Supporting Information

For

Efficient Preparation of Carbamates by Rh-Catalysed Oxidative Carbonylation: Unveiling the Role of the Oxidant

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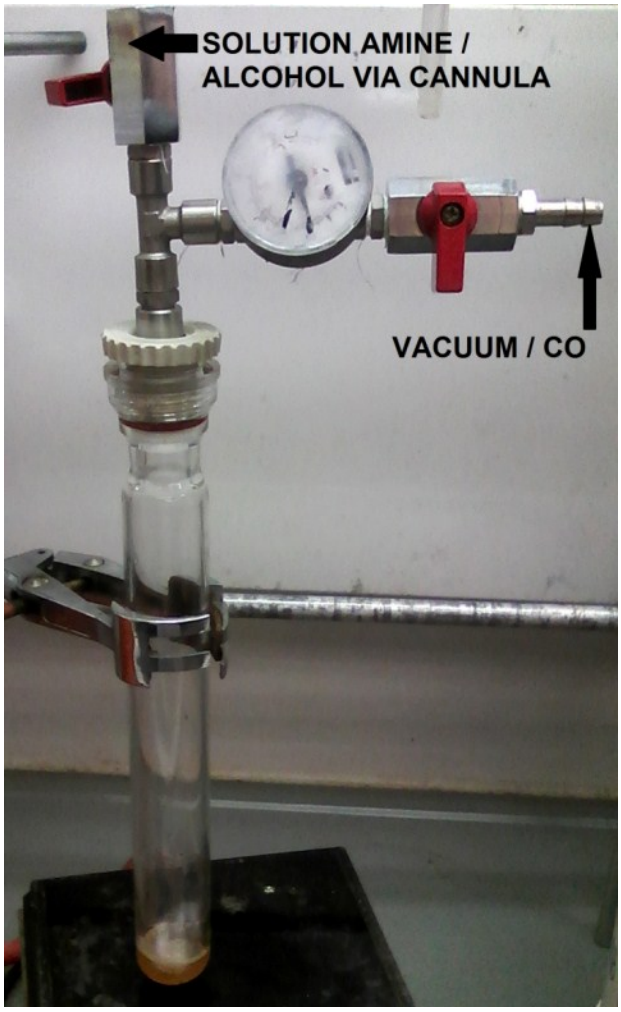
Synthesis and characterization of carbamates

General.

All experiments were carried out under an inert atmosphere by using standard Schlenk techniques. The solvents were obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). $CDCl_2$, $CDCl_3$ and toluene-d_8 (Eurisotop) were dried using activated molecular sieves. The catalysts were prepared according to literature procedures $[Rh(\mu\text{-}Cl)(COD)]_2$, $[Rh(\mu\text{-}MeO)(COD)]_2$ and $[Rh(\mu\text{-}Cl)(Cl)(Cp^*)]_2$.[1] All other commercially available starting materials were purchased from Sigma-Aldrich, Merck and J. T. Baker and were used without further purification. CO gas (>99.5 %) was obtained from Air Liquide. ^1H, $^{13}C\{1H\}$, ^{19}F, ^1H-^{29}Si HMBC, ^1H-^{13}C HMBC, ^1H-^{13}C HSQC and 1H-1H COSY NMR spectra were recorded either on a Bruker ARX 300 MHz or a Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks for ^1H and $^{13}C\{1H\}$, and to an external reference of $CFCl_3$ for ^{19}F. Coupling constants, J, are given in Hz. Spectral assignments were achieved by combination of ^1H-^1H COSY, ^{13}C APT and 1H-13C HSQC/HMBC experiments. Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formiate as reference. FT-IR spectra were collected on a Nicolet Nexus 5700 FT spectrophotometer equipped with a Nicolet Smart Collector diffuse reflectance accessory. Column chromatography was performed using silica gel (70-230 mesh).

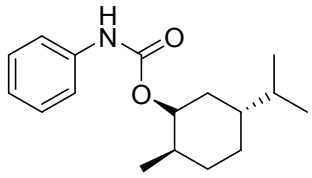
General procedure for the preparation of carbamates

Oxone (0.6 mmol, 184 mg) and the catalyst (2 mol %) were placed in a Fisher-Porter reactor under vacuum. A solution of amine (0.2 mmol) and alcohol (1 mmol) in toluene (4 mL) was prepared in a Schlenk flask and transferred into the reactor via cannula. The resulting suspension was frozen with liquid N_2, placed under vacuum and, after allowing it to reach room temperature, the reactor was charged with CO (2 bar). Subsequently, the temperature was increased to 100 ºC and stirred for 18 h. Then, the CO was released carefully and the resulting suspension filtered through celite. The residue remaining in the reaction vessel was extracted with CH_2Cl_2 (3×2 mL) and the solution was filtered through celite. The solution thus obtained was evaporated in vacuo to afford the desired product. Purification by flash chromatography in hexane / ethyl acetate (9/1) was performed when reaction byproducts were obtained. In the case of compound **3h** the impurities were eluted with a mixture in hexane / ethyl acetate (9/1) and the product was extracted with pure CH_2Cl_2.



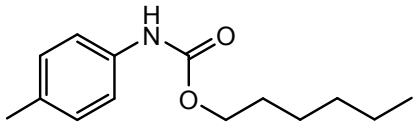
Characterisation

(1R,2R,5R)-5-isopropyl-2-methylcyclohexyl phenylcarbamate (1f)



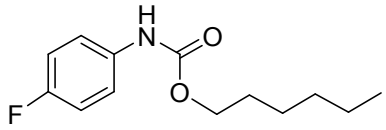
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.37 (m, 2H, CH_{Ar}), 7.33-7.27 (m, 2H, CH_{Ar}), 7.09-7.01 (m, 2H, CH_{Ar}), 7.56 (s, 1H, NH), 4.67 (td, J_{H-H} = 10.9, 4.4 Hz, 1H, CHO), 2.16-2.07 (m, 1H, $CH_{menthol}$), 2.16-2.07 (m, 1H, $CH_{menthol}$), 2.05-1.89 (m, 1H, $CH_{menthol}$), 1.75-1.64 (m, 2H, $CH_{2\ menthol}$), 1.57-1.44 (m, 1H, $CH_{menthol}$), 1.43-1.31 (m, 1H, $CH_{menthol}$), 1.14-0.98 (m, 2H, $CH_{2\ menthol}$), 0.95-0.88 (m, 6H, $CH_{3\ menthol}$), 0.82 (d, J_{H-H} = 6.9 Hz, 3H, $CH_{3\ menthol}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.4 (s, $COOCH_2$), 138.3 (s, CN), 129.2 (s, CH_{Ar}), 129.1 (s, CH_{Ar}), 123.3 (s, CH_{Ar}), 118.6 (s, CH_{Ar}), 75.3 (s, CHO), 47.5 (s, $CH_{menthol}$), 41.5 (s, $CH_{2\ menthol}$), 34.4 (s, $CH_{2\ menthol}$), 31.5 (s, $CH_{menthol}$), 26.4 (s, $CH_{menthol}$), 23.6 (s, $CH_{2\ menthol}$), 22.2 (s, $CH_{3\ menthol}$), 21.0 (s, $CH_{3\ menthol}$), 16.6 (s, $CH_{3\ menthol}$). IR (ATR, cm^{-1}): ν 1694vs (CO). HRMS (ESI) m/z calcd. for $C_{17}H_{25}NO_2$ (M+Na) 298.1778 found 298.1786.

Hexyl (4-methylphenyl)carbamate (2a)



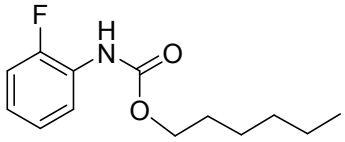
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, J_{H-H} = 8.2, 2H, CH_{Ar}), 7.10 (d, J_{H-H} = 8.2, 2H, CH_{Ar}), 6.51 (bs, 1H, NH), 4.15 (t, J_{H-H} = 6.7, 2H, $COOCH_2$), 2.30 (s, CH_3), 1.71-1.61 (m, 2H, CH_2), 1.43-1.27 (m, 6H, CH_2), 0.90 (t, J_{H-H} = 6.7, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154 (s, COO), 135.5 (s, CN), 129.7 (s, CCH_3), 129.7 (s, CH_{Ar}), 129.7 (s, CH_{Ar}), 118.9 (bs, CH_{Ar}), 65.5 (s, $COOCH_2$), 31.6 (s, CH_2), 29.1 (s, CH_2), 25.7 (s, CH_2), 22.7 (s, CH_2), 20.9 (s, CH_3), 14.1(s, CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): –119.8 (s, CF_3). IR (ATR, cm^{-1}): ν 1704vs (CO). HRMS (ESI) m/z calcd. for $C_{14}H_{21}NO_2$ (M+Na) 258.1465 found 258.1452.

Hexyl (4-fluorophenyl)carbamate (2b)



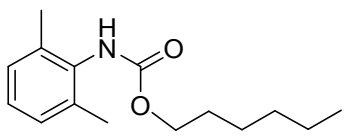
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.27 (m, 2H, CH_{Ar}), 6.98 (t, J_{H-H} = 8.7, 2H, CH_{Ar}), 6.67 (bs, 1H, NH), 4.15 (t, J_{H-H} = 6.7, 2H, $COOCH_2$), 1.72-1.60 (m, 2H, CH_2), 1.43-1.24 (m, 6H, CH_2), 0.89 (t, J_{H-H} = 6.7, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1 (d, J_{C-F} = 242.4, CF), 154.1 (s, COO), 134.1 (s, CN), 120.6 (bs, CH_{Ar}), 115.7 (d, J_{C-F} = 22.6, $CH_{Ar}CF$), 118.3 (bs, CH_{Ar}), 65.7 (s, $COOCH_2$), 31.6 (s, CH_2), 29.0 (s, CH_2), 25.6 (s, CH_2), 22.7 (s, CH_2), 14.1(s, CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): –119.8 (s, CF_3). IR (ATR, cm^{-1}): ν 1696vs (CO). HRMS (ESI) m/z calcd. for $C_{13}H_{18}NO_2F$ (M+Na) 262.1214 found 262.1198.

Hexyl (2-fluorophenyl)carbamate (**2c**)



^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (t, J_{H-H}=7.3, 1H, CH_{Ar}), 7.17-6.93 (m, 3H, CH_{Ar}), 6.81 (bs, 1H, NH), 4.18 (t, J_{H-H} = 6.7, 2H, $COOCH_2$), 1.75-1.62 (m, 2H, CH_2), 1.45-1.27 (m, 6H, CH_2), 0.90 (t, J_{H-H} = 6.1, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.6 (s, COO), 152.3 (d, J_{C-F} = 242.4, CF), 126.7 (d, J_{C-F} = 9.9, CN), 124.7 (d, J_{C-F} = 3.5, CH_{Ar}), 123.4 (d, J_{C-F} = 7.5, CH_{Ar}), 120.3 (s, CH_{Ar}), 114.9 (d, J_{C-F} = 19.1, CH_{Ar}), 65.9 (s, $COOCH_2$), 31.6 (s, CH_2), 29.0 (s, CH_2), 25.7 (s, CH_2), 22.7 (s, CH_2), 14.1(s, CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): -132.73 (bs, CF_3). IR (ATR, cm^{-1}): ν 1726s (CO). HRMS (ESI) m/z calcd. for $C_{13}H_{18}NO_2F$ (M+Na) 262.1214 found 262.1200

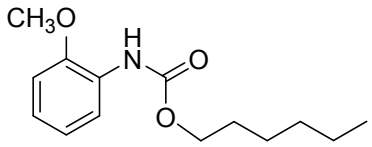
Hexyl (2,6-dimethylphenyl)carbamate (**2d**)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.22 (m, 3H, CH_{Ar}), 6.26 (bs, 1H, NH), 4.32 (bs, 2H, $COOCH_2$), 2.45 (s, 3H, CH_3), 1.94-1.77 (m, 2H, CH_2), 1.69-1.34 (m, 6H, CH_2), 1.09 (bs, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155 (s, COO), 136 (s, CN), 133.9 (s, CCH_3), 128.3 (s, CH_{Ar}), 127.2 (s, CH_{Ar}), 65.6 (s, $COOCH_2$), 31.6 (s, CH_2), 29.1 (s,

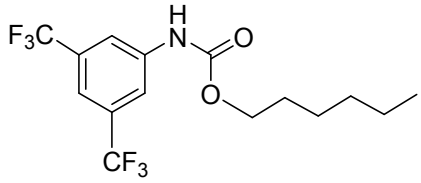
CH_2), 25.6 (s, CH_2), 22.7 (s, CH_2), 18.4 (s, CH_3), 14.1 (s, CH_3). IR (ATR, cm^{-1}): ν 1698vs (CO). HRMS (ESI) m/z calcd. for $C_{15}H_{23}NO_2$ (M+Na) 272.1621 found 272.1611.

