1249, 1230, 1067, 997, 834, 784.

^1H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.35 (m, 4H), 7.33 – 7.21 (m, 1H), 7.06 – 6.89 (m, 2H), 4.93 (s, 2H), 4.12 (qd, *J* = 7.1, 1.4 Hz, 2H), 1.52 (d, *J* = 6.5 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 160.3 (dd, *J* = 248.6, 7.2 Hz), 156.0, 143.8, 130.7 (t, *J* = 2.0 Hz), 129.0 (t, *J* = 10.4 Hz), 128.3, 126.0, 118.3 (t, *J* = 18.6 Hz), 113.0 – 110.9 (m), 61.0, 50.5, 22.6, 14.7.

HRMS (ESI): $[M+Na]^+$ $C_{17}H_{17}O_2NF_2Na^+$: calcd. 328.11196 found 328.11069.

5-((ethoxycarbonyl)amino)-5,6,7,8-tetrahydronaphthalen-2-yl acetate (3u)



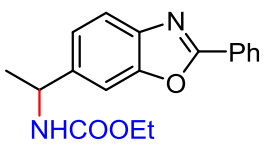
Rf = 0.25-0.3 (PE : EA = 5:1).

FT-IR **ν**max (cm^{-1}) = 3323, 2936, 1761, 1703, 1523, 1495, 1209, 1067.

^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 1H), 6.94 – 6.74 (m, 2H), 4.87 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.76 (q, *J* = 6.8 Hz, 2H), 2.27 (s, 3H), 2.10 – 1.97 (m, 1H), 1.88 – 1.75 (m, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 169.7, 156.2, 149.7, 139.1, 134.7, 130.0, 121.8, 119.7, 77.6, 77.2, 76.7, 61.0, 48.8, 30.5, 29.4, 21.2, 19.8, 14.8.

HRMS (ESI): $[M+Na]^+$ $C_{15}H_{19}O_4NNa^+$: calcd. 300.12063 found 300.12021.

Ethyl (1-(2-phenylbenzo[d]oxazol-6-yl)ethyl)carbamate (3v)



Rf = 0.35 (PE : EA = 5:1).

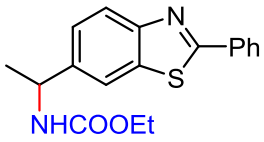
m.p. = 119-121°C

FT-IR **ν**max (cm^{-1}) = 3321, 2978, 1702, 1529, 1246,1062.

^1H NMR (300 MHz, $CDCl_3$) δ 8.29 – 8.13 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.51 (tt, *J* = 5.5, 2.7 Hz, 4H), 7.31 (dd, *J* = 8.2, 1.7 Hz, 1H), 5.31 – 4.79 (m, 2H), 4.10 (qd, *J* = 7.1, 2.2 Hz, 2H), 1.53 (d, *J* = 6.9 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 163.4,

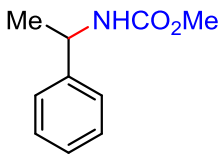
155.9, 151.1, 141.9, 141.4, 131.6, 129.0, 127.7, 127.2, 122.8, 112.0, 108.2, 61.0, 50.8, 22.9, 14.7.
HRMS (ESI): $[M+H]^+$ $[C_{18}H_{19}O_3N_2]^+$: calcd. 311.13902 found 311.13849.

Ethyl (1-(2-phenylbenzo[d]thiazol-6-yl)ethyl)carbamate (3w)



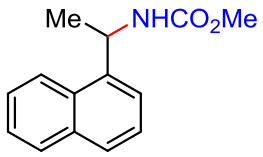
Rf = 0.3 (PE : EA = 5:1).
m.p. = 113-115°C
FT-IR **ν**max (cm^{-1}) = 3319, 2976, 1700, 1524, 1244, 1068, 764, 689.
^1H NMR (300 MHz, $CDCl_3$) δ 8.12 – 7.96 (m, 3H), 7.83 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.37 (m, 4H), 5.06 (dd, *J* = 46.1, 7.9 Hz, 2H), 4.11 (qd, *J* = 7.1, 3.1 Hz, 2H), 1.53 (d, *J* = 6.9 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H) ^{13}C NMR (76 MHz, $CDCl_3$) δ 168.2, 155.9, 153.5, 141.4, 135.5, 133.7, 131.1, 129.1, 127.6, 124.7, 123.3, 118.9, 61.0, 50.7, 22.8, 14.7.
HRMS (ESI): $[M+H]^+$ $C_{18}H_{19}O_2N_2SNa^+$: calcd. 327.11618 found 327.11582.

Methyl (1-phenylethyl)carbamate (4a)



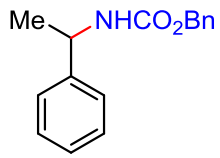
Rf = 0.25 (PE : EA = 10:1).
FT-IR **ν**max (cm^{-1}) = 3324, 2975, 1704, 1532, 1452, 1251, 1070, 700.
^1H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 5H), 5.01 (s, 1H), 4.84 (s, 1H), 3.65 (s, 3H), 1.48 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 143.7, 128.7, 127.4, 126.0, 52.2, 50.7, 22.5.
HRMS (ESI): $[M+Na]^+$ $C_{10}H_{13}O_2NNa^+$: calcd. 202.08385 found 202.08364.

Methyl (1-(naphthalen-1-yl)ethyl)carbamate (4b)



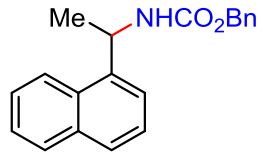
Rf = 0.2 (PE : EA = 10:1).
FT-IR **ν**max (cm^{-1}) = 3325, 2977, 1713, 1695, 1532, 1249, 1067, 778.
^1H NMR (300 MHz, $CDCl_3$) δ 8.20 – 8.07 (m, 1H), 7.87 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.79 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.65 – 7.37 (m, 4H), 5.86 – 5.40 (m, 1H), 5.07 (d, *J* = 8.4 Hz, 1H), 3.68 (s, 3H), 1.65 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.3, 138.9, 134.1, 131.0, 129.0, 128.3, 126.5, 125.9, 125.4, 123.3, 122.3, 52.3, 46.8, 21.8.
HRMS (ESI): $[M+Na]^+$ $C_{14}H_{15}O_2NNa^+$: calcd. 252.09950 found 252.09896.

Benzyl (1-phenylethyl)carbamate (4c)



Rf = 0.3 (PE : EA = 10:1).
FT-IR **ν**max (cm^{-1}) = 3324, 2974, 1702, 1530, 1243, 1056, 697.
^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.23 (m, 10H), 5.18 – 4.98 (m, 3H), 4.93 – 4.81 (m, 1H), 1.49 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 155.6, 143.6, 136.6, 128.8, 128.6, 128.3, 127.5, 126.1, 66.9, 50.8, 22.6.
HRMS (ESI): $[M+Na]^+$ $C_{16}H_{17}O_2NNa^+$: calcd. 278.11515 found 278.11477.

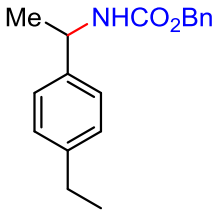
Benzyl (1-(naphthalen-1-yl)ethyl)carbamate (4d)



Rf = 0.3 (PE : EA = 10:1).
m.p. = 85-88°C
FT-IR **ν**max (cm^{-1}) = 3326, 2975, 1703, 1518, 1241, 1058, 777.
^1H NMR (300 MHz, $CDCl_3$) δ 8.20 – 8.09 (m, 1H), 7.92 – 7.84 (m, 1H), 7.79

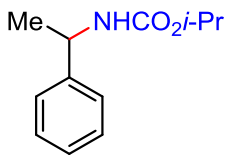
(dt, *J* = 7.9, 1.2 Hz, 1H), 7.57 – 7.41 (m, 4H), 7.41 – 7.27 (m, 5H), 5.77 – 5.59 (m, 1H), 5.19 – 5.07 (m, 3H), 1.66 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 138.8, 136.6, 134.0, 130.9, 129.0, 128.62 128.3, 128.2, 126.6, 125.9, 125.4, 123.4, 122.3, 66.9, 46.8, 21.8.
HRMS (ESI): $[M+Na]^+$ $C_{20}H_{19}O_2NNa^+$: calcd. 328.13080 found 328.13005.

Benzyl (1-(4-ethylphenyl)ethyl)carbamate (4e)



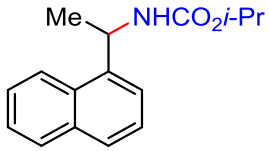
Rf = 0.35 (PE : EA = 10:1).
m.p. = 60-63°C
FT-IR **ν**max (cm^{-1}) = 3324, 2966, 1702, 1513, 1242, 1060, 697.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.08 (m, 9H), 5.19 – 4.92 (m, 3H), 4.91 – 4.75 (m, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.48 (d, *J* = 6.9 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 143.5, 140.8, 136.6, 128.6, 128.25, 128.1, 126.1, 66.8, 50.6, 28.6, 22.5, 15.7.
HRMS (ESI): $[M+Na]^+$ $C_{18}H_{21}O_2NNa^+$: calcd. 306.14645 found 306.14618.

Isopropyl (1-phenylethyl)carbamate (4f)



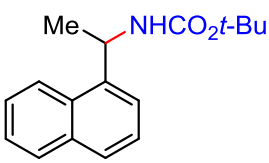
Rf = 0.35-0.4 (PE : EA = 10:1).
FT-IR **ν**max (cm^{-1}) = 3323, 2979, 1695, 1523, 1249, 1112, 699.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 5H), 4.88 (dq, *J* = 11.8, 5.9 Hz, 3H), 1.47 (d, *J* = 6.7 Hz, 3H), 1.20 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 143.9, 128.7, 127.3, 126.0, 68.2, 50.6, 22.7, 22.3.
HRMS (ESI): $[M+Na]^+$ $C_{12}H_{17}O_2NNa^+$: calcd. 230.11515 found 230.11495.

Isopropyl (1-(naphthalen-1-yl)ethyl)carbamate (4g)



Rf = 0.25-0.3 (PE : EA = 10:1).
m.p. = 74-76°C
FT-IR **ν**max (cm^{-1}) = 3326, 2978, 1695, 1529, 1512, 1247, 1111, 1055, 778.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.78 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.64 – 7.38 (m, 4H), 5.65 (s, 1H), 4.93 (ddd, *J* = 11.5, 6.8, 5.7 Hz, 2H), 1.64 (d, *J* = 6.9 Hz, 3H), 1.20 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.5, 139.2, 134.1, 131.0, 129.0, 128.2, 126.5, 125.8, 125.4, 123.4, 122.3, 68.3, 46.6, 22.3, 22.0.
HRMS (ESI): $[M+Na]^+$ $C_{16}H_{19}O_2NNa^+$: calcd. 280.13080 found 280.13016.

Tert-butyl (1-(naphthalen-1-yl)ethyl)carbamate

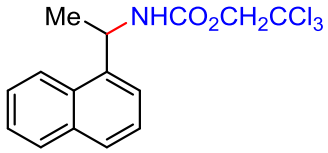


Rf = 0.3-0.35 (PE : EA = 10:1).
m.p. = 65-67°C
FT-IR **ν**max (cm^{-1}) = 3342, 2976, 1699, 1506, 1365, 1245, 1169, 1056, 777.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.78 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.57 – 7.42 (m, 4H), 5.61 (s, 1H), 4.89 (s, 1H), 1.62 (d, *J* = 10.0 Hz, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 139.4, 134.1, 131.0, 128.9, 128.1,

126.4, 125.8, 125.4, 123.5, 122.2, 79.6, 46.3, 28.5, 22.0.

HRMS (ESI): $[M+Na]^+$ $C_{17}H_{21}O_2NNa^+$: calcd. 294.14645 found 294.14621.

2,2,2-trichloroethyl (1-(naphthalen-1-yl)ethyl)carbamate (4i)



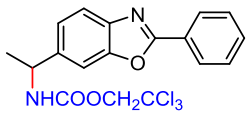
Rf = 0.4 (PE : EA = 10:1).

FT-IR **ν**max (cm^{-1}) = 3332, 2954, 1724, 1515, 1235, 1115, 777.

^1H NMR (300 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 1H), 7.88 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.41 (m, 4H), 5.70 (p, *J* = 7.0 Hz, 1H), 5.31 (d, *J* = 8.4 Hz, 1H), 4.76 (s, 2H), 1.71 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 153.7, 137.9, 134.0, 130.9, 128.9, 128.5, 126.6, 125.9, 125.3, 123.1, 122.4, 95.6, 77.5, 77.0, 76.6, 74.5, 47.0, 21.4.

HRMS (ESI): $[M+Na]^+$ $C_{15}H_{14}O_2NCl_3Na^+$: calcd. 367.99823 found 367.99797.

2,2,2-trichloroethyl (1-(2-phenylbenzo[d]oxazol-6-yl)ethyl)carbamate (4j)



Rf = 0.35 (PE : EA = 5:1).

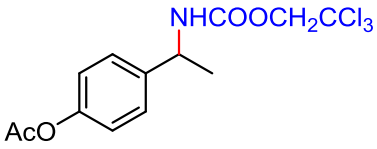
m.p. = 92-95°C

FT-IR **ν**max (cm^{-1}) = 3325, 2976, 2953, 1738, 1731, 1326, 1244, 1116, 1056, 821, 725.

^1H NMR (300 MHz, $CDCl_3$) δ 8.32 – 8.12 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.52 (tt, *J* = 6.1, 2.9 Hz, 4H), 7.32 (dd, *J* = 8.2, 1.6 Hz, 1H), 5.56 (d, *J* = 7.7 Hz, 1H), 5.00 (t, *J* = 7.0 Hz, 1H), 4.72 (s, 2H), 1.58 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 163.6, 153.9, 151.0, 141.6, 140.8, 131.7, 129.0, 127.7, 127.1, 122.8, 120.1, 108.3, 95.6, 74.7, 51.3, 22.7.

HRMS (ESI): $[M+H]^+$ $[C_{18}H_{16}O_3N_2Cl_3]^+$: calcd. 413.02210 found 413.02147.

4-(1-(((2,2,2-trichloroethoxy)carbonyl)amino)ethyl)phenyl acetate (4k)



Rf = 0.3 (PE : EA = 5:1).

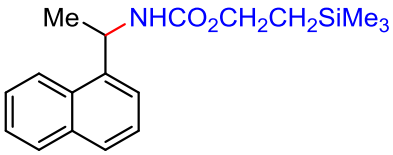
m.p. = 90-92°C

FT-IR **ν**max (cm^{-1}) = 3342, 2977, 1738, 1733, 1508, 1219, 1199, 728.

^1H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 2H), 7.13 – 7.01 (m, 2H), 5.24 (d, *J* = 7.9 Hz, 1H), 4.88 (p, *J* = 7.0 Hz, 1H), 4.78 – 4.63 (m, 2H), 2.29 (s, 3H), 1.52 (d, *J* = 6.9 Hz, 3H). 13C NMR (76 MHz, CDCl3) δ 169.6, 153.8, 150.1, 140.5, 127.3, 122.0, 95.7, 74.7, 50.6, 22.3, 21.3.

HRMS (ESI): $[M+Na]^+$ $C_{13}H_{14}O_4NCl_3Na^+$: calcd. 375.98806 found 375.98758.

2-(trimethylsilyl)ethyl (1-(naphthalen-1-yl)ethyl)carbamate (4l)



Rf = 0.5 (PE : EA = 10:1).

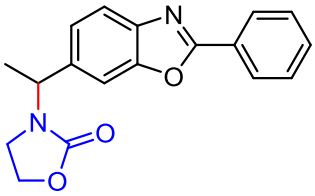
FT-IR **ν**max (cm^{-1}) = 3325, 2953, 1697, 1523, 1510, 1248, 1060, 836, 777.

^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.9 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.78 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.65 – 7.35 (m, 4H), 5.65 (s, 1H), 4.94 (d, *J* = 9.2 Hz, 1H), 4.17 (td, *J* = 8.0, 2.6 Hz, 2H), 1.65 (d, *J* = 6.7 Hz, 3H), 1.04 – 0.90 (m, 2H), 0.02 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0, 139.1, 134.1, 131.0, 129.0, 128.3, 126.5, 125.9, 125.4, 123.4, 122.3, 63.3, 46.6, 21.9, 17.9, -1.3.

HRMS (ESI): $[M+Na]^+$ $C_{18}H_{25}O_2NSiNa^+$: calcd. 338.15468 found 338.15416.

3-(1-(2-phenylbenzo[d]oxazol-6-yl)ethyl)oxazolidin-2-one (4m)



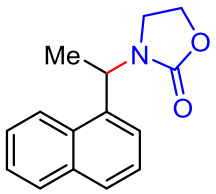
Rf = 0.2 (PE : EA = 2:1).

FT-IR **ν**max (cm^{-1}) = 3505, 2978, 1745, 1484, 1423, 1249, 1056, 706.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 – 8.15 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.59 (dt, *J* = 1.6, 0.7 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.35 (ddd, *J* = 8.3, 1.7, 0.6 Hz, 1H), 5.35 (q, *J* = 7.1 Hz, 1H), 4.27 (dtd, *J* = 23.3, 8.7, 6.8 Hz, 2H), 3.53 (ddd, *J* = 9.3, 8.3, 6.7 Hz, 1H), 3.18 (ddd, *J* = 9.2, 8.3, 6.9 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 163.8, 158.0, 151.1, 141.9, 137.3, 131.8, 129.1, 127.7, 127.0, 123.8, 120.0, 109.4, 62.1, 51.7, 40.1, 16.8.

HRMS (ESI): $[M+H]^+$ $[C_{18}H_{17}O_3N_2]^+$: calcd. 309.12337 found 309.12280.

3-(1-(naphthalen-1-yl)ethyl)oxazolidin-2-one (4n)



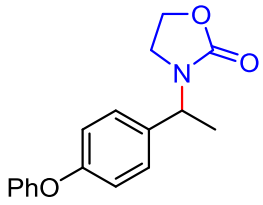
Rf = 0.15-0.2 (PE : EA = 5:1).

FT-IR **ν**max (cm^{-1}) = 3484, 2979, 1742, 1421, 1252, 781.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dq, *J* = 8.6, 1.0 Hz, 1H), 7.96 – 7.77 (m, 2H), 7.63 – 7.41 (m, 4H), 5.93 (q, *J* = 6.9 Hz, 1H), 4.24 (ddd, *J* = 9.4, 8.5, 5.8 Hz, 1H), 4.04 (ddd, *J* = 9.3, 8.5, 7.6 Hz, 1H), 3.61 – 3.33 (m, 1H), 2.73 (ddd, *J* = 9.3, 8.4, 5.8 Hz, 1H), 1.73 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.6, 134.8, 134.0, 131.7, 129.2, 128.9, 127.2, 126.3, 124.9, 123.9, 123.6, 62.1, 47.7, 40.1, 16.1.

HRMS (ESI): $[M+Na]^+$ $C_{15}H_{15}O_2NNa^+$: calcd. 264.09950 found 264.09891.

3-(1-(4-phenoxyphenyl)ethyl)oxazolidin-2-one (4o)



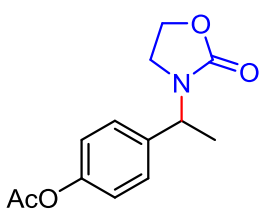
Rf = 0.3 (PE : EA = 5:2).

FT-IR **ν**max (cm^{-1}) = 3496, 2977, 1745, 1588, 1507, 1489, 1420, 1237.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 4H), 7.15 – 7.08 (m, 1H), 7.05 – 6.93 (m, 4H), 5.21 (q, *J* = 7.1 Hz, 1H), 4.46 – 4.17 (m, 2H), 3.50 (ddd, *J* = 9.1, 8.3, 6.7 Hz, 1H), 3.19 (ddd, *J* = 9.1, 8.3, 7.0 Hz, 1H), 1.57 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 158.1, 157.1, 157.0, 134.3, 129.9, 128.6, 123.7, 119.2, 118.8, 62.0, 51.10 40.1, 16.7.

HRMS (ESI): $[M+Na]^+$ $C_{17}H_{17}O_3NNa^+$: calcd. 306.11006 found 306.10963.

4-(1-(2-oxooxazolidin-3-yl)ethyl)phenyl acetate (4p)



Rf = 0.1 (PE : EA = 5:2).

FT-IR **ν**max (cm^{-1}) = 3496, 2980, 1747, 1422, 1202.

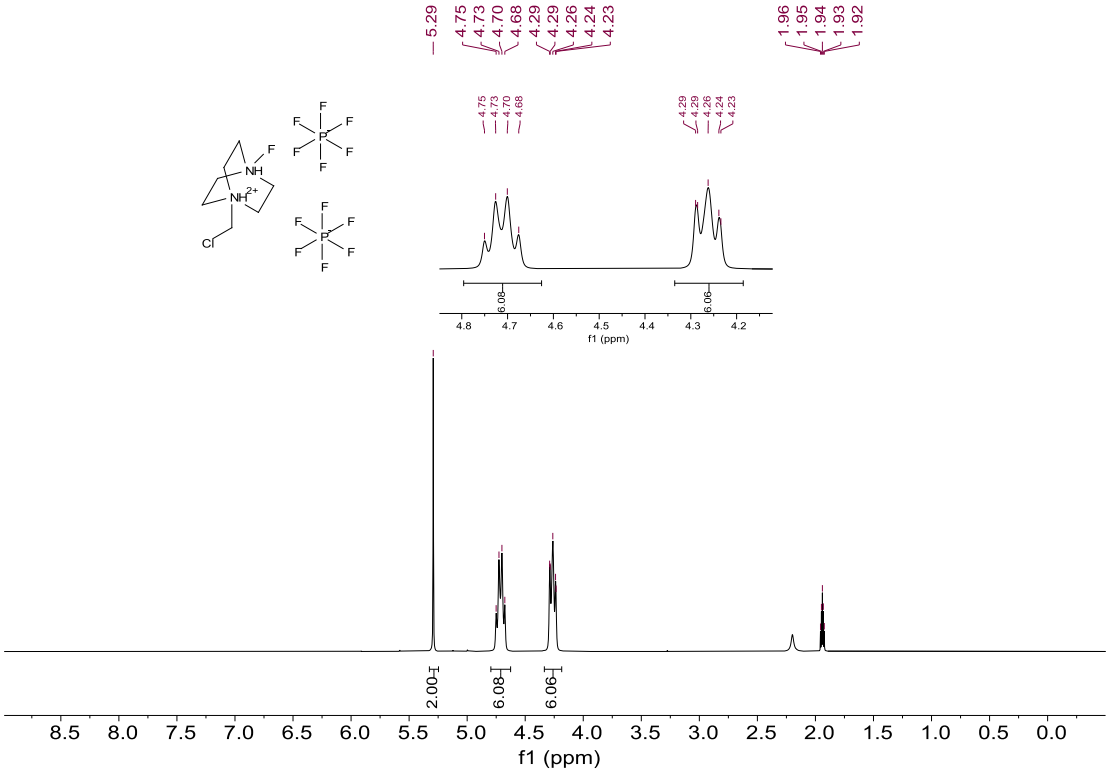
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 2H), 7.12 – 7.02 (m, 2H), 5.21 (q, *J* = 7.1 Hz, 1H), 4.26 (dddd, *J* = 21.9, 9.2, 8.5, 6.8 Hz, 2H), 3.49 (ddd, *J* = 9.2, 8.3, 6.8 Hz, 1H), 3.17 (ddd, *J* = 9.2, 8.3, 6.8 Hz, 1H), 2.29 (s, 3H), 1.57

(d, J = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 169.5, 158.0, 150.3, 137.2, 128.3, 121.9, 62.0, 51.0, 40.1, 21.2, 16.5.

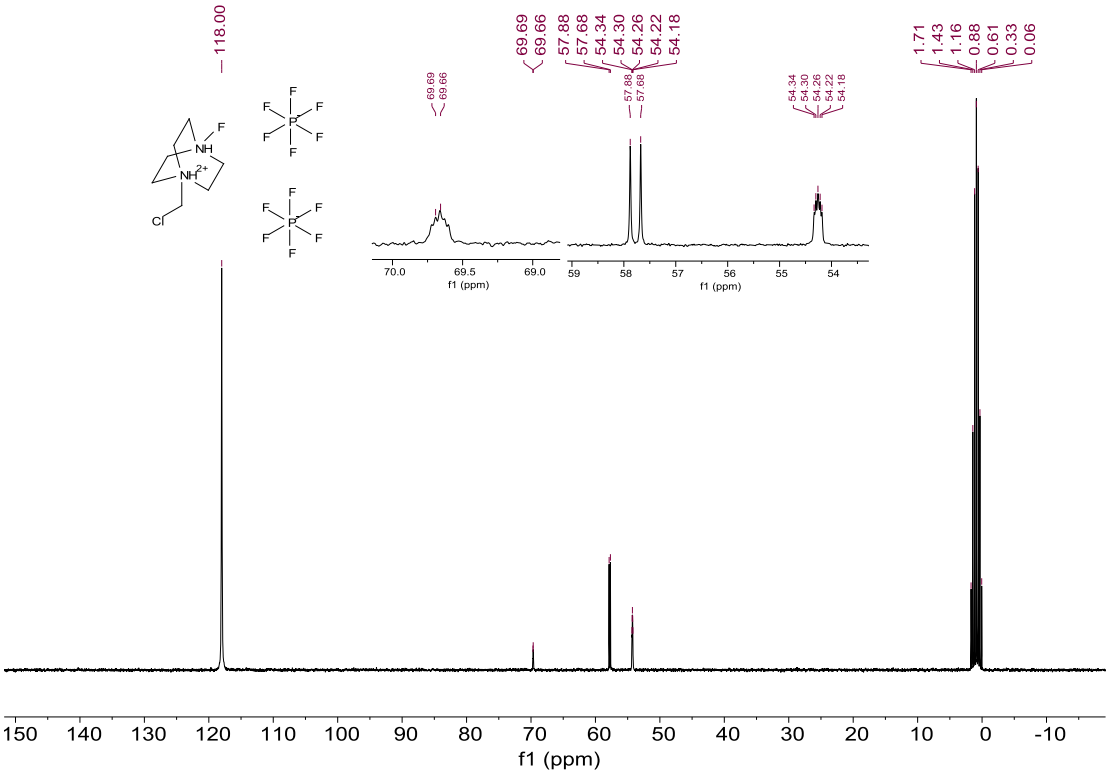
HRMS (ESI): $[M+Na]^+$ $C_{13}H_{15}O_4NNa^+$: calcd. 272.08933 found 272.08872.