Hexyl (2-methoxyphenyl)carbamate (**2e**)



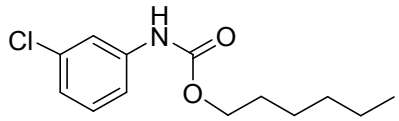
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, J_{H-H} = 6.2, 1H, CH_{Ar}), 7.21 (bs, 1H, NH), 7.04-6.91 (m, 2H, CH_{Ar}), 6.89-6.83 (m, 1H, CH_{Ar}), 4.16 (t, J_{H-H} = 6.7, 2H, $COOCH_2$), 3.87 (s, 3H, CH_3), 1.74-1.60 (m, 2H, CH_2), 1.46-1.27 (m, 6H, CH_2), 0.90 (t, J_{H-H} = 6.8, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8 (s, COO), 147.7 (s, $COCH_3$), 127.9 (s, CN), 122.7 (s, CH_{Ar}), 121.3 (s, CH_{Ar}), 118.3 (s, CH_{Ar}), 110.1 (s, CH_{Ar}), 65.4 (s, $COOCH_2$), 55.8 (s, OCH_3), 31.6 (s, CH_2), 29.0 (s, CH_2), 25.7 (s, CH_2), 22.7 (s, CH_2), 14.1(s, CH_3). IR (ATR, cm^{-1}): ν 1732vs (CO). HRMS (ESI) m/z calcd. for $C_{14}H_{21}NO_3$ (M+Na) 274.1414 found 274.1405.

Hexyl (3,5-bis(trifluoromethyl)phenyl)carbamate (**2f**)



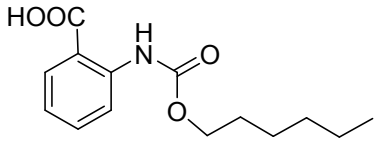
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (s, 2H, CH_{Ar}), 7.55 (s, 1H, CH_{Ar}), 6.93 (bs, 1H, NH), 4.20 (t, J_{H-H} = 6.7, 2H, $COOCH_2$), 1.75-1.60 (m, 2H, CH_2), 1.42-1.27 (m, 6H, CH_2), 0.90 (t, J_{H-H}=6.7, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3 (s, COO), 139.7 (s, CN), 133.3-132 (q, J_{C-F} = 33.3, CCF_3), 128.7- 117.8 (q, J_{C-F} = 272.8, CF_3), 118.3 (bs, CH_{Ar}, 2CH), 116.9-116.6 (m, CH_{Ar}, 1CH), 66.4 (s, $COOCH_2$), 31.6 (s, CH_2), 28.9 (s, CH_2), 25.6 (s, CH_2), 22.7 (s, CH_2), 14.1(s, CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): -63.2 (s, CF_3). IR (ATR, cm^{-1}): ν 1704s (CO). HRMS (ESI) m/z calcd. for $C_{15}H_{17}F_6NO_2$ (M-H) 356.1091 found 356.1107.

Hexyl (3-chlorophenyl)carbamate (**2g**)



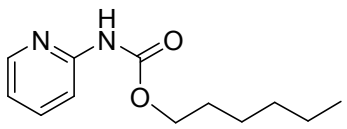
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (s, 1H, CH_{Ar}), 7.22-7.18 (m, 2H, CH_{Ar}), 7.05-7.00 (m, 1H, CH_{Ar}), 6.66 (bs, 1H, NH), 4.16 (t, J_{H-H} = 6.7, 2H, $COOCH_2$), 1.69-1.62 (m, 2H, CH_2), 1.38-1.28 (m, 6H, CH_2), 0.90 (t, J_{H-H} = 6.8, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.6 (s, CO), 139.4 (s, CCl), 134.9 (s, CN), 130.1 (s, CH_{Ar}), 123.5 (s, CH_{Ar}), 118.8 (s, CH_{Ar}), 116.7 (s, CH_{Ar}), 65.9 (s, $COOCH_2$), 31.6 (s, CH_2), 29 (s, CH_2), 25.7 (s, CH_2), 22.7 (s, CH_2), 14.1 (s, CH_3). IR (ATR, cm^{-1}): ν 1701vs (CO). HRMS (ESI) m/z calcd. for $C_{13}H_{18}NO_2Cl$ (M+Na) 278.0918 found 278.0907.

2-(((Hexyloxy)carbonyl)amino)benzoic acid (**2h**)



^{1}H NMR (300 MHz, $CDCl_3$): 10.22 (s, 1H, COOH), 8.48 (d, J_{H-H} = 8.5, 1H, CH_{Ar}), 8.12 (dd, J_{H-H} = 8.0, 1.5, 1H, CH_{Ar}), 7.62-7.56 (m, 1H, CH_{Ar}), 7.10-7.04 (m, 1H, CH_{Ar}), 4.19 (J_{H-H} = 6.8, 2H, $COOCH_2$), 1.74-167 (m, 2H, CH_2), 1.41-1.30 (m, 6H, C*H*$_2$), 0.93-0.88 (m, 6H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): 172.7 (s, COOH), 154.0 (s, CO), 142.7 (s, CN), 135.7 (s, CH_{Ar}), 132.0 (s, CH_{Ar}), 121.8 (s, CH_{Ar}), 119.1 (s, CH_{Ar}), 113.5 (s, CCOOH), 65.8 (s, CH_2O), 31.6 (s, CH_2), 29.0 (s, CH_2), 25.7 (s, CH_2), 22.6 (s, CH_2), 14.1 (s, *C*H$_3$). IR (ATR, cm^{-1}) ν 1735vs (CO), 1672 vs (CO). HRMS (ESI) m/z calcd. for $C_{14}H_{19}NO_4$ (M+Na) 288.1206 found 288.1192.

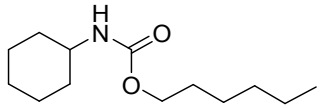
Hexyl pyridin-2-ylcarbamate (**2i**)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78-7.54 (m, 3H, CH_{Ar}), 7.16 (d, J_{H-H} = 1H, CH_{Ar}), 6.71 (t, J_{H-H} = 1H, CH_{Ar}), 4.08 (t, J_{H-H}= 6.4, 2H, $COOCH_2$), 1.77-1.59 (m, 2H, CH_2), 1.38-1.20 (m, 6H, CH_2), 0.85 (t, J_{H-H} = 6.6, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.6 (s, CN), 143.6 (s, CH_{Ar}), 134.9 (s, CH_{Ar}), 114.8 (s, CH_{Ar}), 112.3 (s, CH_{Ar}), 65.6 (s, $COOCH_2$), 31.6 (s, CH_2), 29.4 (s, CH_2), 25.5 (s, CH_2), 22.6 (s, CH_3), 14.1 (s, CH_3).

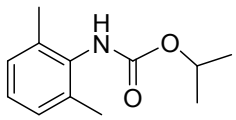
IR (ATR, cm^{-1}): ν 1667vs (CO). HRMS (ESI) m/z calcd. for $C_{12}H_{18}N_2O_2$ ($M+H^+$) 223.1441 found 223.1429.

Hexyl (cyclohexyl)carbamate (2j)



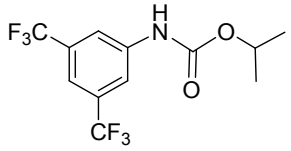
^1H NMR (300 MHz, $CDCl_3$): δ 4.02 (t, J_{H-H}= 6.7, 2H, $COOCH_2$), 3.22-3 (m, 1H, CHNH), 2.14-2.02 (m, 2H, CH_2), 1.85-1.73 (m, 2H, CH_2), 1.70-1.55 (m, 4H, CH_2), 1.42-1.14 (m, 10H, CH_2), 0.88 (t, J_{H-H} = 6.6, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.8 (s, $COOCH_2$), 51.0 (s, CHNH), 31.6 (s, CH_2), 30.8 (s, CH_2), 29.4 (s, CH_2), 25.6 (s, CH_2), 24.8 (s, CH_2), 24.4 (s, CH_2), 22.7 (s, CH_2), 14.1 (s, CH_3). IR (ATR, cm^{-1}): ν 1694s (CO). HRMS (ESI) m/z calcd. for $C_{13}H_{25}N_2O_2$ (M) 227.1880 found 226.9513.

Isopropyl (2,6-dimethylphenyl)carbamate (3d)



^1H NMR (300 MHz, $CDCl_3$): δ 7.12-7.02 (m, 3H, CH_{Ar}), 5.92 (bs, 1H, NH), 5.05-4.92 (h, J_{H-H}= 6.3, 1H, COOCH), 2.27 (s, 6H, CH_3), 1.36-1.19 (m, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136 (s, CN), 133.5 (CCH_3), 128.3 (s, CH_{Ar}), 127.2 (s, CH_{Ar}), 68.7 (s, COOCH), 22.2 (s, CH_3), 18.5 (s, CH_3). IR (ATR, cm^{-1}): ν 1688vs (CO). HRMS (ESI) m/z calcd. for $C_{12}H_{17}NO_2$ (M+Na) 230.1151 found 230.1160.

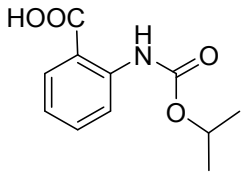
Isopropyl (3,5-bis(trifluoromethyl)phenyl)carbamate (3f)



^1H NMR (300 MHz, $CDCl_3$): δ 7.89 (s, 2H, CH_{Ar}), 7.54 (s, 1H, CH_{Ar}), 6.85 (bs, 1H, NH), 5.11-4.98 (h, J_{H-H} = 6.3, 1H, COOCH), 1.32 (d, J_{H-H}=6.3, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.9 (s, COO), 139.8 (s, CN), 133.3-131.9 (q, J_{C-F} = 33.6, CCF_3), 128.7-117.8 (q, J_{C-F} = 272.8, CF_3), 118.3 (bs, $CH_{Ar,}$ 2CH), 117.0-116.5 (m, $CH_{Ar,}$ 1CH),

70.1 (s, COOCH), 22.1(s, CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): -63.1 (s, CF_3). IR (ATR, cm^{-1}): ν 1702s (CO). HRMS (ESI) m/z calcd. for $C_{12}H_{11}F_6NO_2$ (M+Na) 338.0586 found 338.0597.

2-(((Isopropyloxy)carbonyl)amino)benzoic acid (3h)



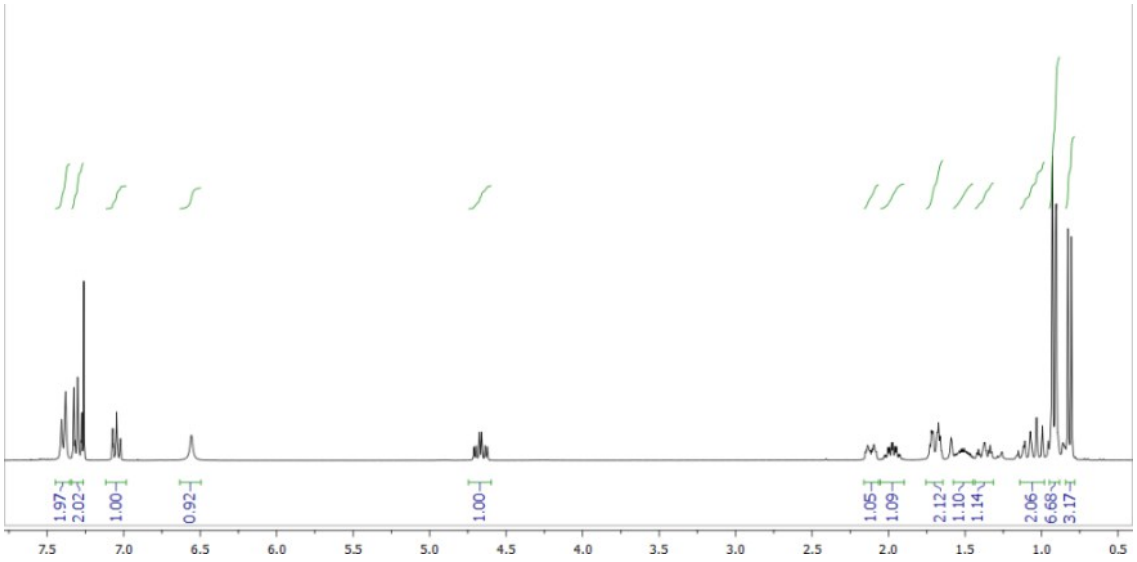
^1H NMR (300 MHz, $CDCl_3$): 10.19 (s, 1H, COOH), 8.50 (d, J_{H-H} = 8.5, 1H, CH_{Ar}), 8.10 (dd, J_{H-H} = 8.0, 1.6, 1H, CH_{Ar}), 7.63-7.53 (m, 1H, CH_{Ar}), 7.10-7.0 (m, 1H, CH_{Ar}), 5.10-4.97 (m, 1H, COOCH), 1.33 (d, J_{H-H}=6.3, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 171.4 (s, COOH), 153.4 (s, CO), 142.8 (s, CN), 135.6 (s, CH_{Ar}), 132.0 (s, CH_{Ar}), 121.6 (s, CH_{Ar}), 119.1 (s, CH_{Ar}), 113.4 (s, CCOOH), 69.1 (s, COOCH), 22.2 (s, CH_3). IR (ATR, cm^{-1}) ν 1731vs (CO), 1673 vs (CO). HRMS (ESI) m/z calcd. for $C_{11}H_{13}NO_4$ (M+Na) 246.0737 found 246.0714.

Compounds **1a**,[2] **1b**,[3] **1c**,[4] **1d**,[5] **1e**,[6] **3a**,[4] **3b**,[4] and **3g**[7] have been previously reported and characterised in the literature.

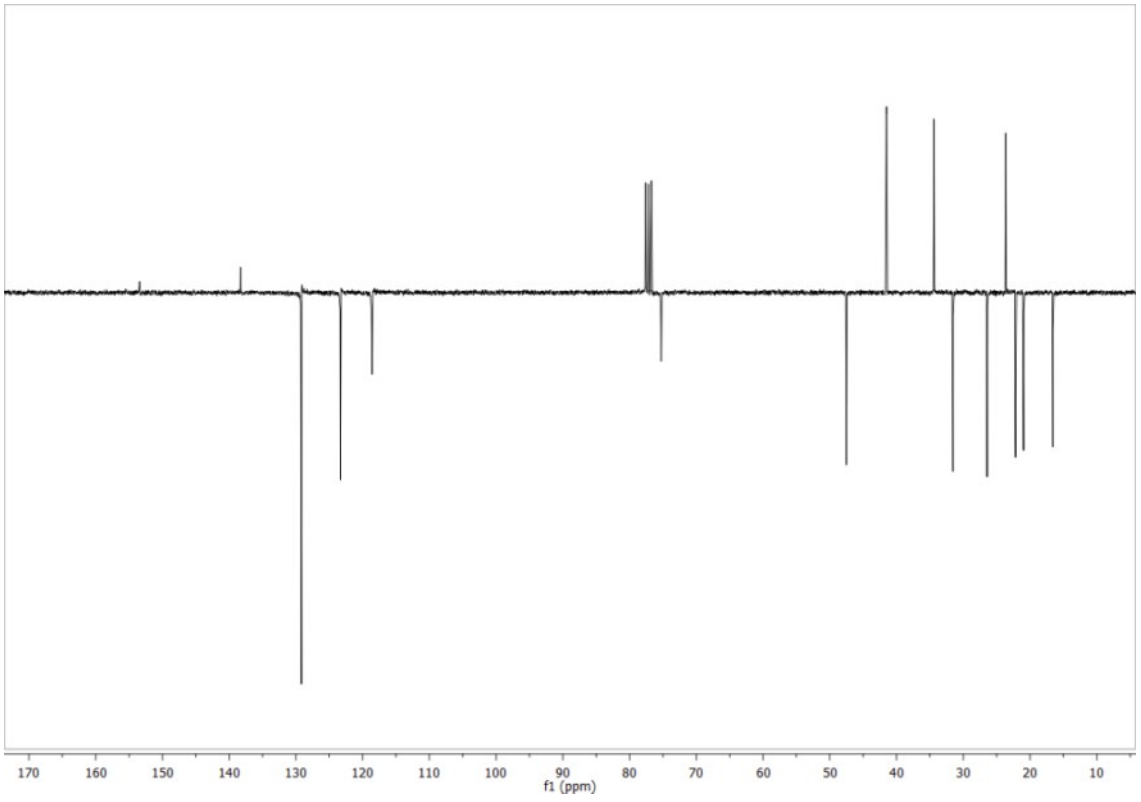
NMR spectra

- (1R,2R,5R)-5-isopropyl-2-methylcyclohexyl phenylcarbamate (**1f**)

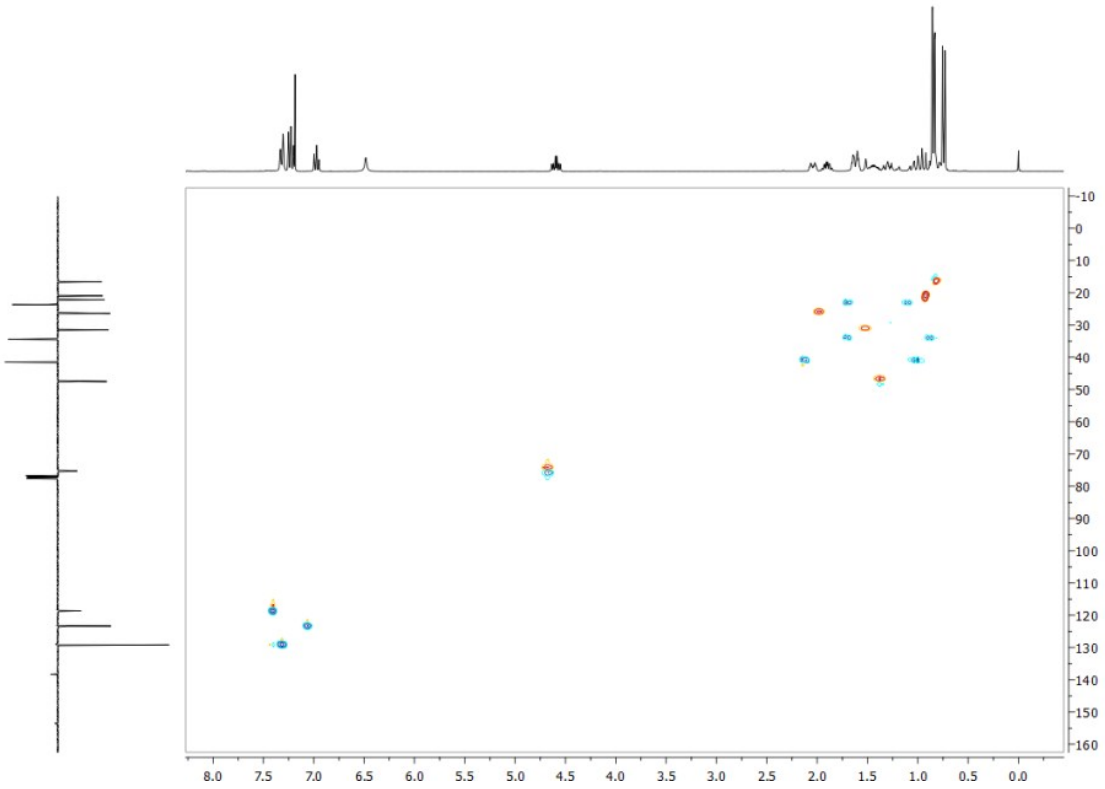
^{1}H NMR



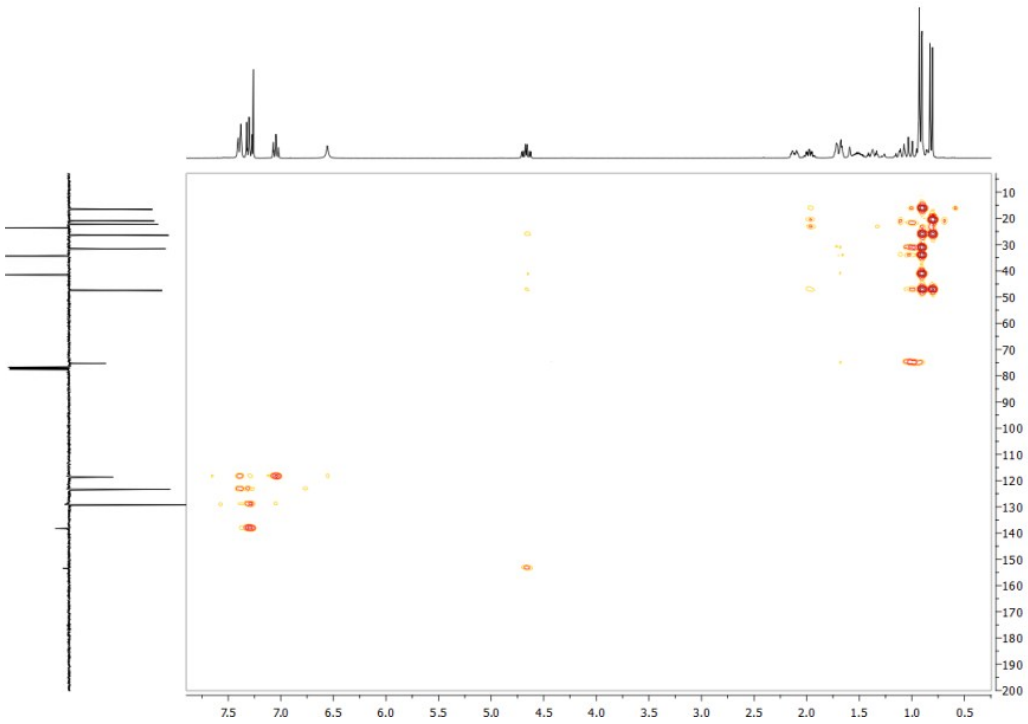
^{13}C NMR (APT)