7. NMR Spectra of Substrates and Products

^{1}HMNR

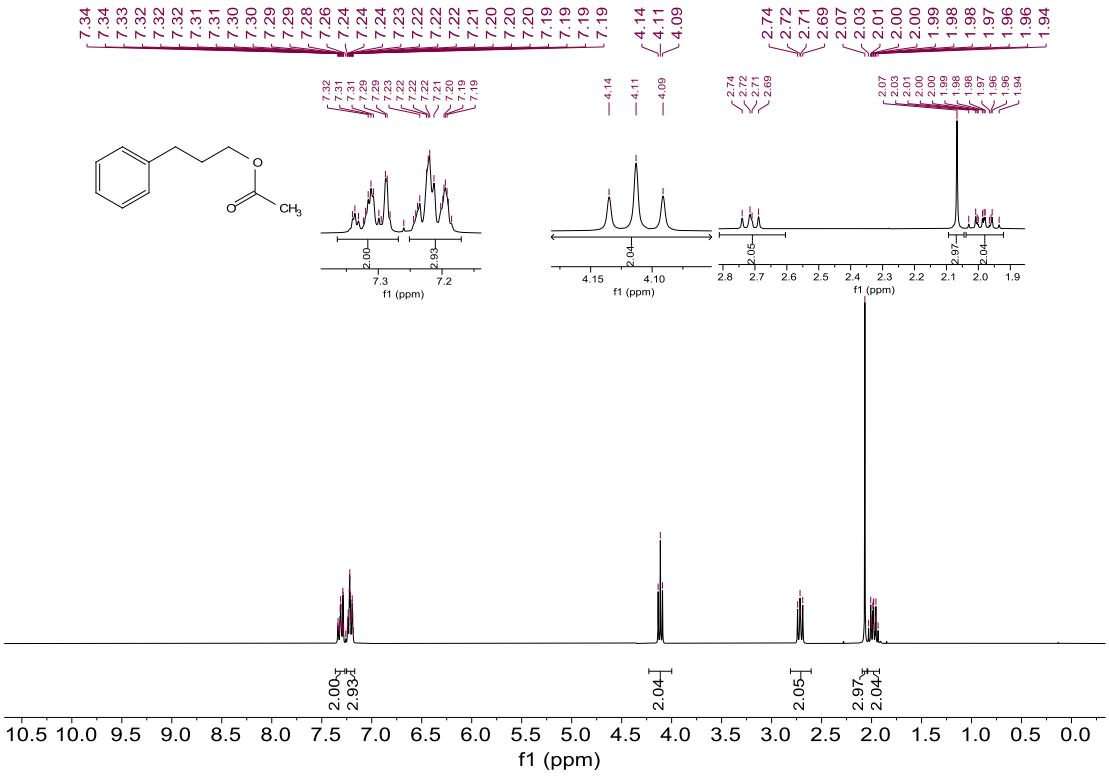


^{13}CNMR

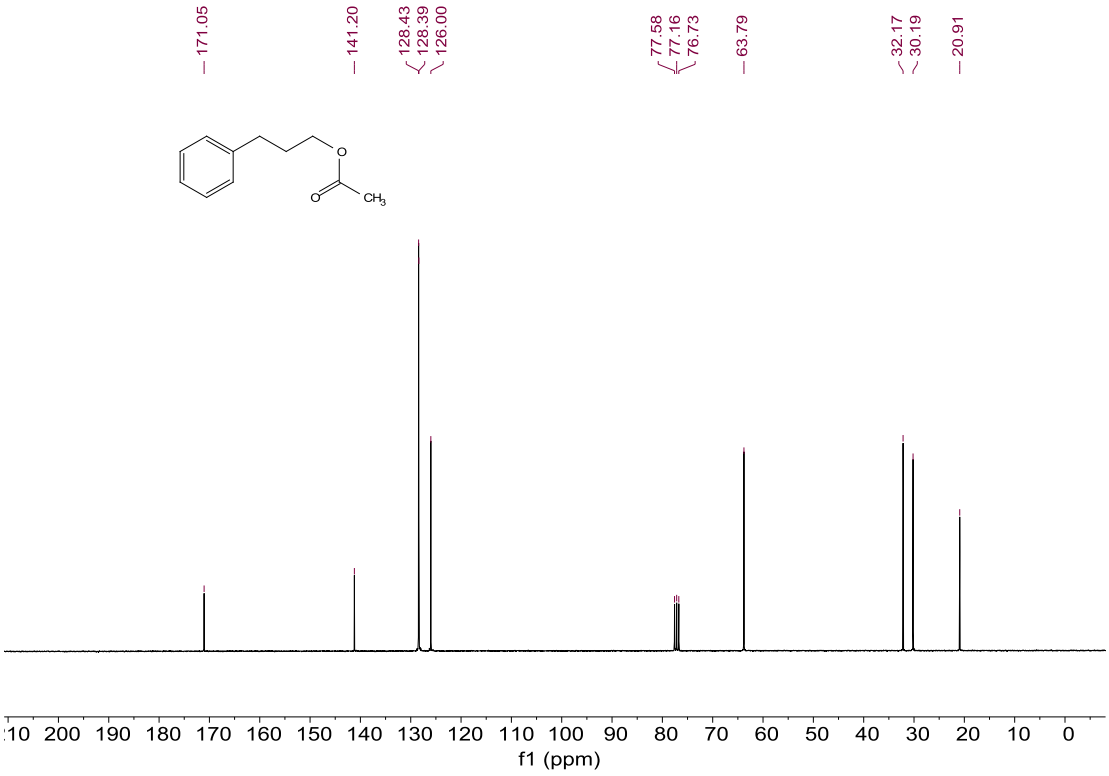


Compound 1e

^{1}HMNR

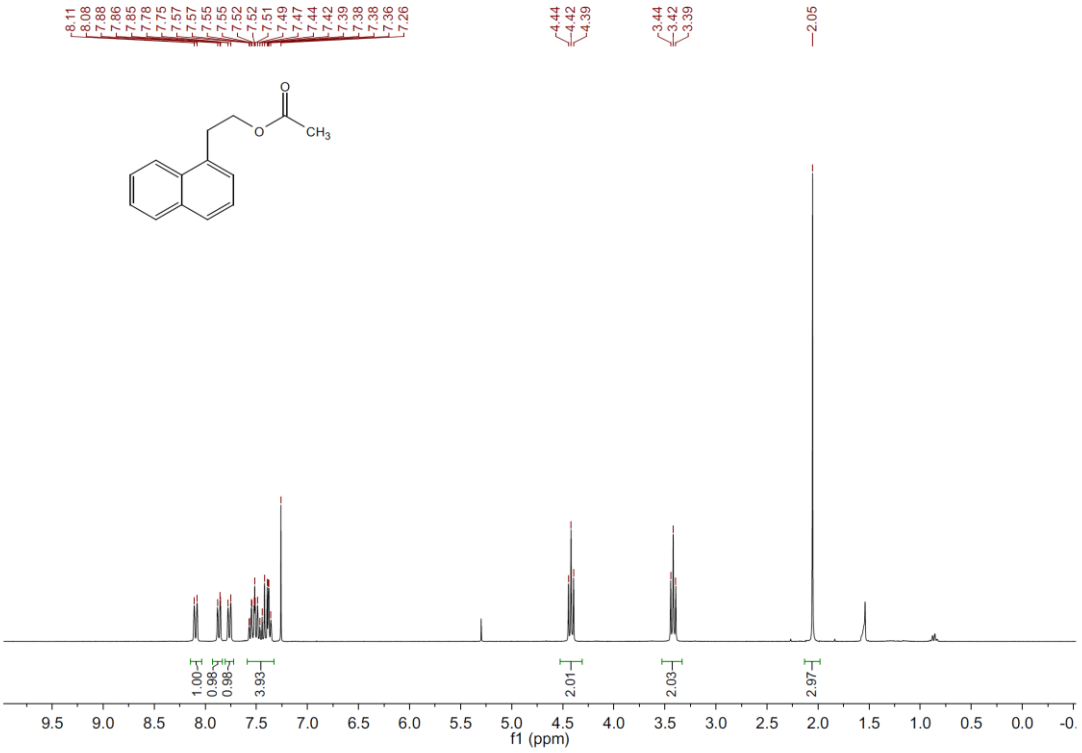


^{13}CNMR

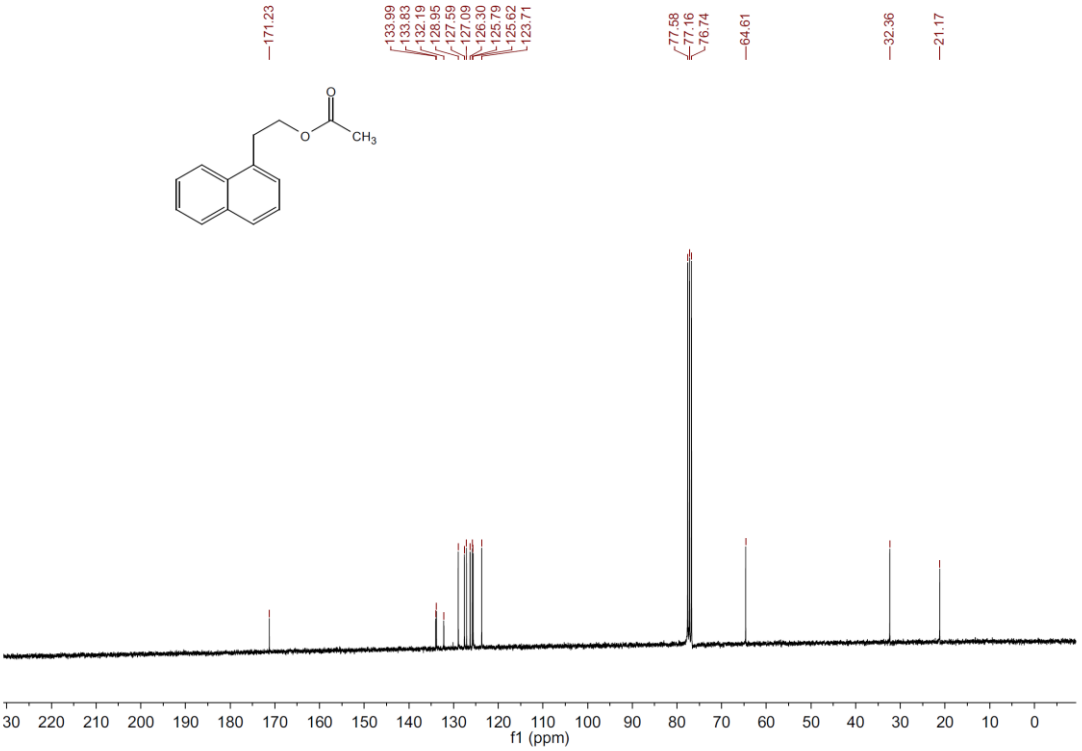


Compound 1f

^{1}HMNR

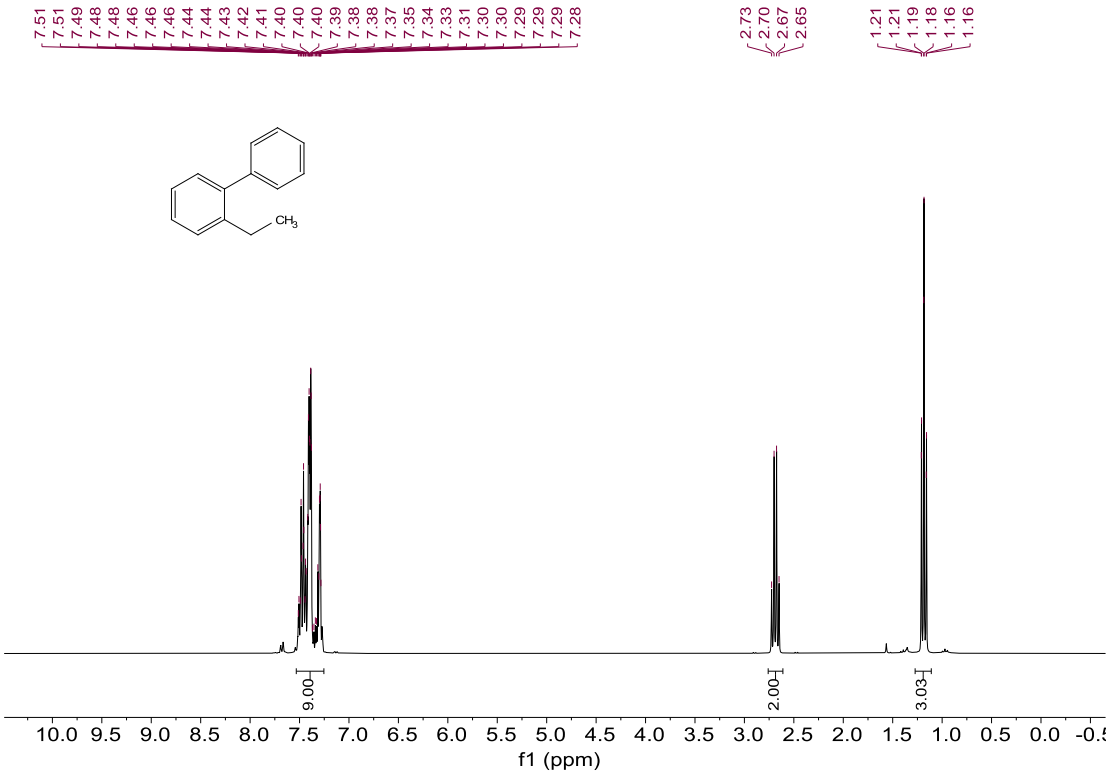


^{13}CNMR

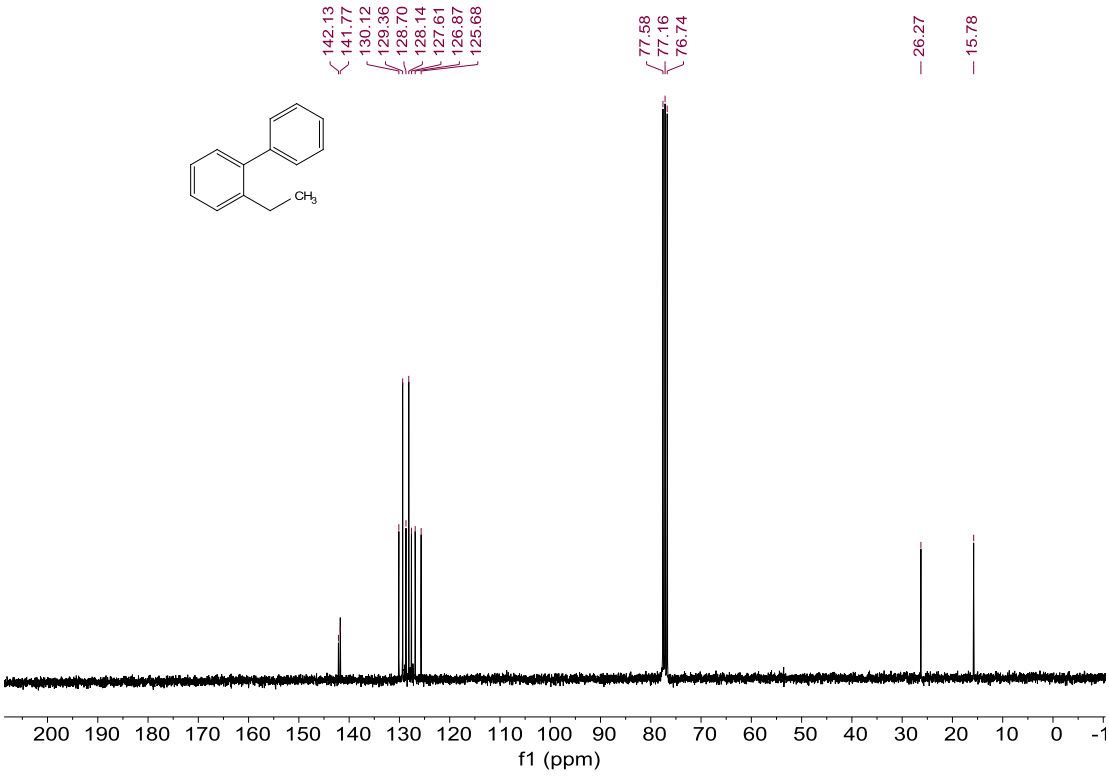


Compound 1o

^{1}HMNR

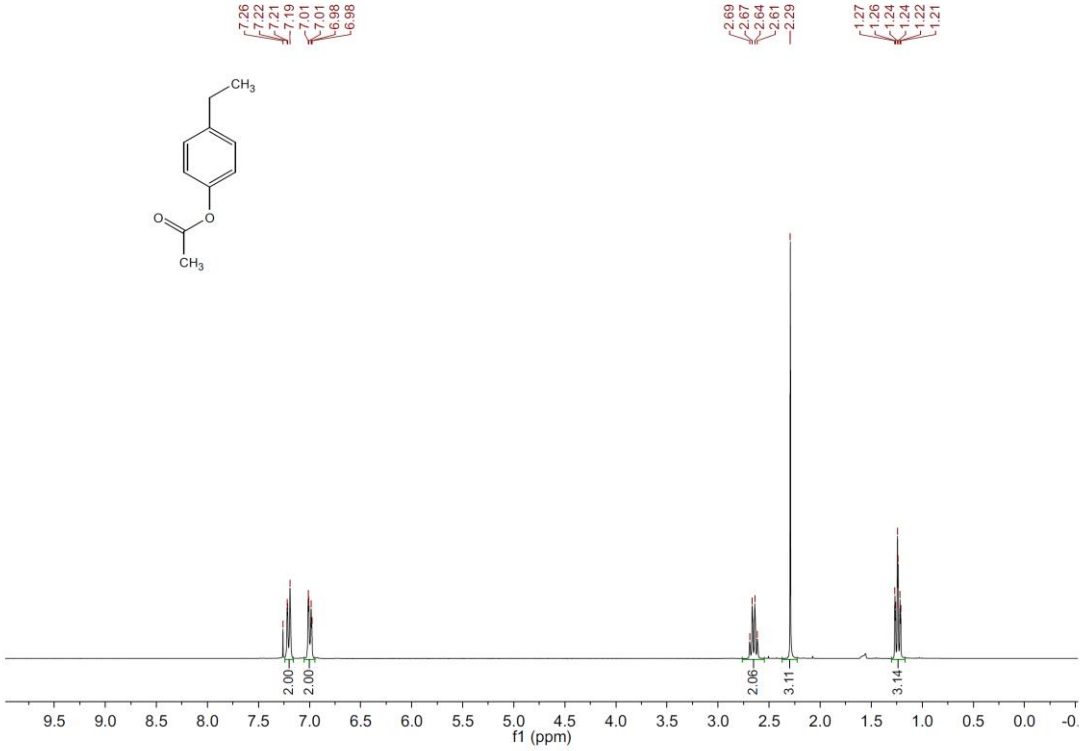


^{13}CNMR

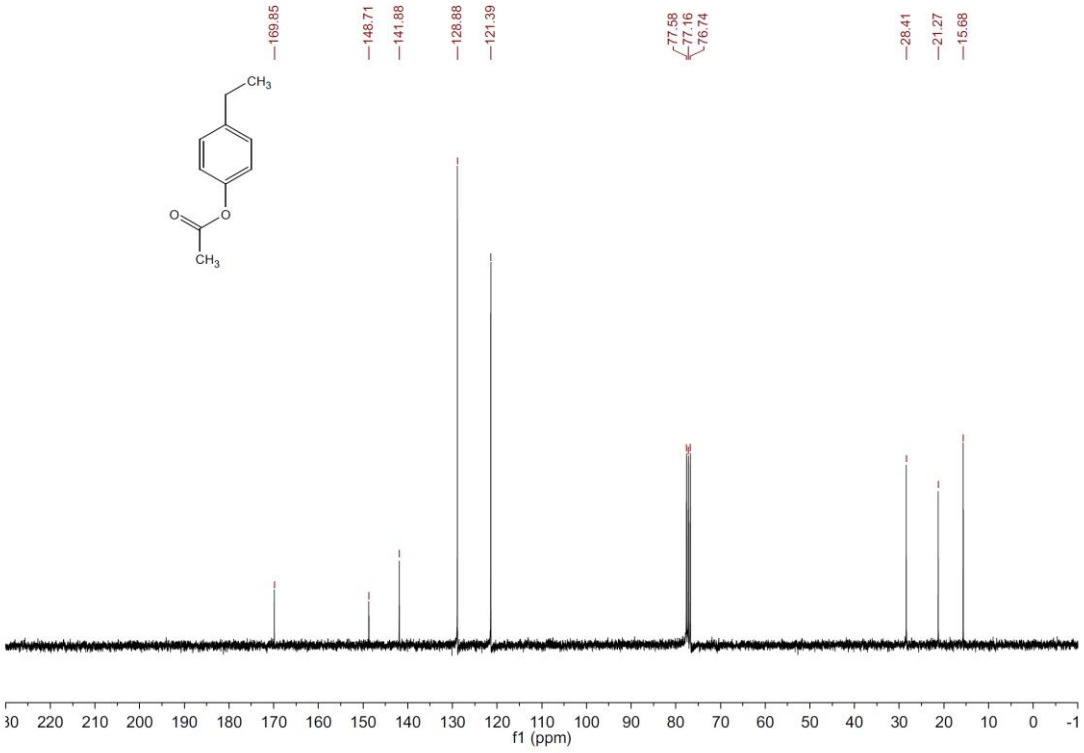


Compound 1p

^{1}HNMR

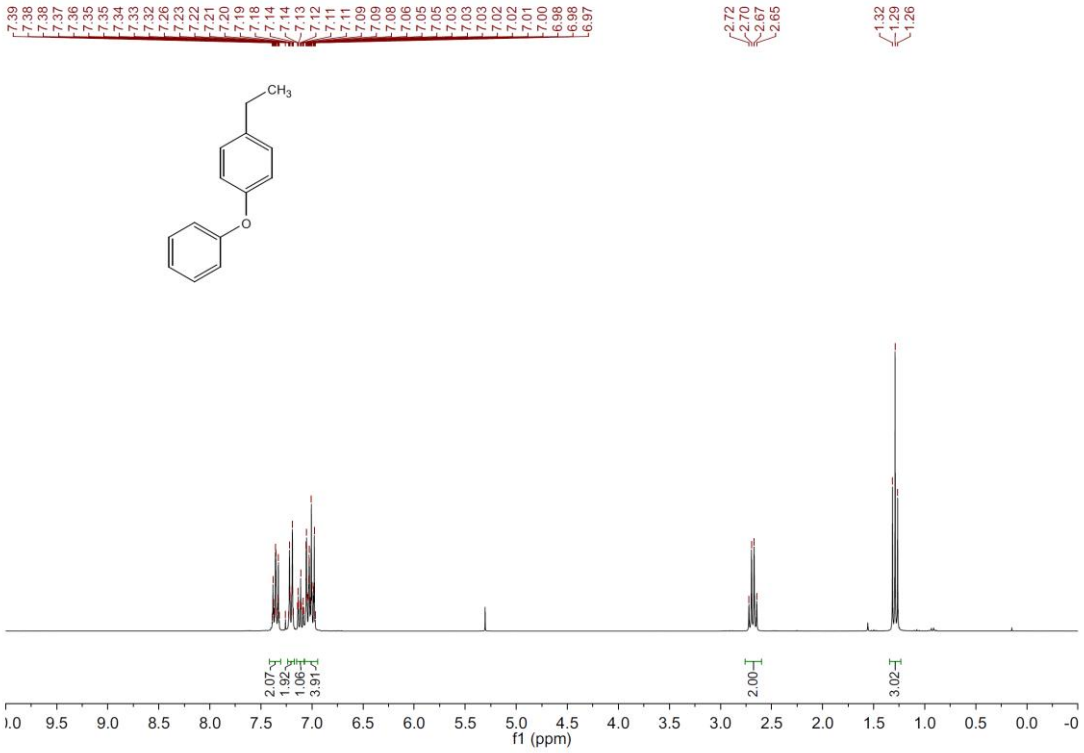


^{13}CNMR

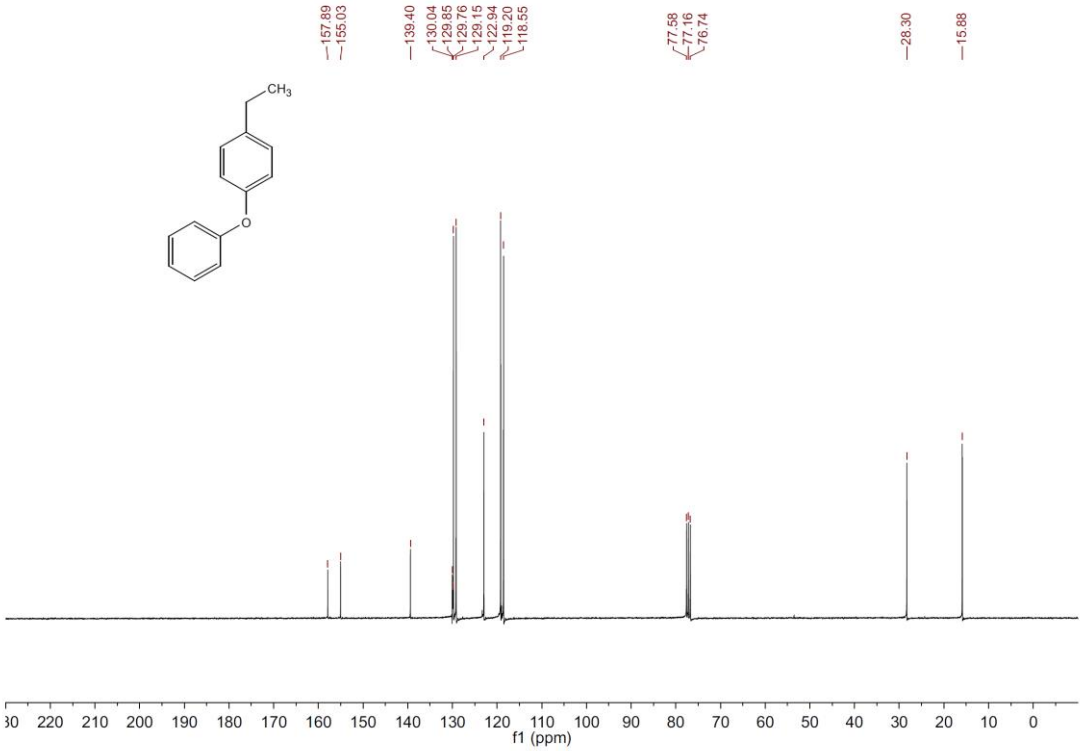


Compound 1q

^{1}HNMR

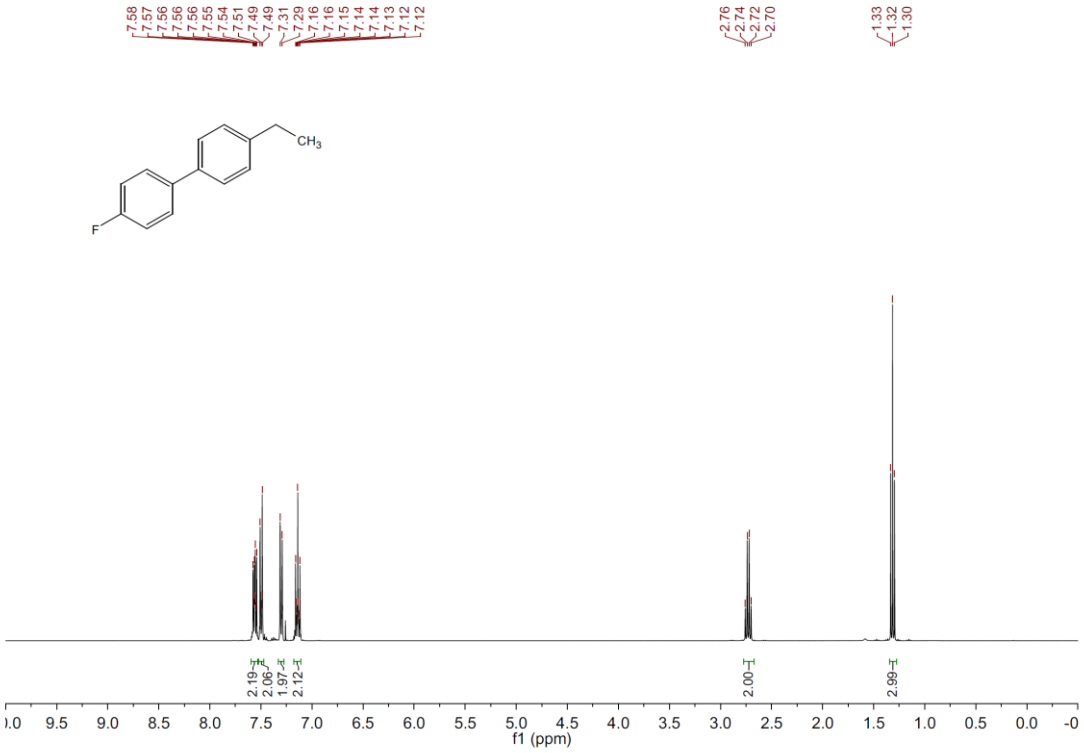


^{13}CNMR

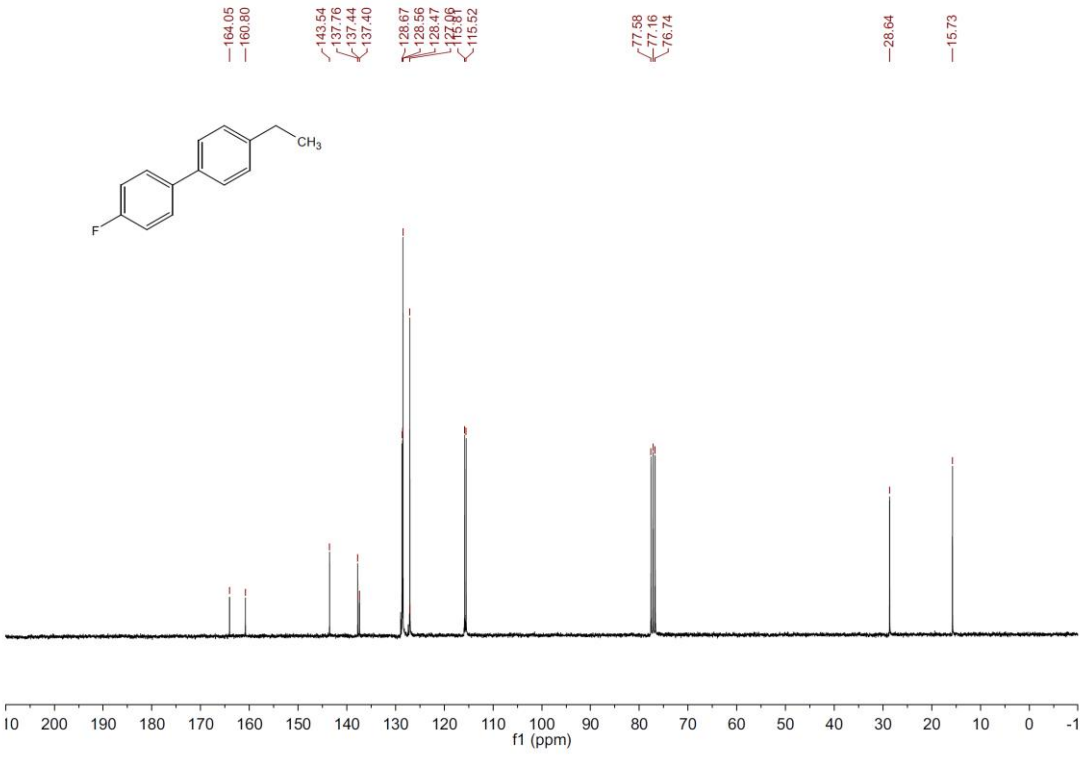


Compound 1r

^{1}HNMR

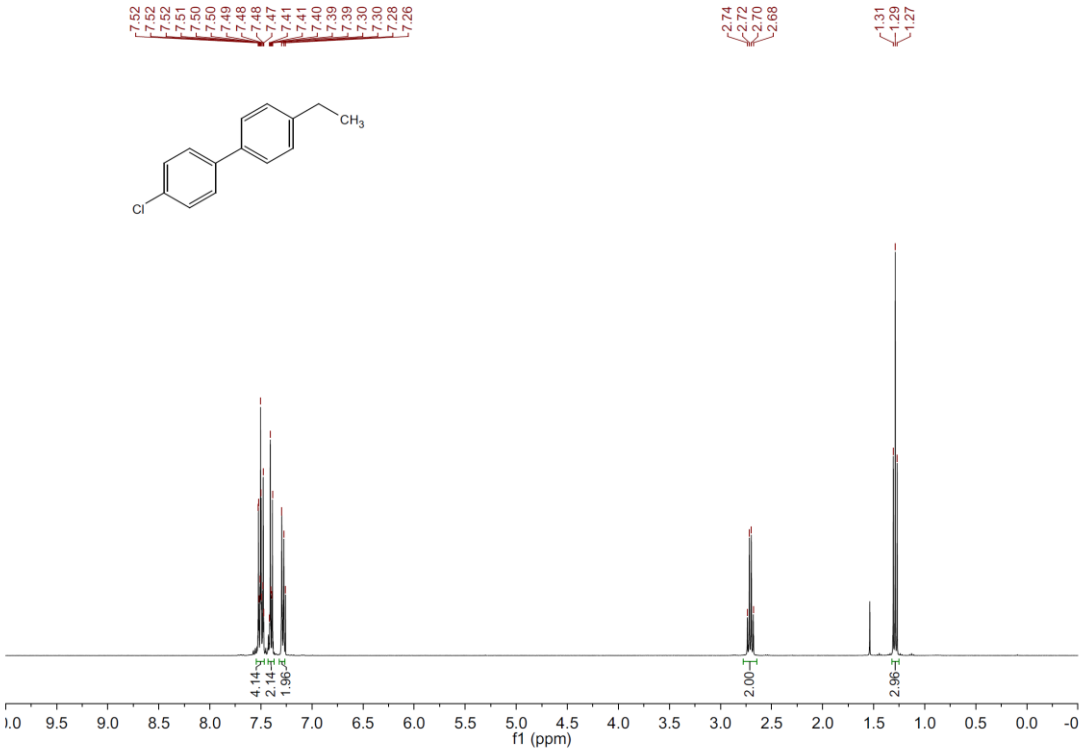


^{13}CNMR

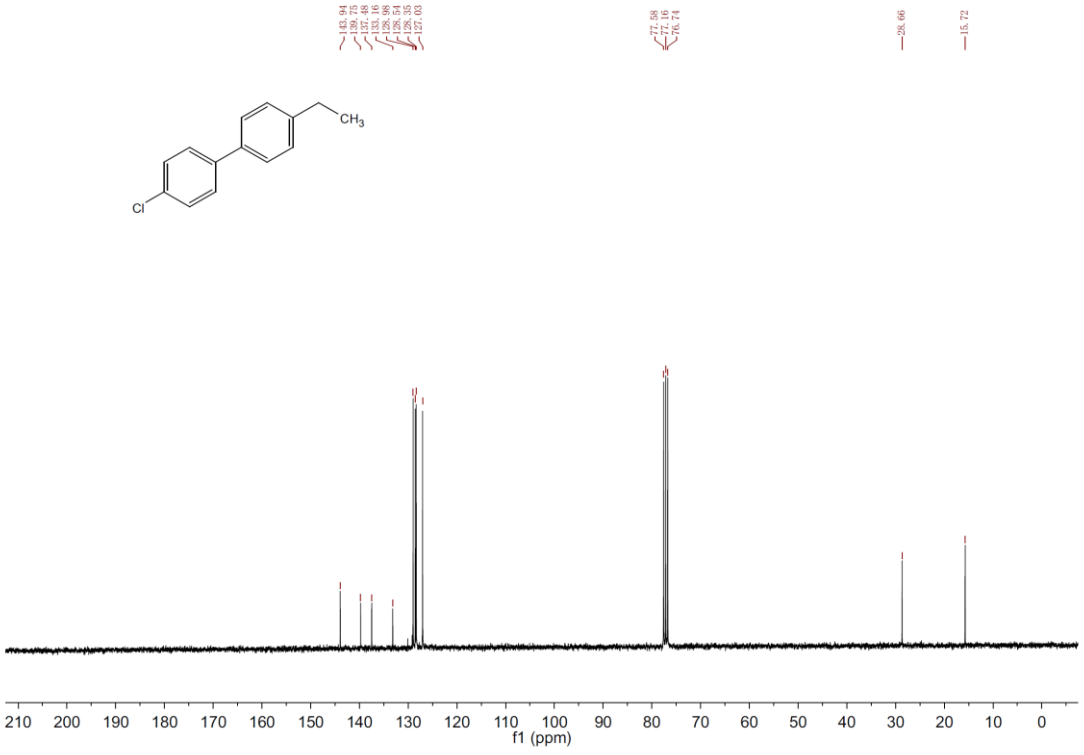


Compound 1s

^{1}HNMR

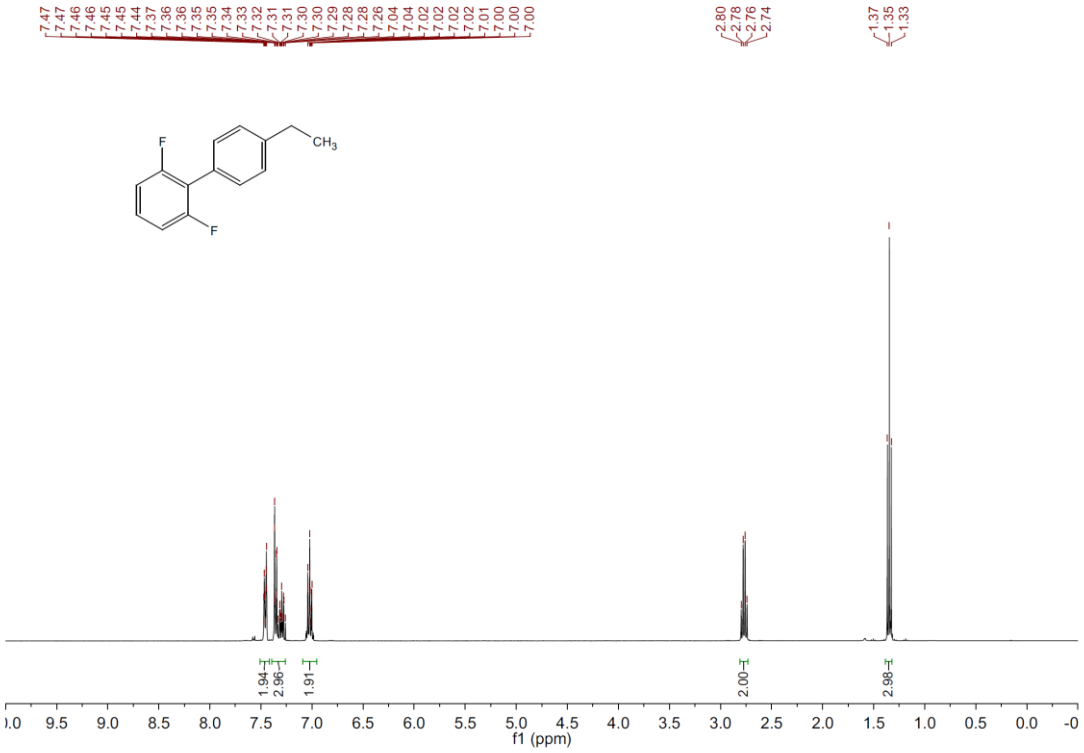


^{13}CNMR

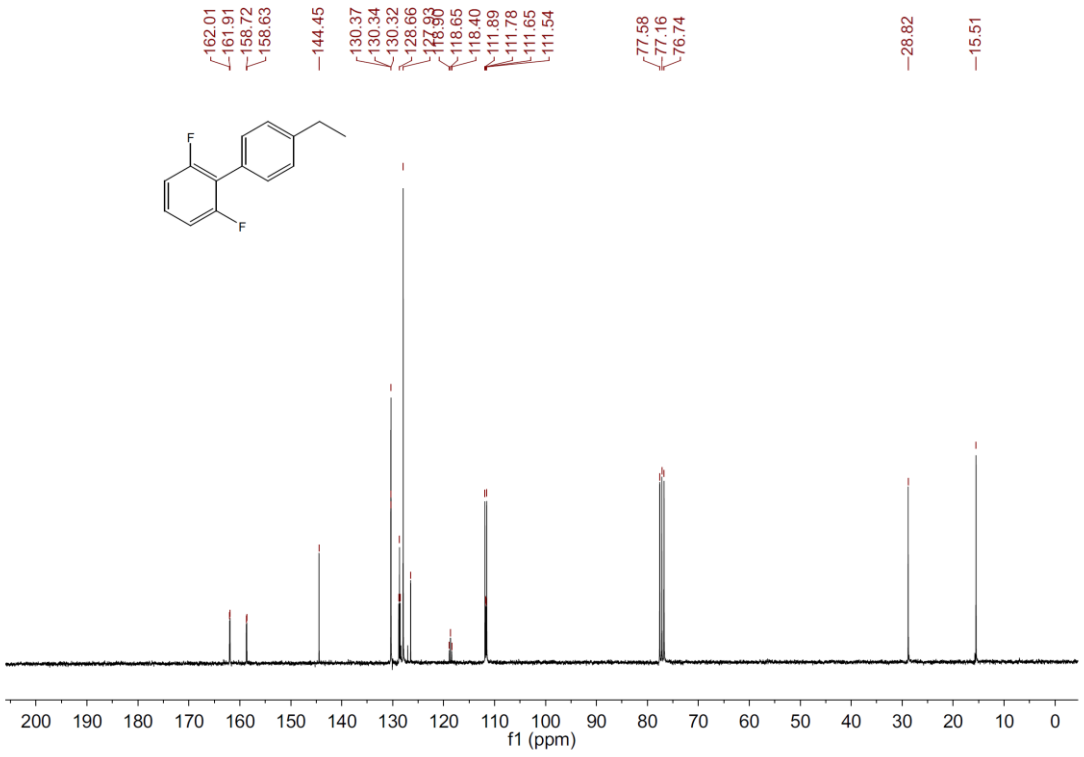