^{1}H-^{13}C HSQC NMR

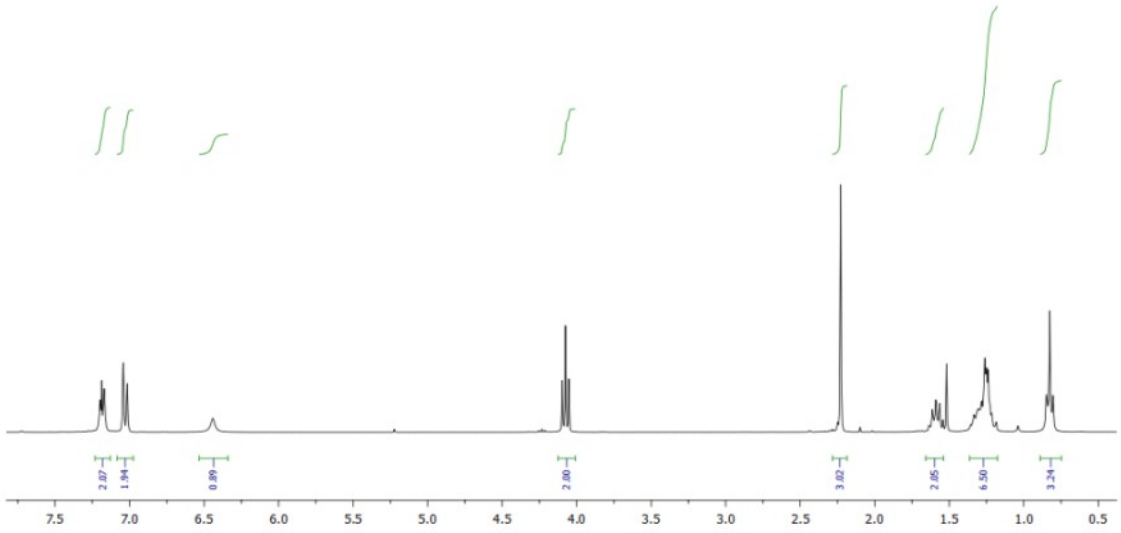


^{1}H-^{13}C HMBC NMR

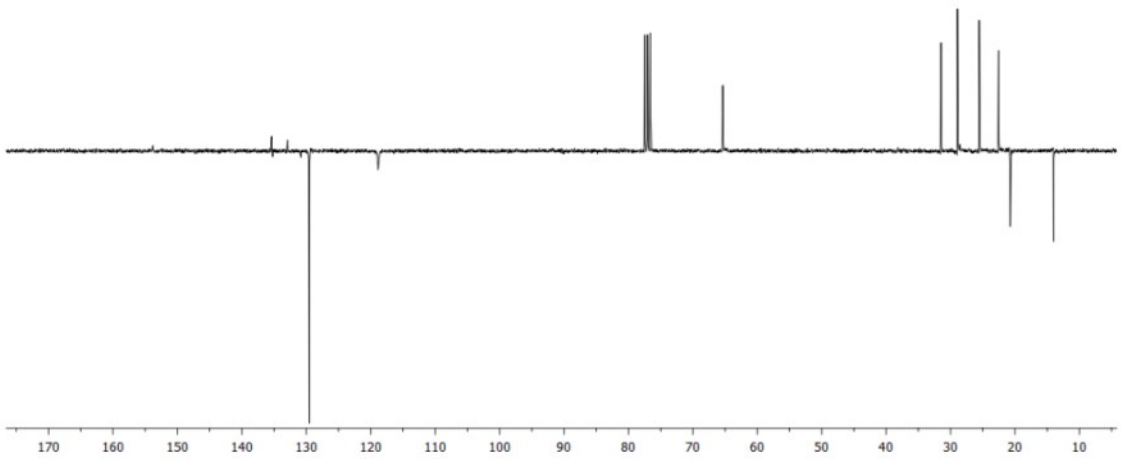


- Hexyl (4-methylphenyl)carbamate **(2a)**

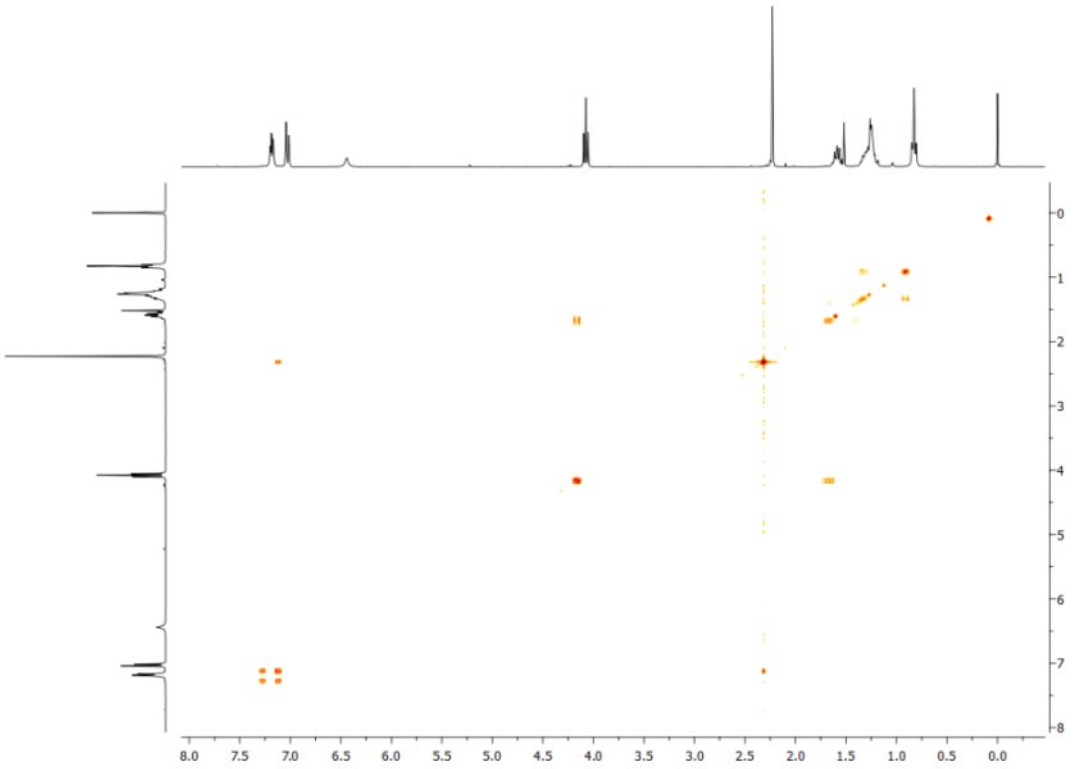
^{1}H NMR



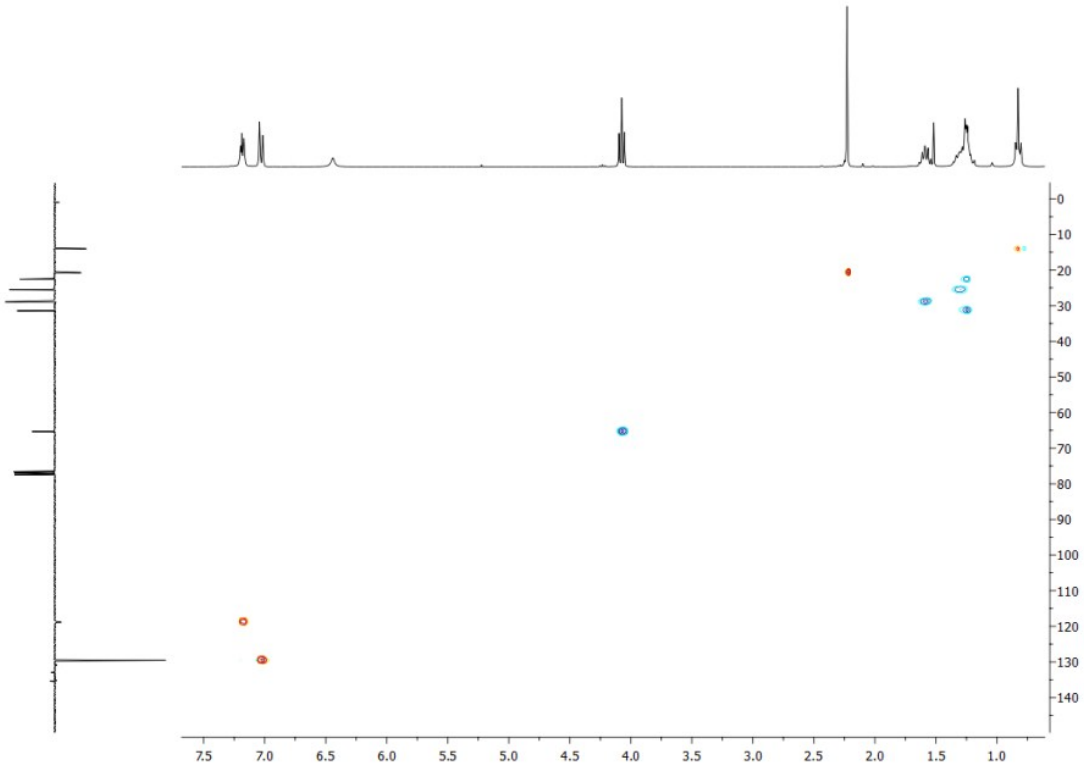
^{13}C NMR (APT)



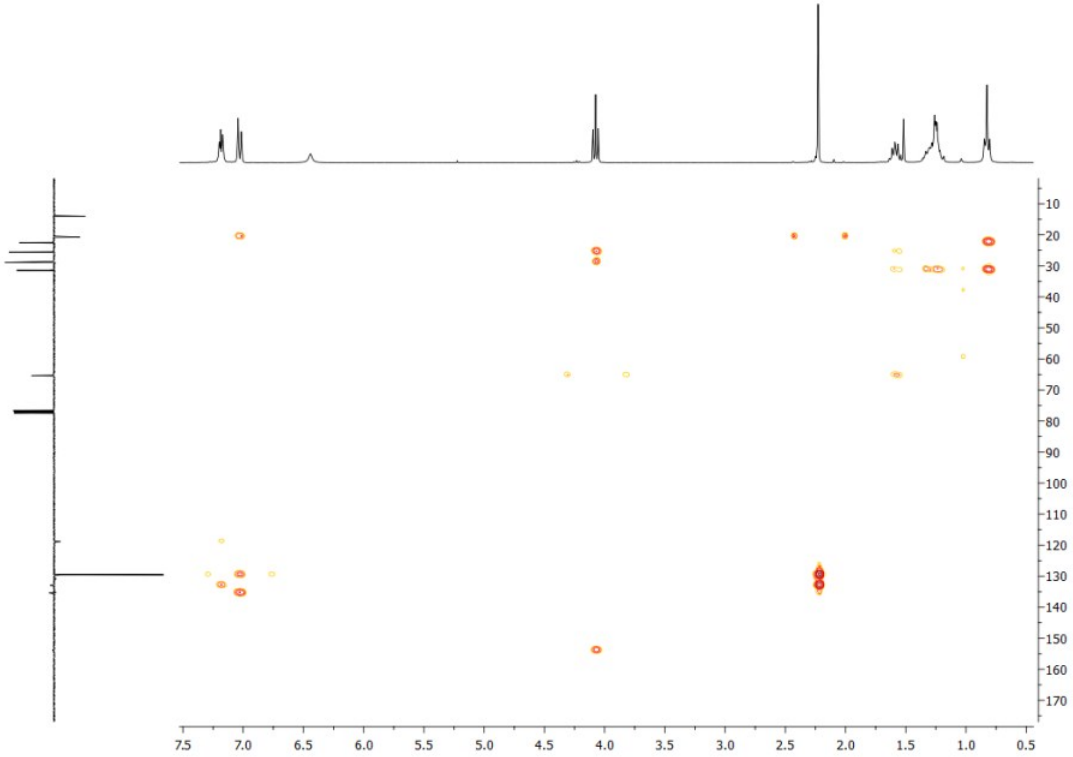
^{1}H-^{1}H COSY NMR



^{1}H-^{13}C HSQC NMR

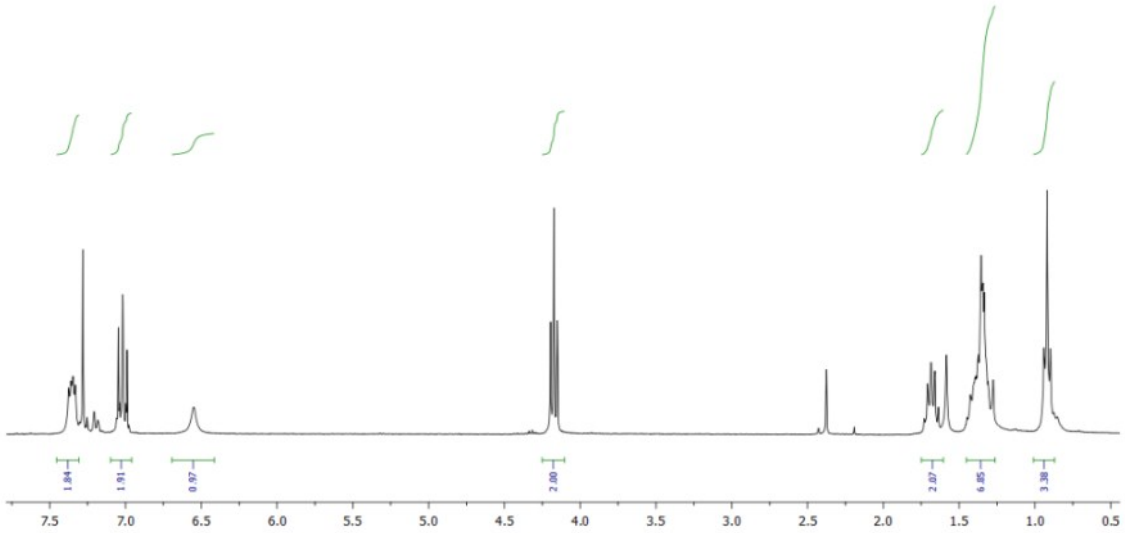


^{1}H-^{13}C HMBC NMR

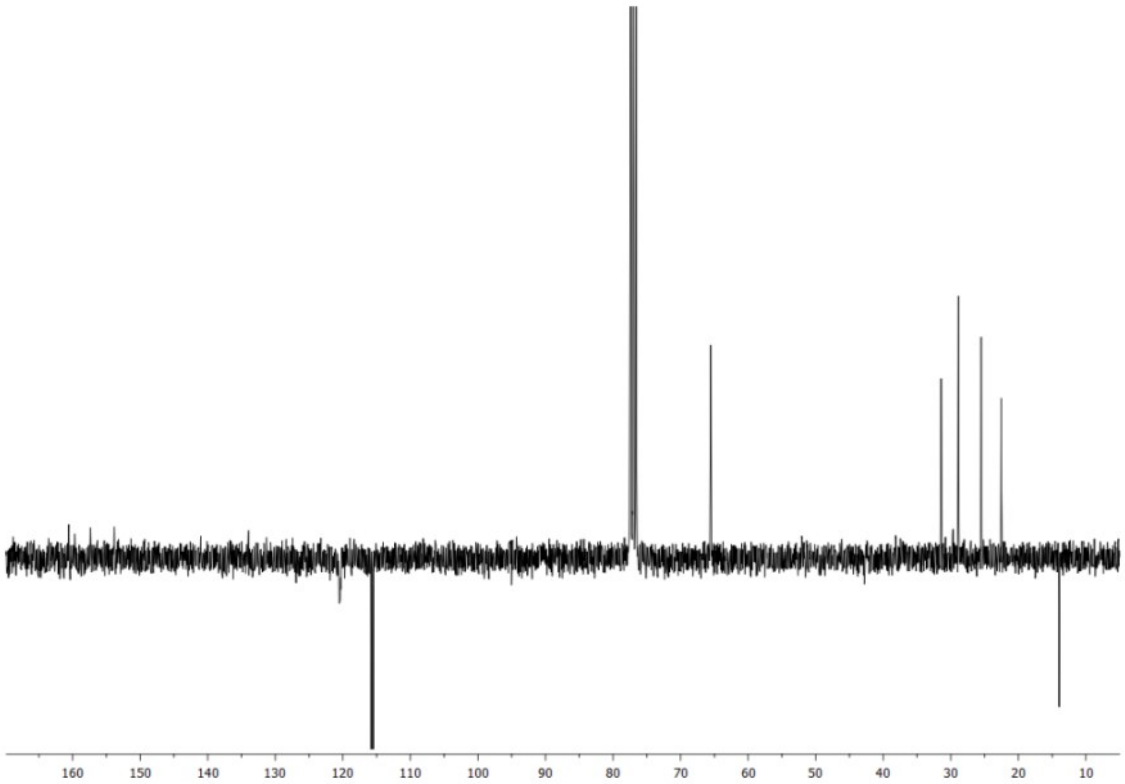


- Hexyl (4-fluorophenyl)carbamate (**2b**)

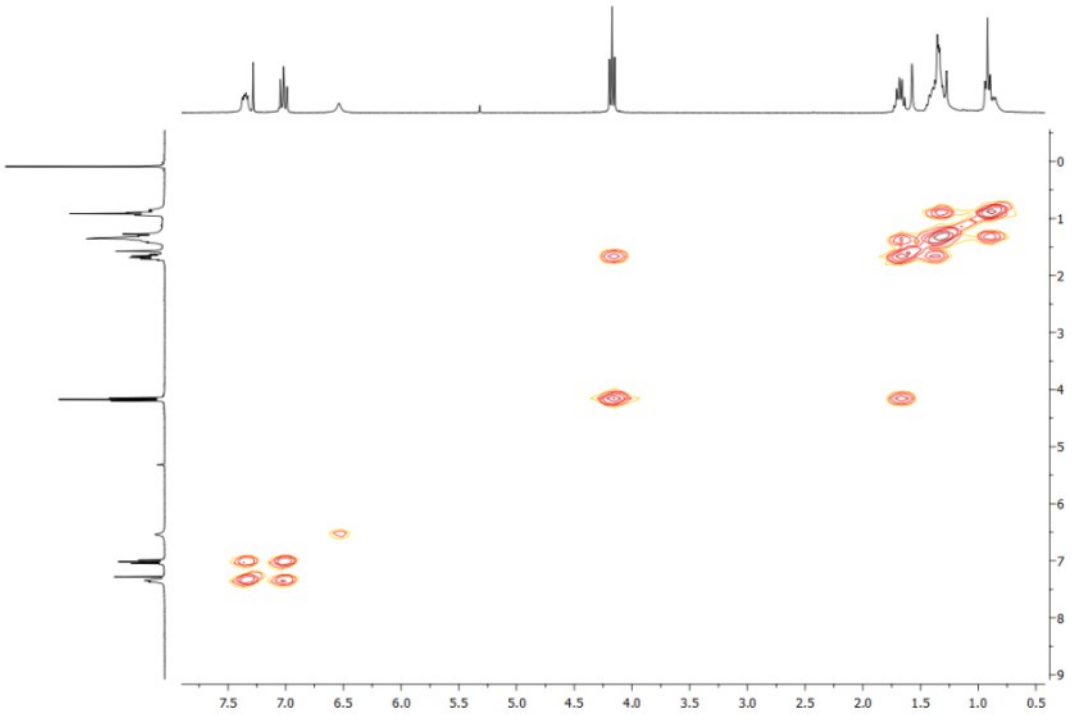
^{1}H NMR



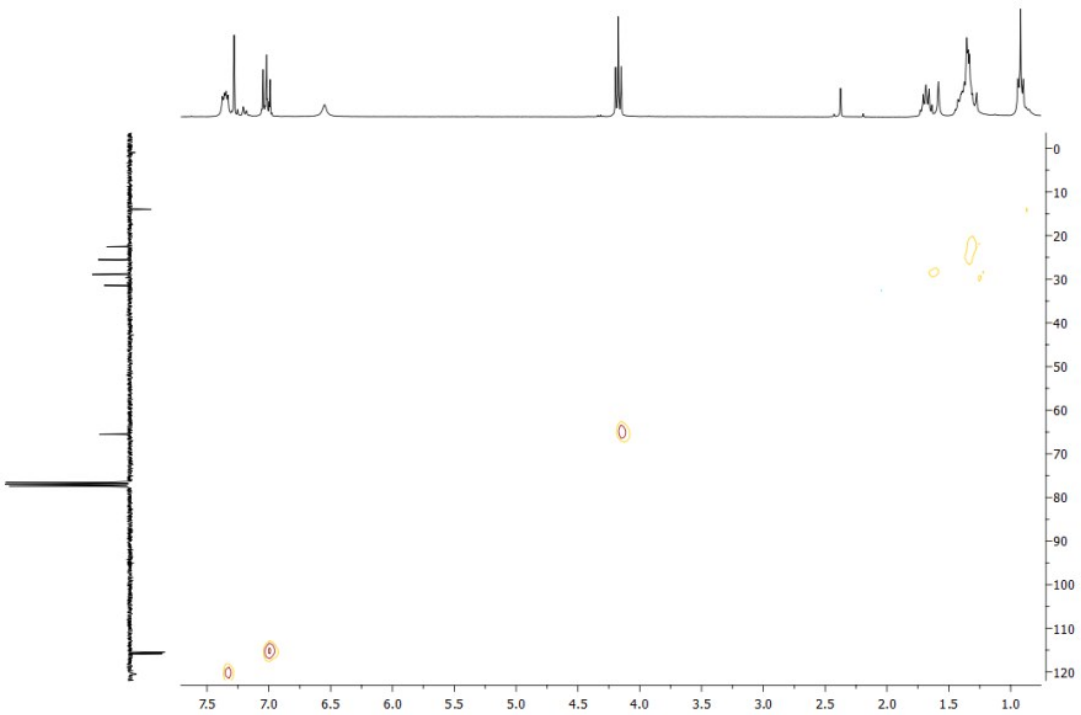
^{13}C NMR (APT)



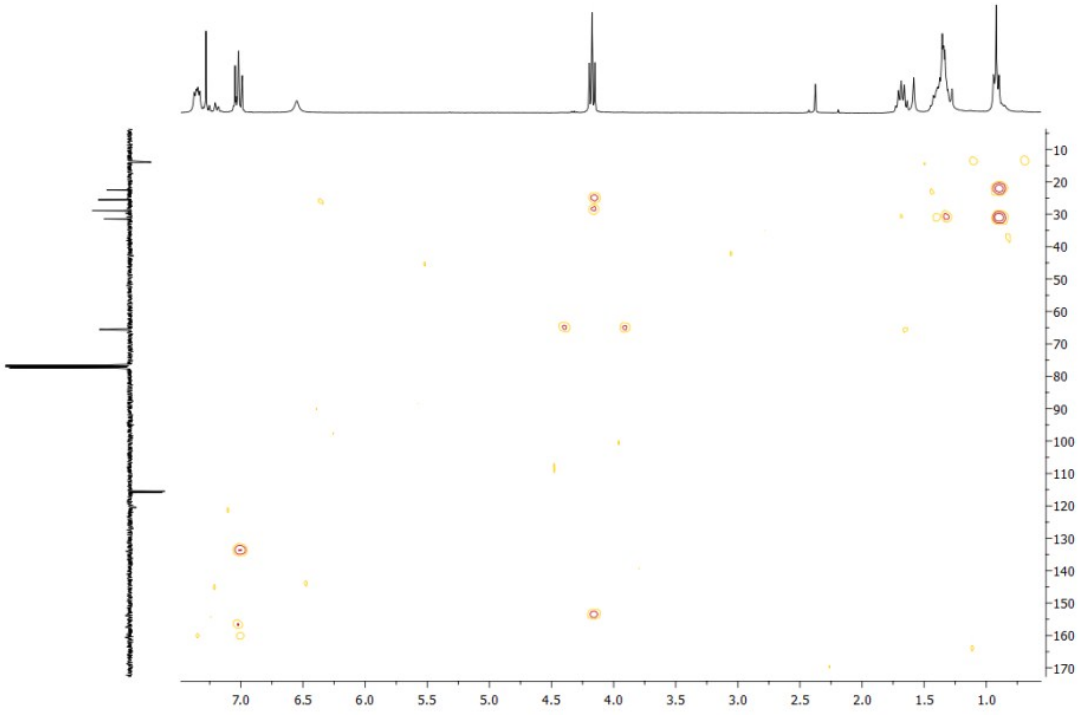
^{1}H-^{1}H COSY NMR



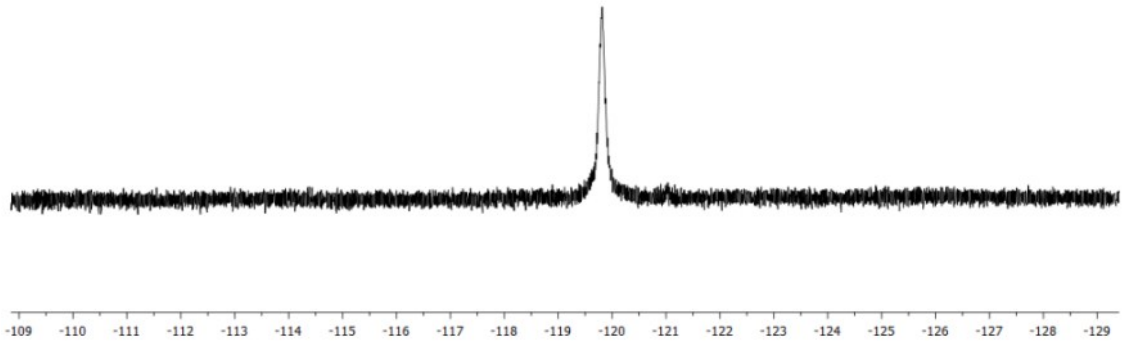
^{1}H-^{13}C HSQC NMR



^{1}H-^{13}C HMBC NMR

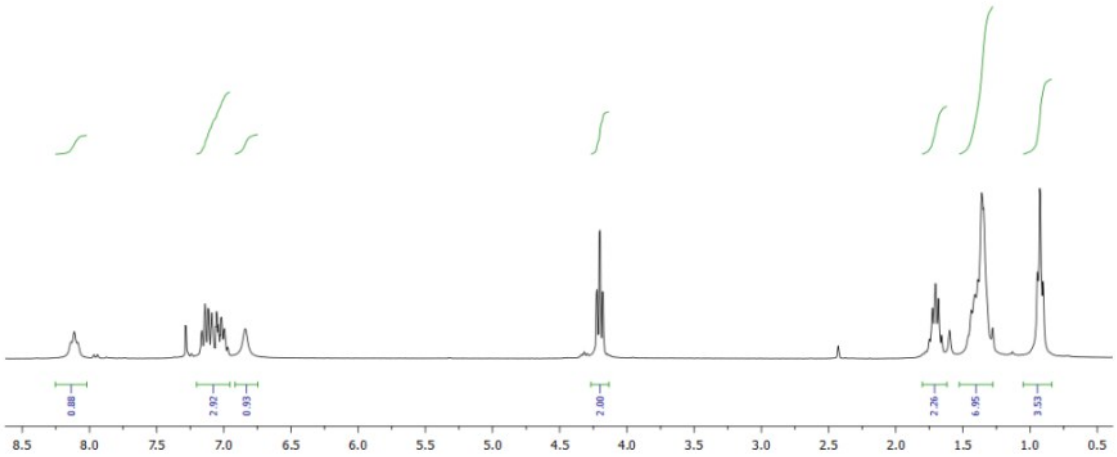


^{19}F NMR

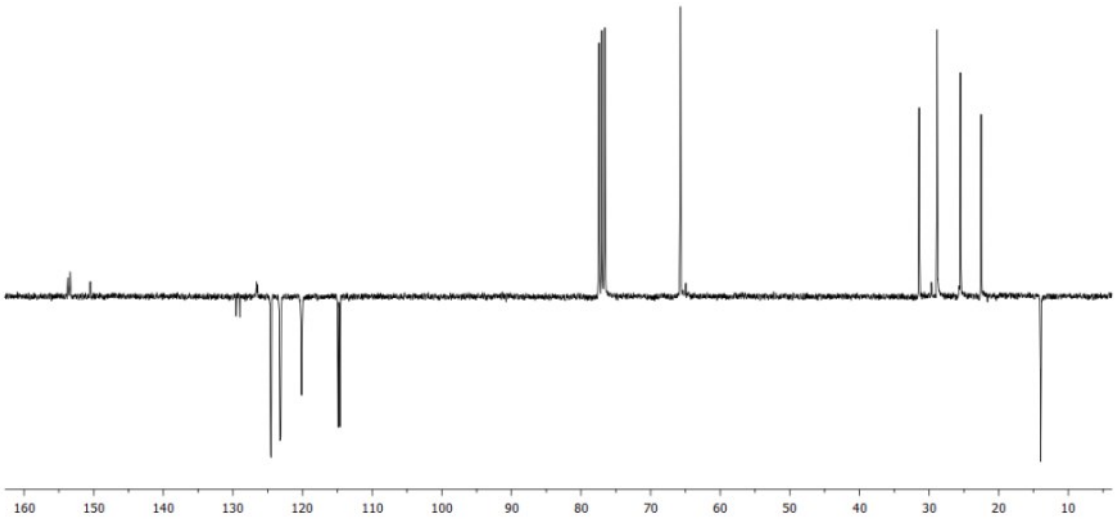


- Hexyl (2-fluorophenyl)carbamate (**2c**)