Compound 1t

^{1}HNMR



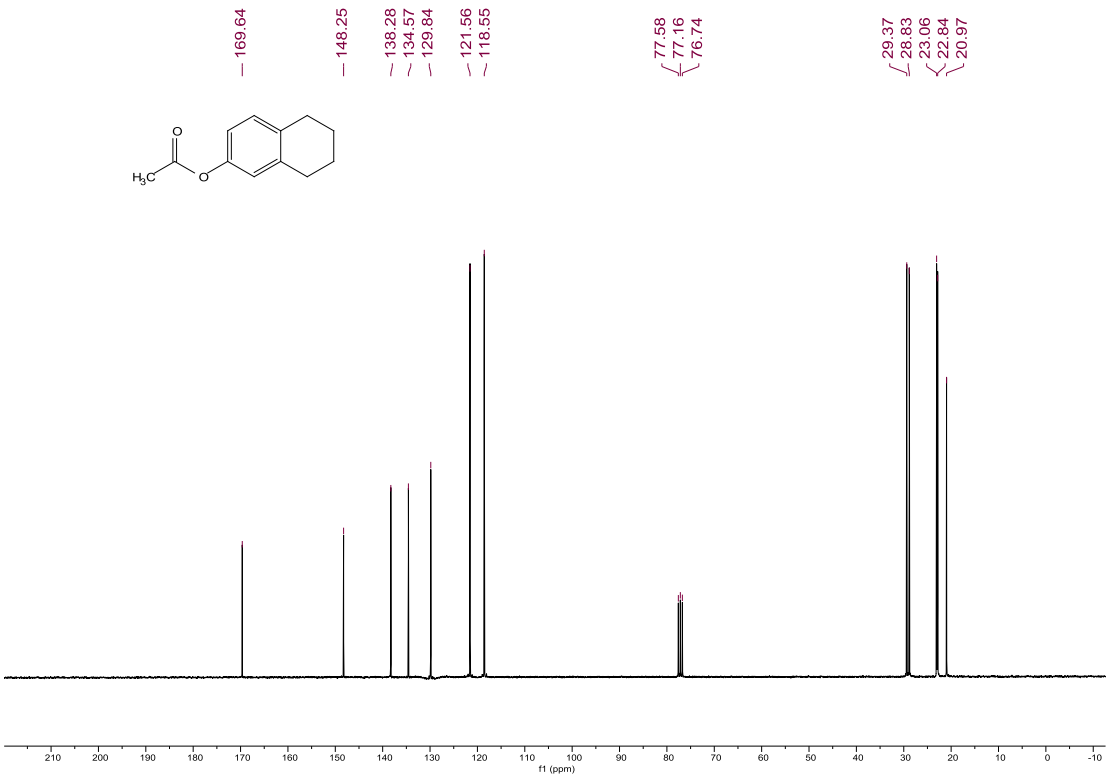
^{13}CNMR



Compound 1u

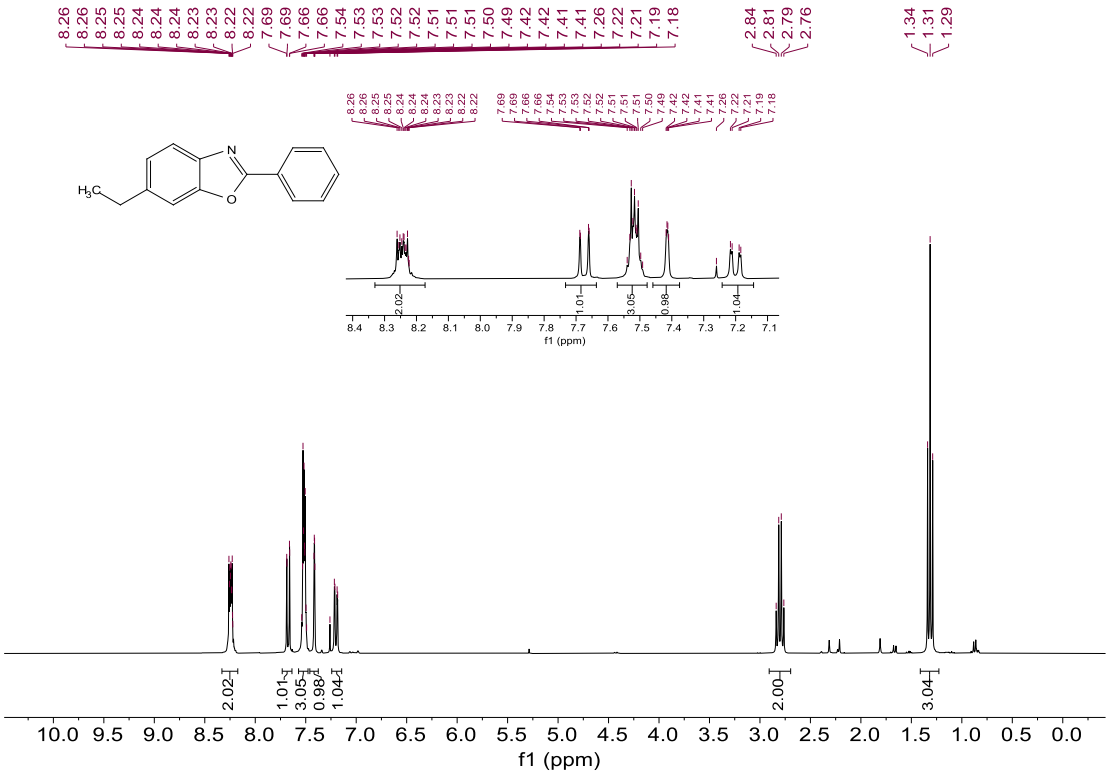
^{1}HNMR

^{13}CNMR

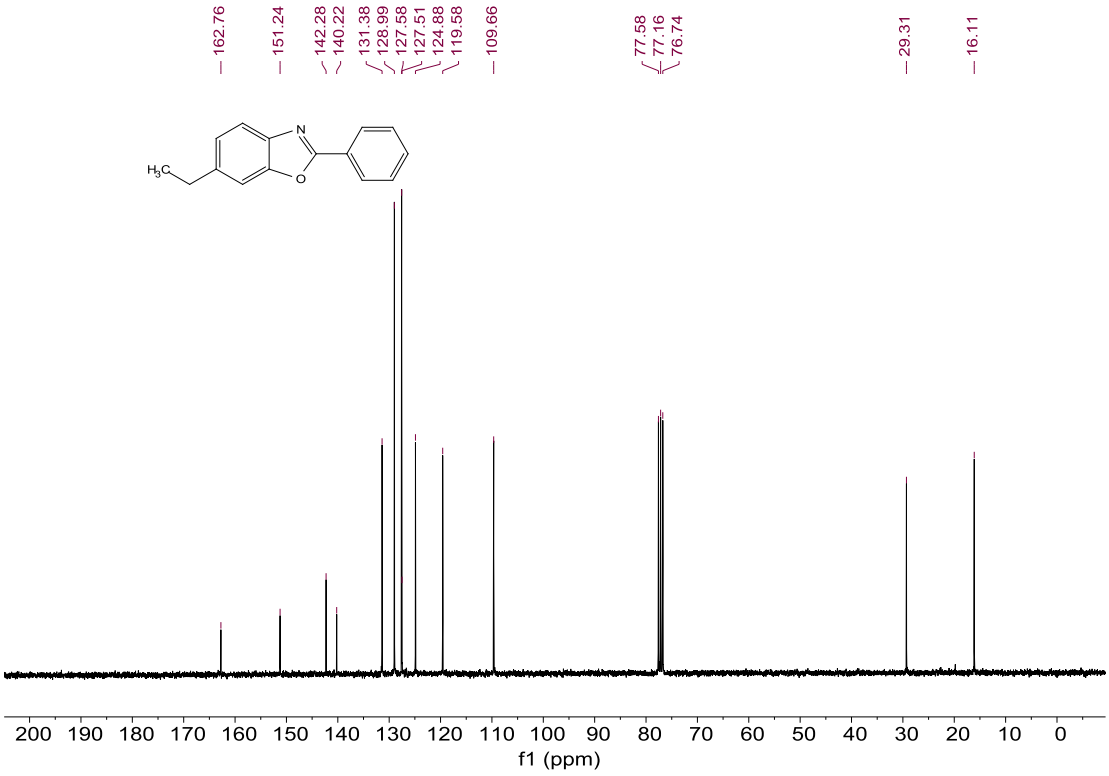


Compound 1v

^{1}HNMR

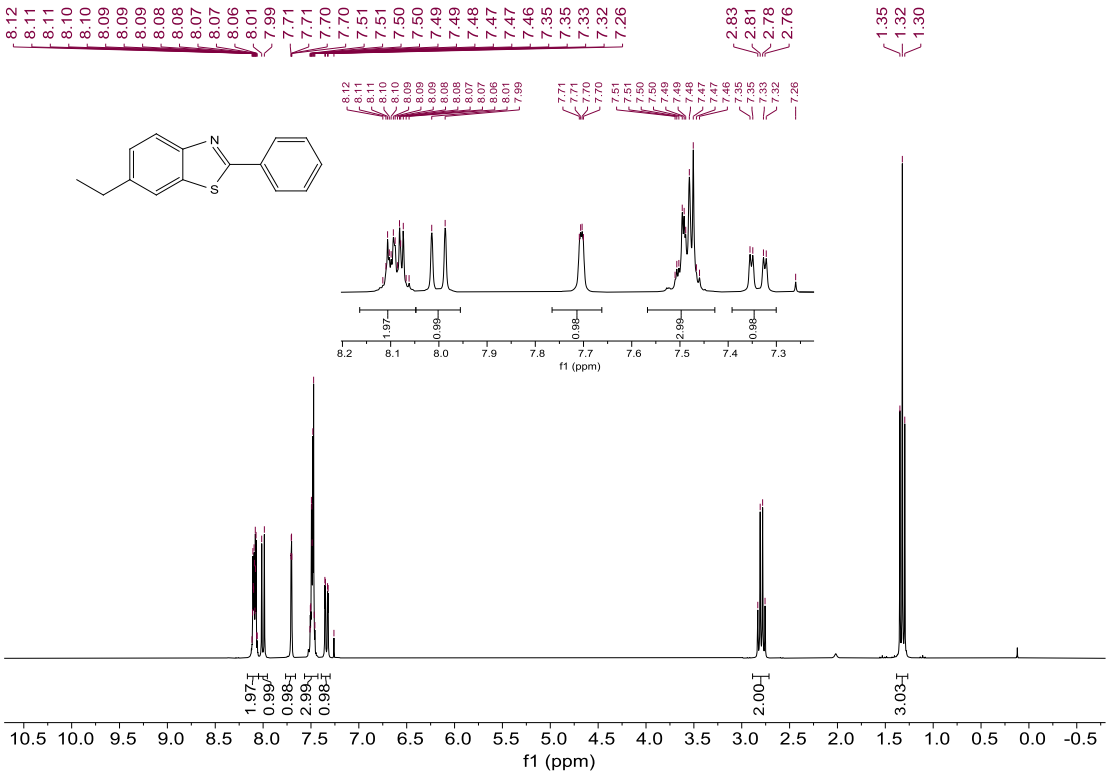


^{13}CNMR

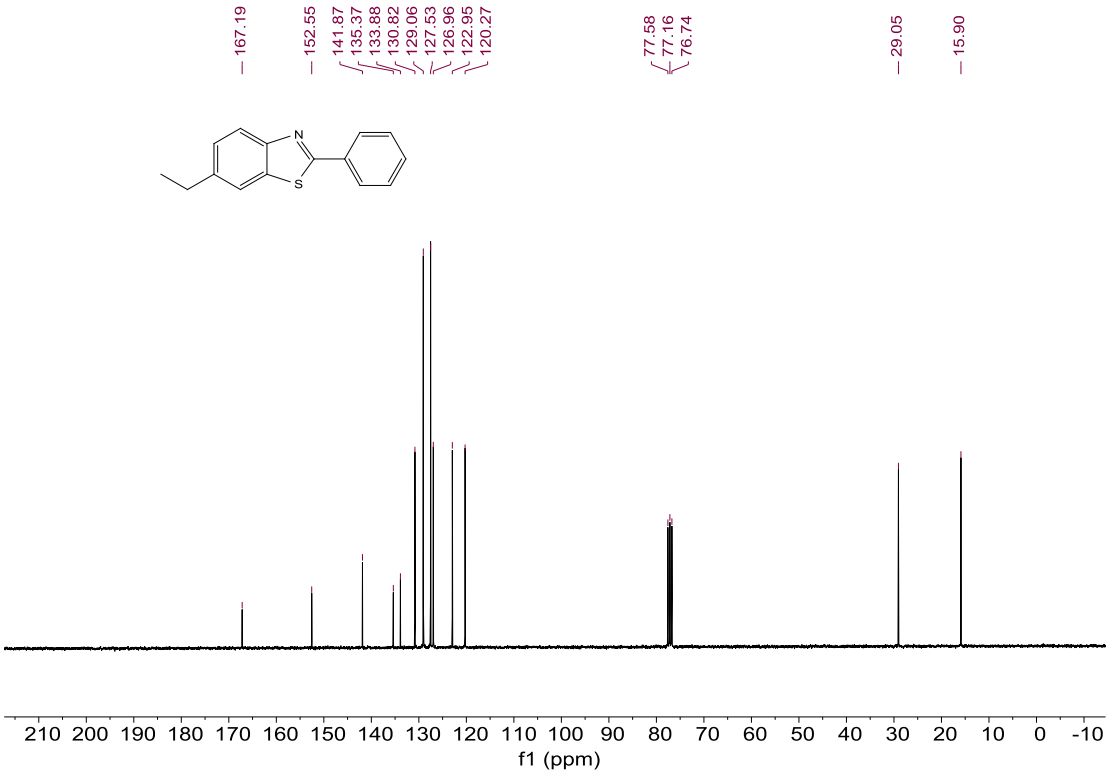


Compound 1w

^{1}HMNR

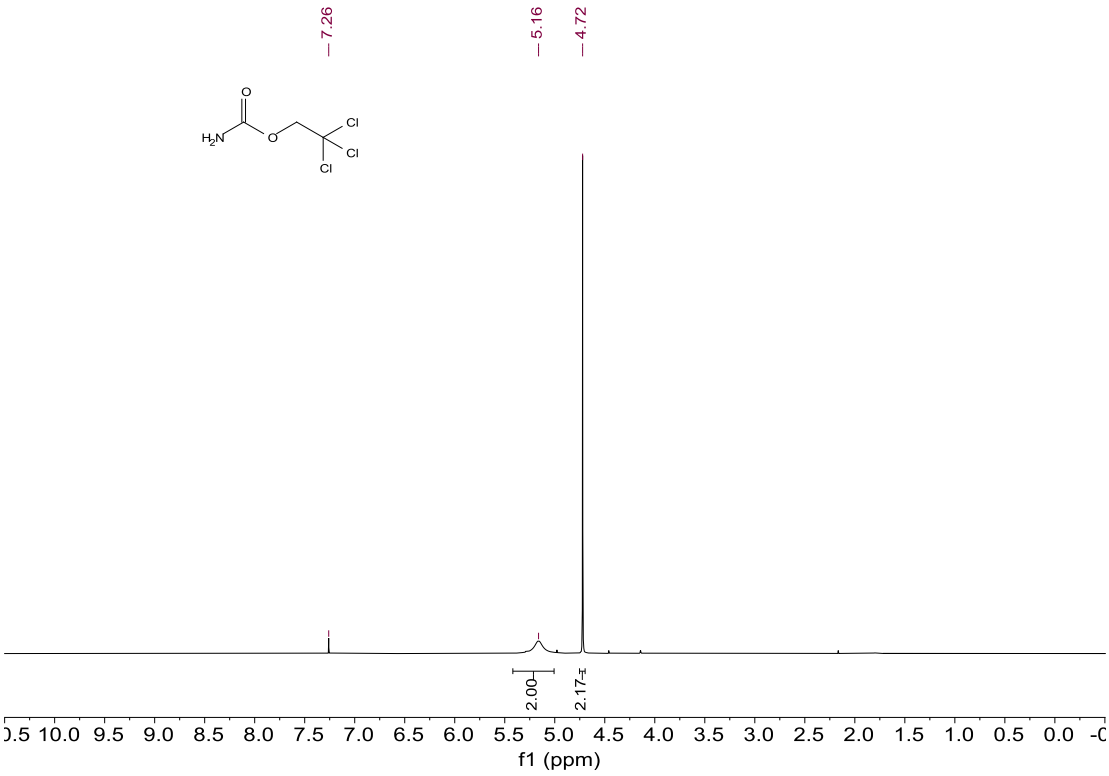


^{13}CNMR

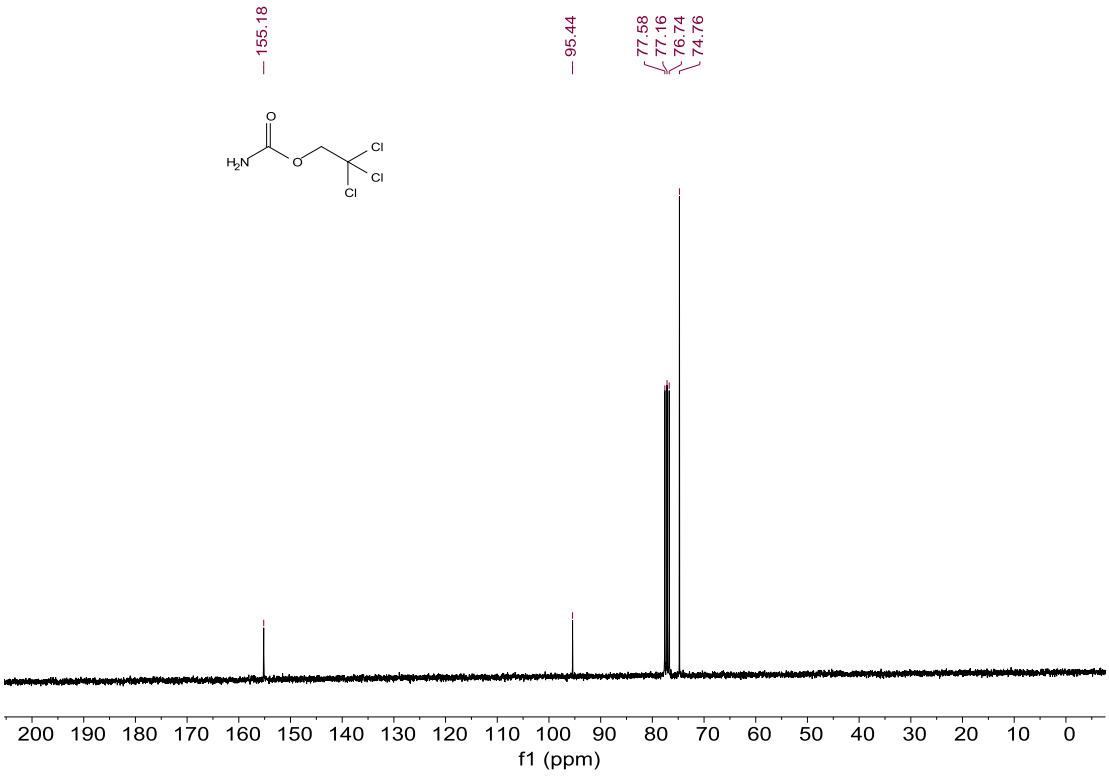


Compound 2i

^{1}HNMR



^{13}CNMR

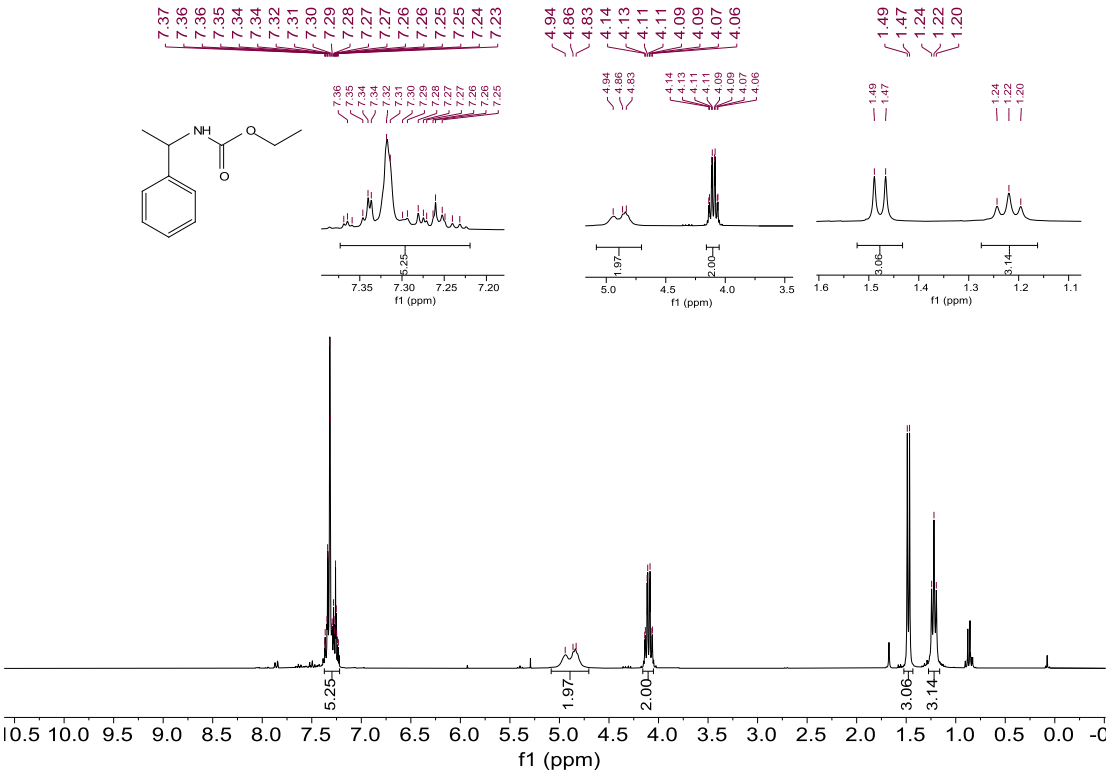


Compound 2l

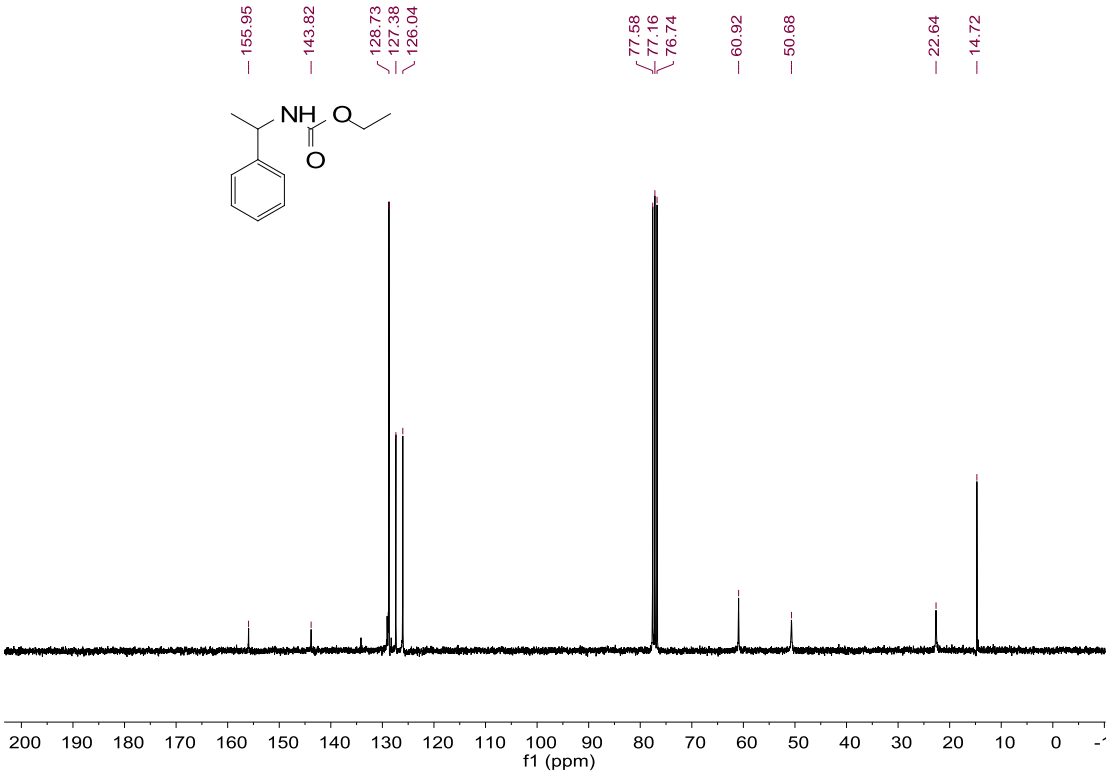
^{1}HNMR

Compound 3a

^{1}HNMR

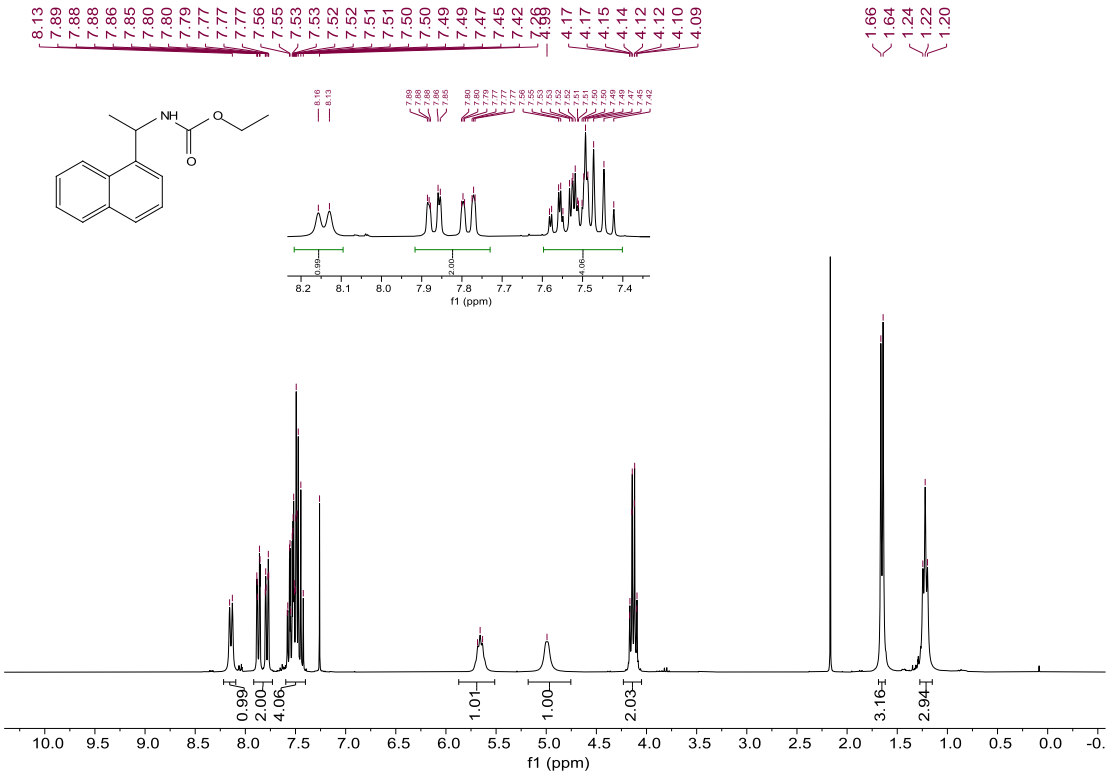


^{13}CNMR

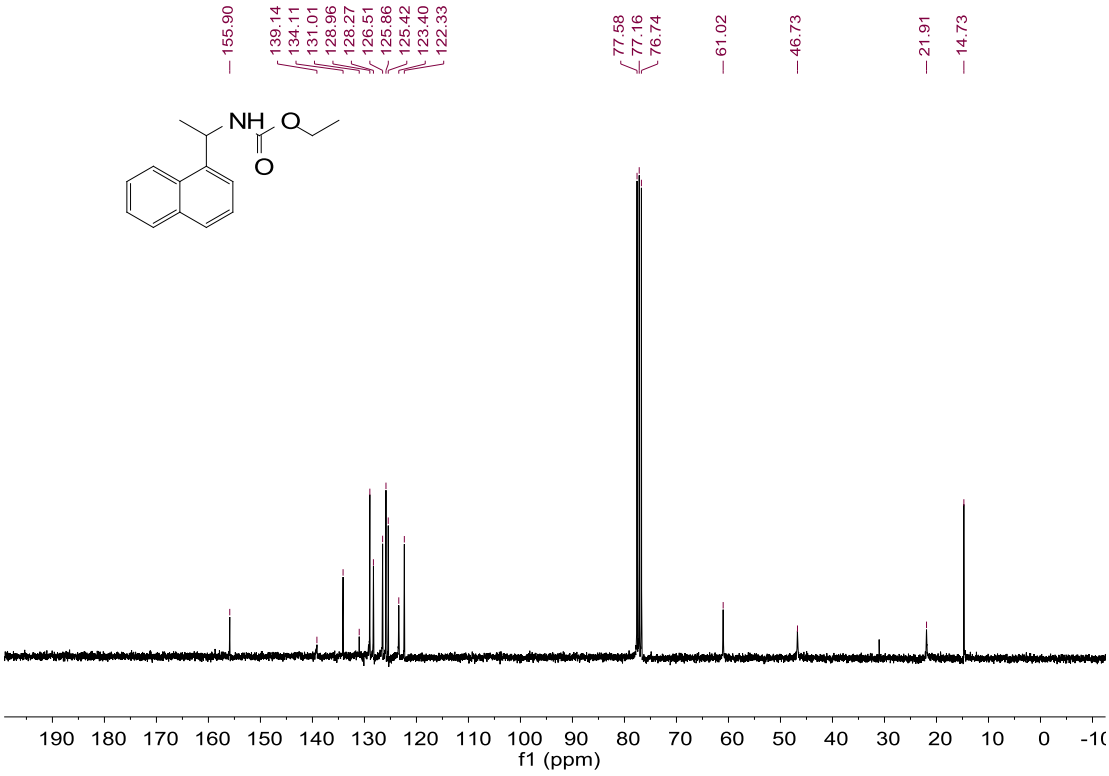


Compound 3b

^{1}HNMR

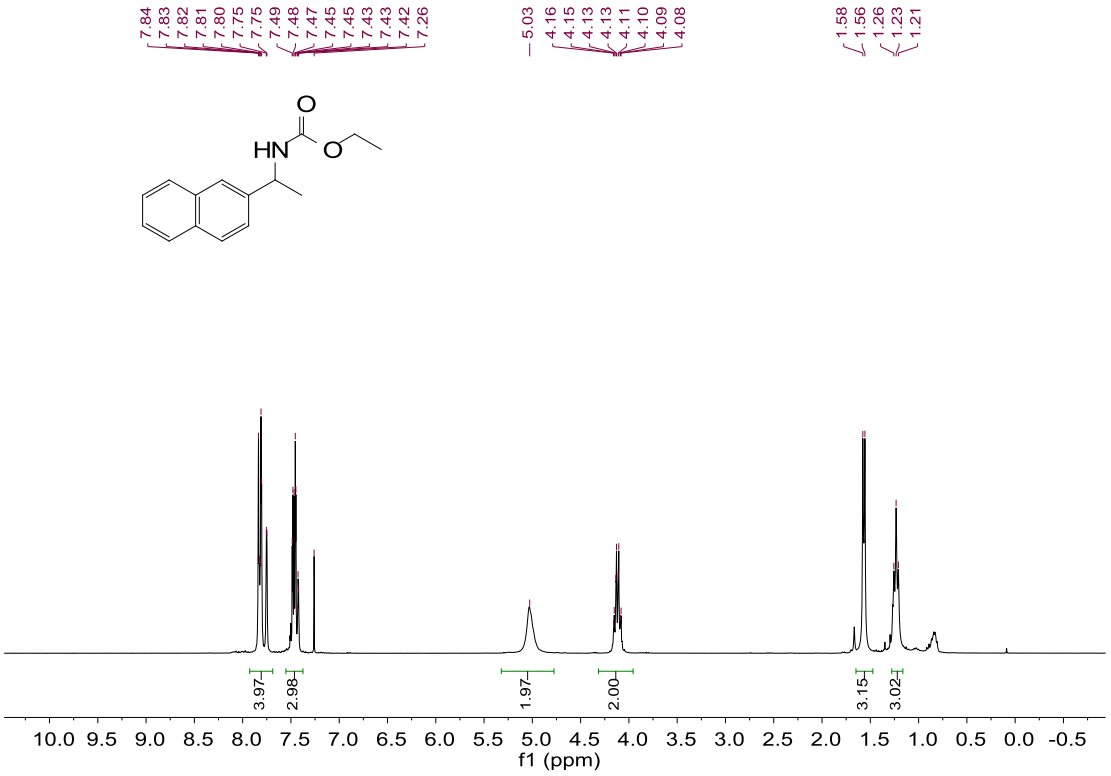


^{13}CNMR



Compound 3c

^{1}HNMR



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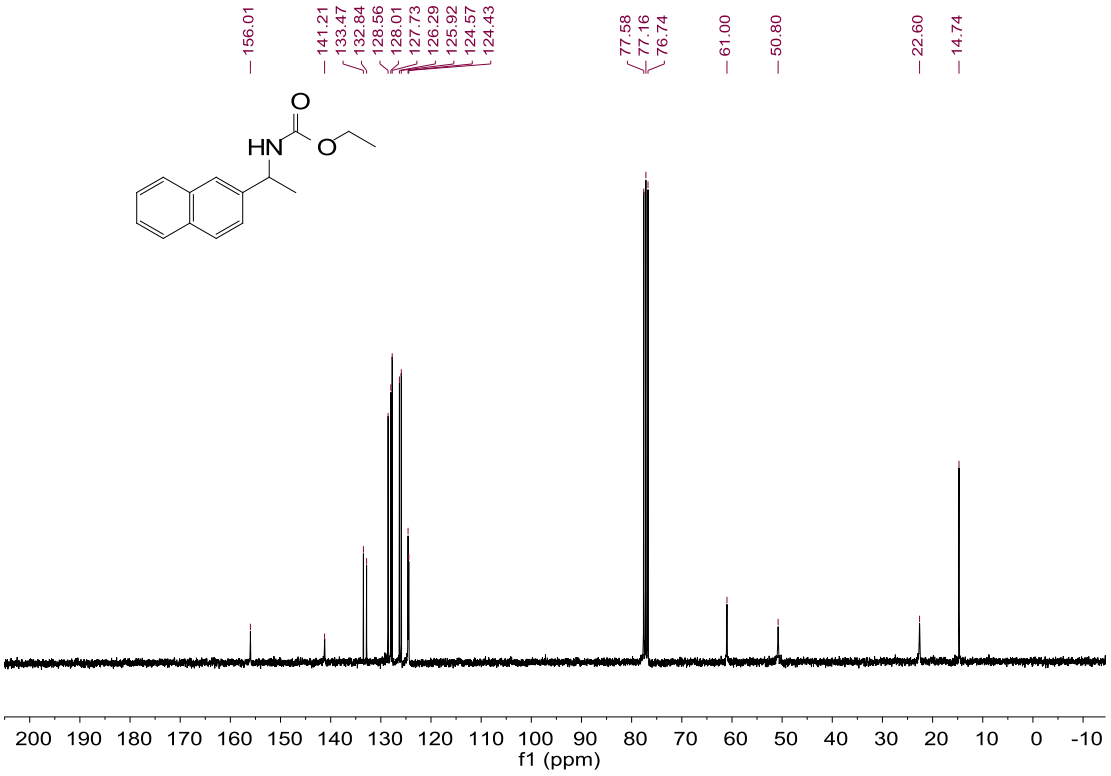
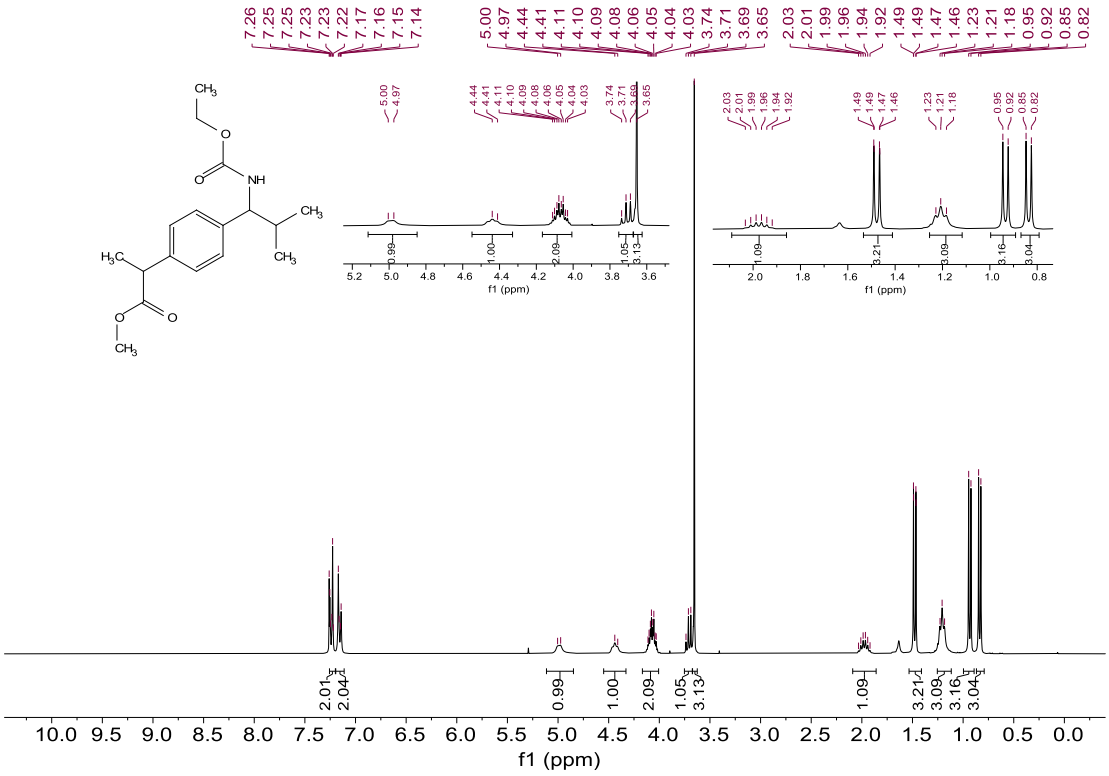
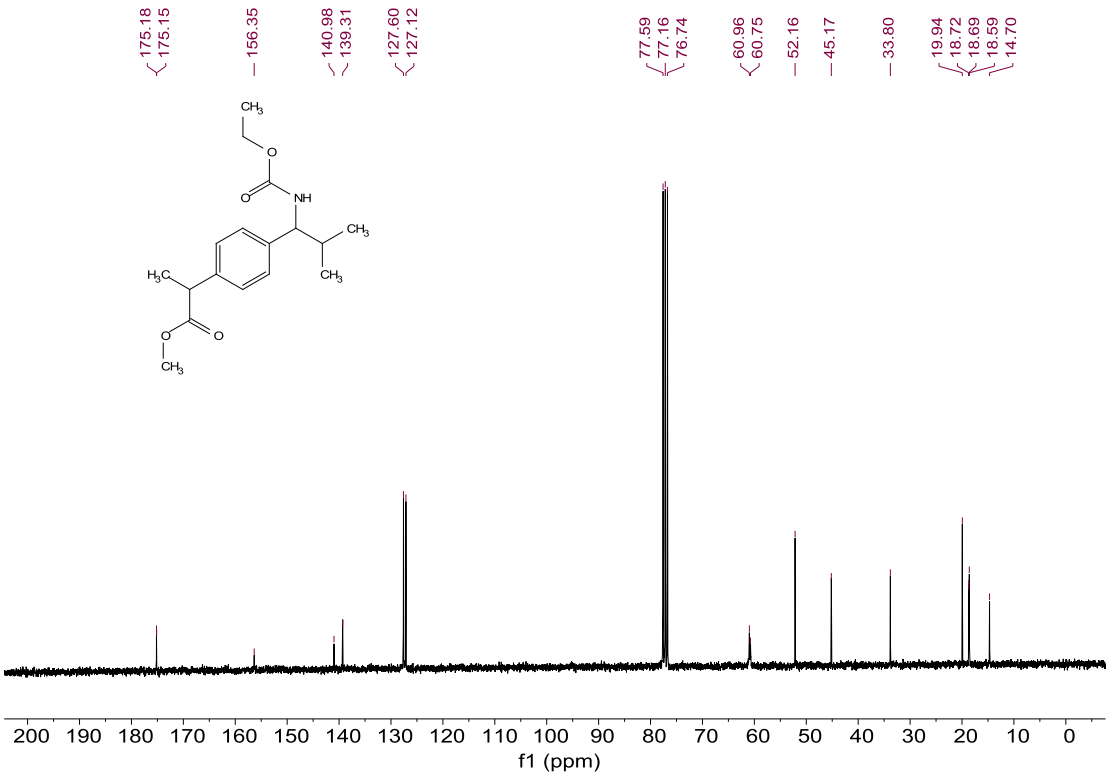