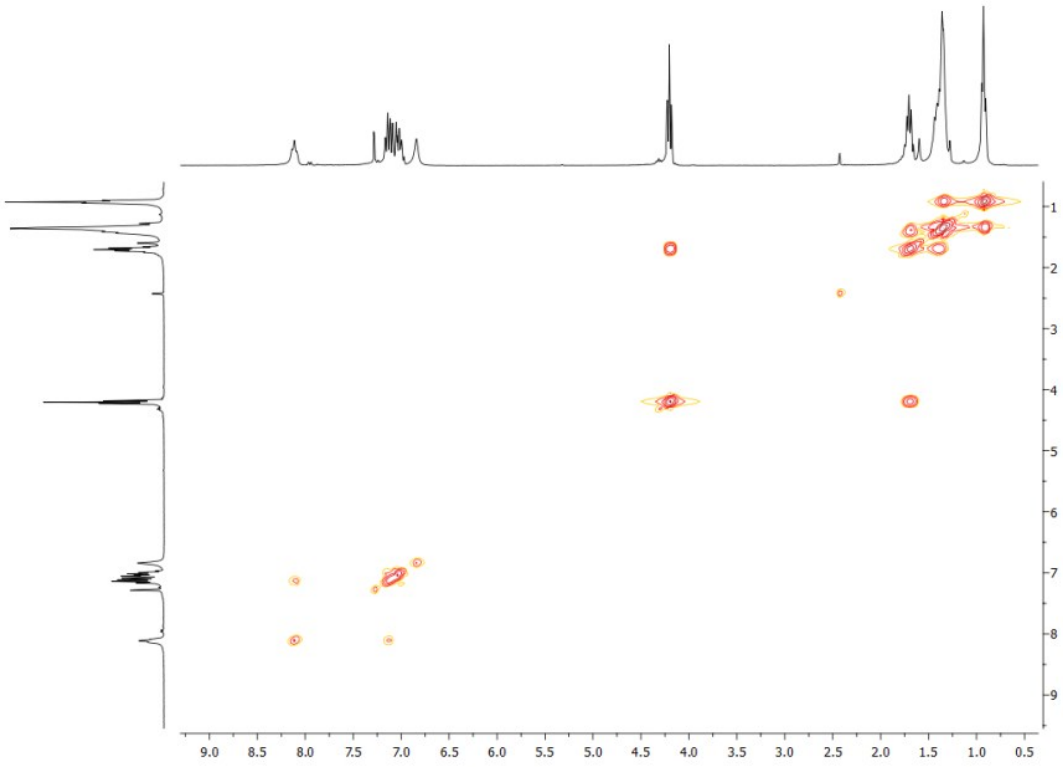
^{1}H NMR



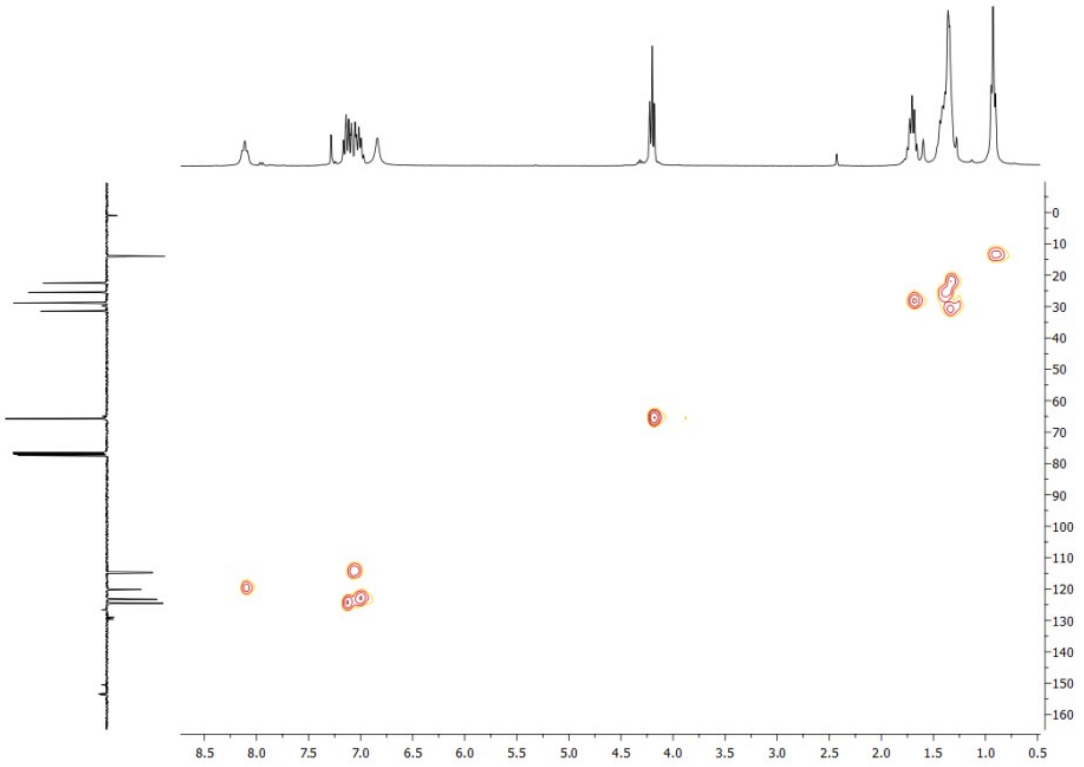
^{13}C NMR (APT)



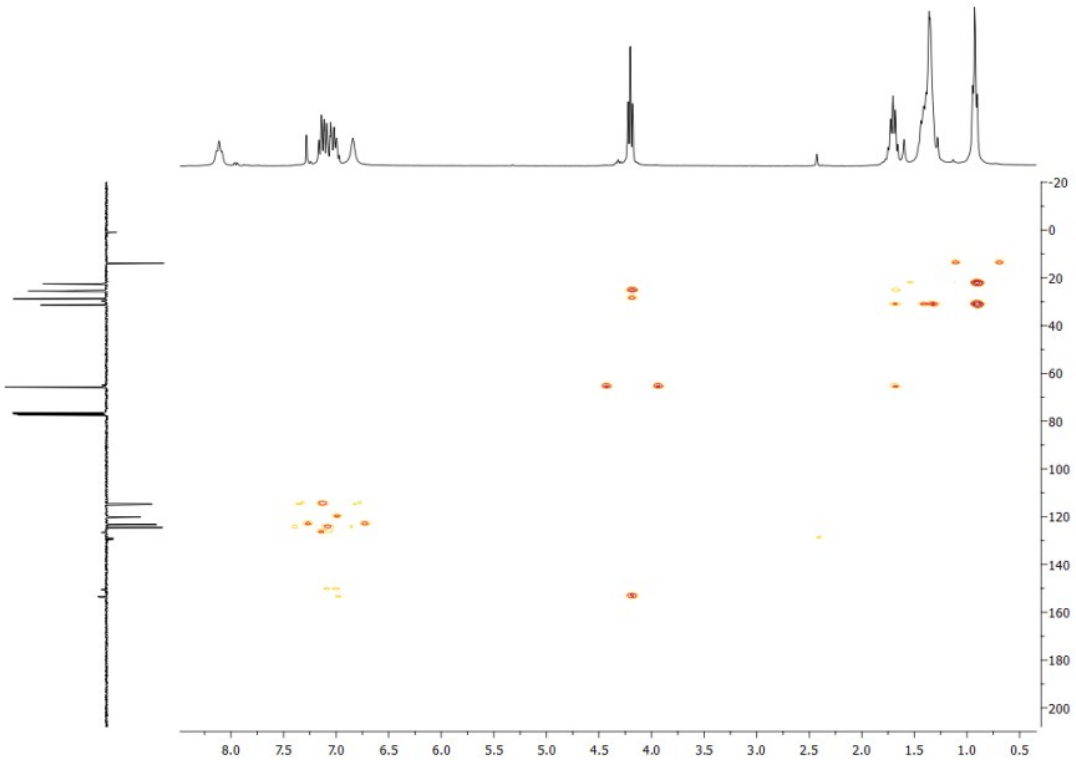
^{1}H-^{1}H COSY NMR



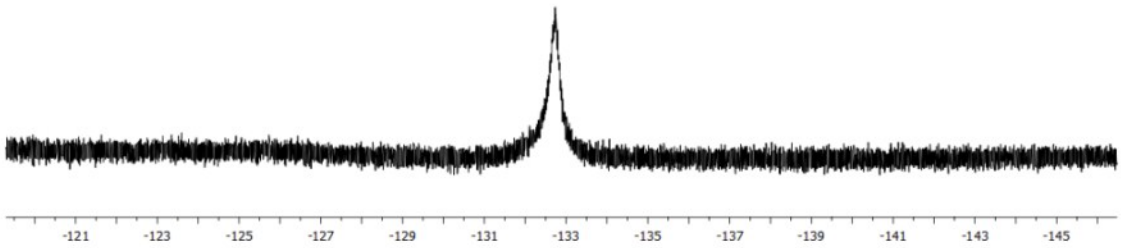
^{1}H-^{13}C HSQC NMR



^{1}H-^{13}C HMBC NMR

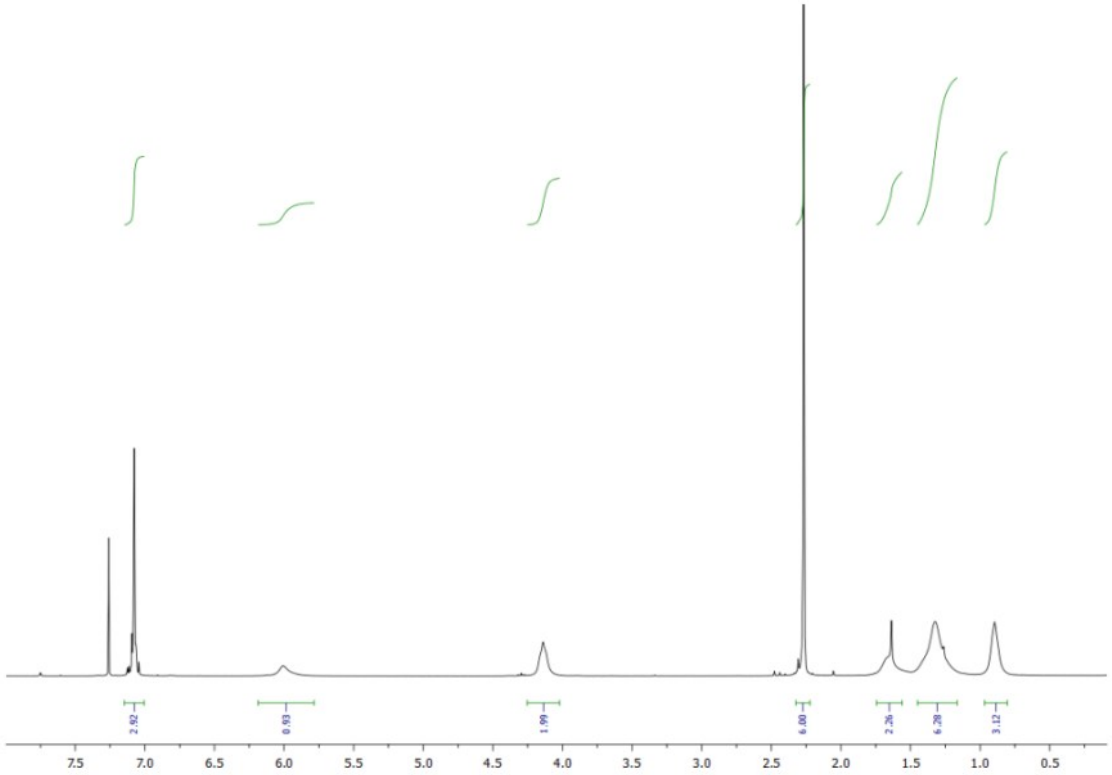

-20
0
20
40
60
80
100
120
140
160
180
200
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

^{19}F NMR

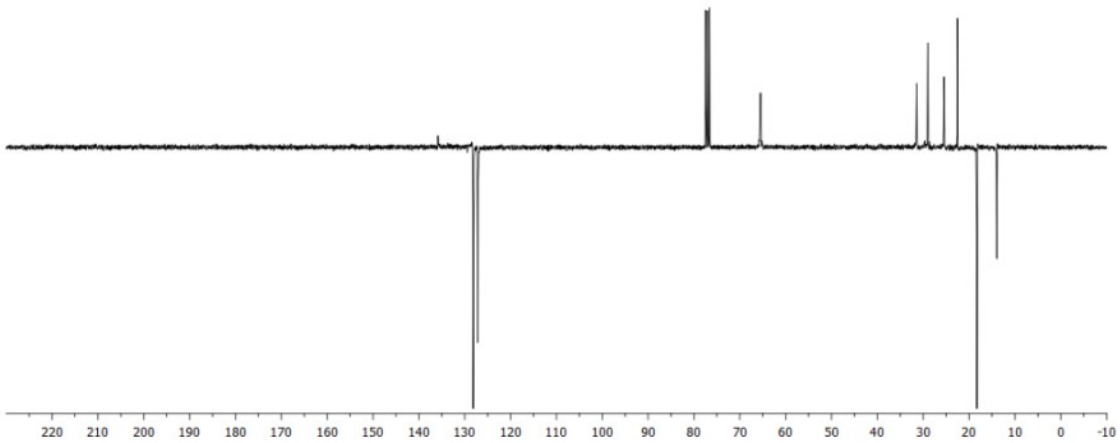

-121
-123
-125
-127
-129
-131
-133
-135
-137
-139
-141
-143
-145

- Hexyl (2,6-dimethylphenyl)carbamate (**2d**)