Compound 3d

^{1}HMNR

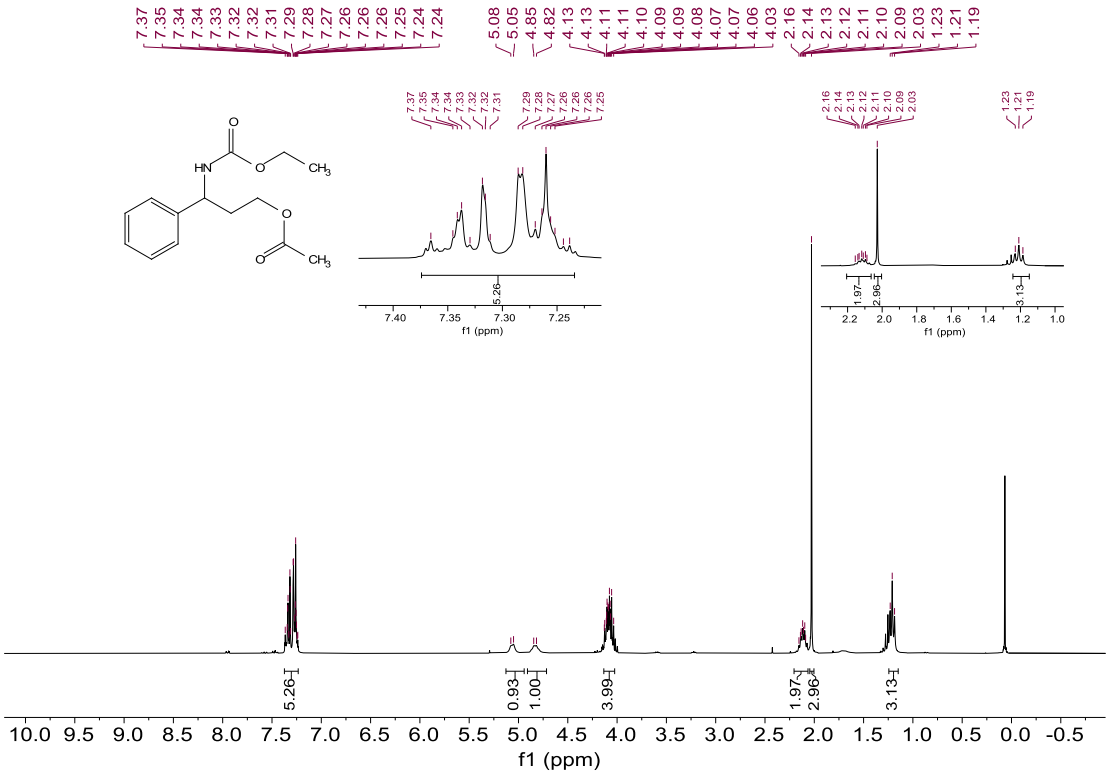


^{13}CNMR

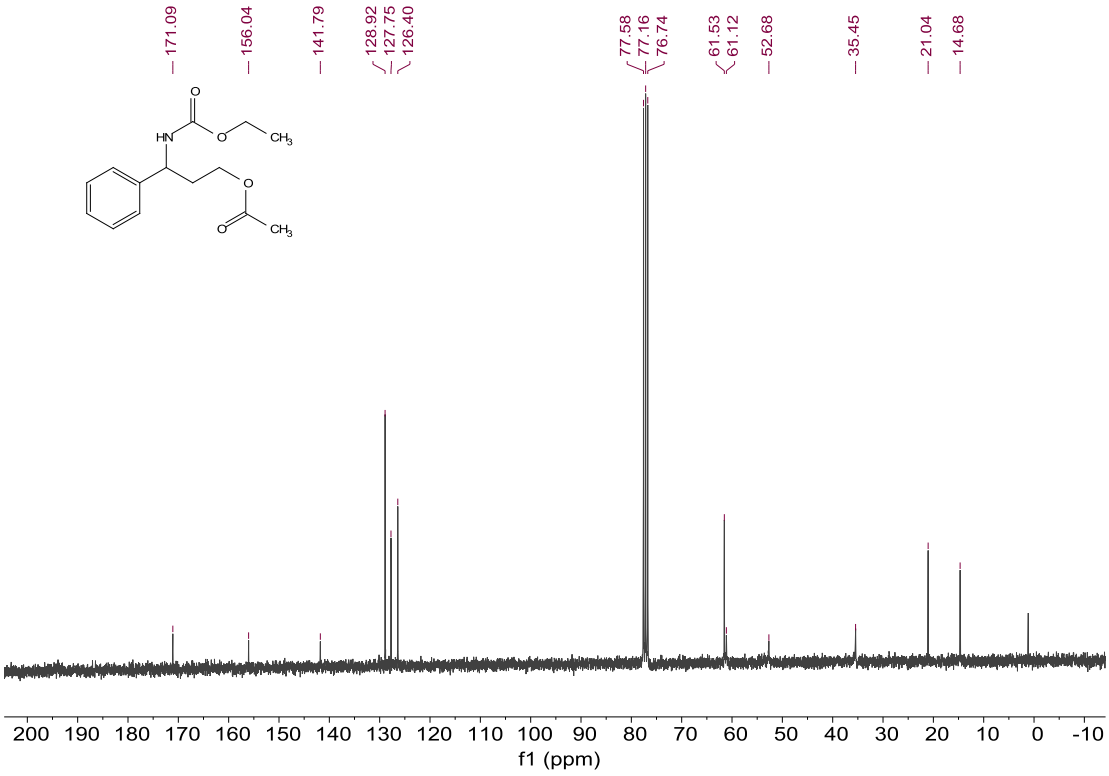


Compound 3e

^{1}HMNR

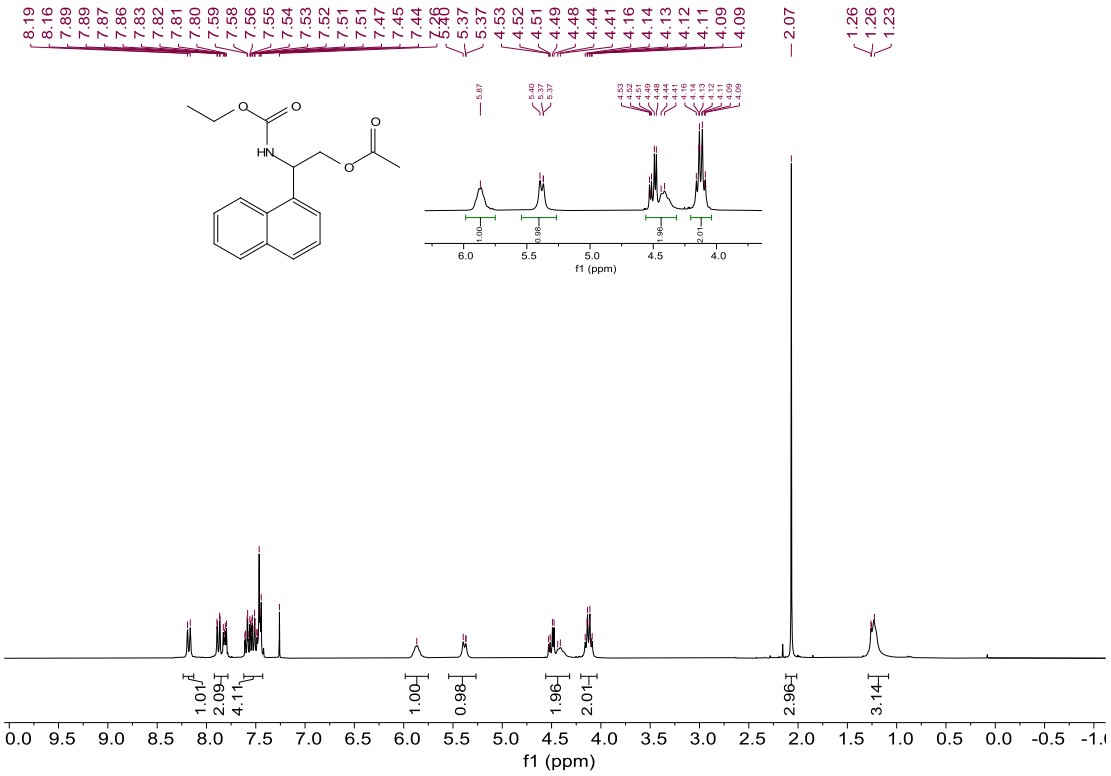


^{13}CNMR

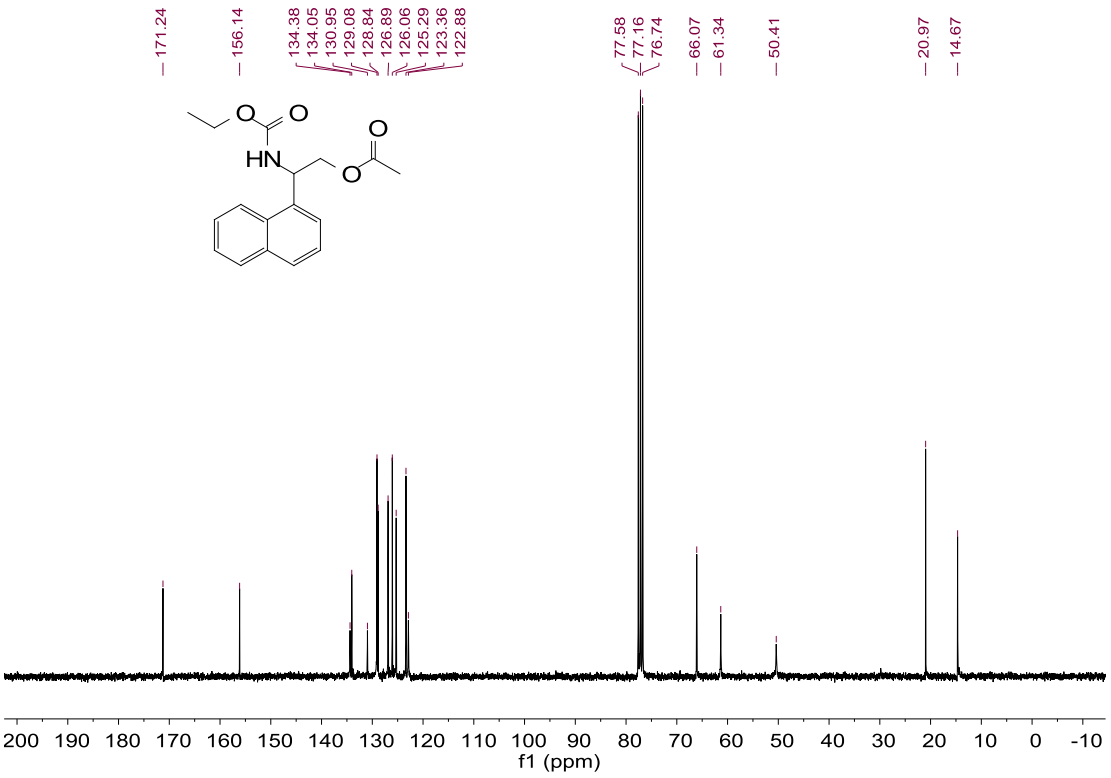


Compound 3f

^{1}HNMR

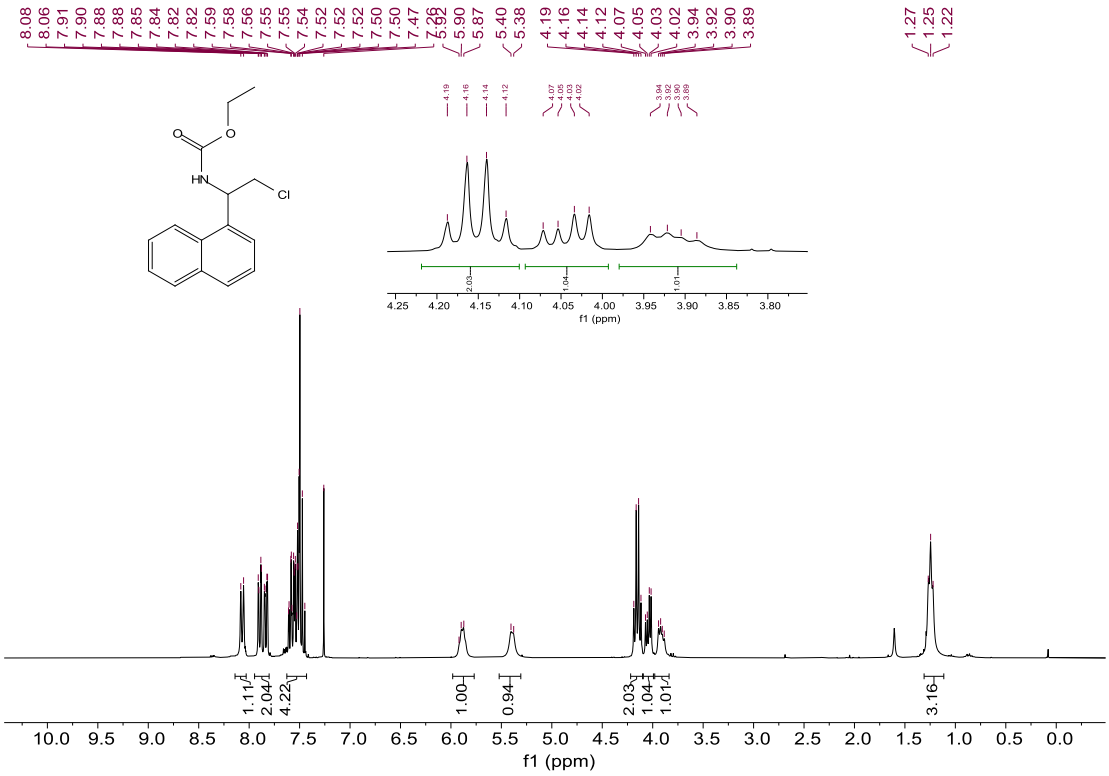


^{13}CNMR

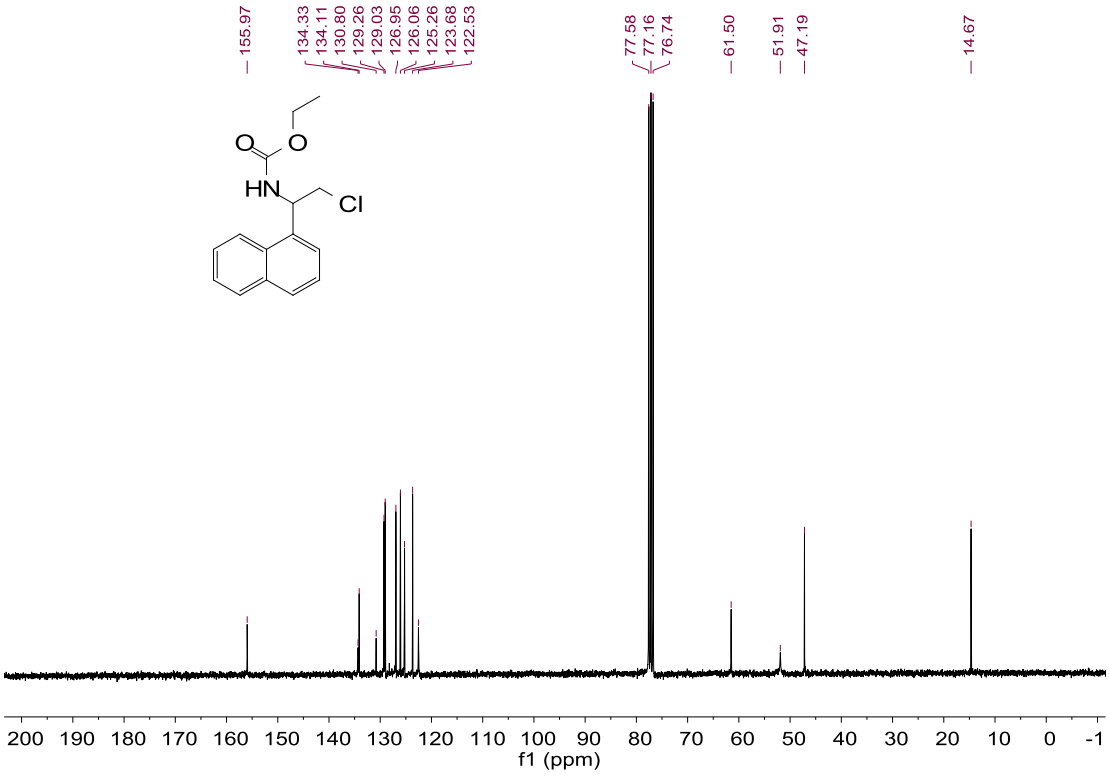


Compound 3g

^{1}HNMR

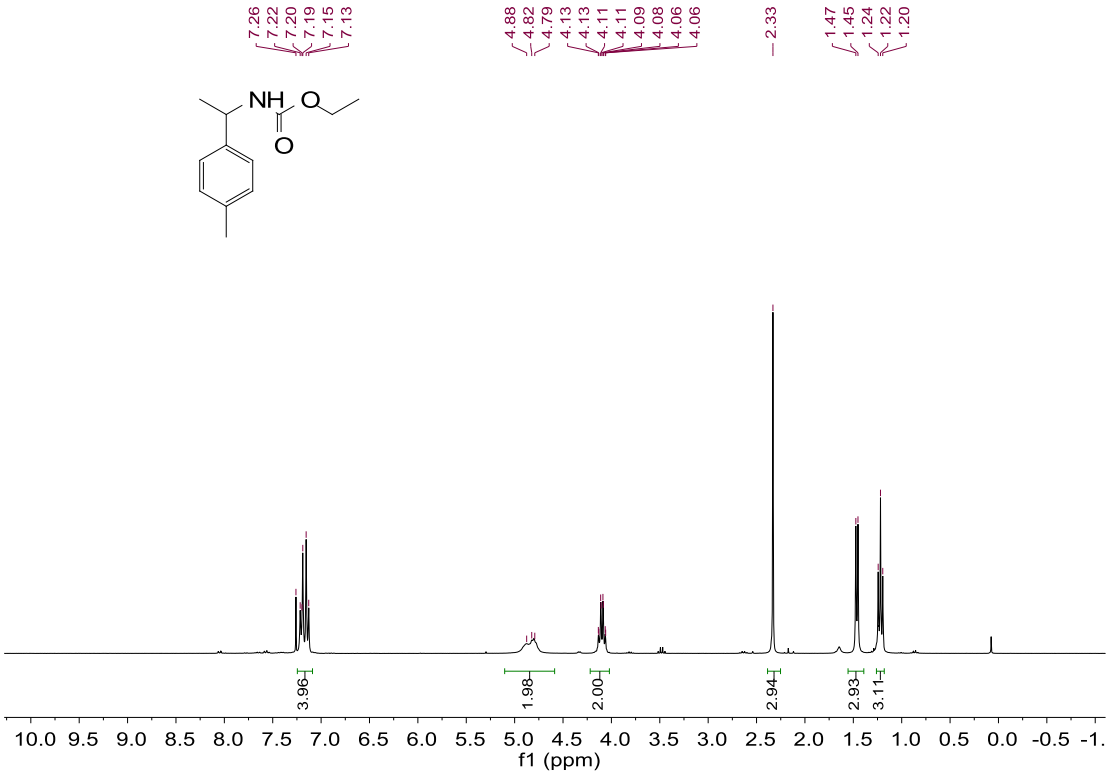


^{13}CNMR

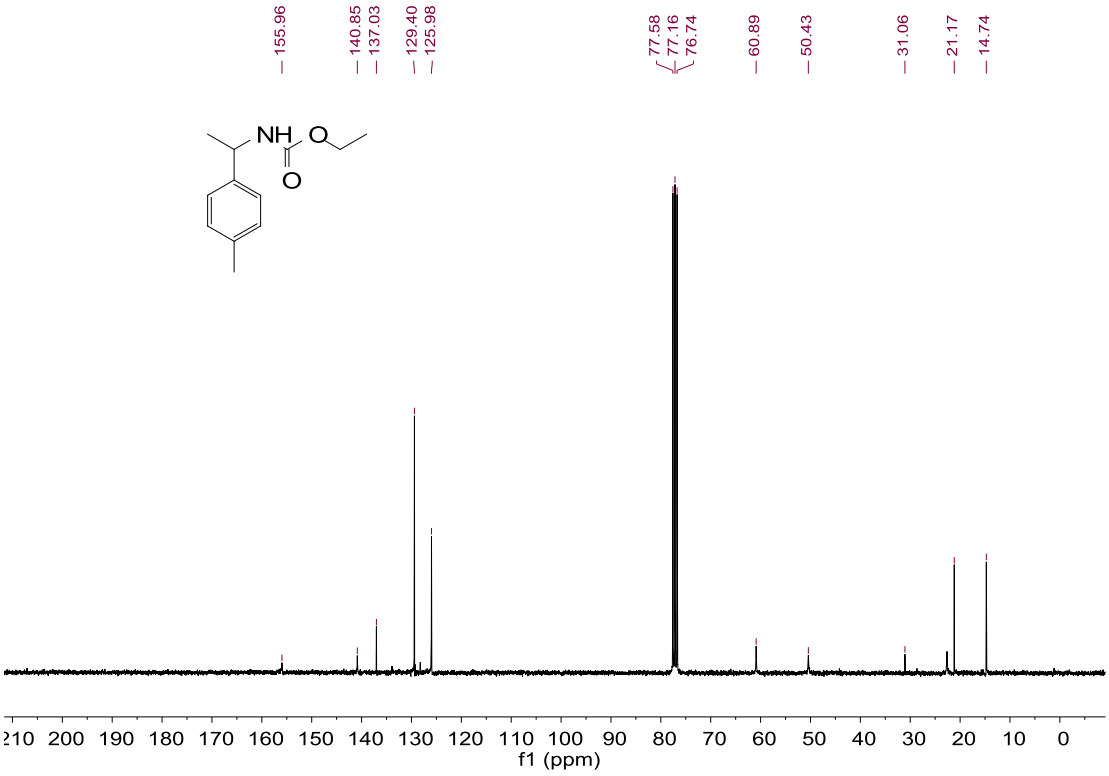


Compound 3h

^{1}HNMR

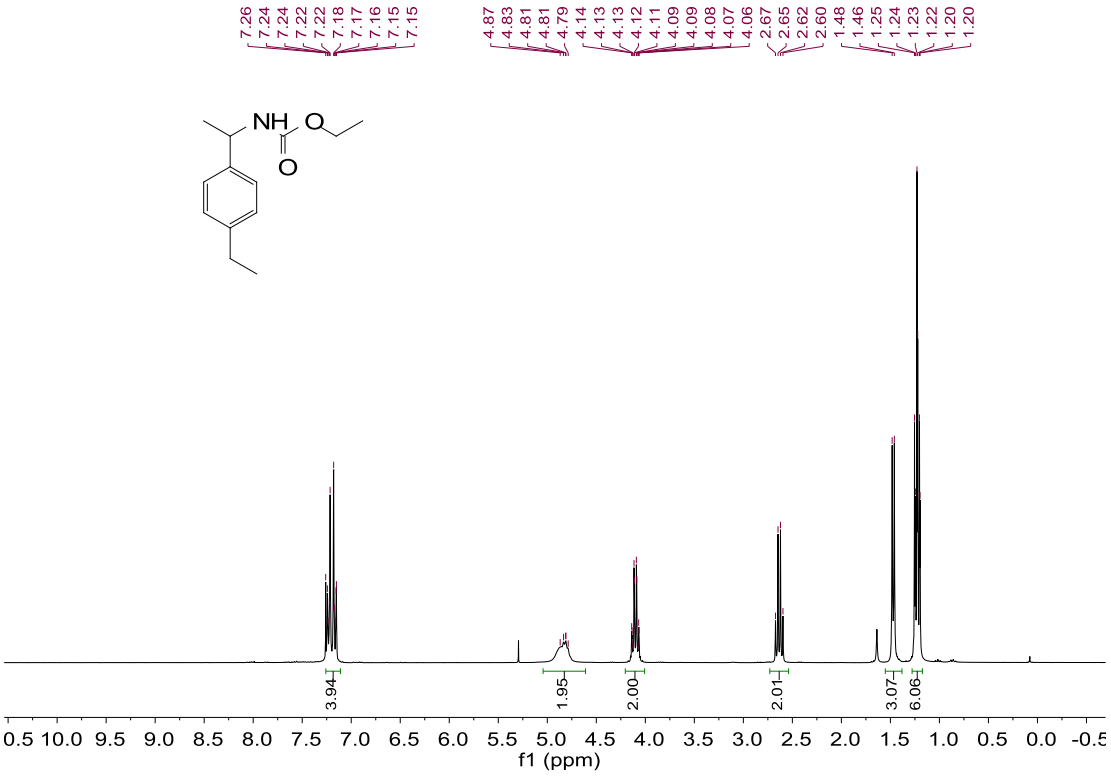


^{13}CNMR

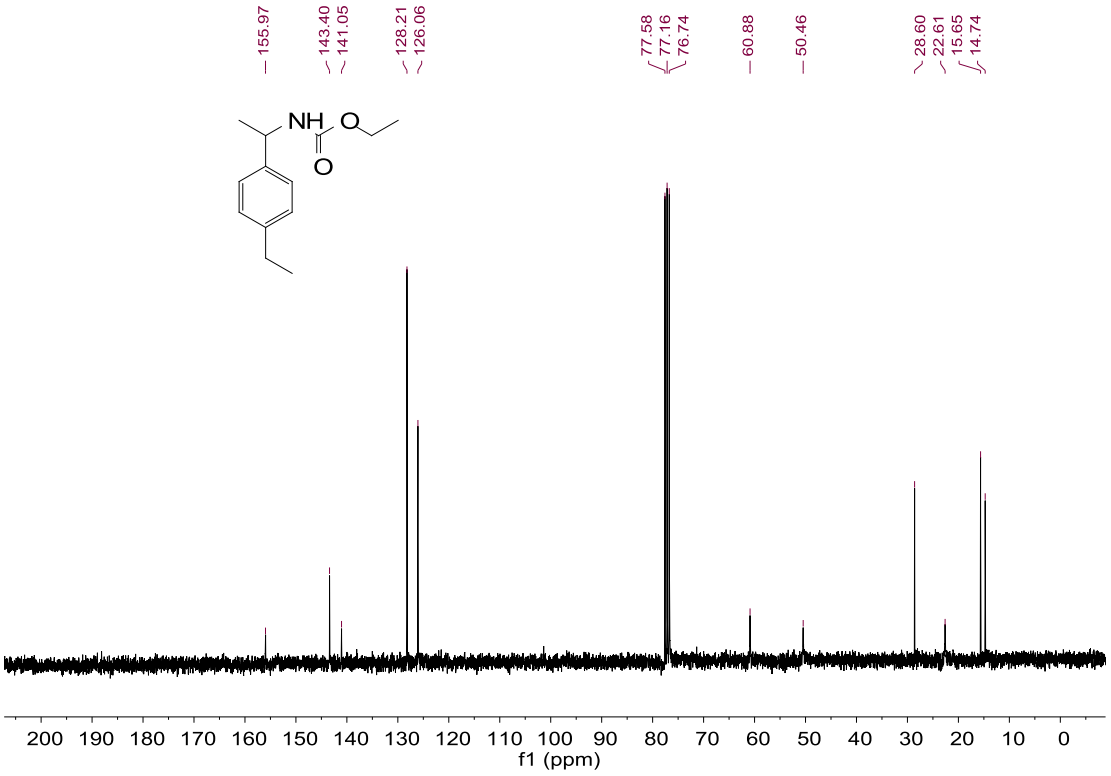


Compound 3i

^{1}HMNR

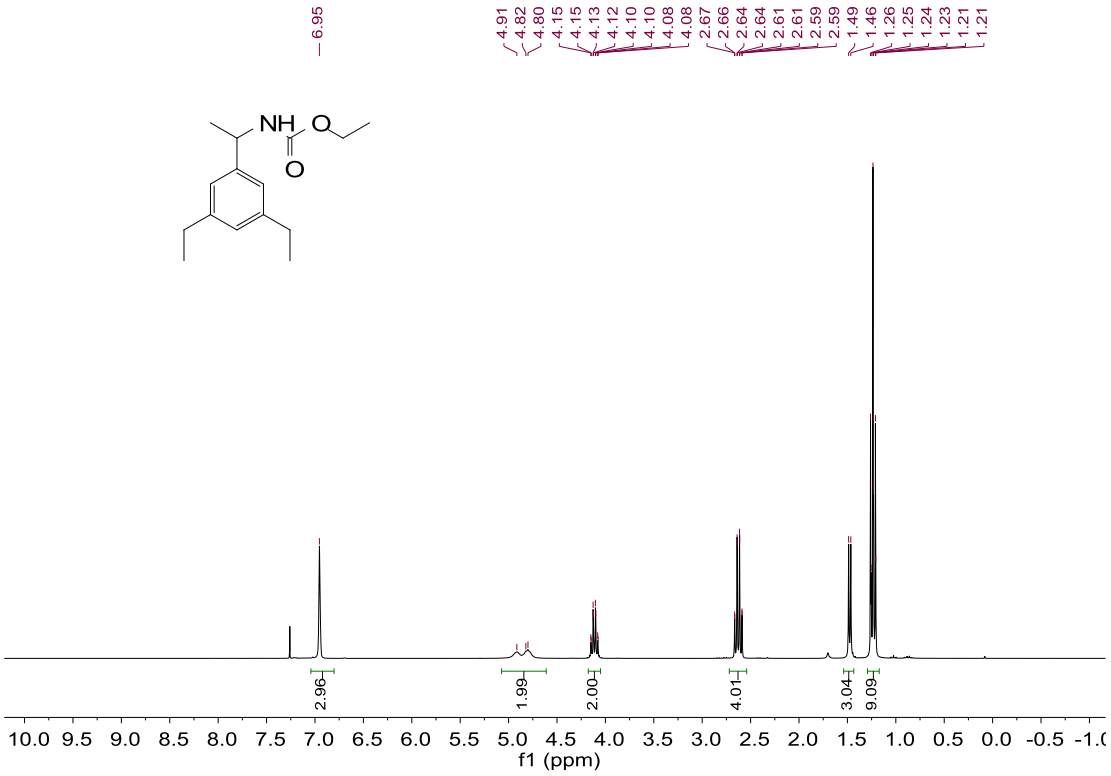


^{13}CNMR

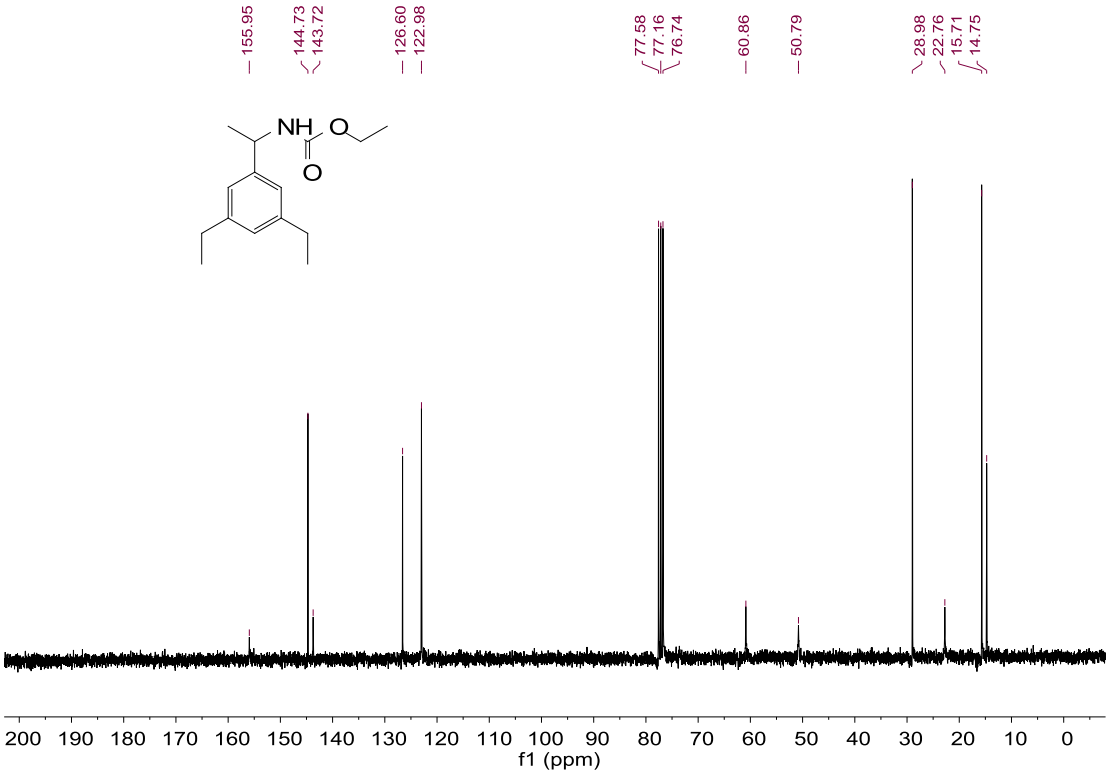


Compound 3j

^{1}HNMR

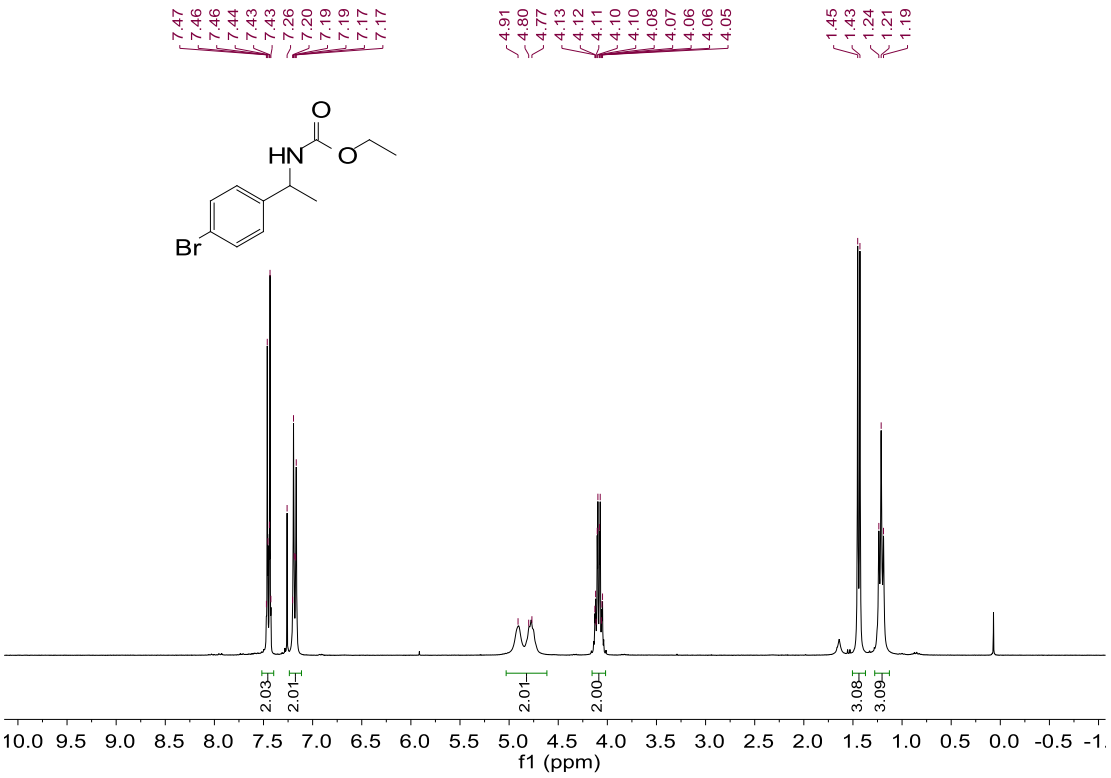


^{13}CNMR

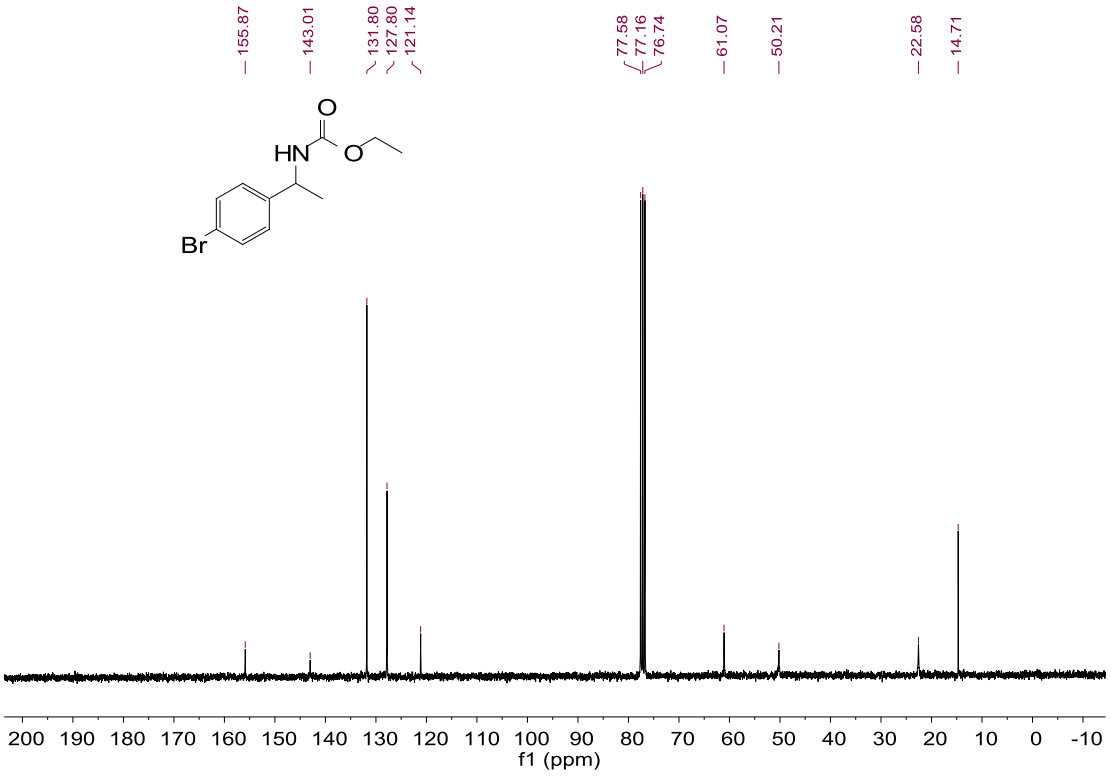


Compound **3k**

^{1}HNMR

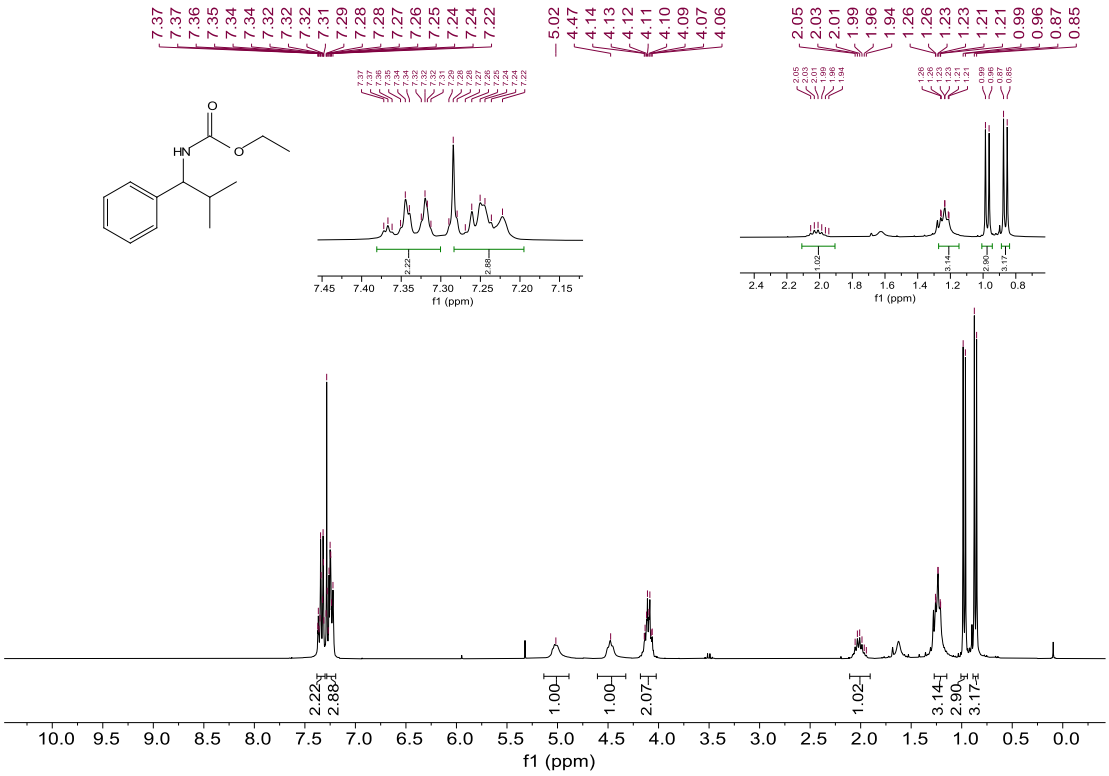


^{13}CNMR

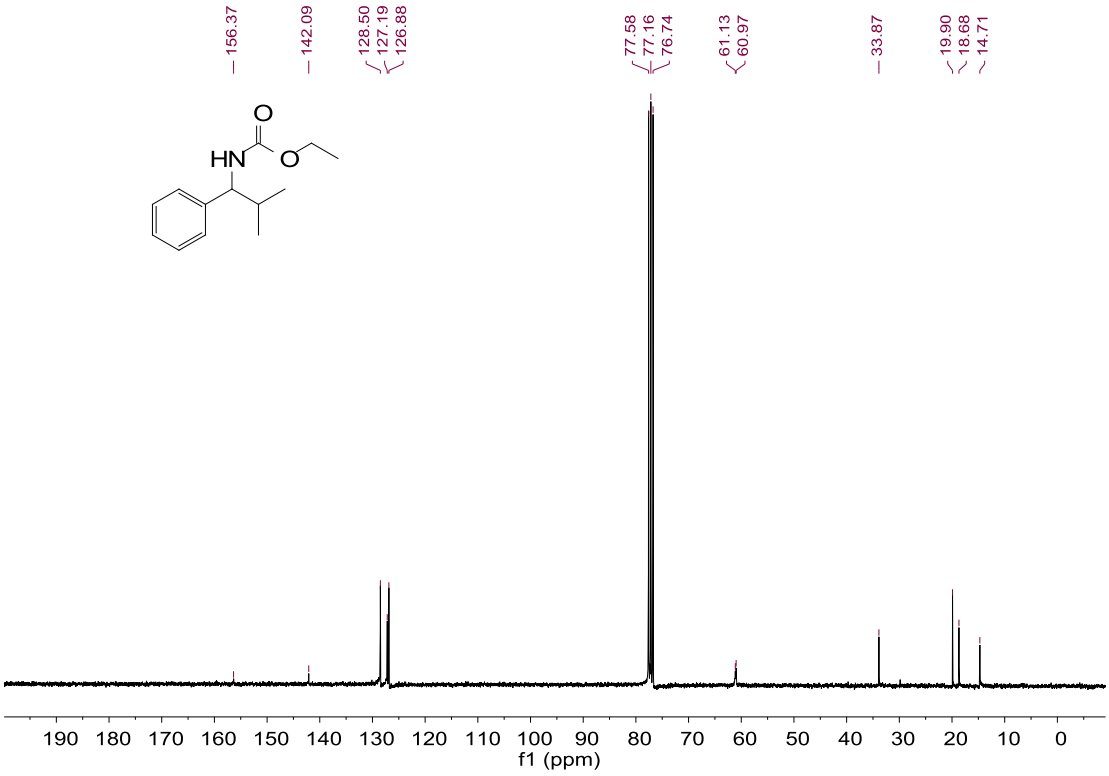


Compound **3l**

^{1}HNMR

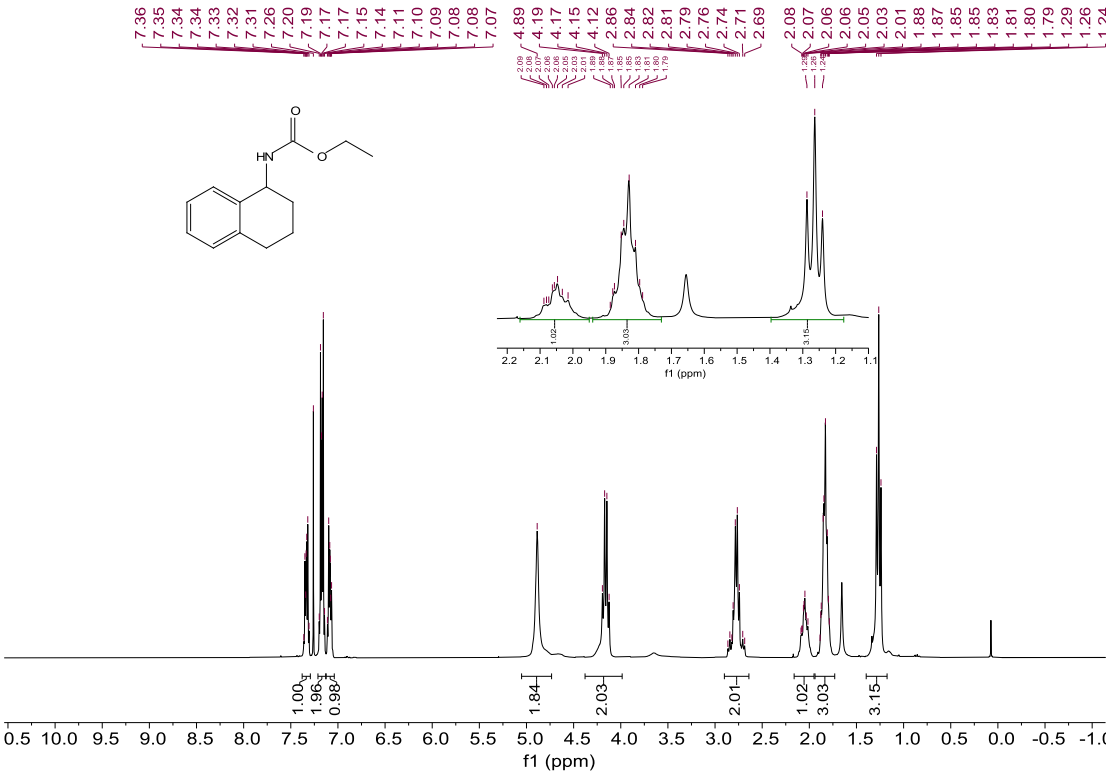


^{13}CNMR