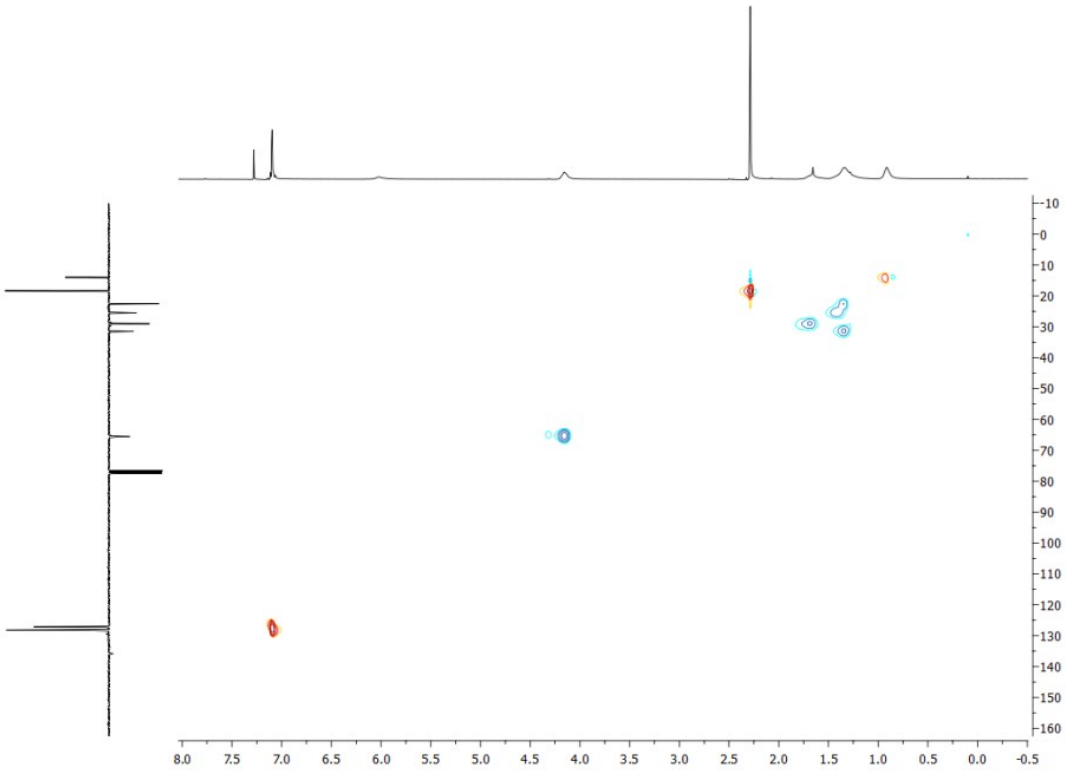
^{1}H NMR



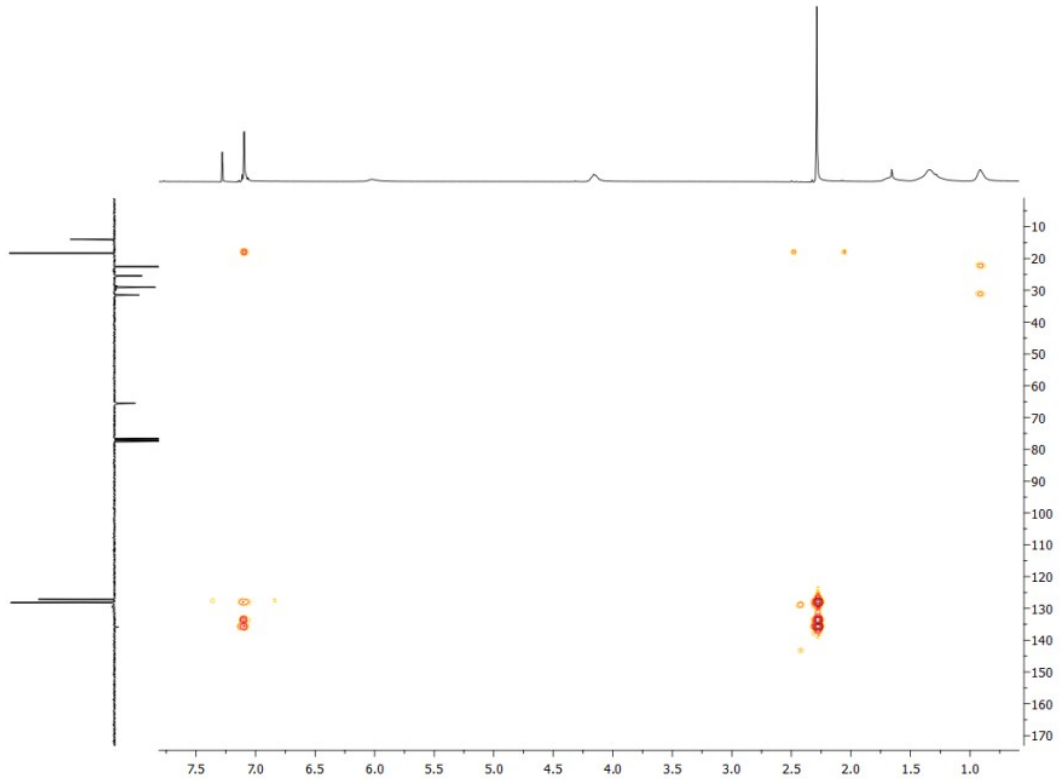
^{13}C NMR (APT)



^{1}H-^{13}C HSQC NMR

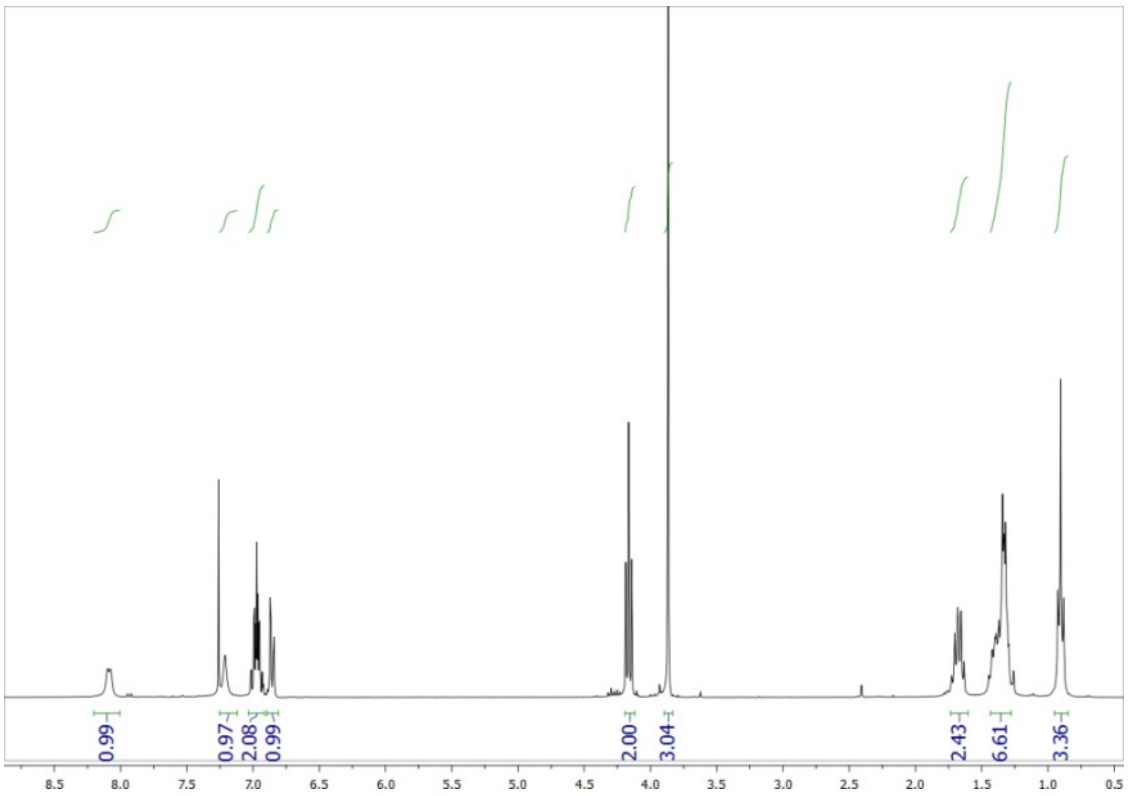


^{1}H-^{13}C HMBC NMR

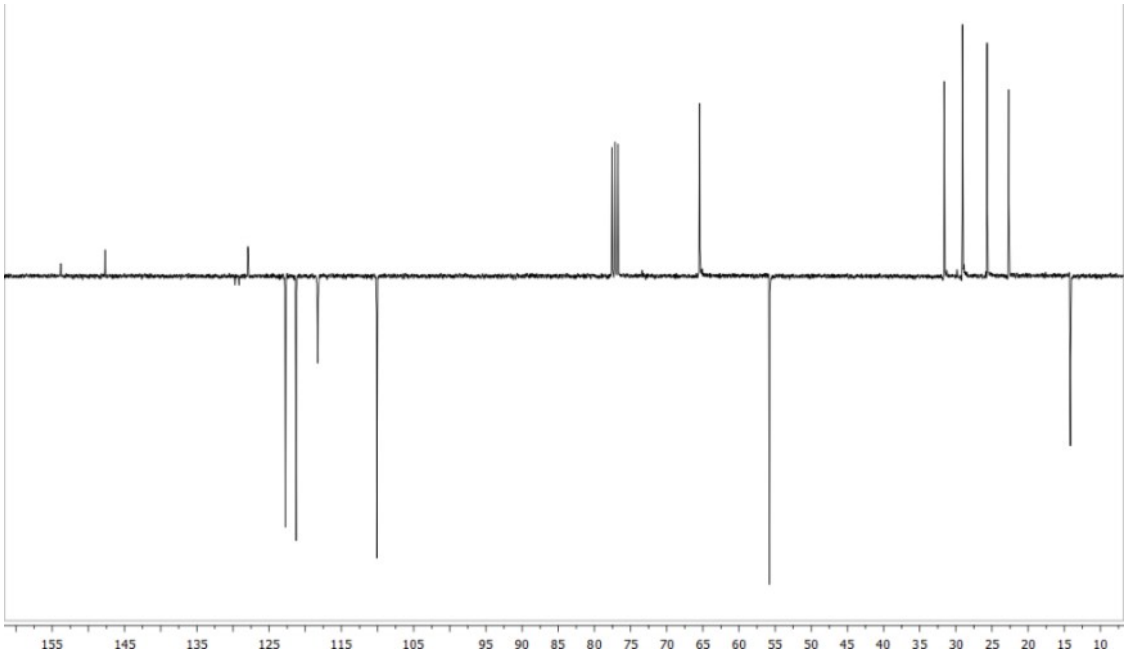


- Hexyl (2-methoxyphenyl)carbamate (**2e**)

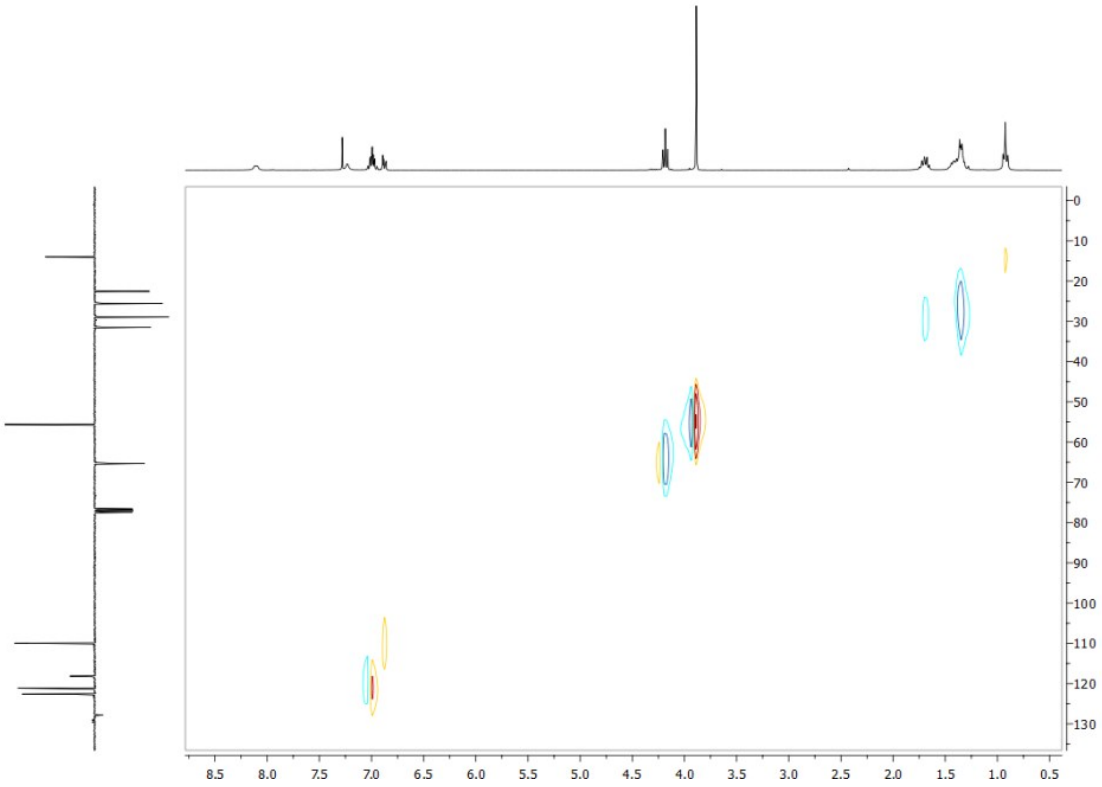
^{1}H NMR



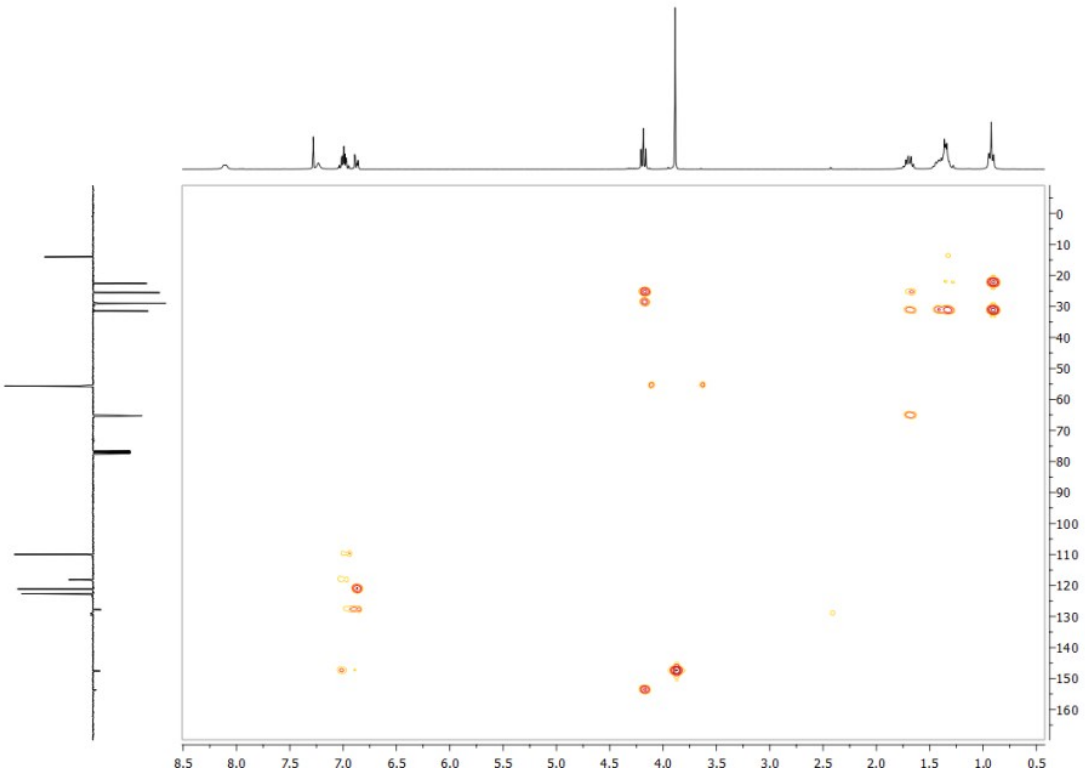
^{13}C NMR (APT)