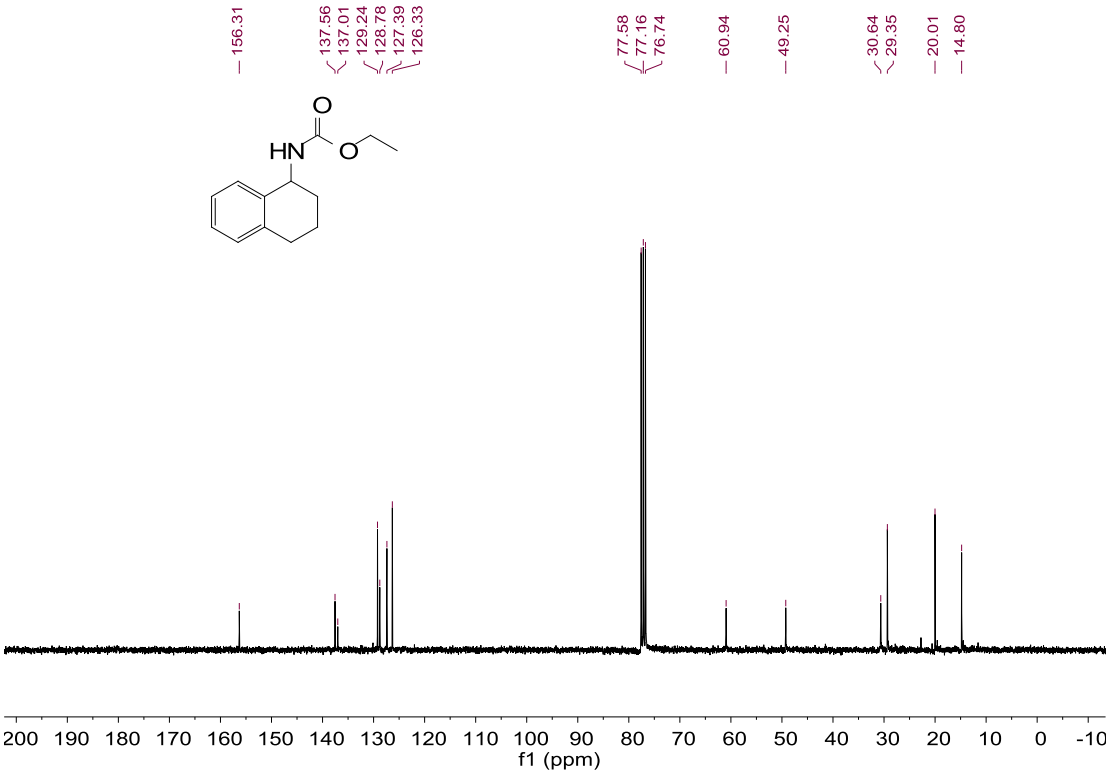


Compound 3m

^{1}HMNR

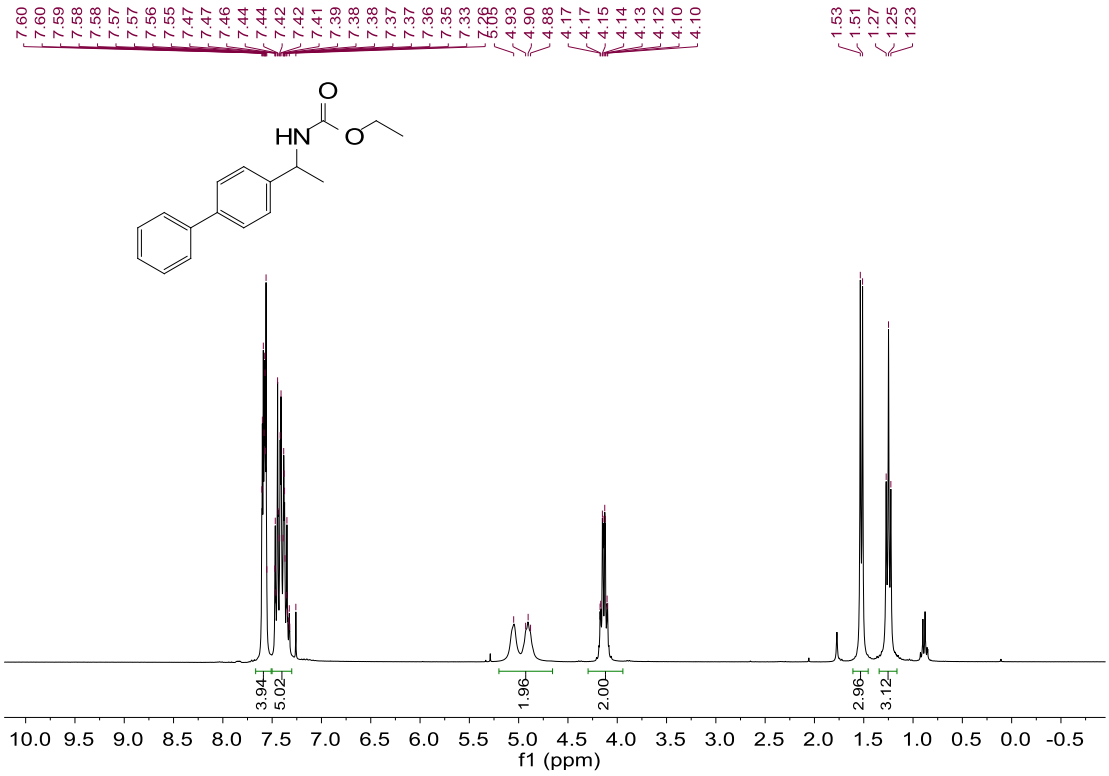


^{13}CNMR

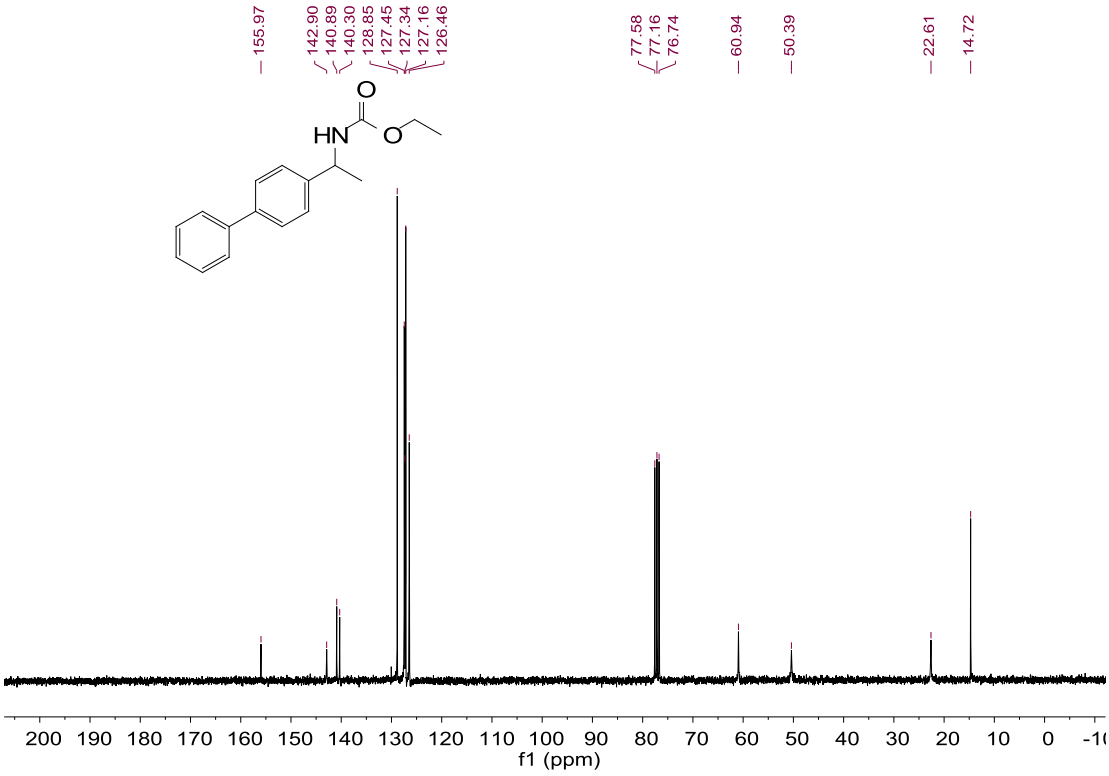


Compound 3n

^{1}HNMR

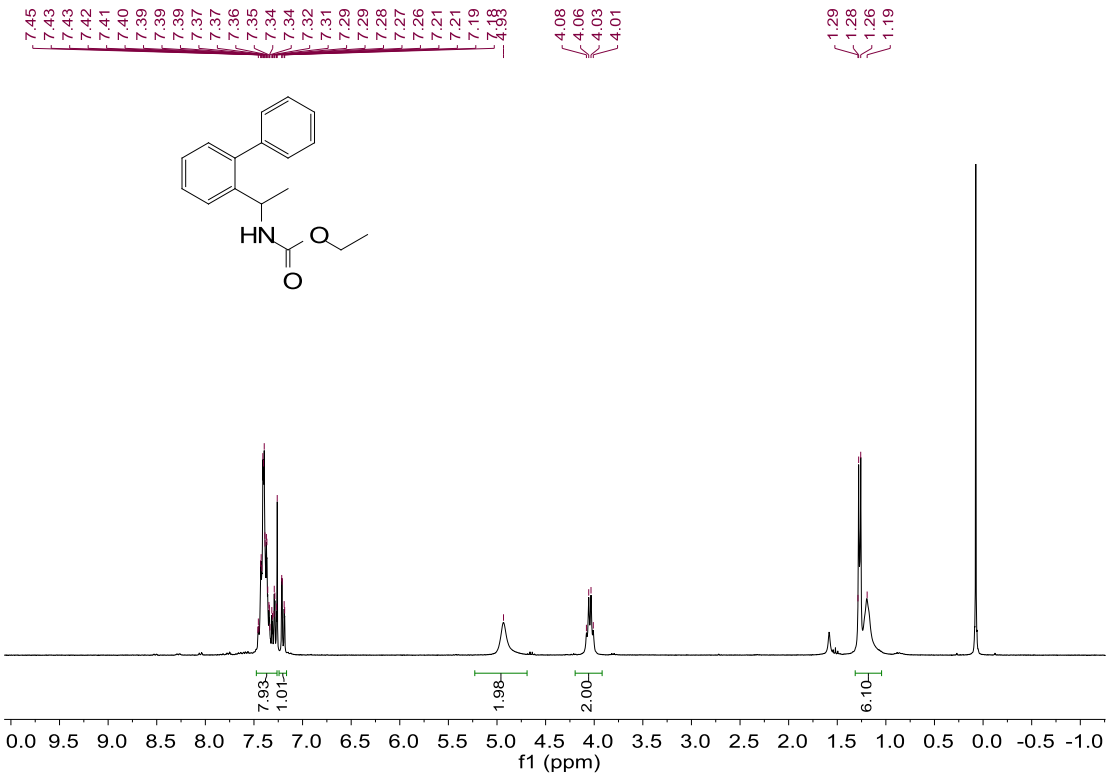


^{13}CNMR

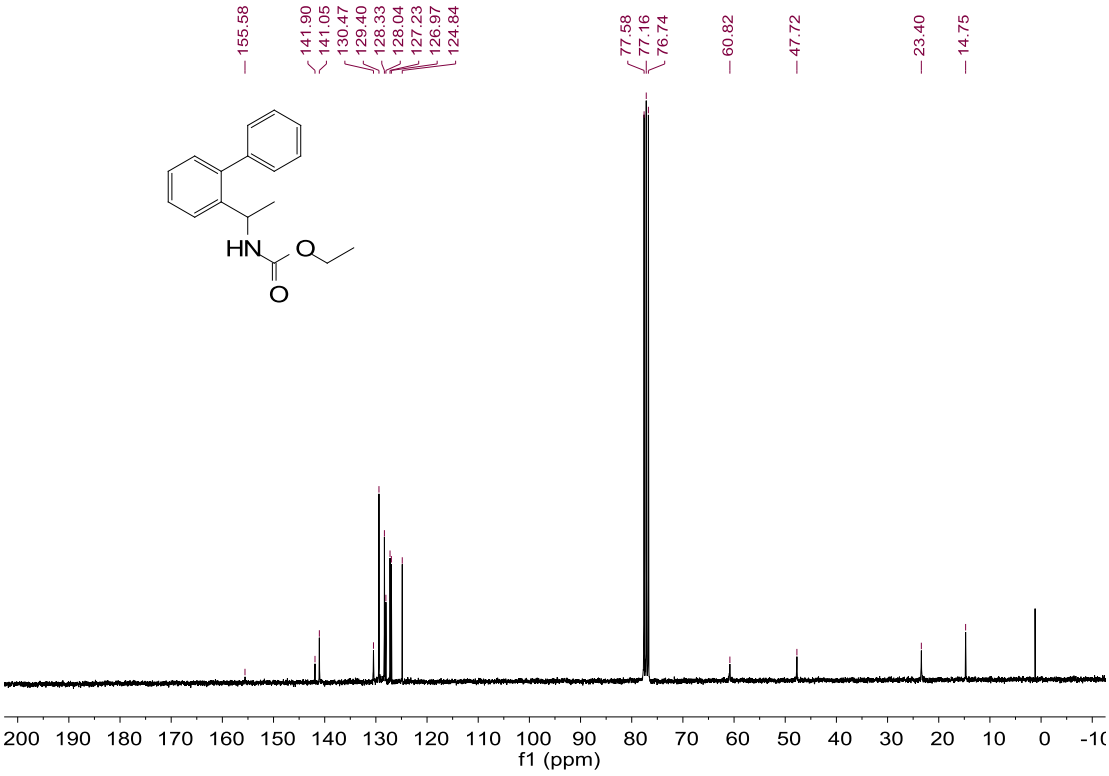


Compound 3o

^{1}HNMR

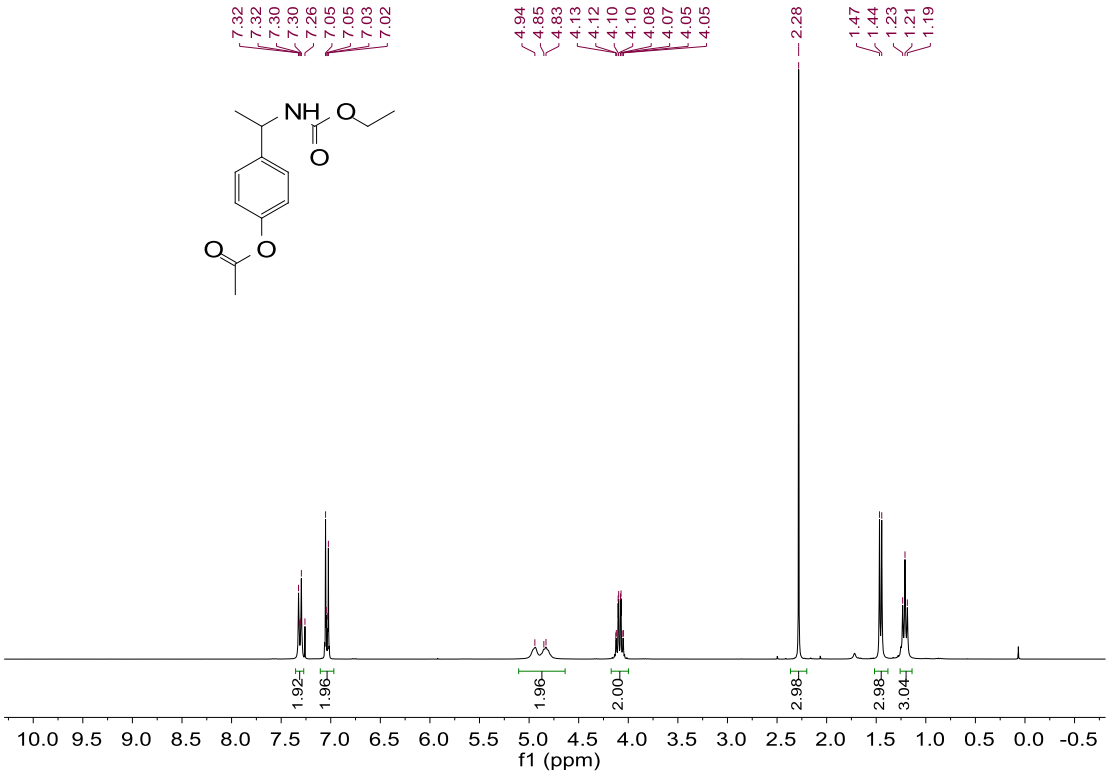


^{13}CNMR

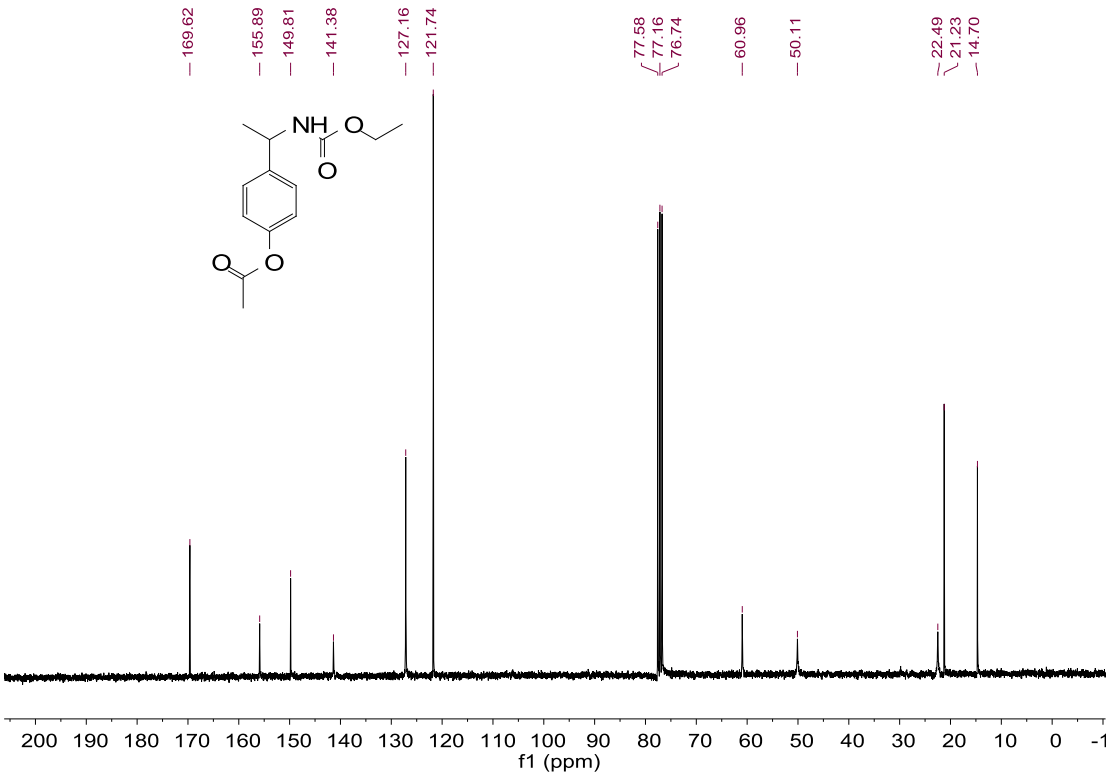


Compound 3p

^{1}HNMR

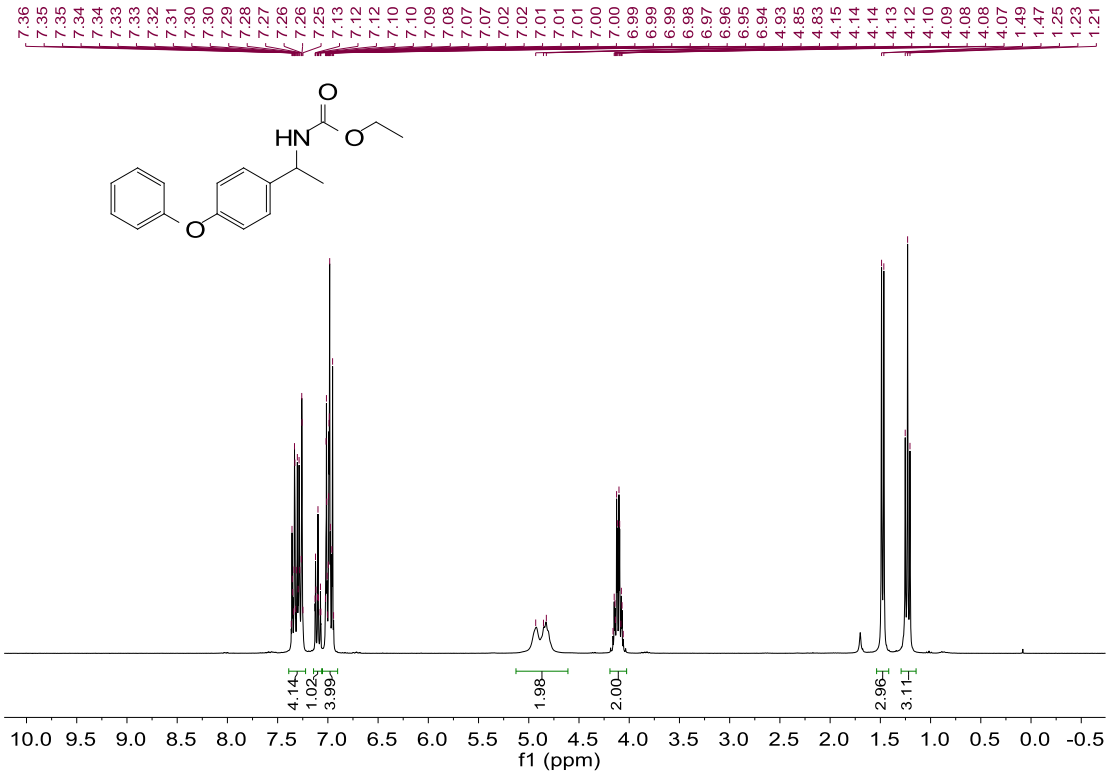


^{13}CNMR



Compound 3q

^{1}HNMR



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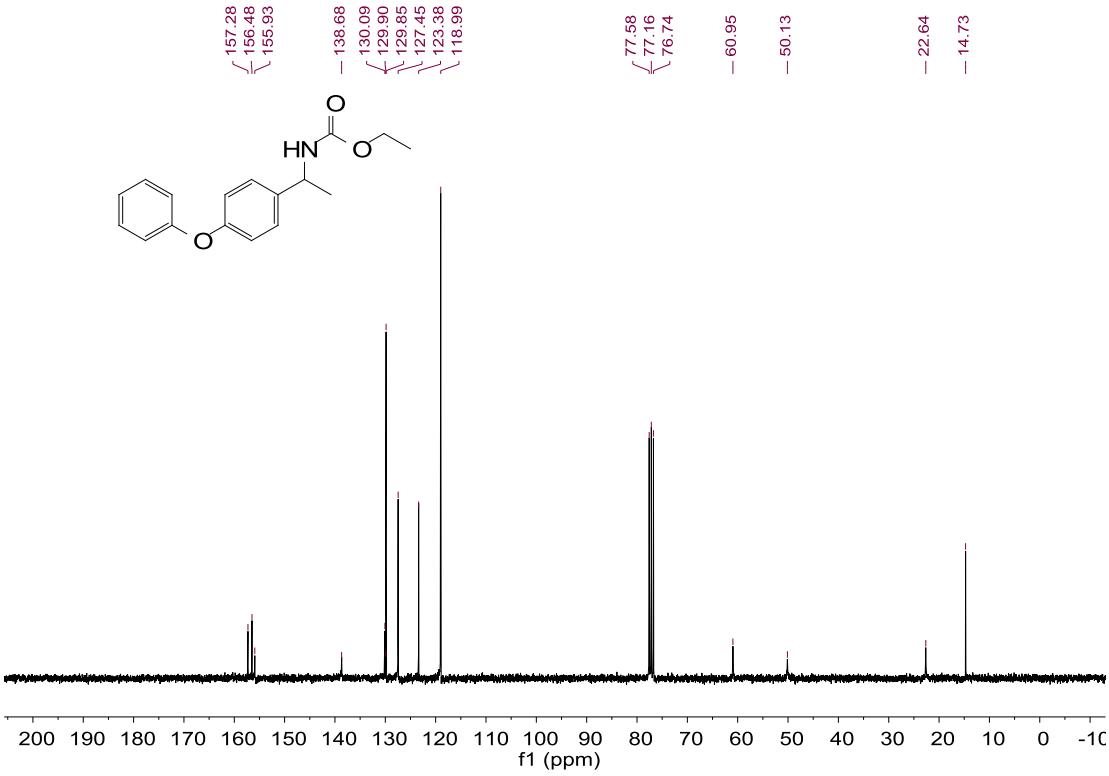
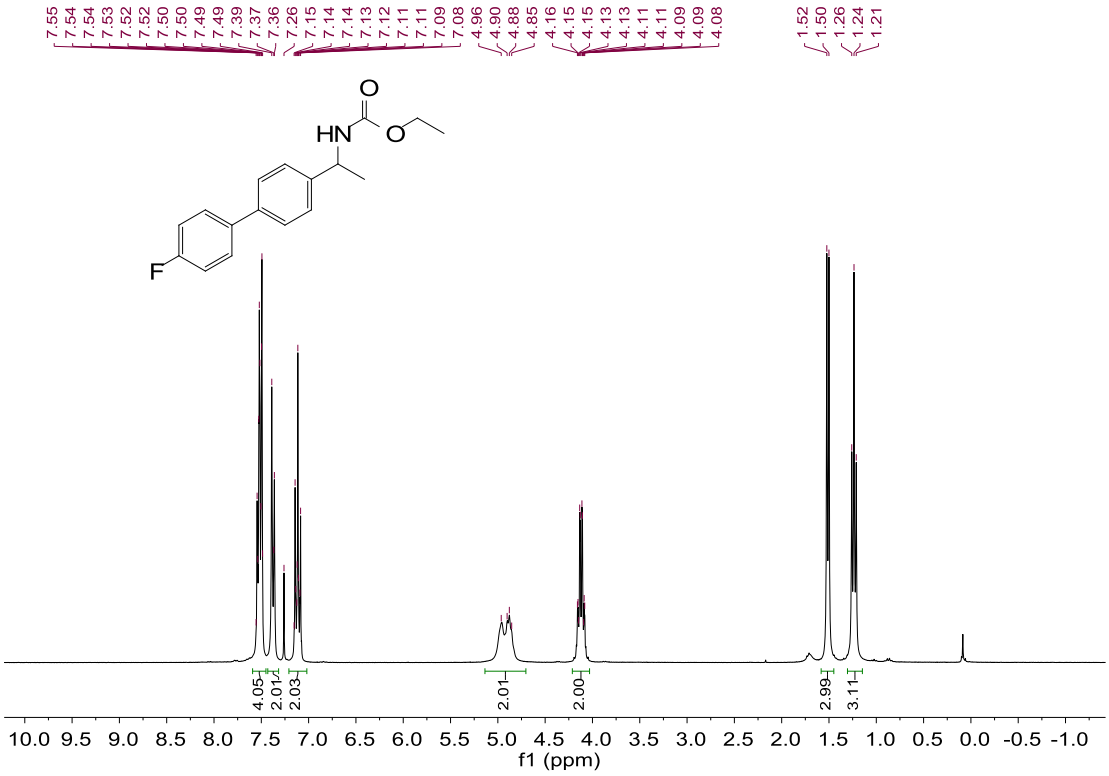
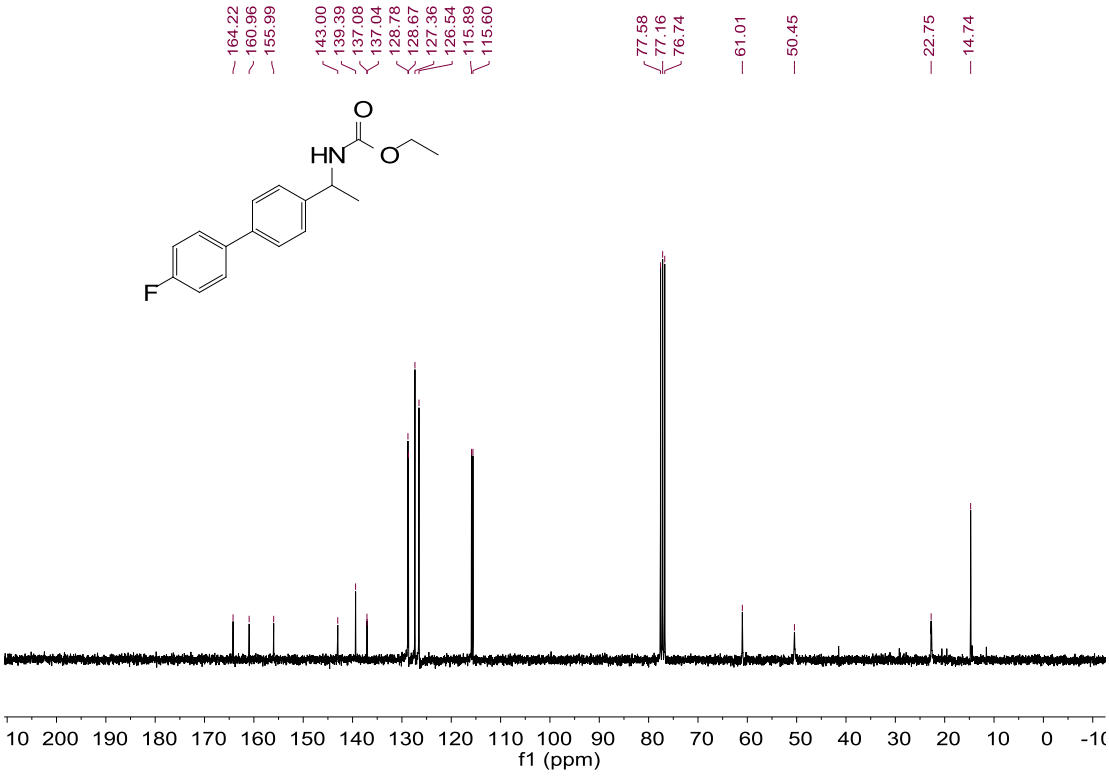


Compound 3r

^{1}HMNR

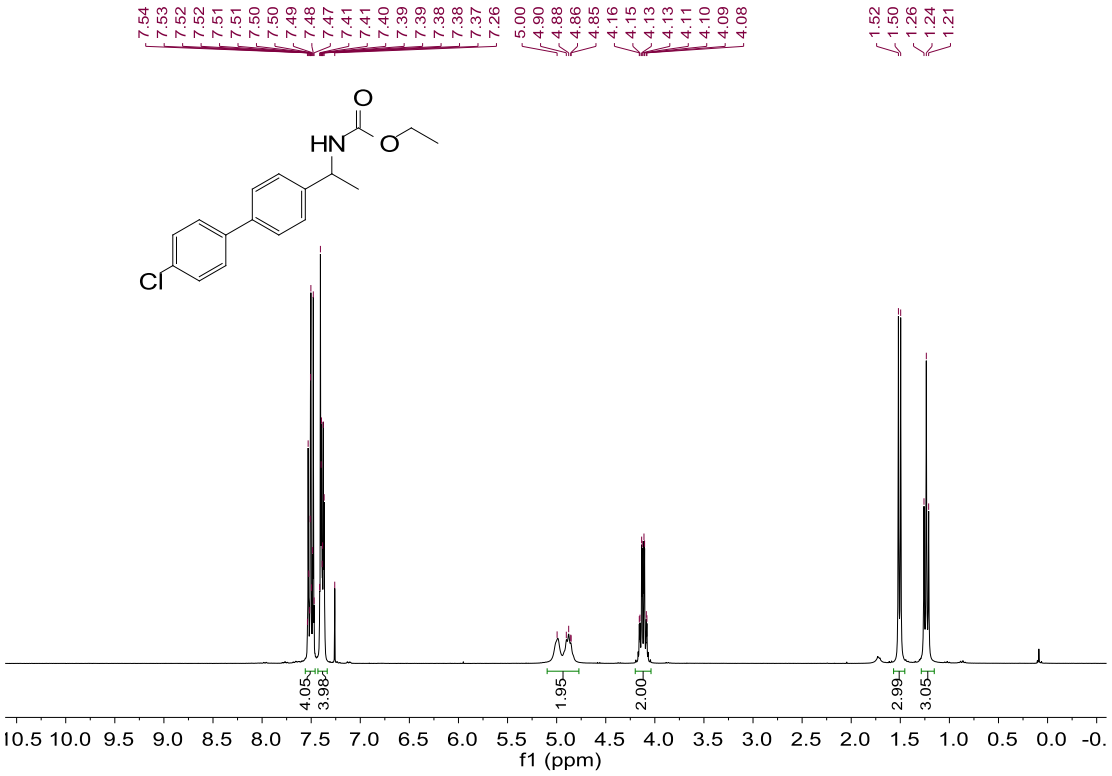


^{13}CNMR

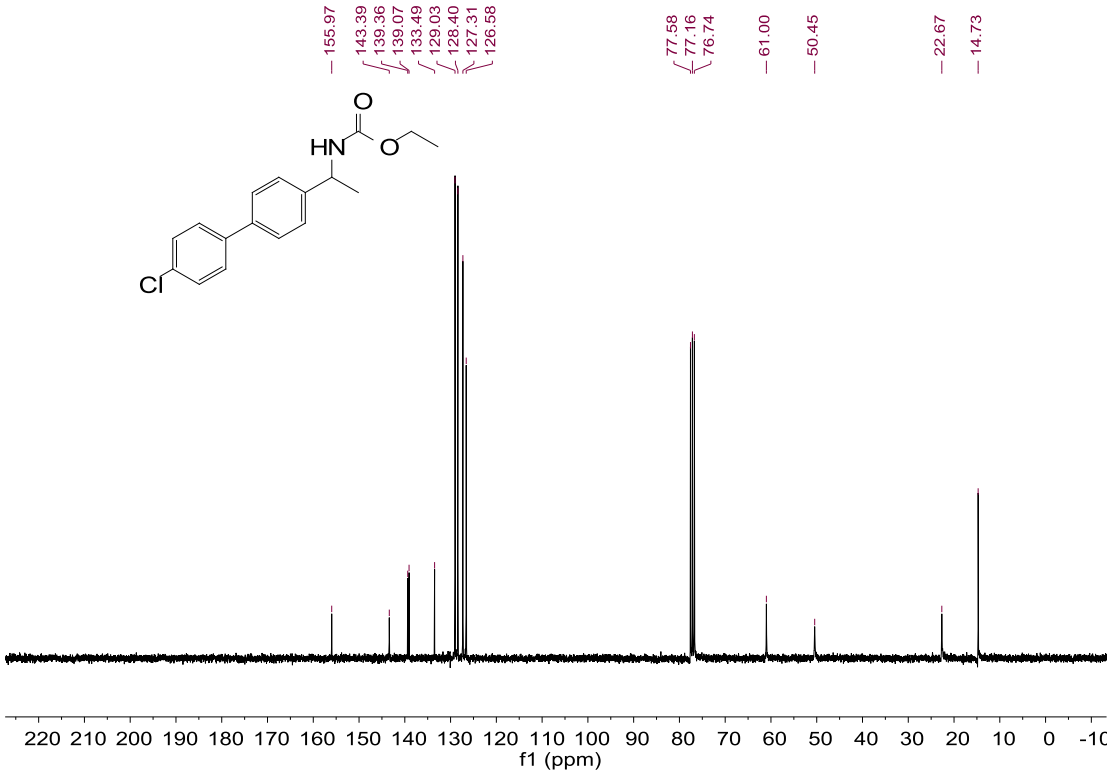


Compound 3s

^{1}HMNR

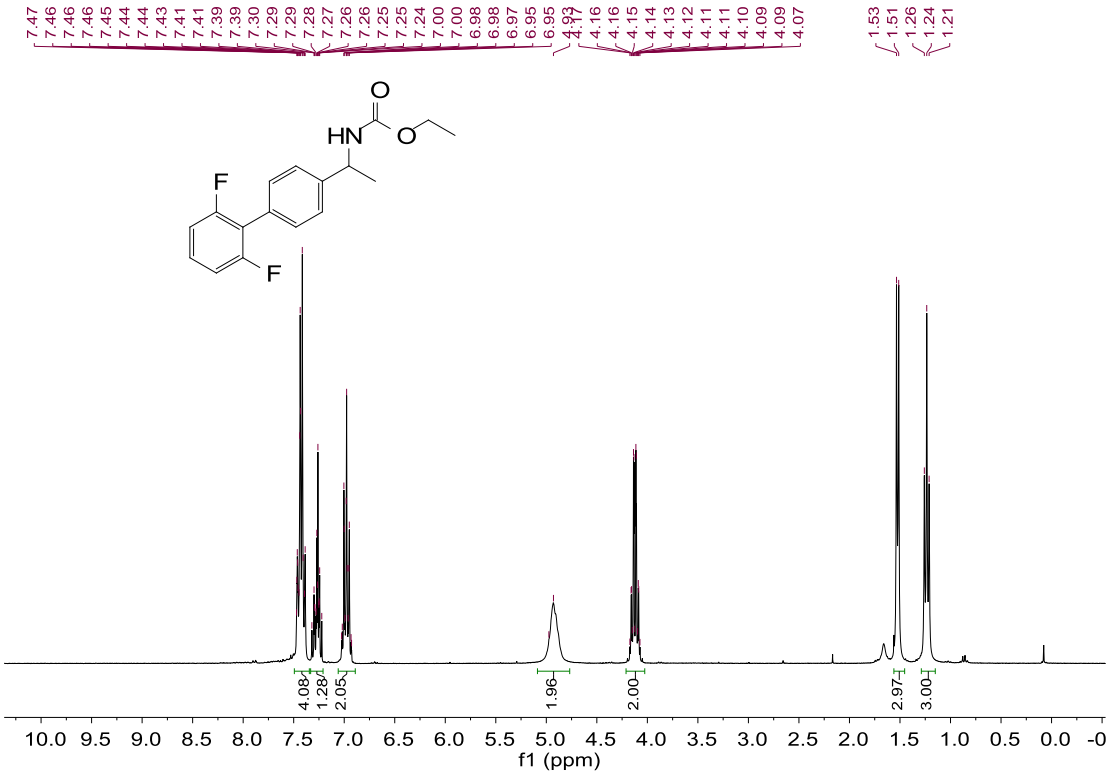


^{13}CNMR



Compound 3t

^{1}HMNR



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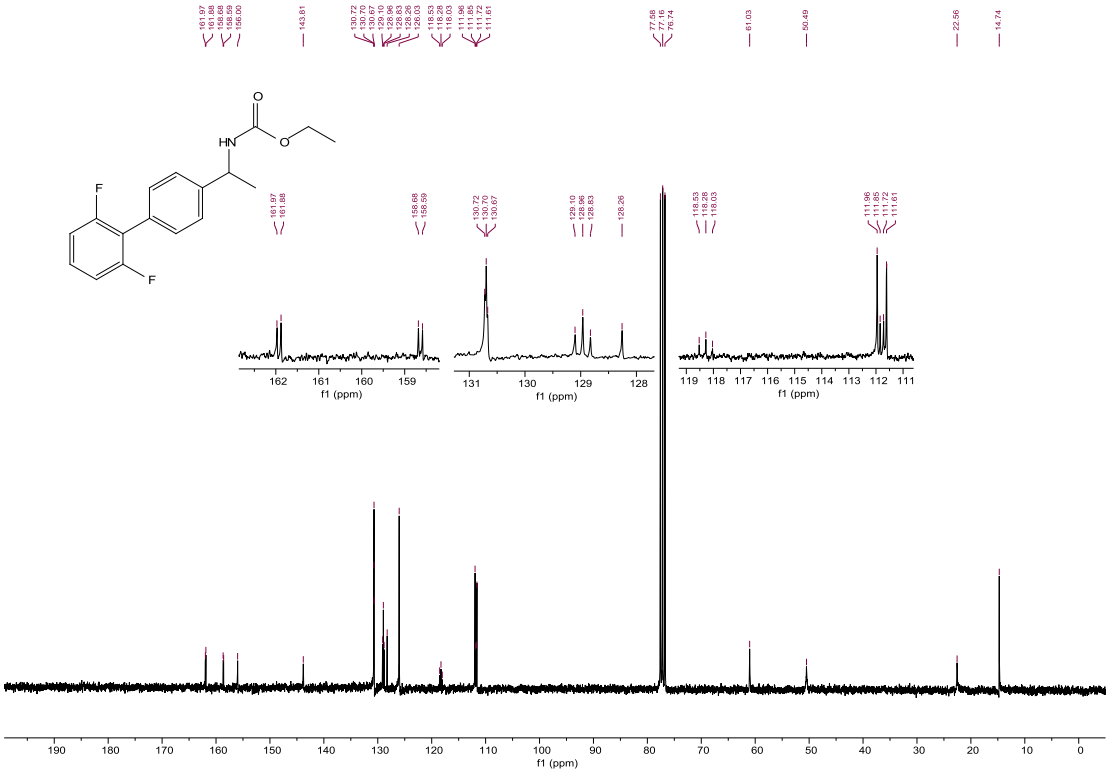
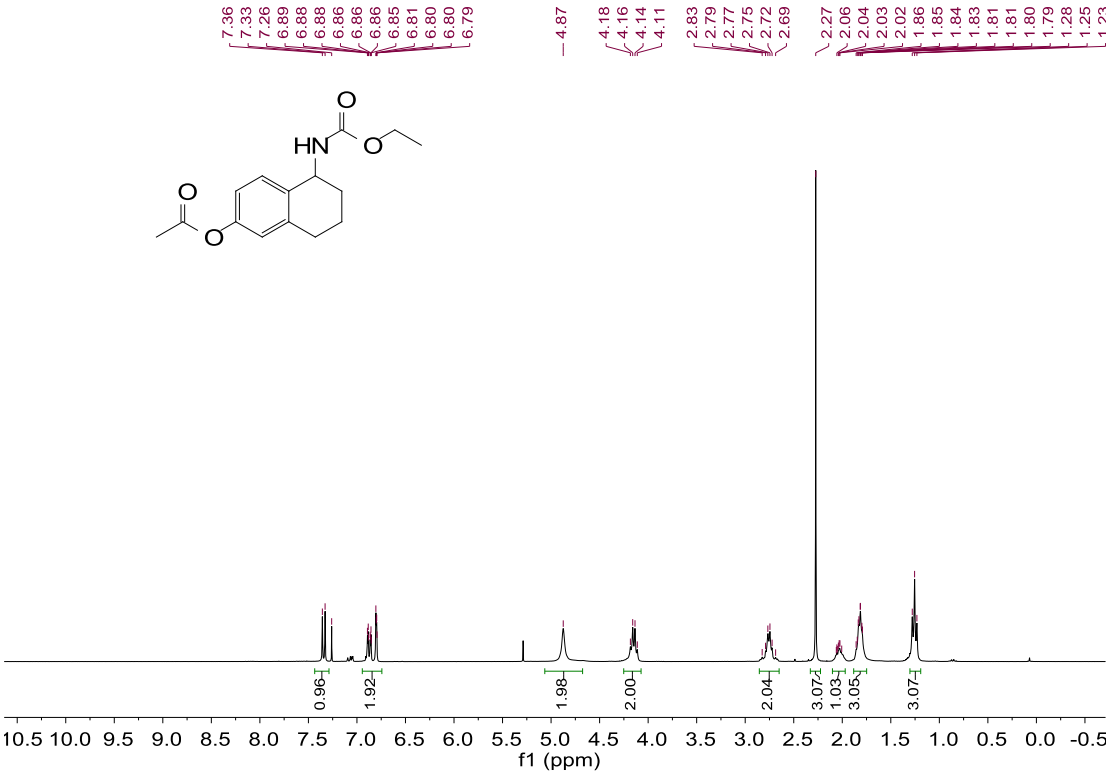
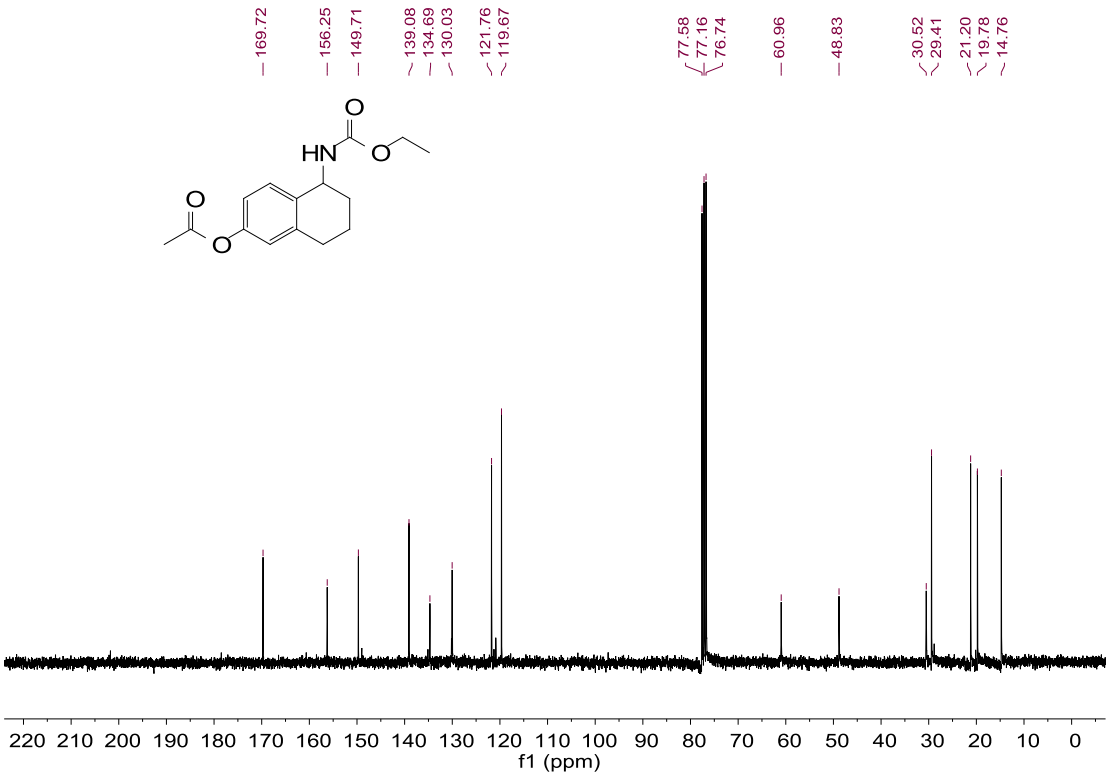


Compound 3u

^{1}HMNR

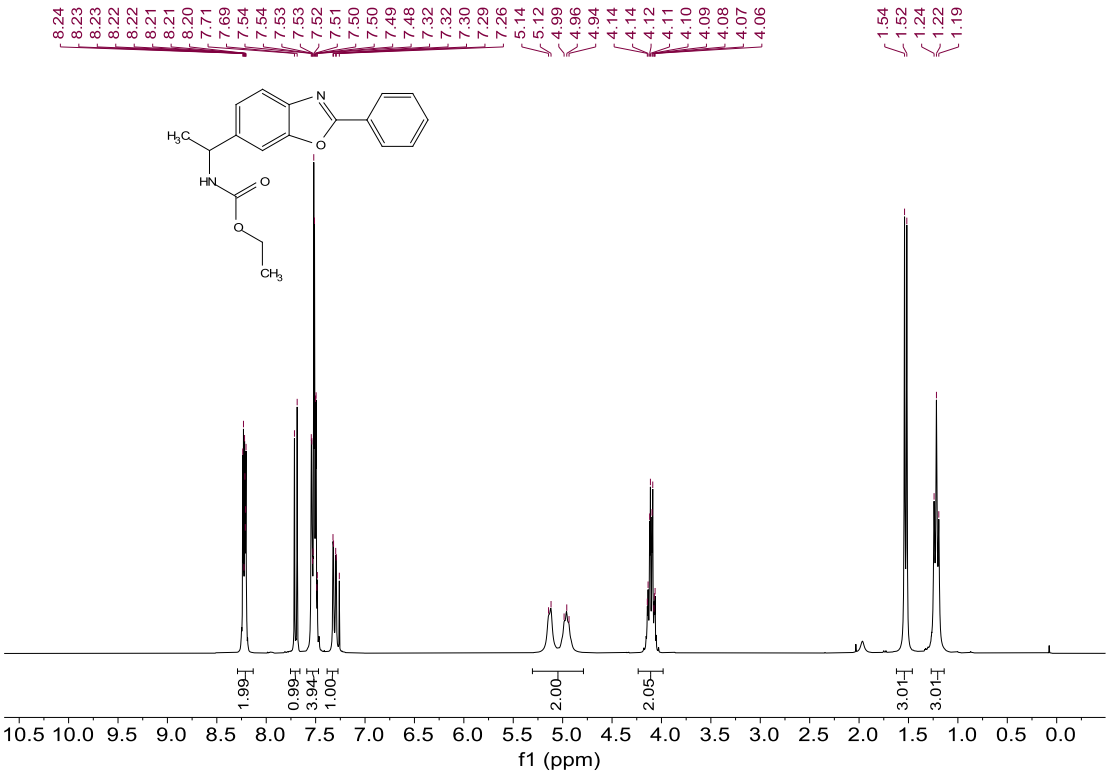


^{13}CNMR

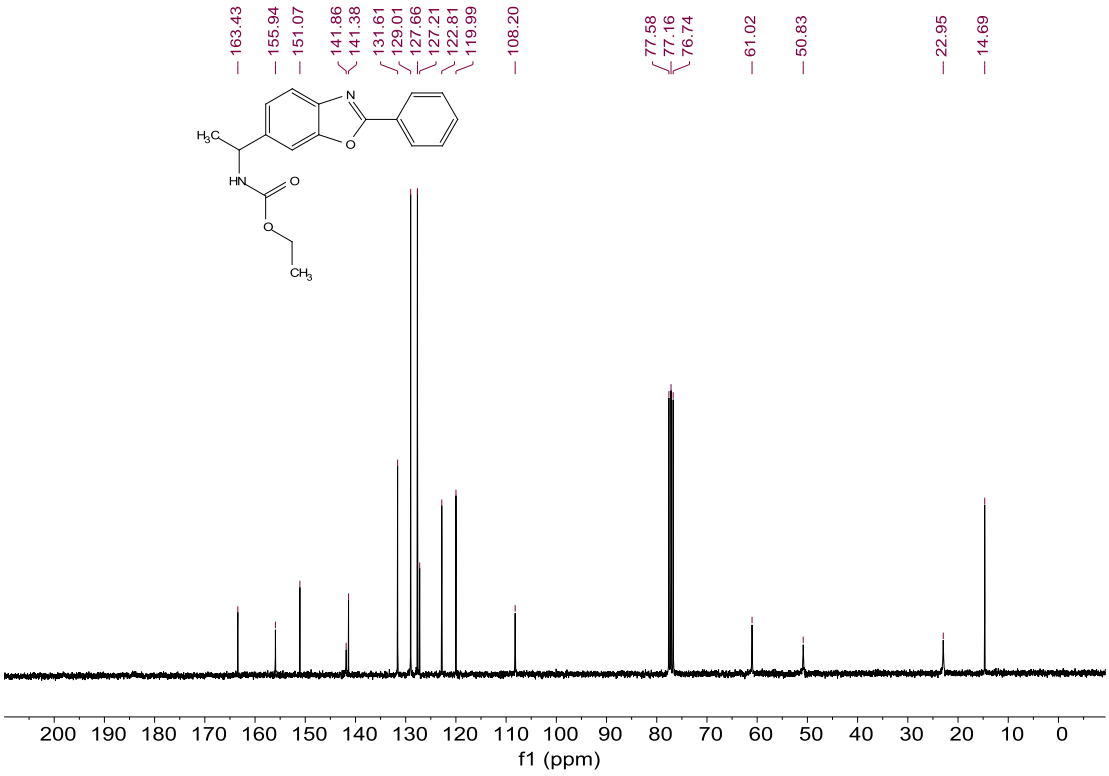


Compound 3v

^{1}HMNR

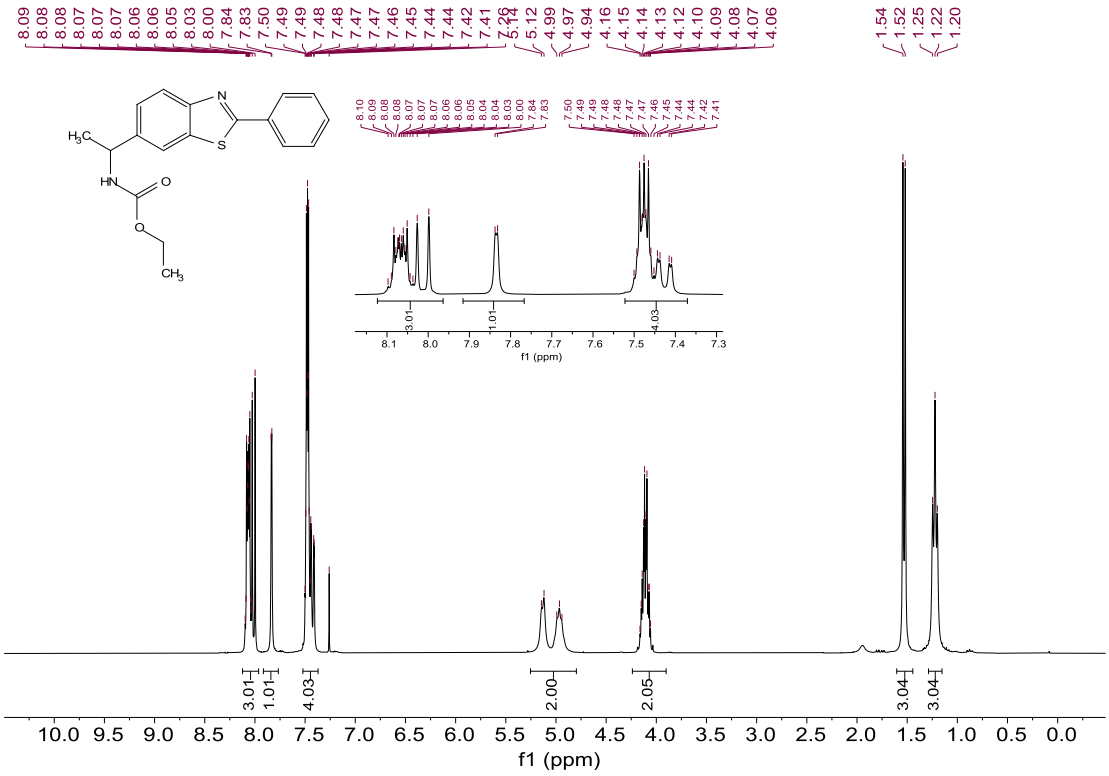


^{13}CNMR

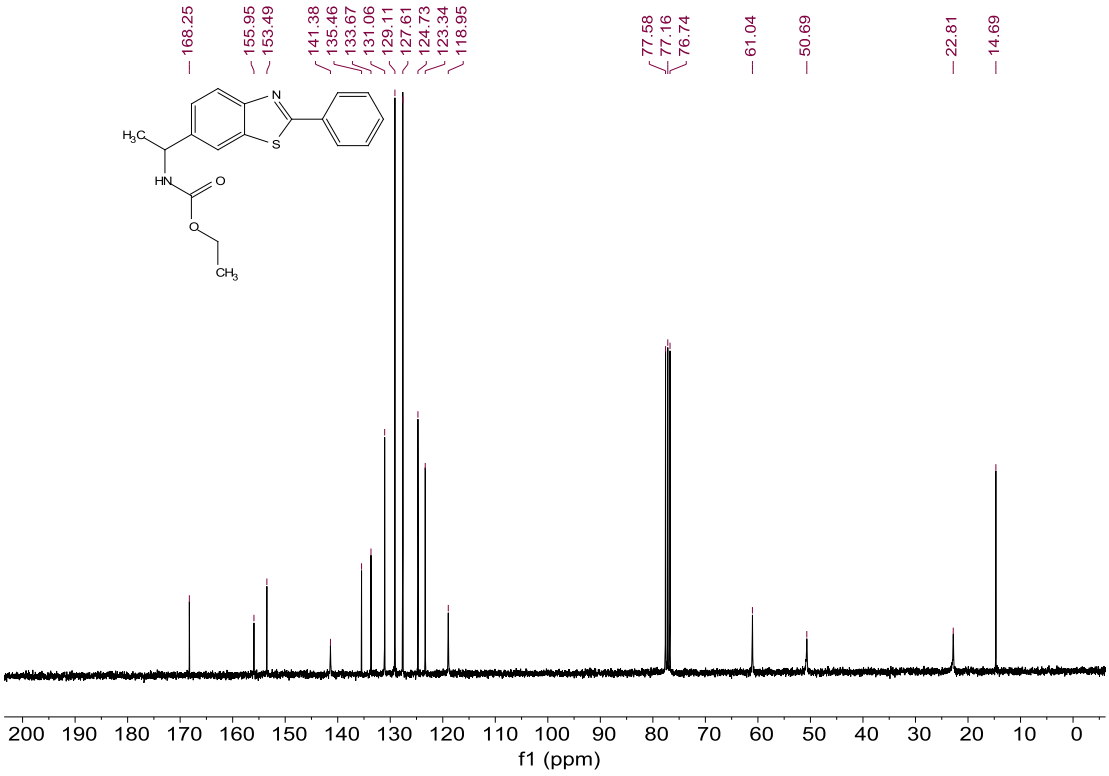


Compound 3w

^{1}HMNR

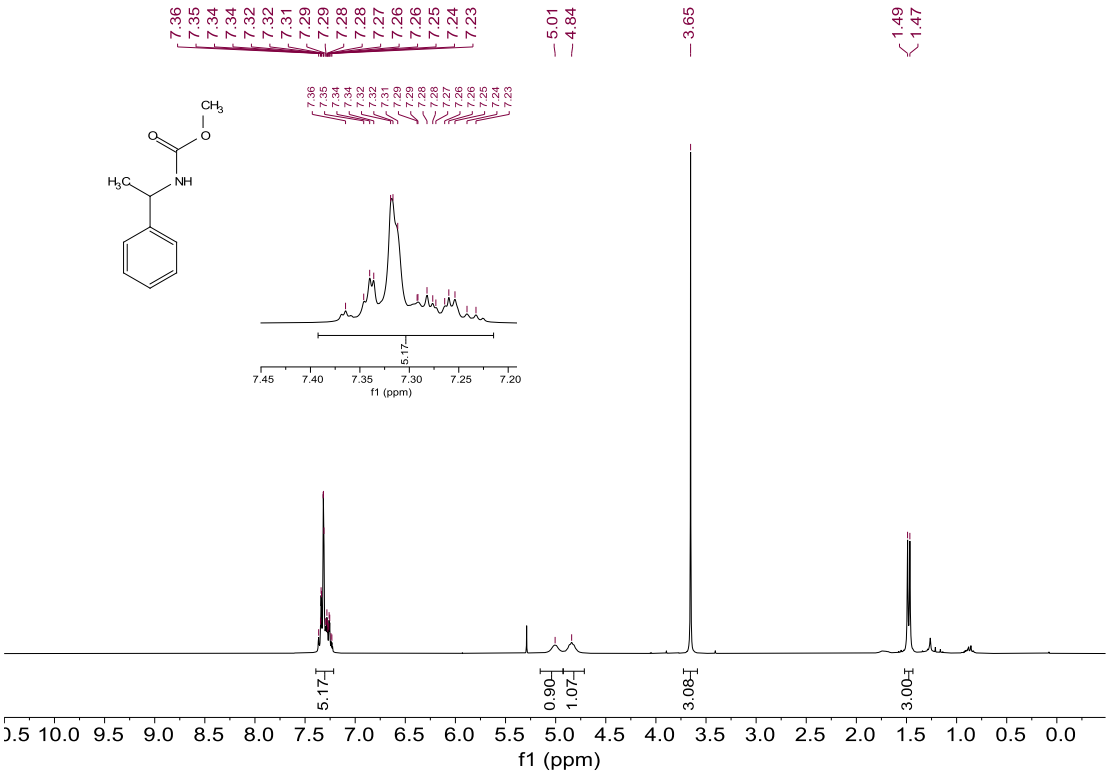


^{13}CNMR

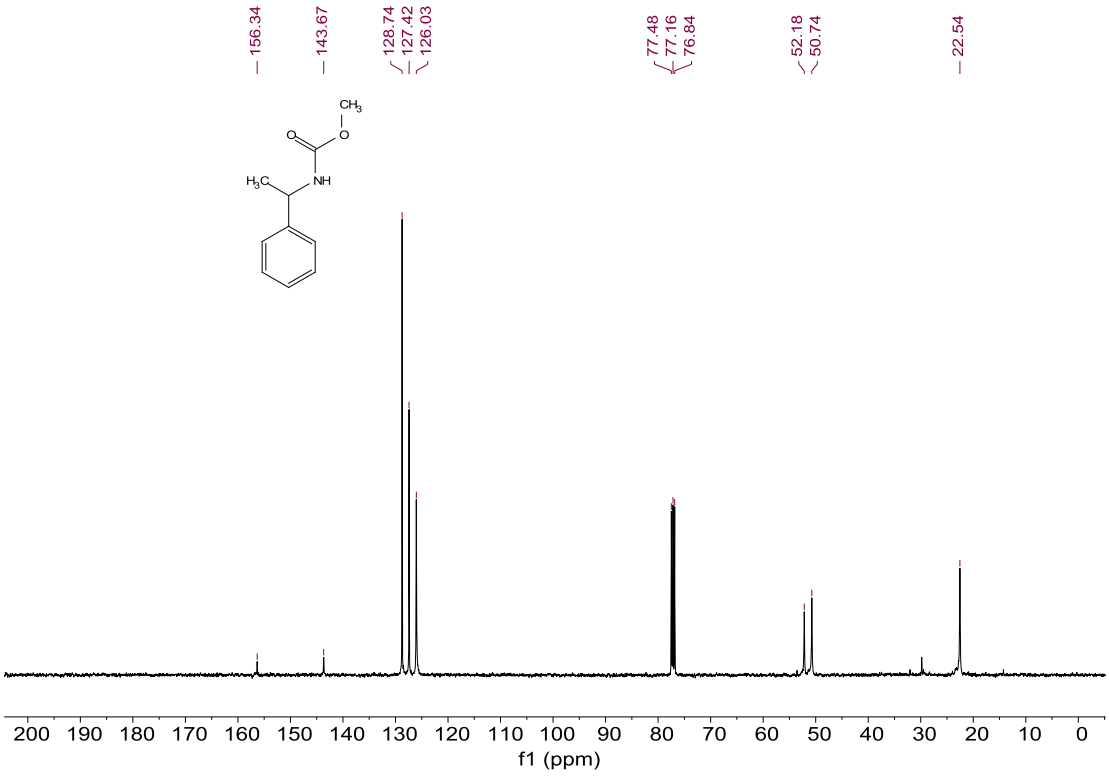


Compound 4a

^{1}HMNR

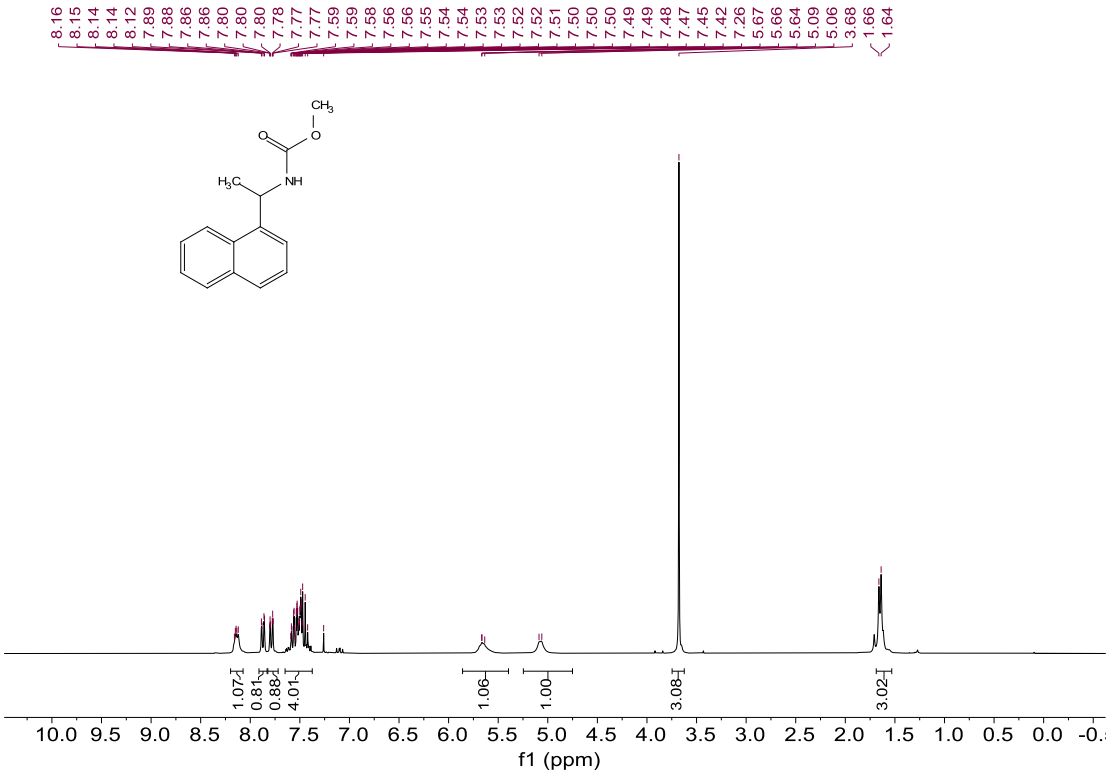


^{13}CNMR

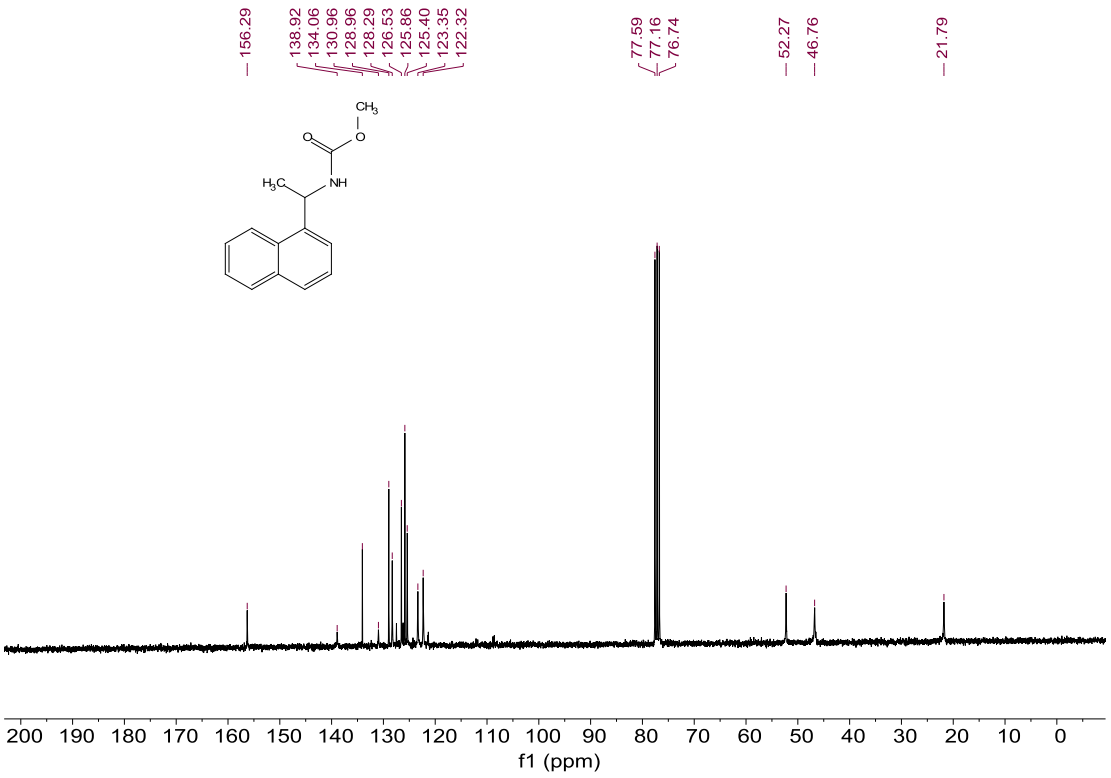


Compound 4b

^{1}HMNR

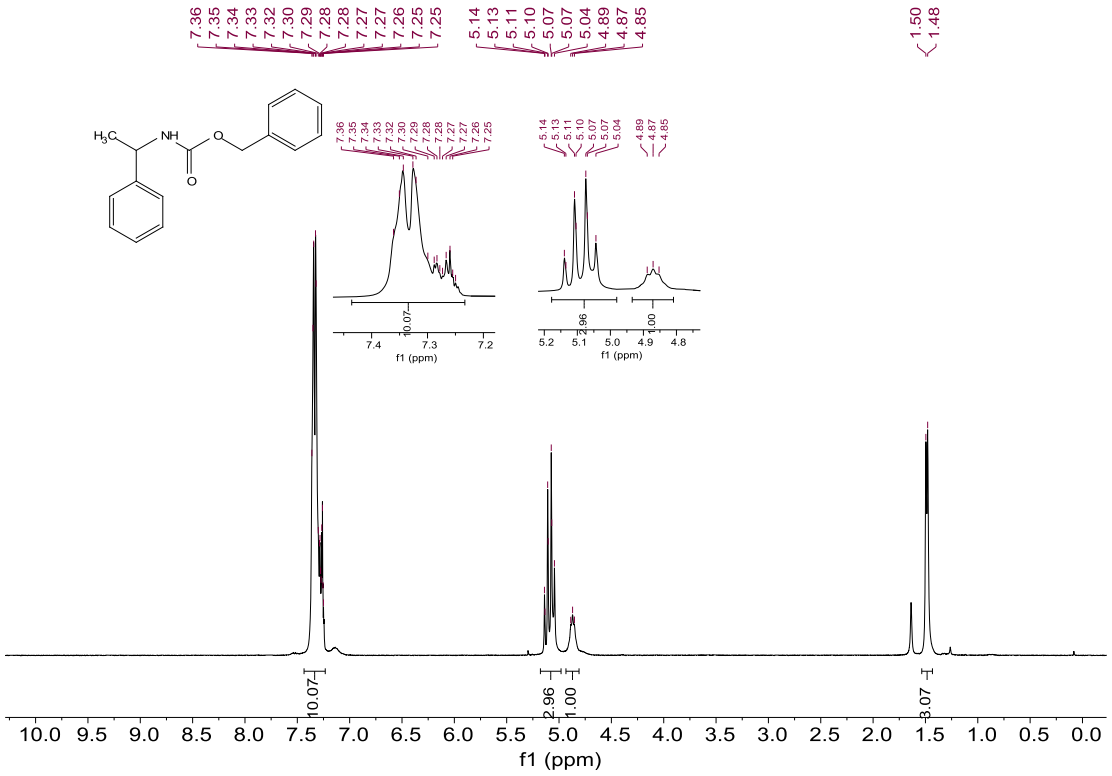


^{13}CNMR



Compound 4c

^{1}HMNR



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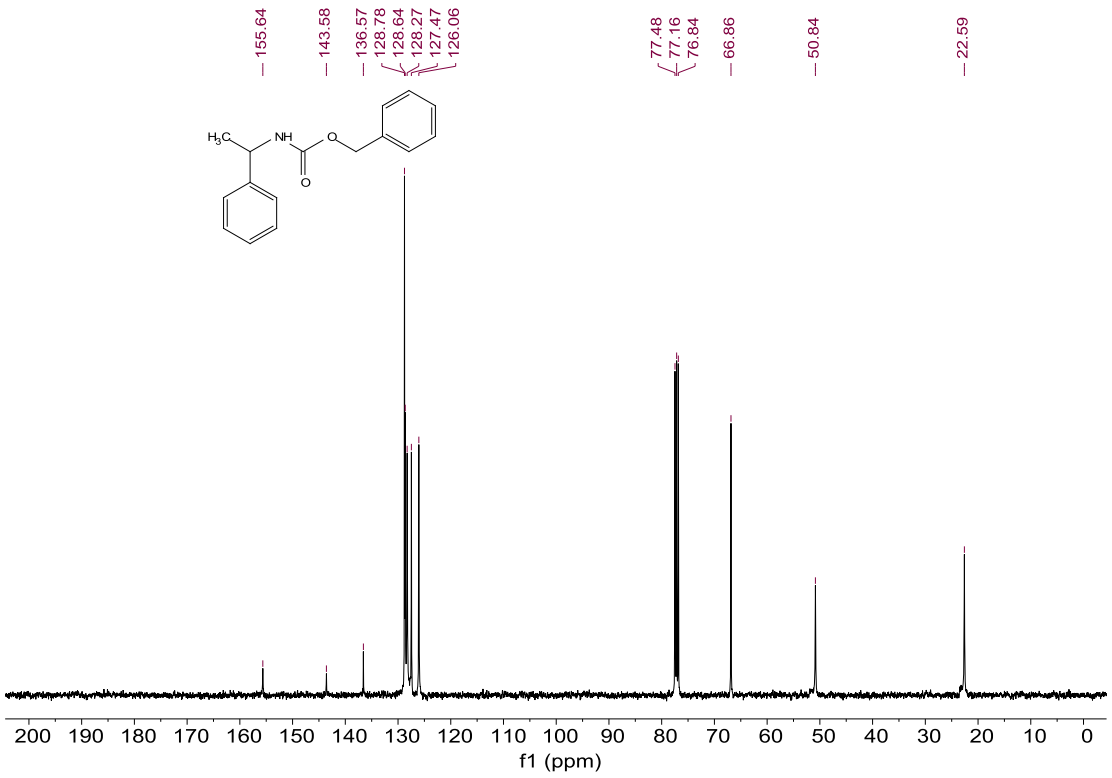
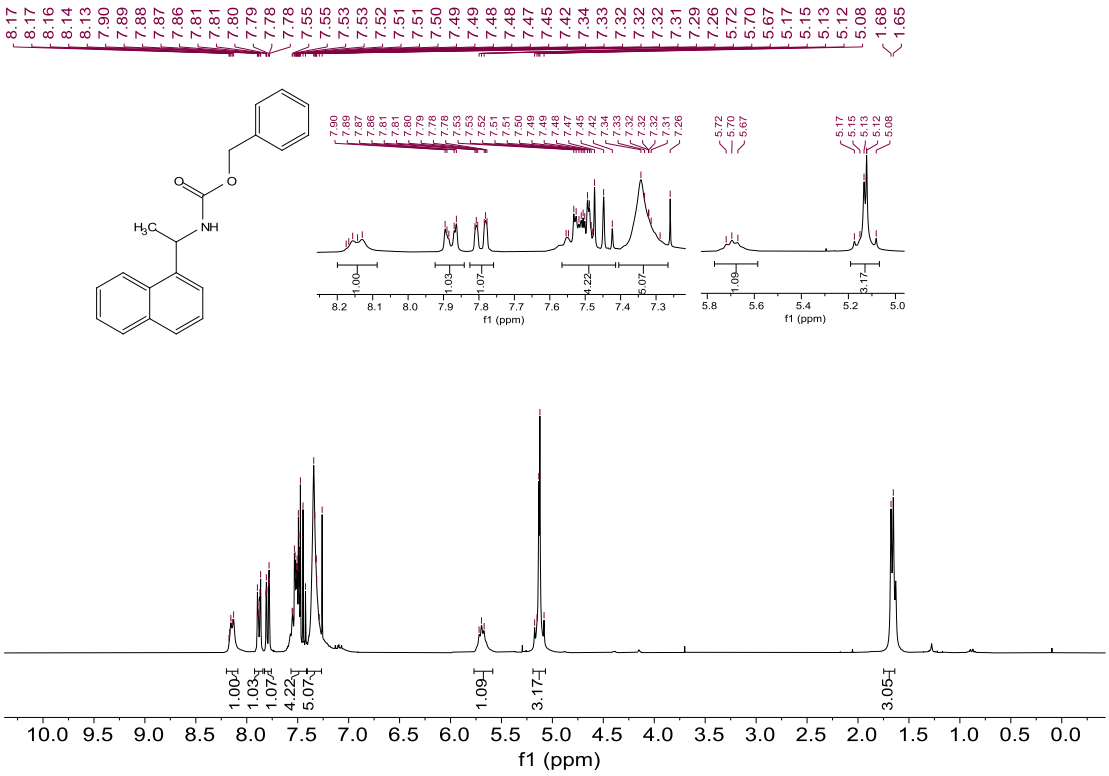
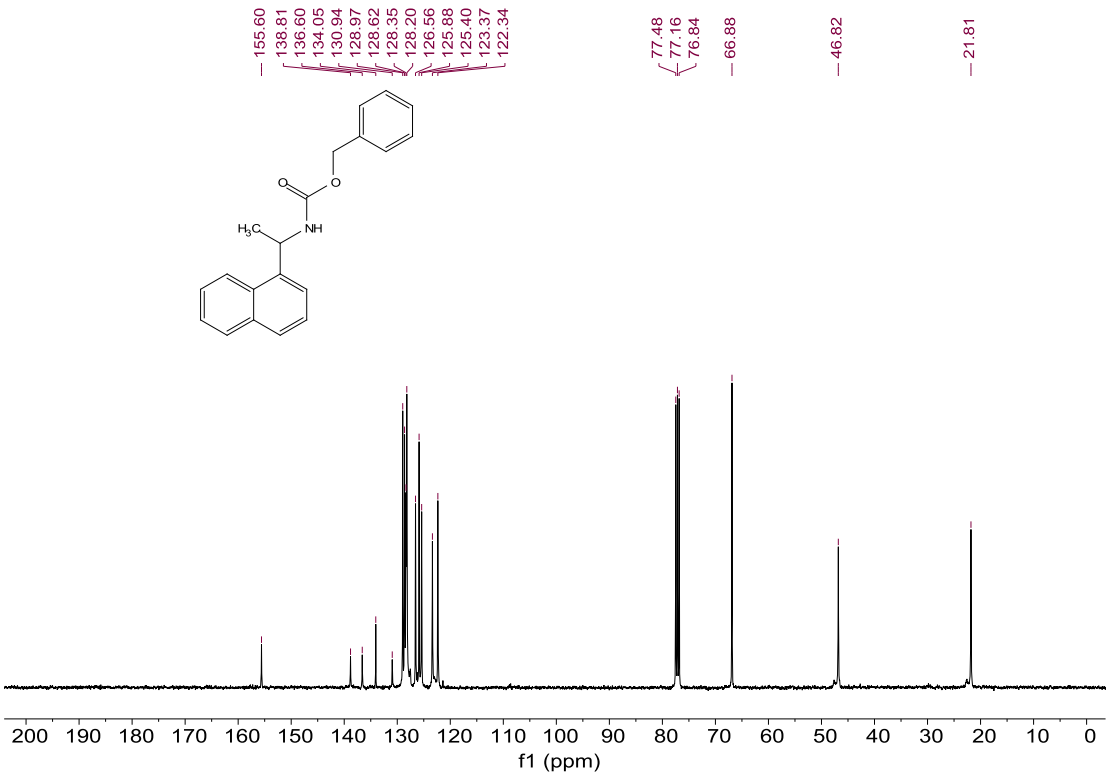


Compound 4d

^{1}HMNR

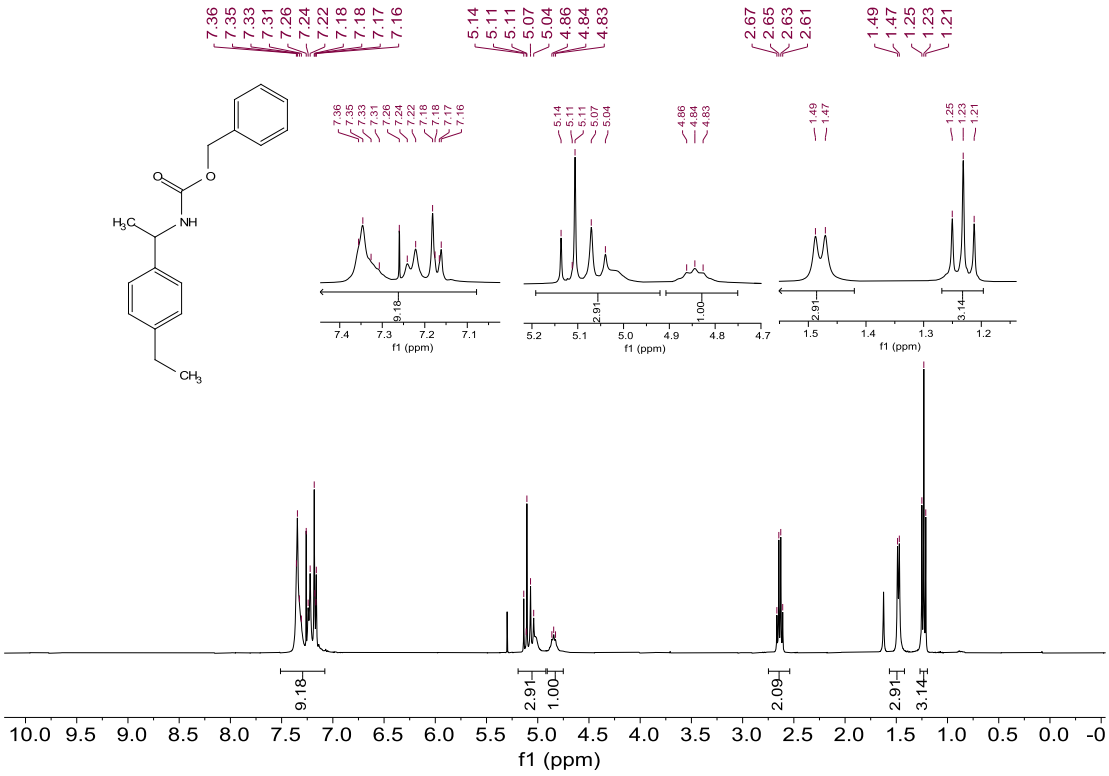


^{13}CNMR

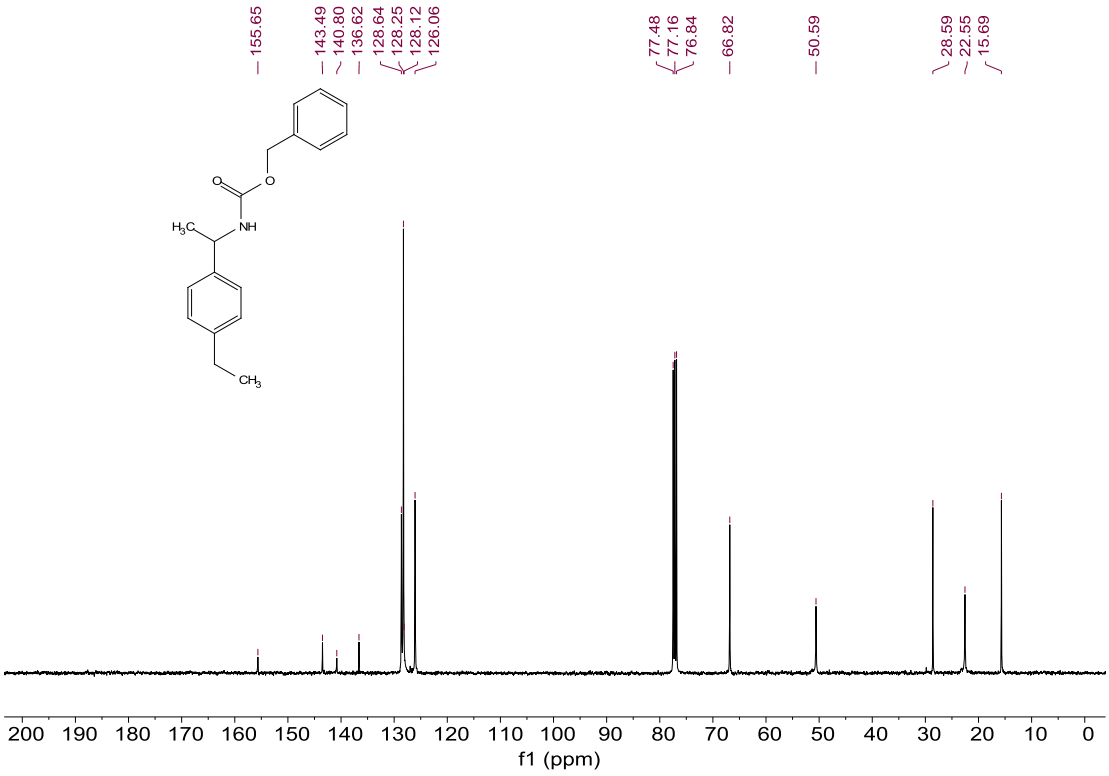


Compound 4e

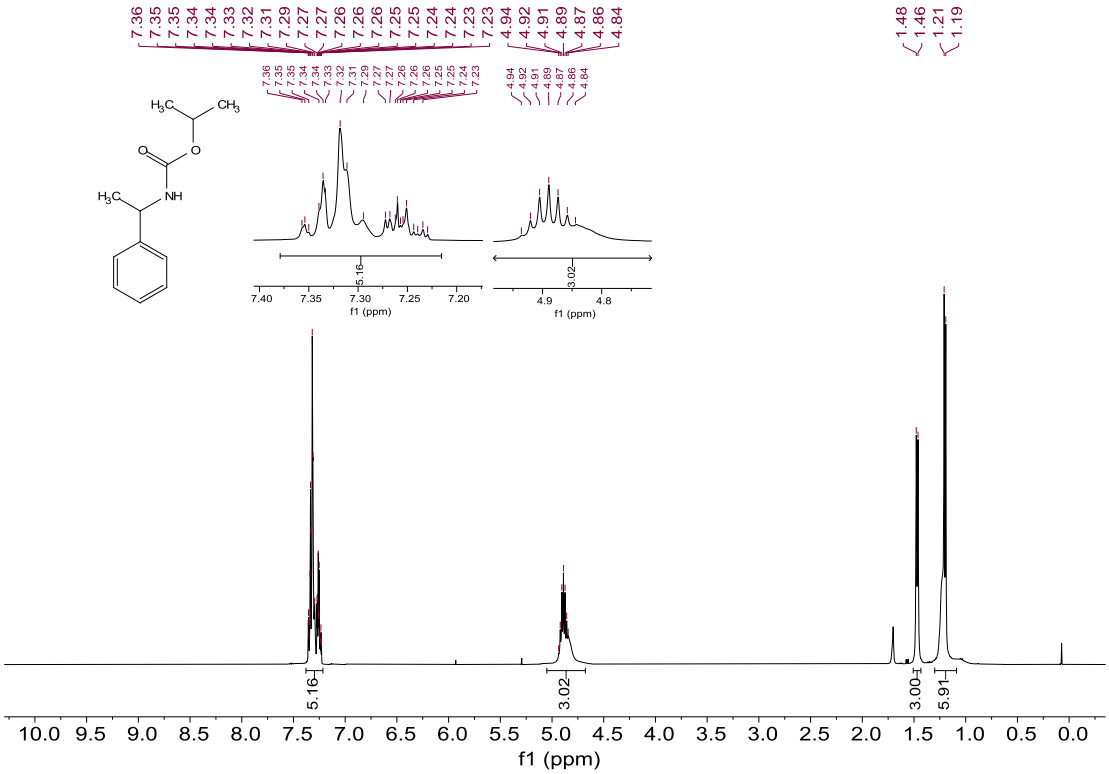
^{1}HMNR



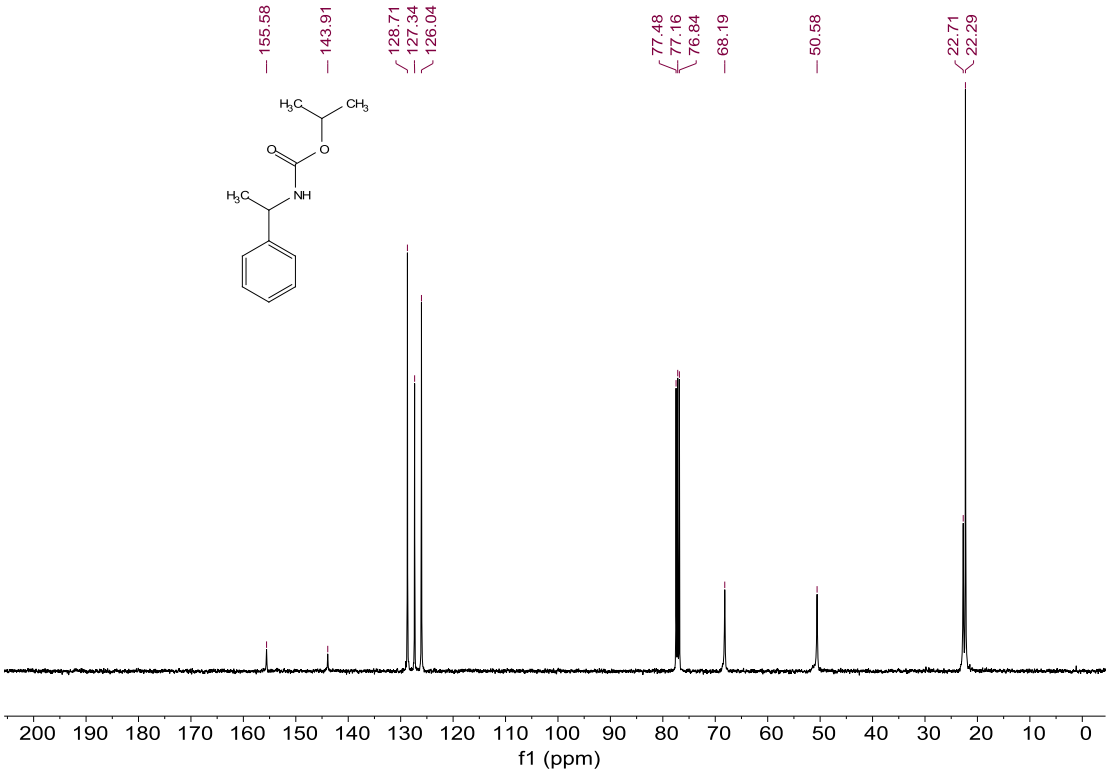
^{13}CNMR



Compound 4f

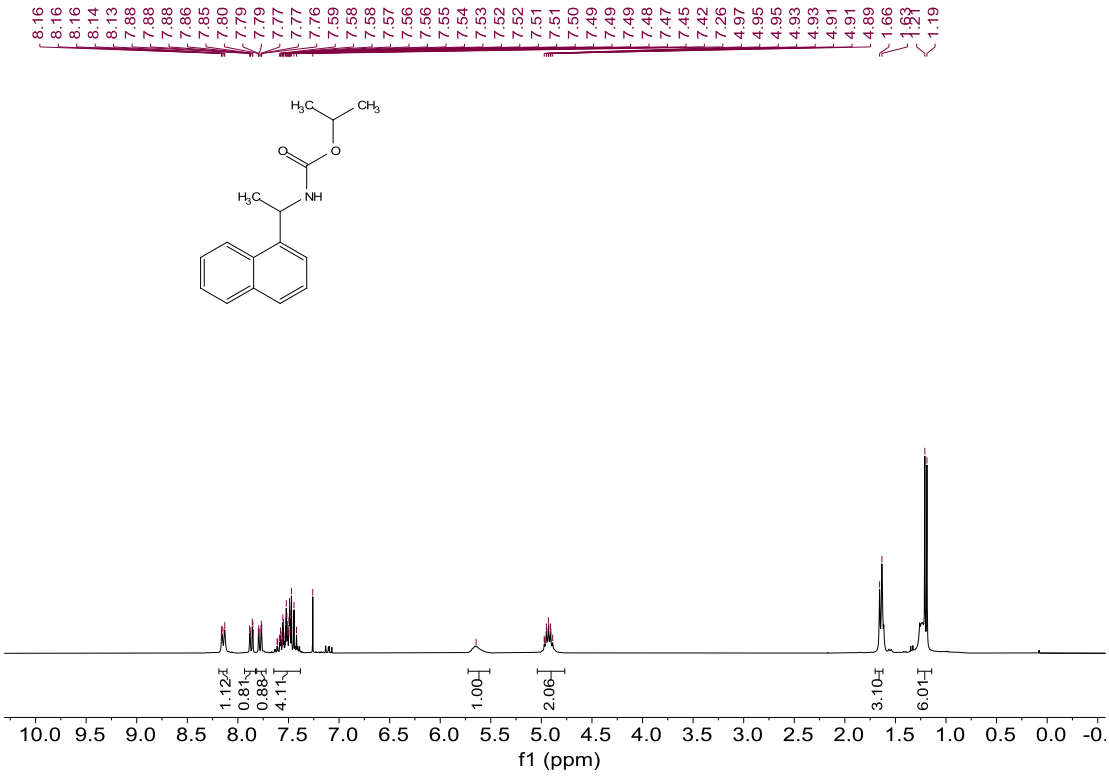


^{13}CNMR

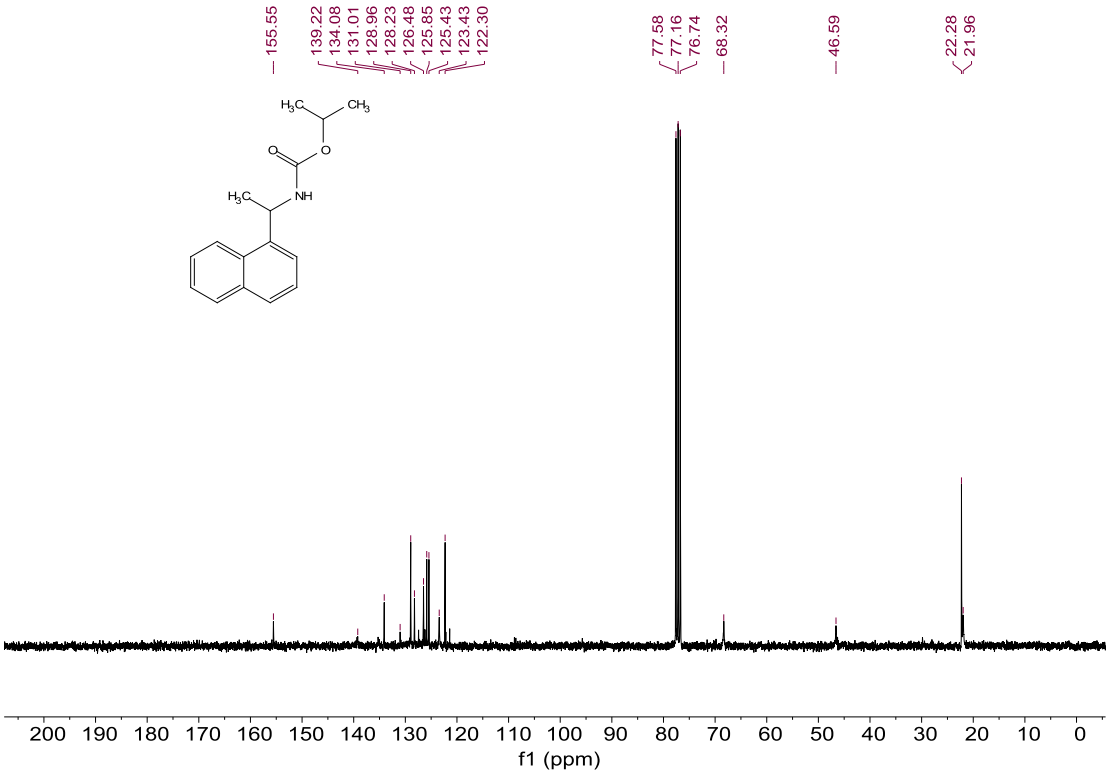


Compound 4g

^{1}HMNR

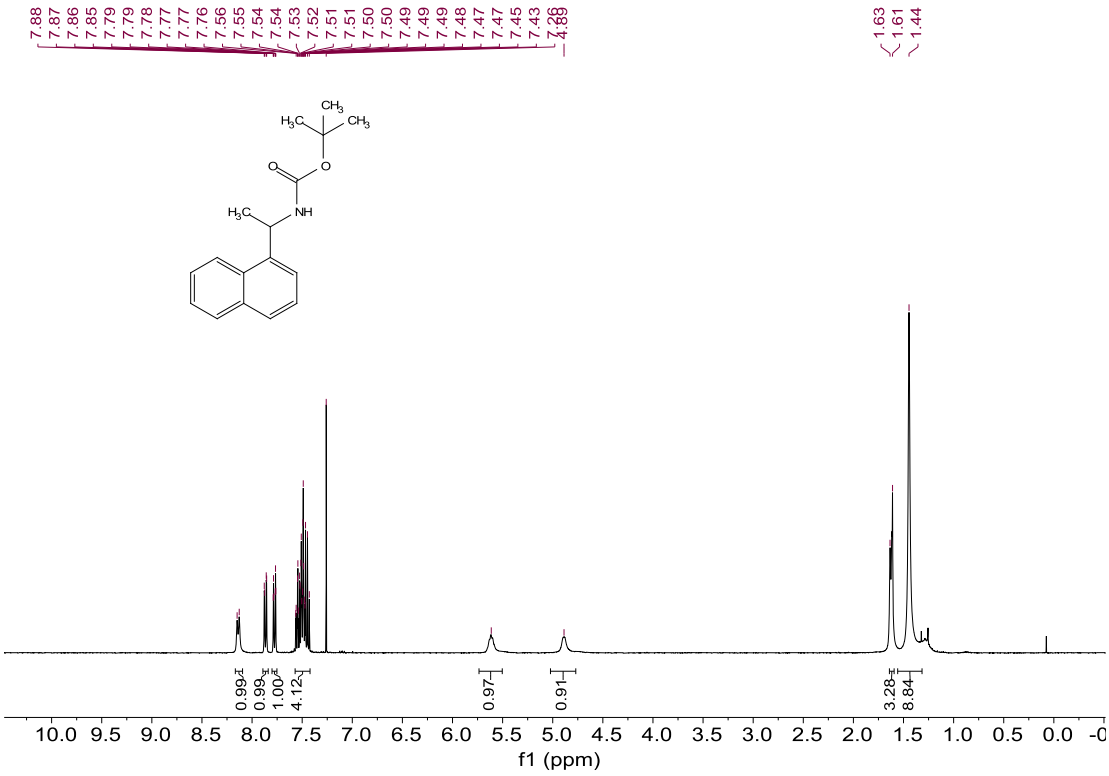


^{13}CNMR

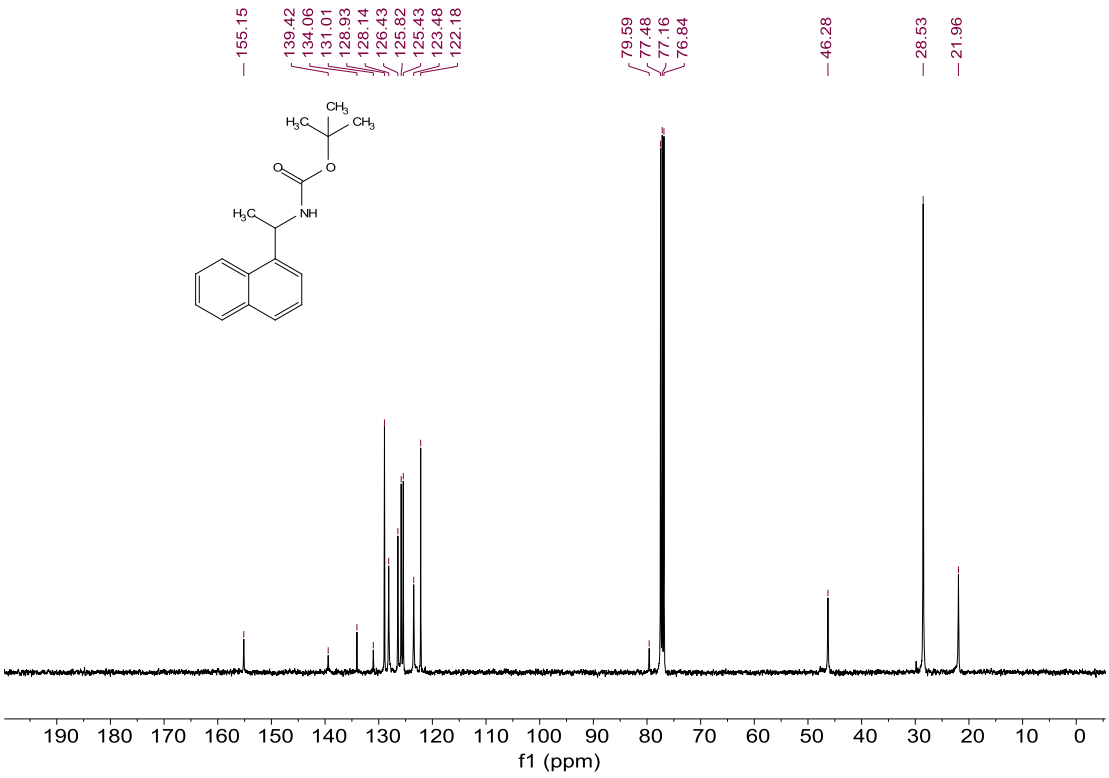


Compound 4h

^{1}HMNR

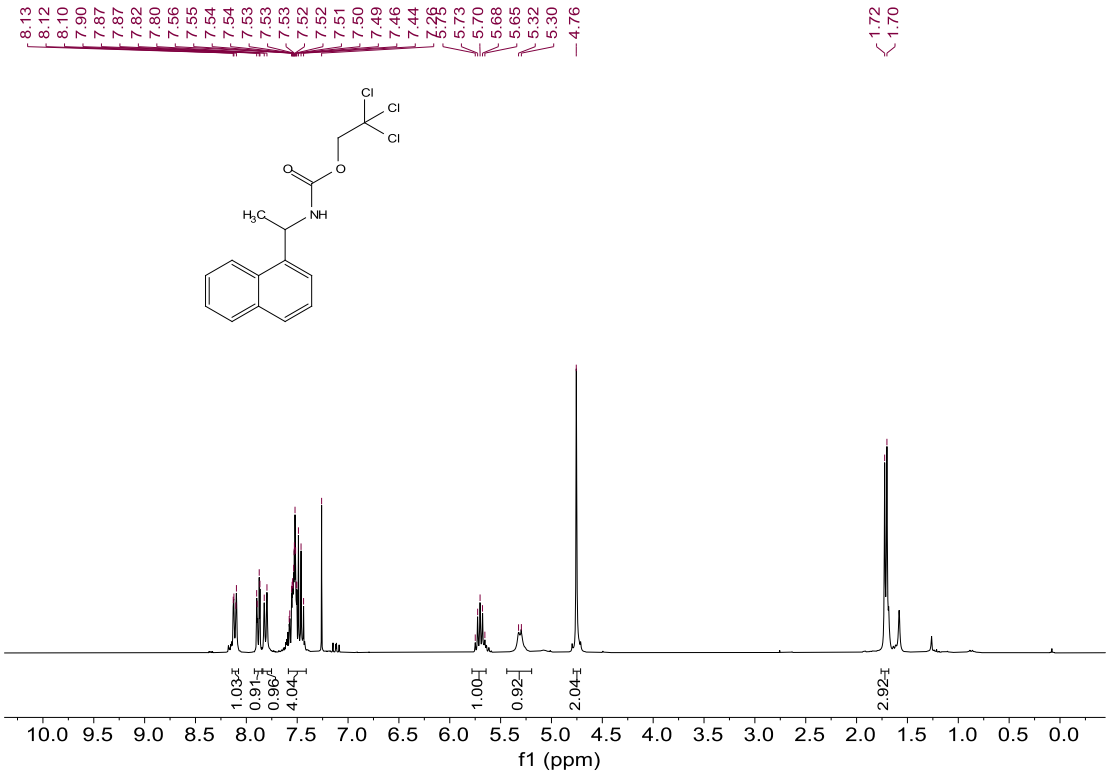


^{13}CNMR

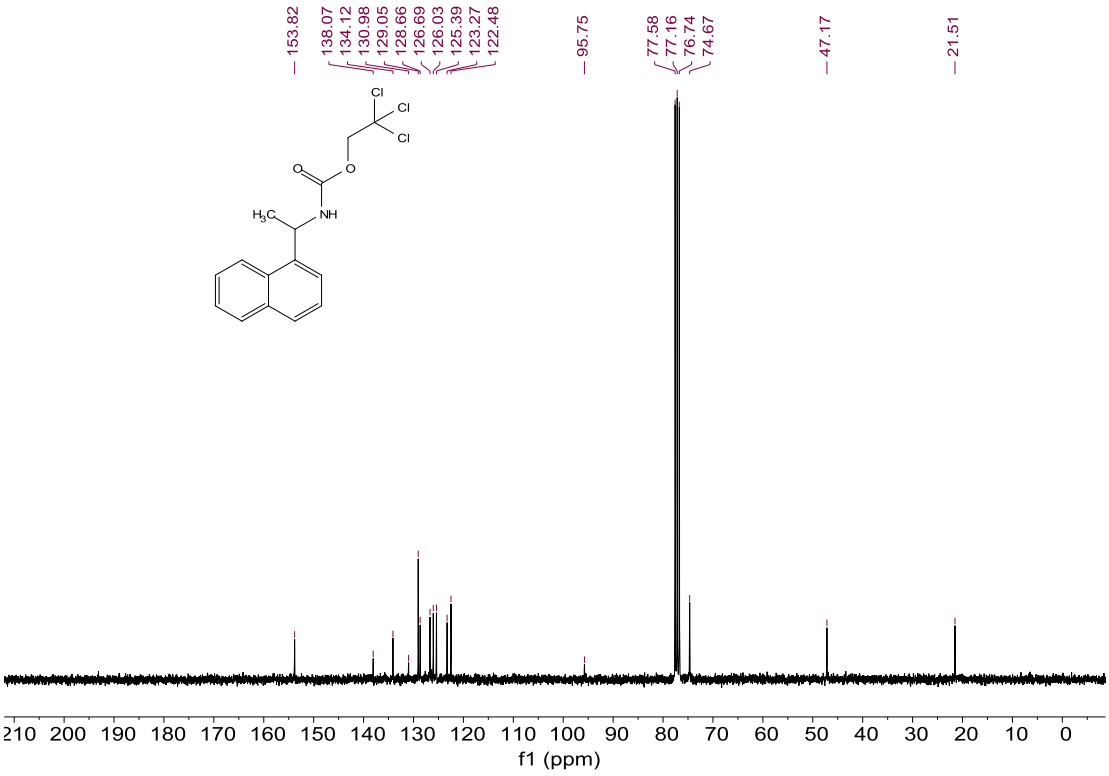


Compound 4i

^{1}HMNR

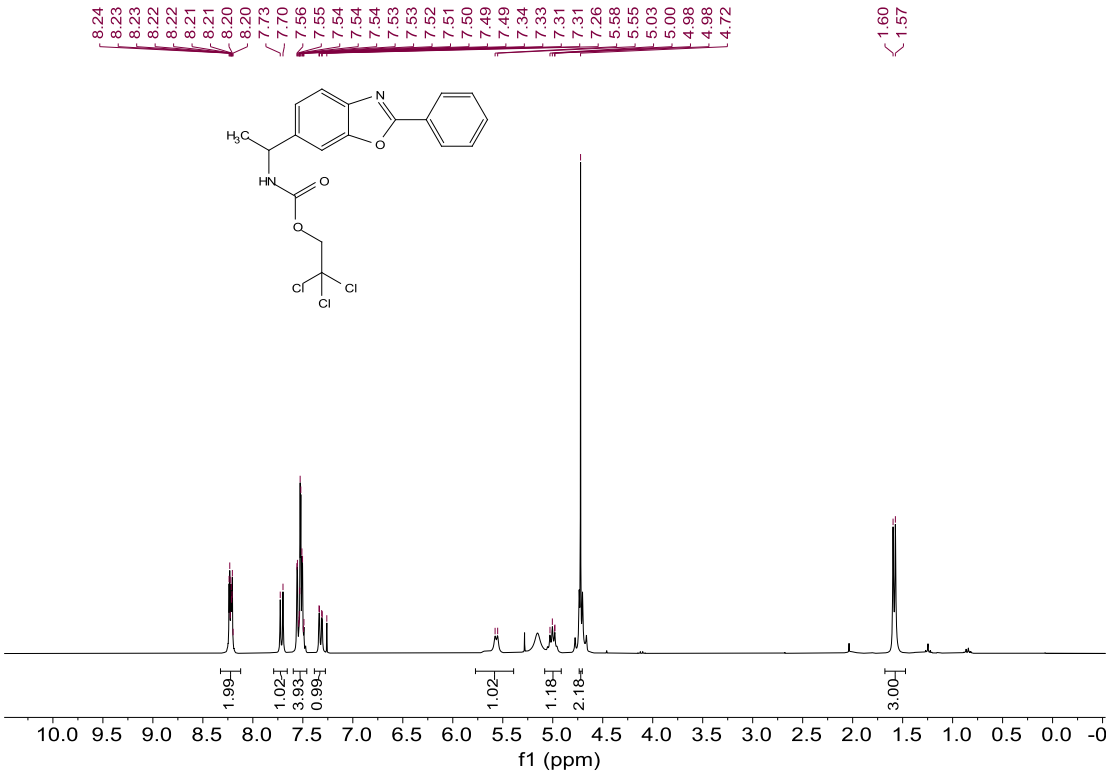


^{13}CNMR

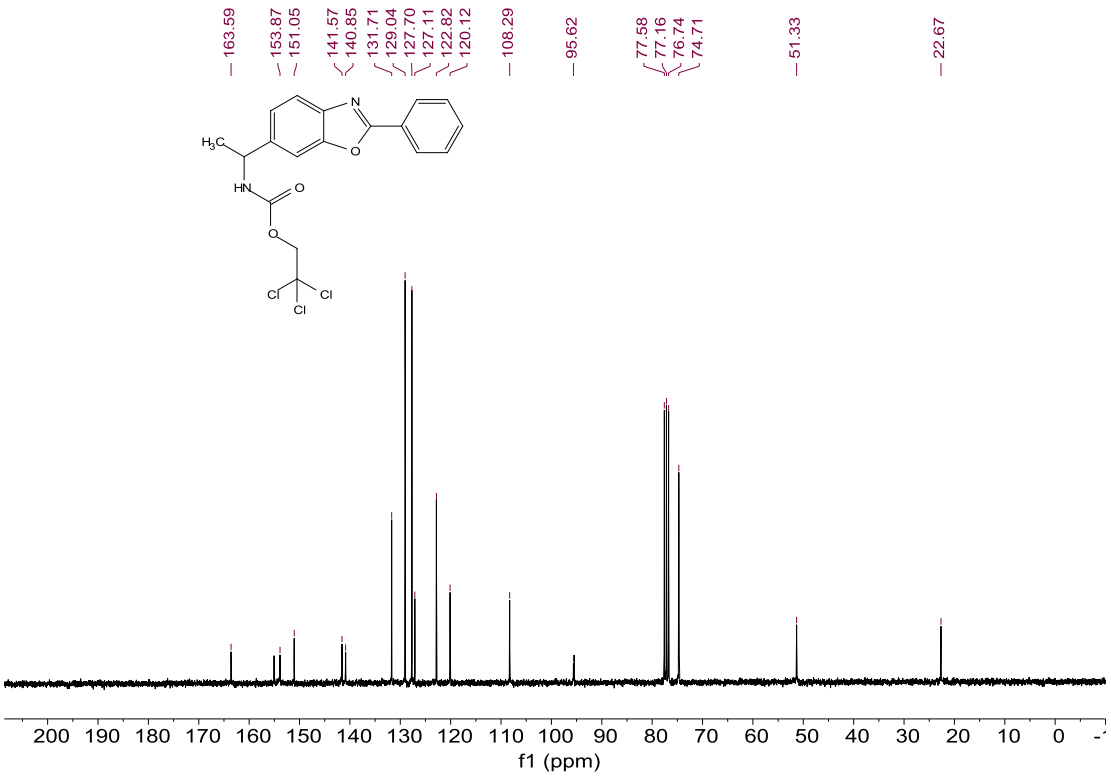


Compound 4j

^{1}HMNR

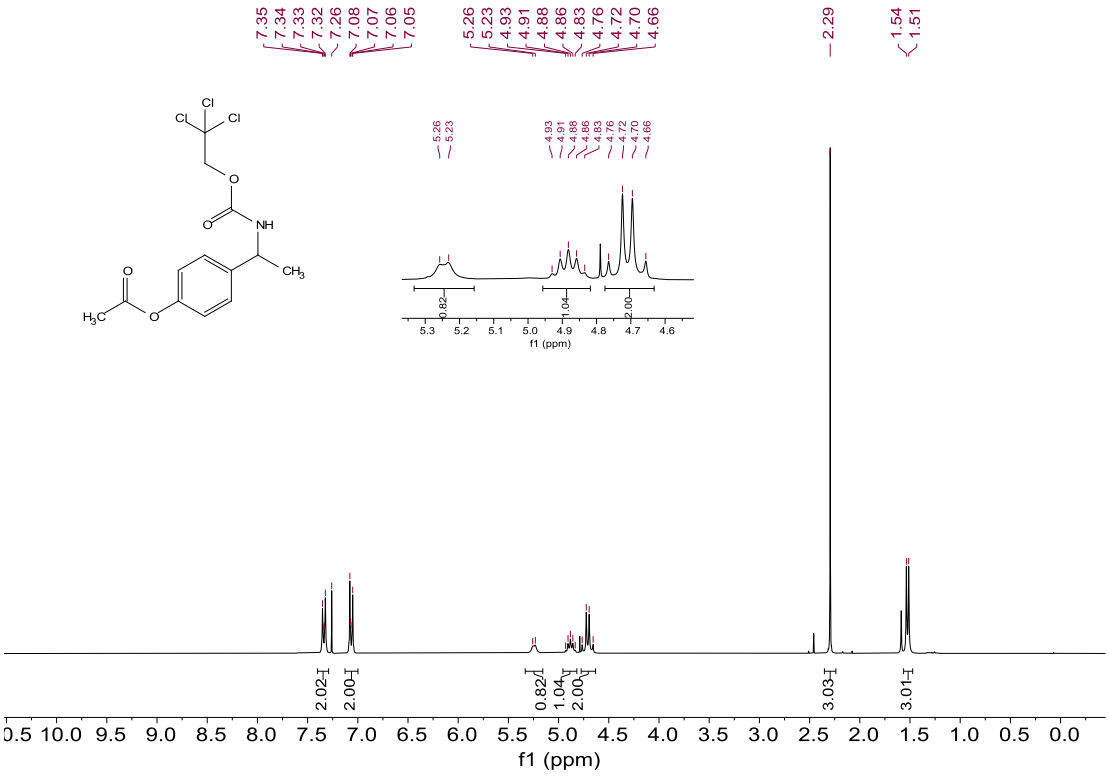


^{13}CNMR

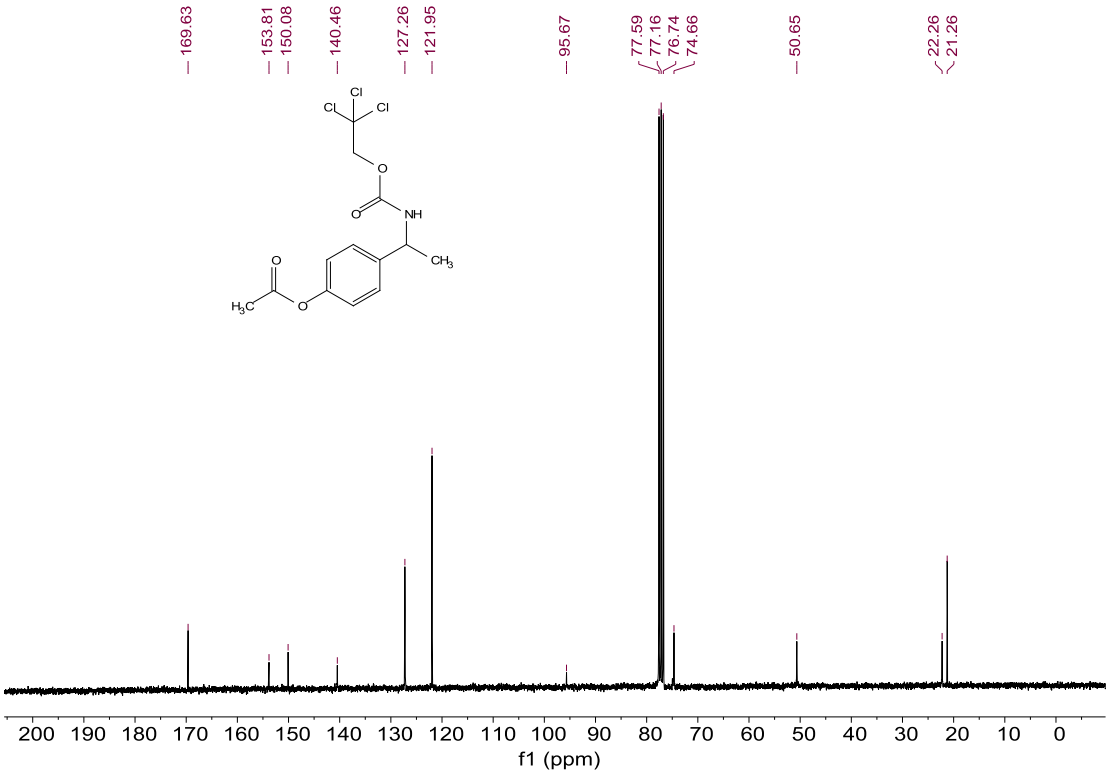


Compound 4k

^{1}HMNR

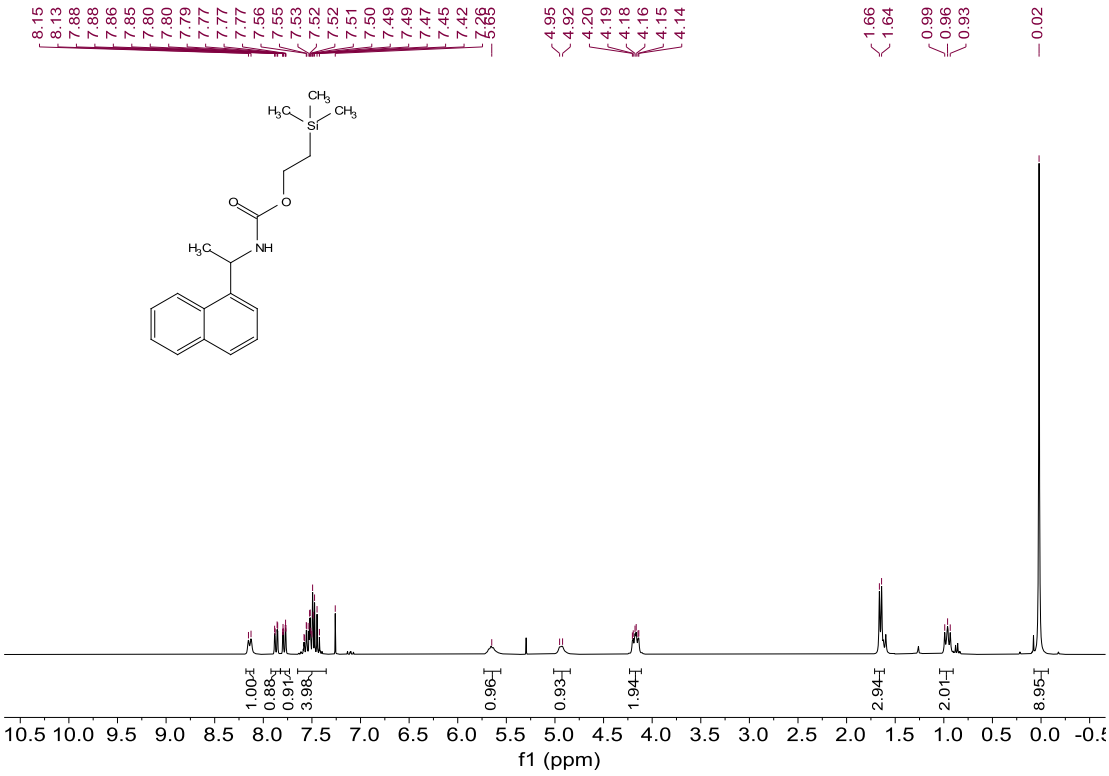


^{13}CNMR

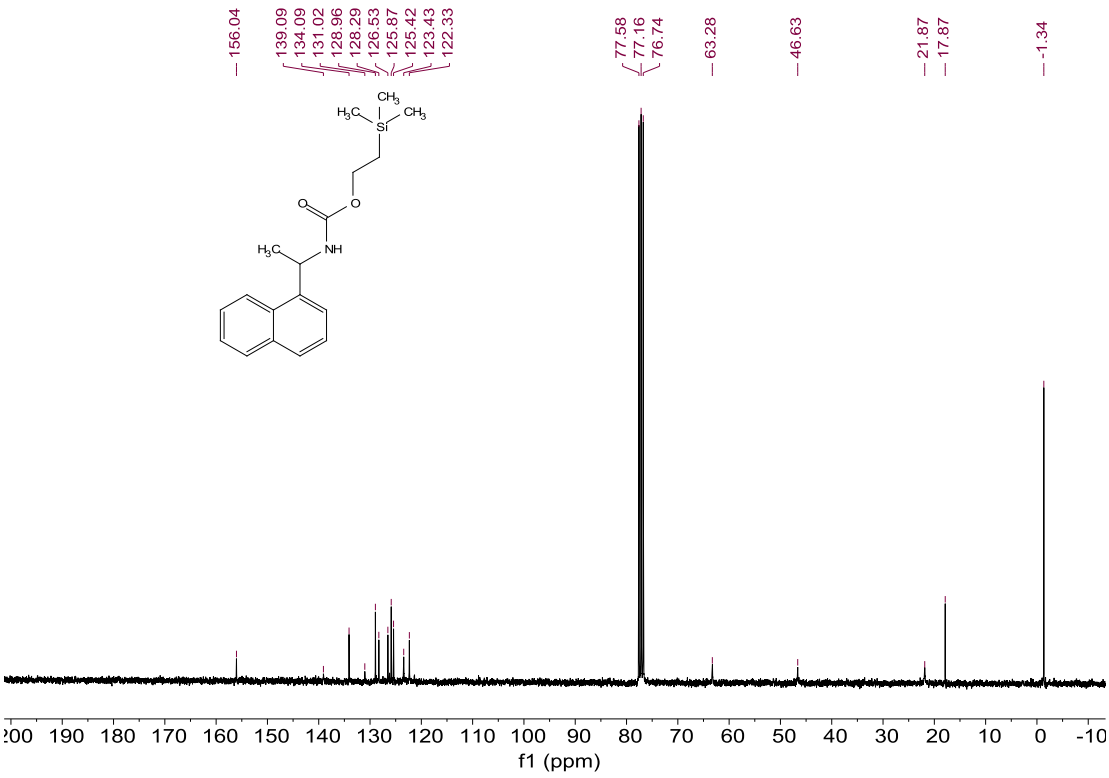


Compound 4l

^{1}HMNR

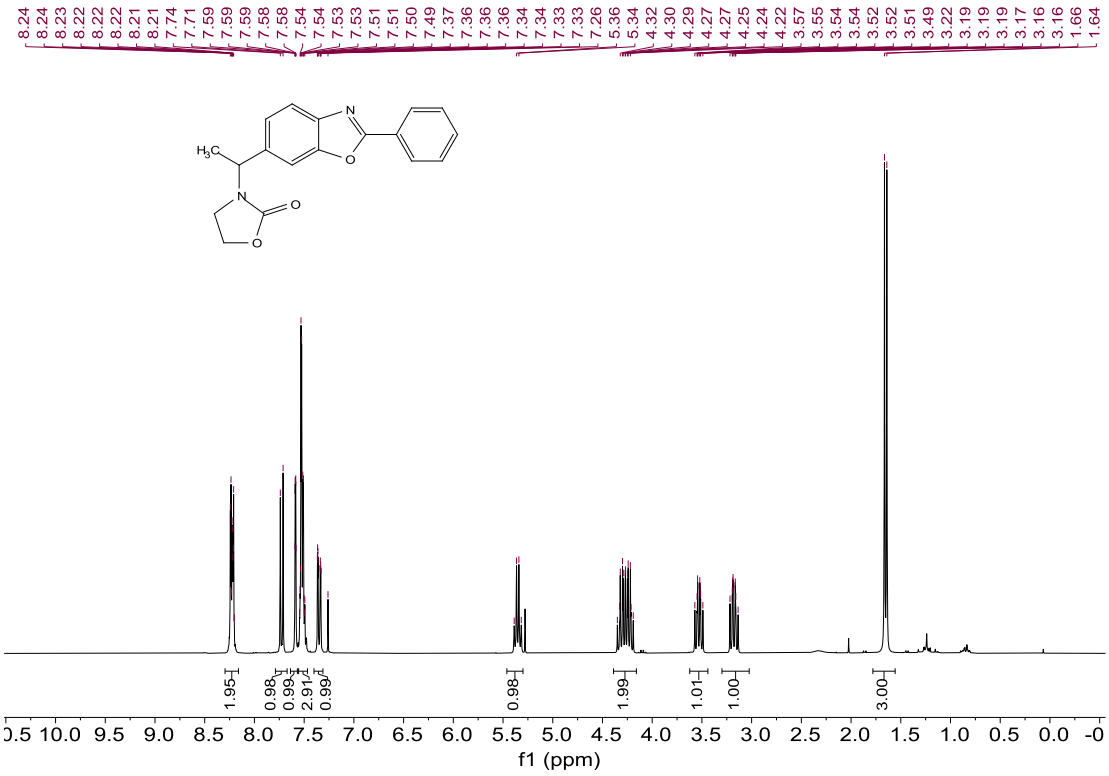


^{13}CNMR

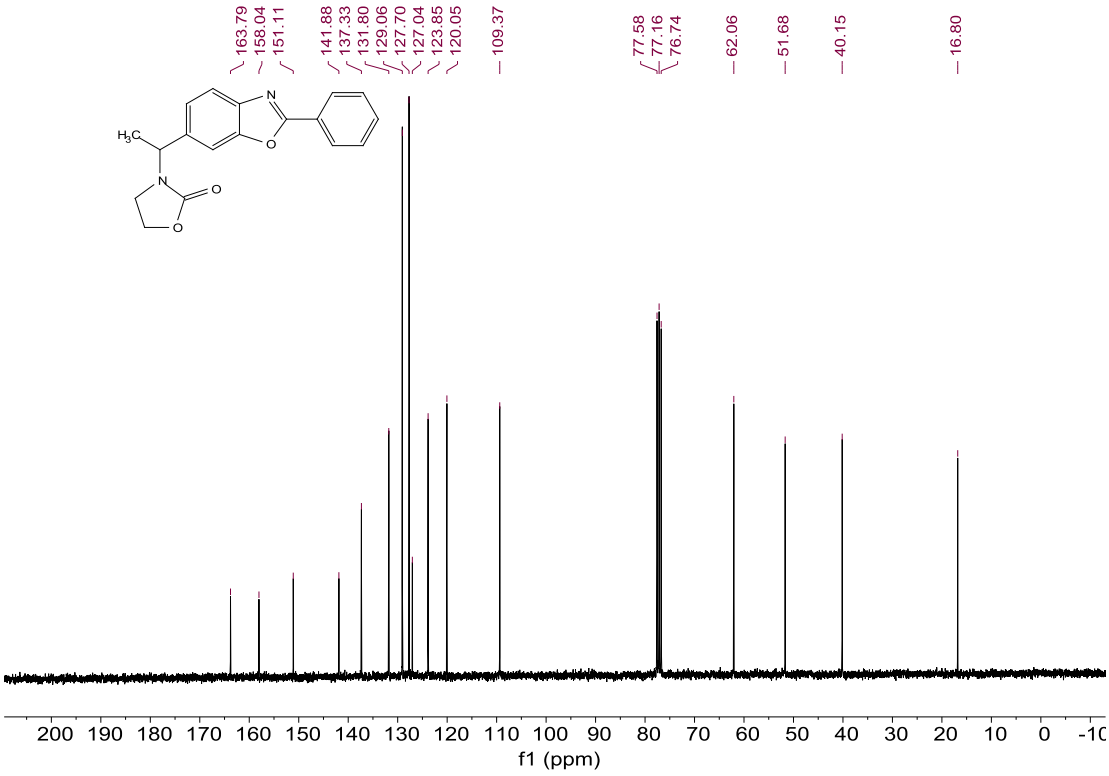


Compound 4m

^{1}HMNR

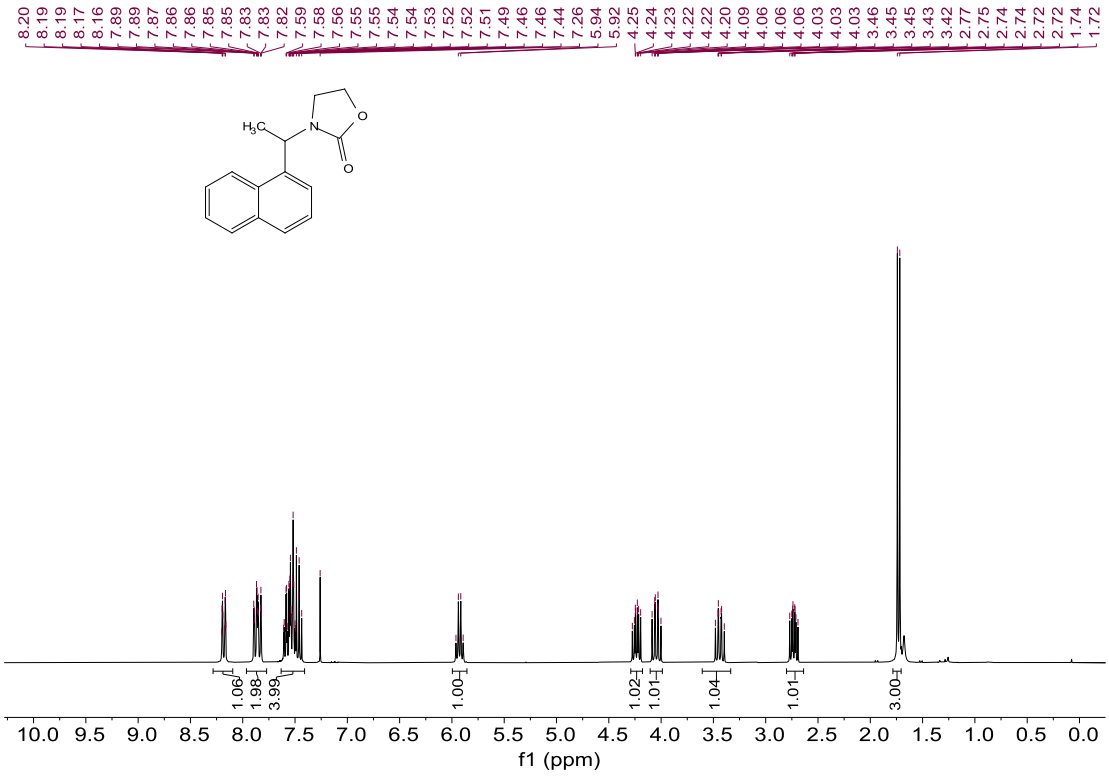


^{13}CNMR

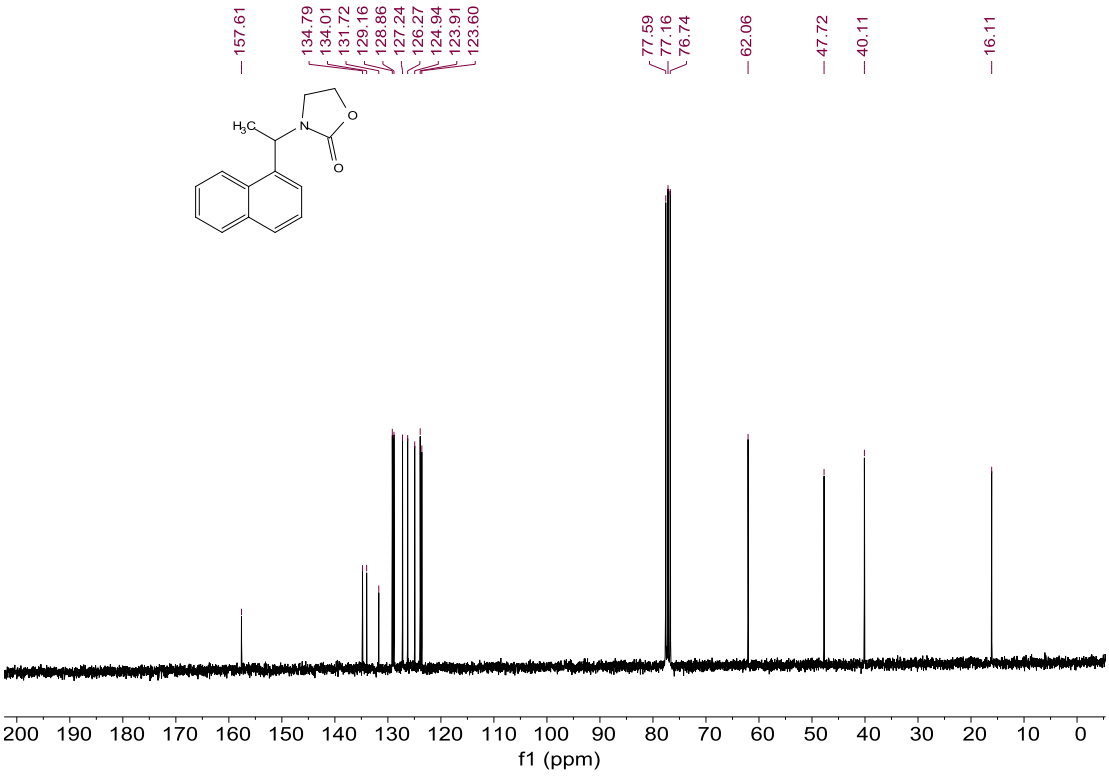


Compound 4n

^{1}HMNR

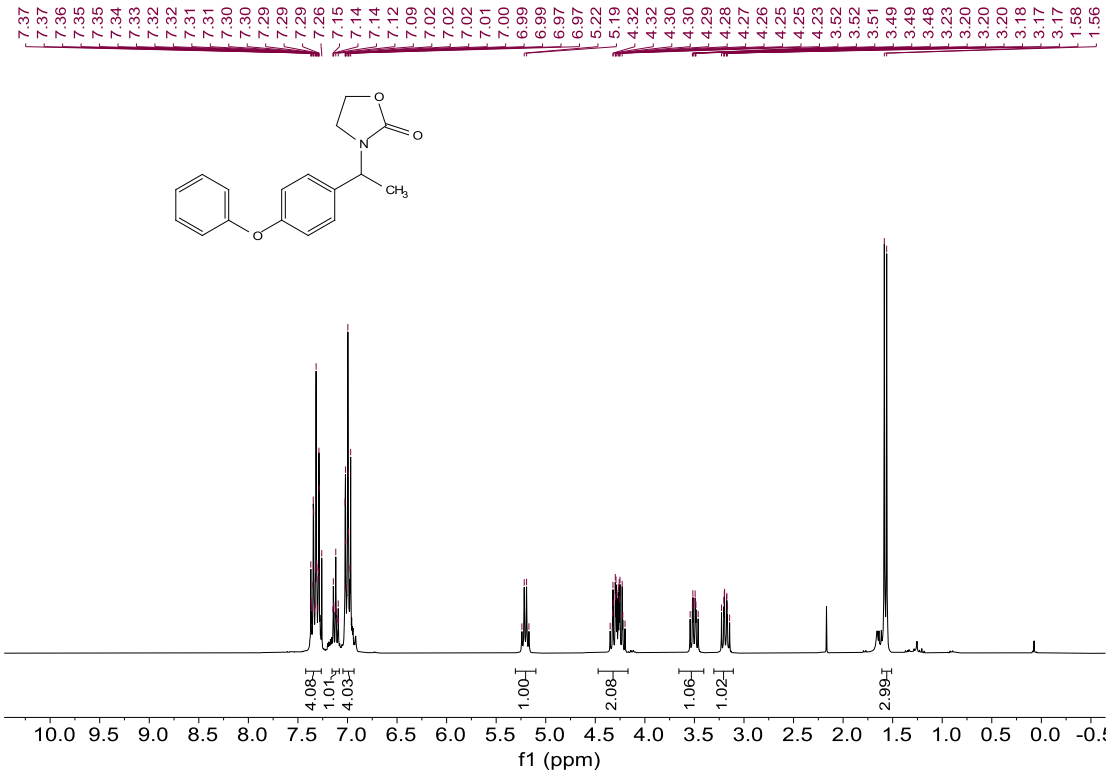


^{13}CNMR

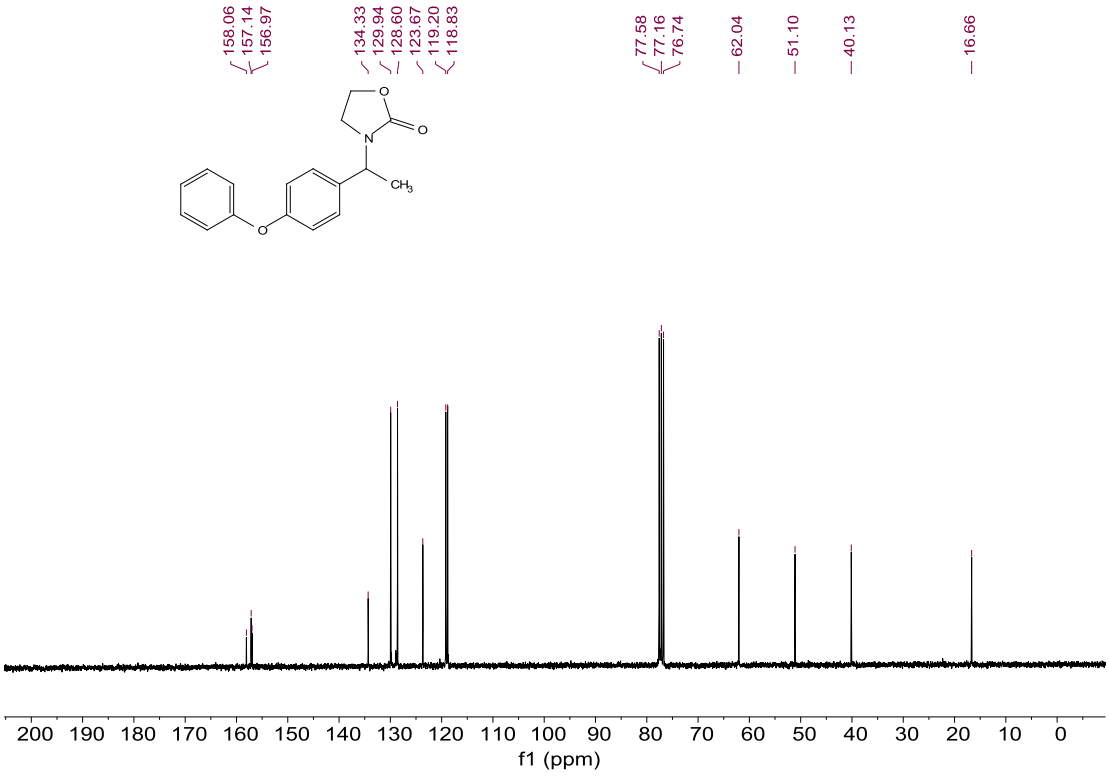


Compound **4o**

^{1}HMNR

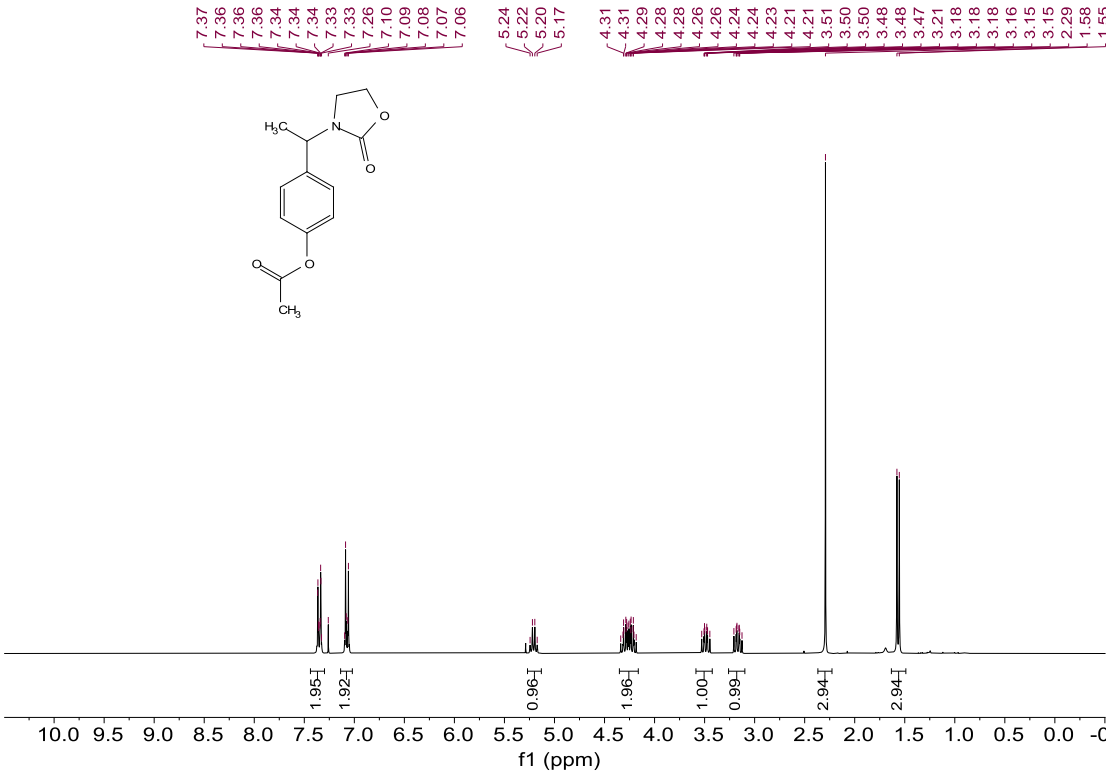


^{13}CNMR

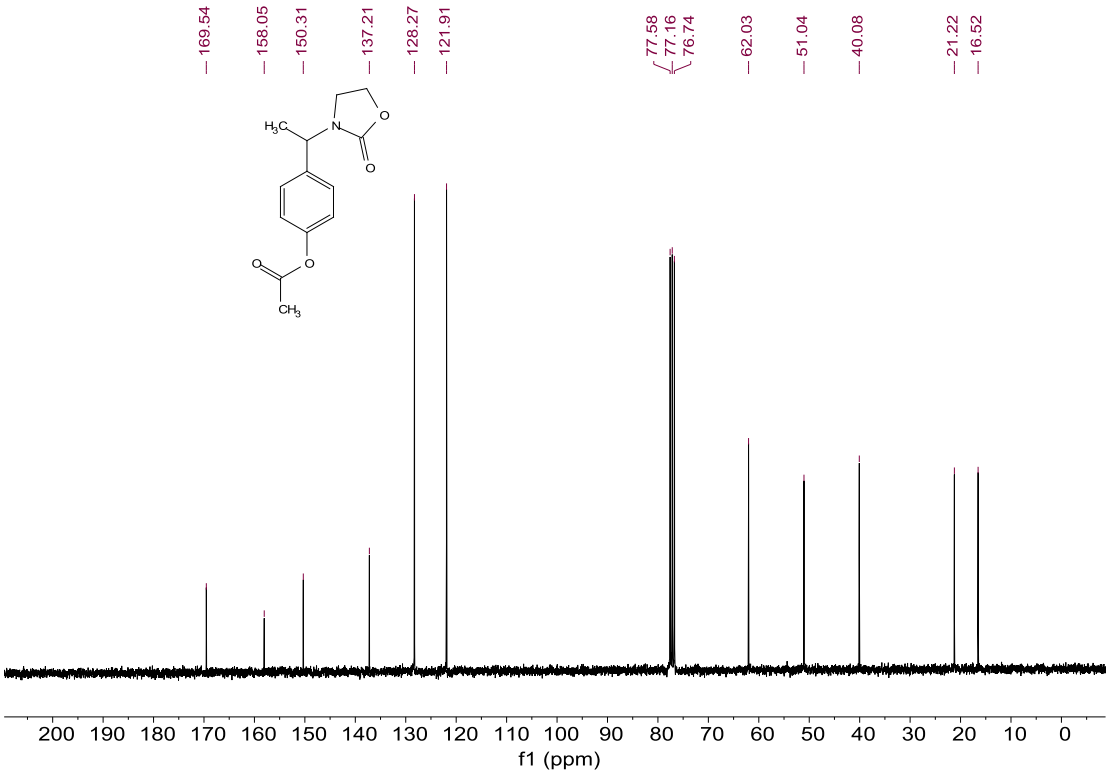


Compound 4p

^{1}HMNR

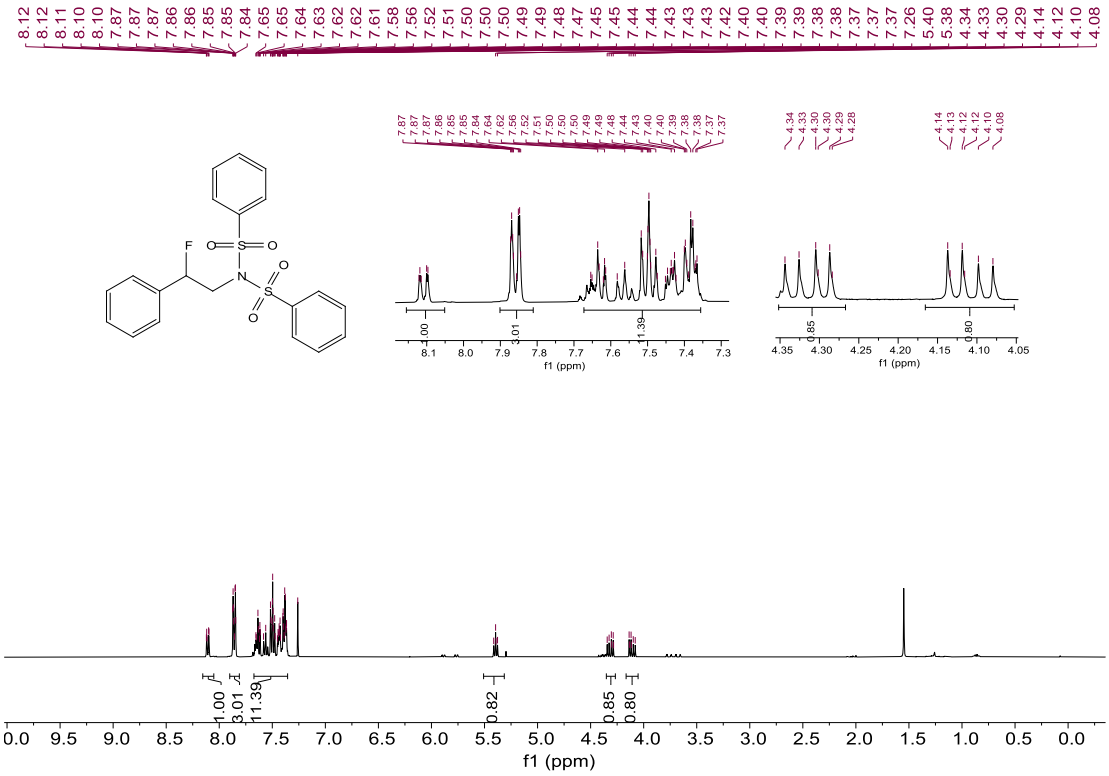


^{13}CNMR

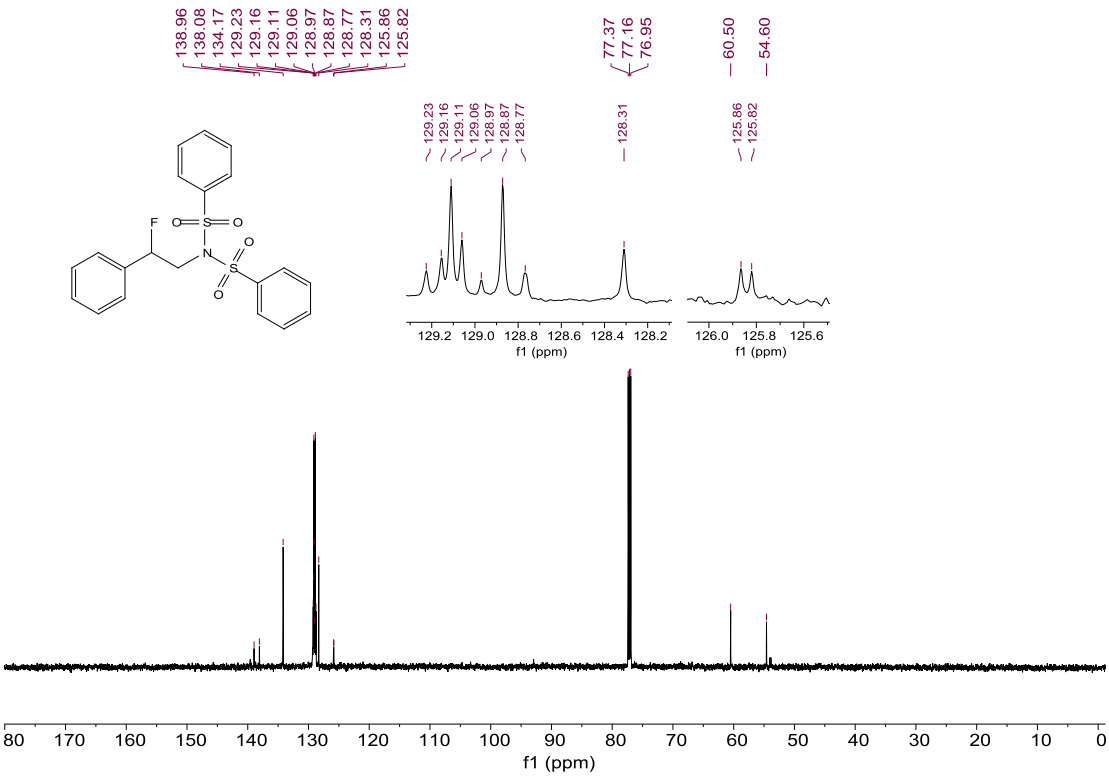


Compound 6a

^{1}HMNR

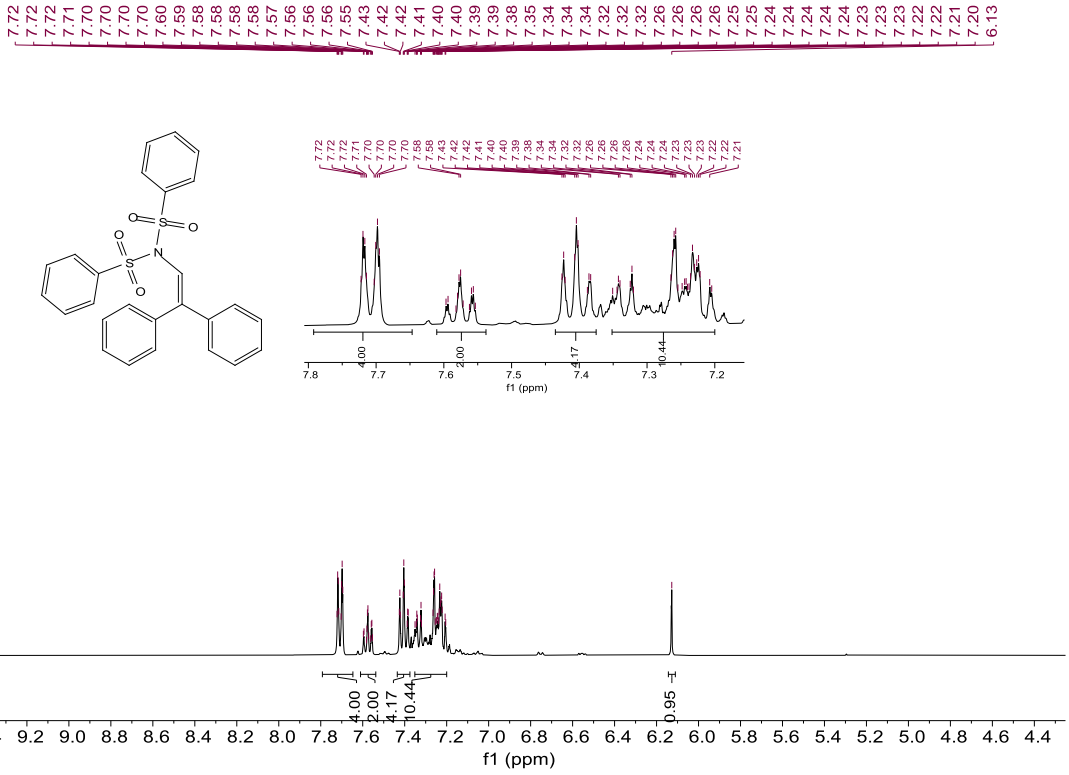


^{13}CNMR

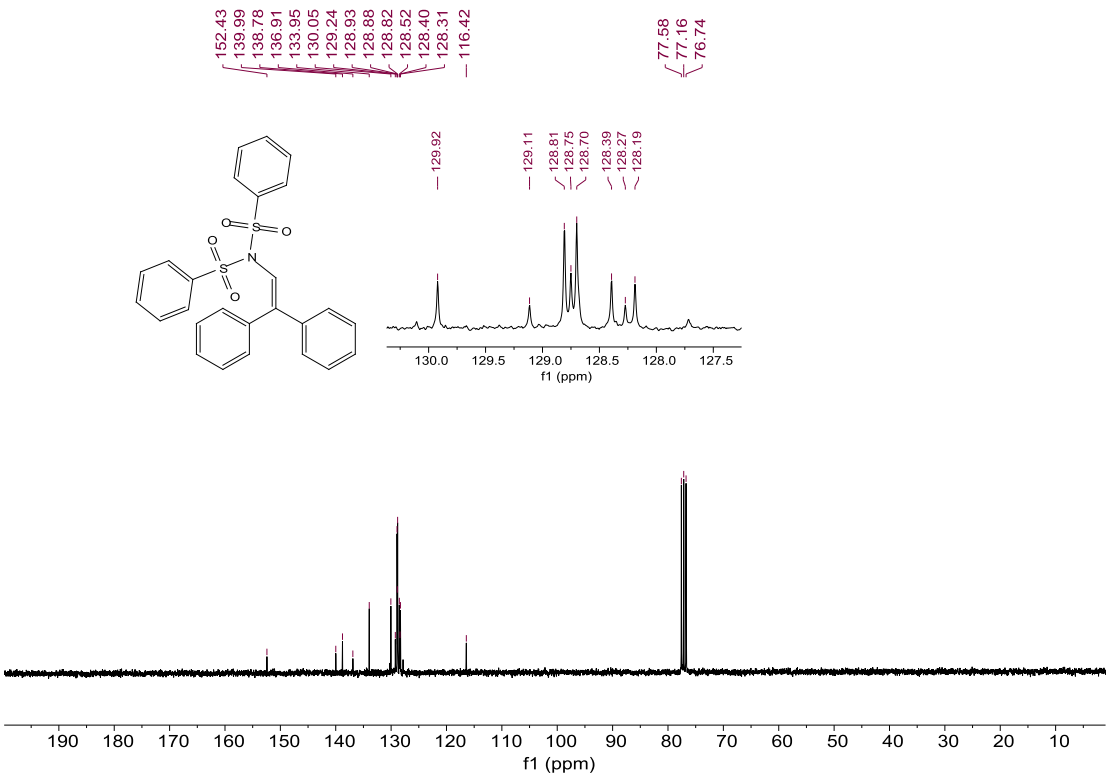


Compound 8a

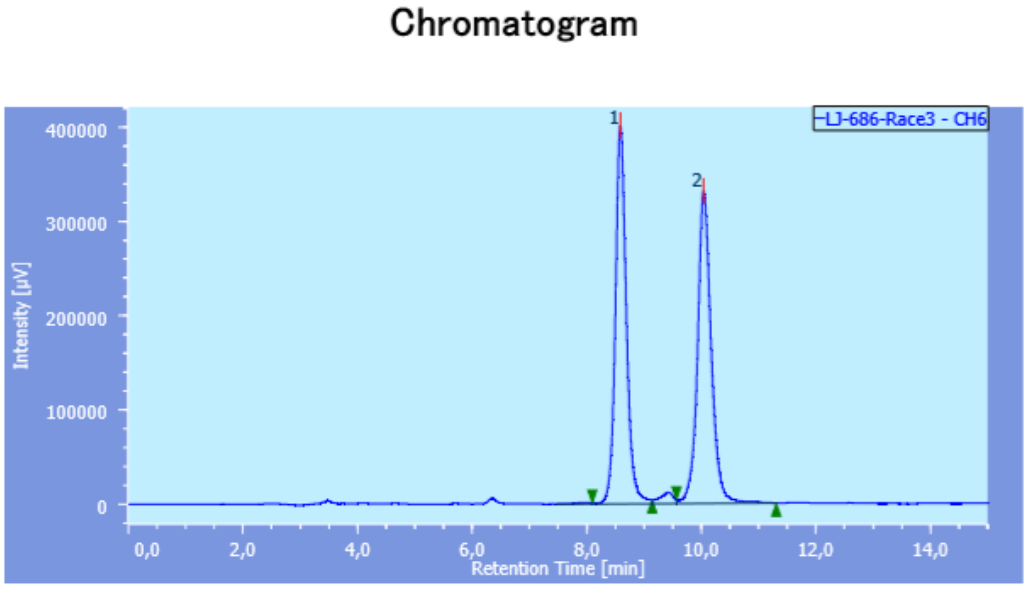
^{1}HMNR



^{13}CNMR



8. HPLC of Carbamate 3c



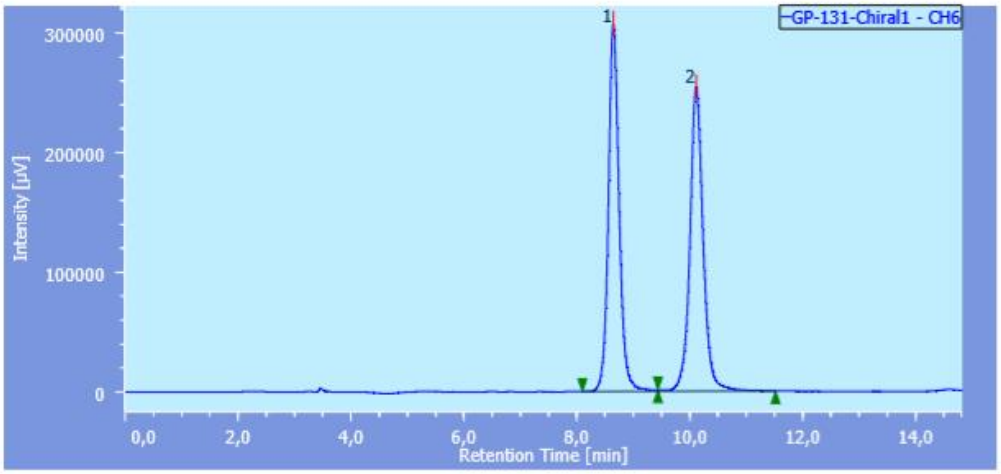
Chromatogram Information	
User Name	Administrator
Date Modified	23/05/2019 12:12:10
Description	
HPLC System Name	Orga
Injection Date	23/05/2019 11:57:08
Volume	20,00 [μL]
Sample Number	9
Project Name	Test
Acquisition Time	15,0 [min]
Acquisition Sequence	LJ-686-race+GP-131-chiral-95-Hx-5-EtOH 1 mL-min 20° C IA
Control Method	95A-Hx 5D-EtOH 16Min-1ml-min 20° C
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	LJ-686-Race3-CH6
Sample Name	
Channel Name	254,0nm
Sampling Interval	100 [msec]
Peak Method	IT (Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	6	8,580	5324382	401230	49,260	54,793	N/A	10948	4,000	1,145	
2	Unknown	6	10,035	5484337	331035	50,740	45,207	N/A	9998	N/A	1,098	

Chromatogram



Chromatogram Information

User Name	Administrator
Date Modified	23/05/2019 14:25:01
Description	
HPLC System Name	Orga
Injection Date	23/05/2019 12:13:38
Volume	20,00 [µL]
Sample Number	10
Project Name	Test
Acquisition Time	15,0 [min]
Acquisition Sequence	LJ-686-race+GP-131-chiral-95-Hx-5-EtOH 1 mL-min 20° C IA
Control Method	95A-Hx 5D-EtOH 16Min-1ml-min 20° C
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	GP-131-Chiral1-CH6
Sample Name	
Channel Name	254,0nm
Sampling Interval	100 [msec]
Peak Method	IT (Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [µV sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	6	8,642	4076716	307000	49,492	54,743	N/A	11091	4,050	1,119	
2	Unknown	6	10,107	4160458	253802	50,508	45,257	N/A	10362	N/A	1,057	

9. References

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