^{1}H-^{13}C HSQC NMR

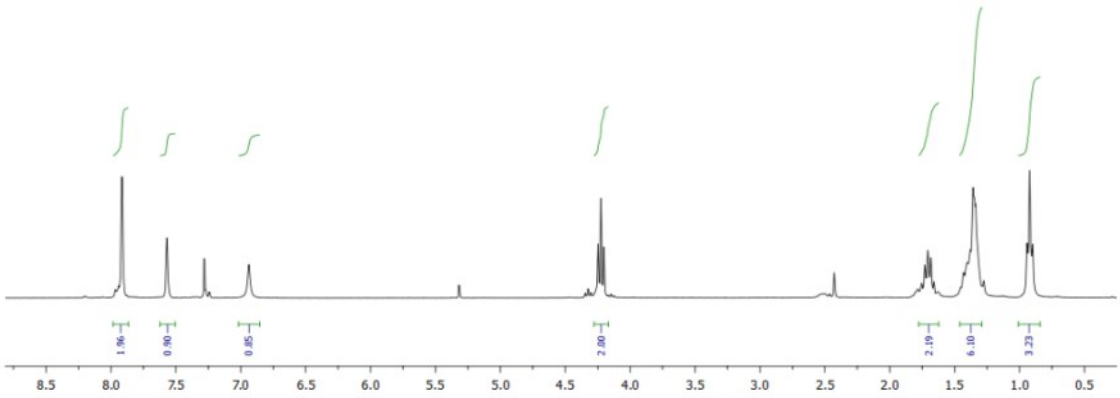


^{1}H-^{13}C HMBC NMR

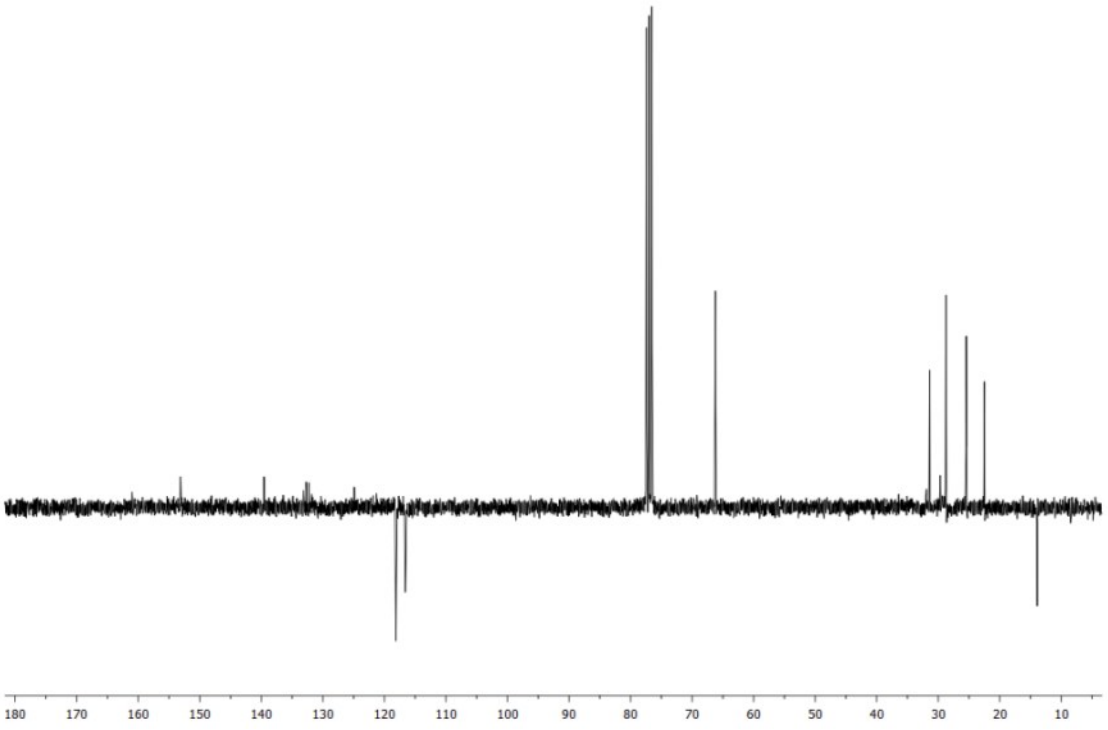


- Hexyl (3,5-bis(trifluoromethyl)phenyl)carbamate (**2f**)

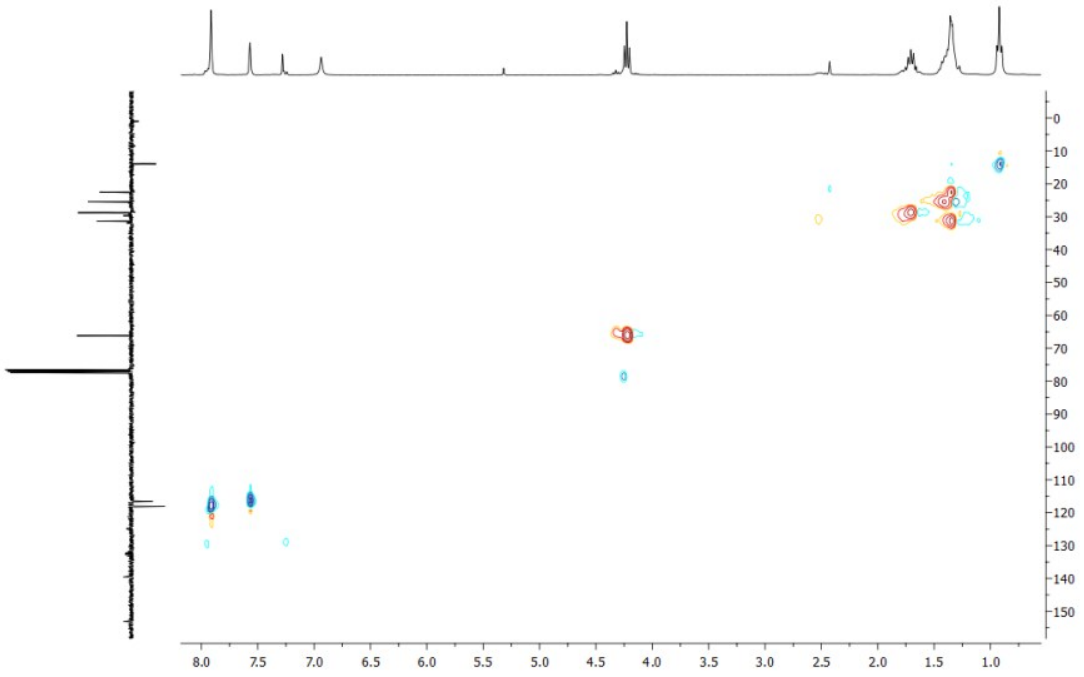
^{1}H NMR



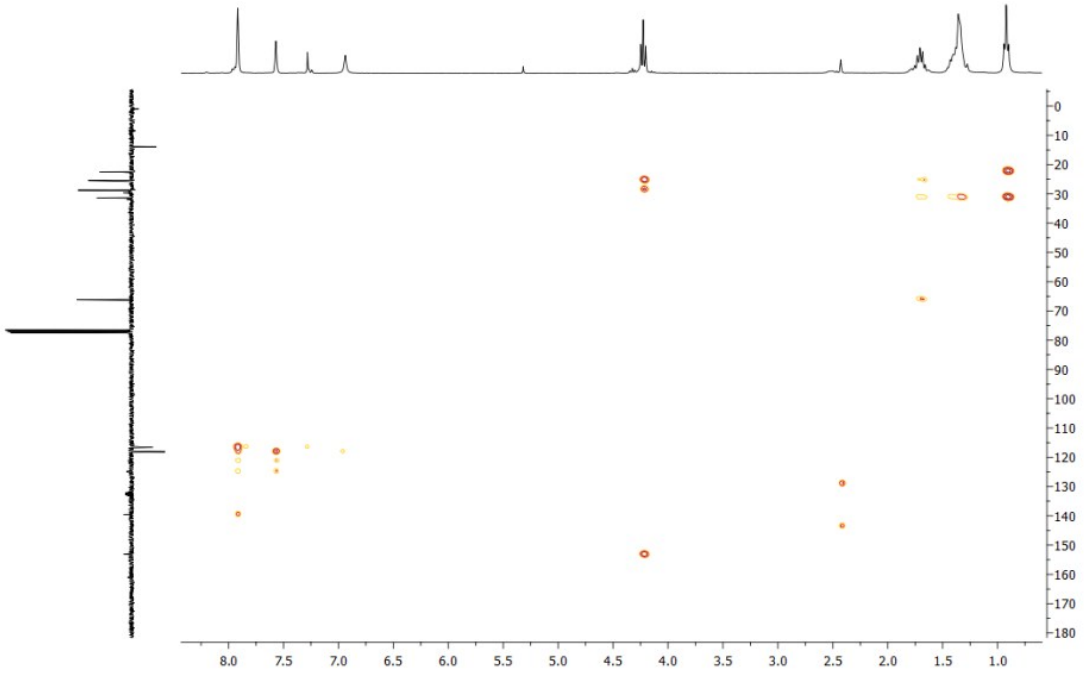
^{13}C NMR (APT)



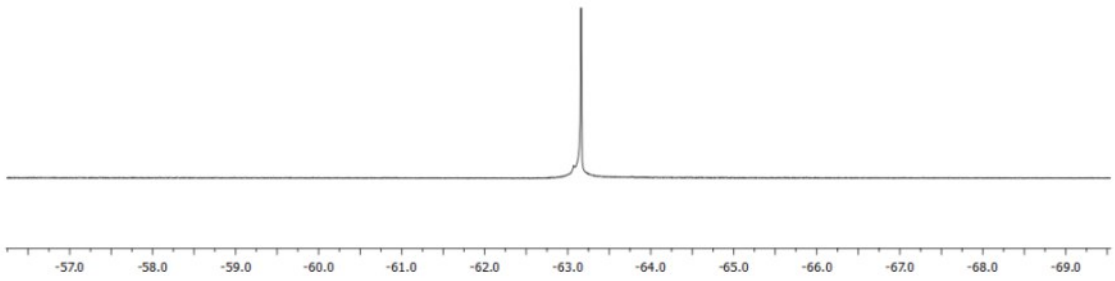
^{1}H-^{13}C HSQC NMR



^{1}H-^{13}C HMBC NMR

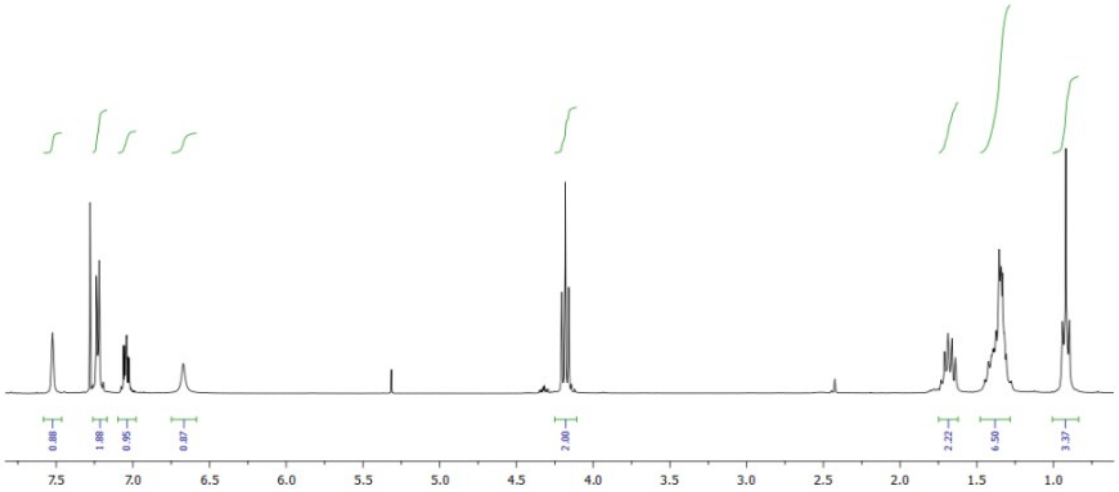


^{19}F NMR

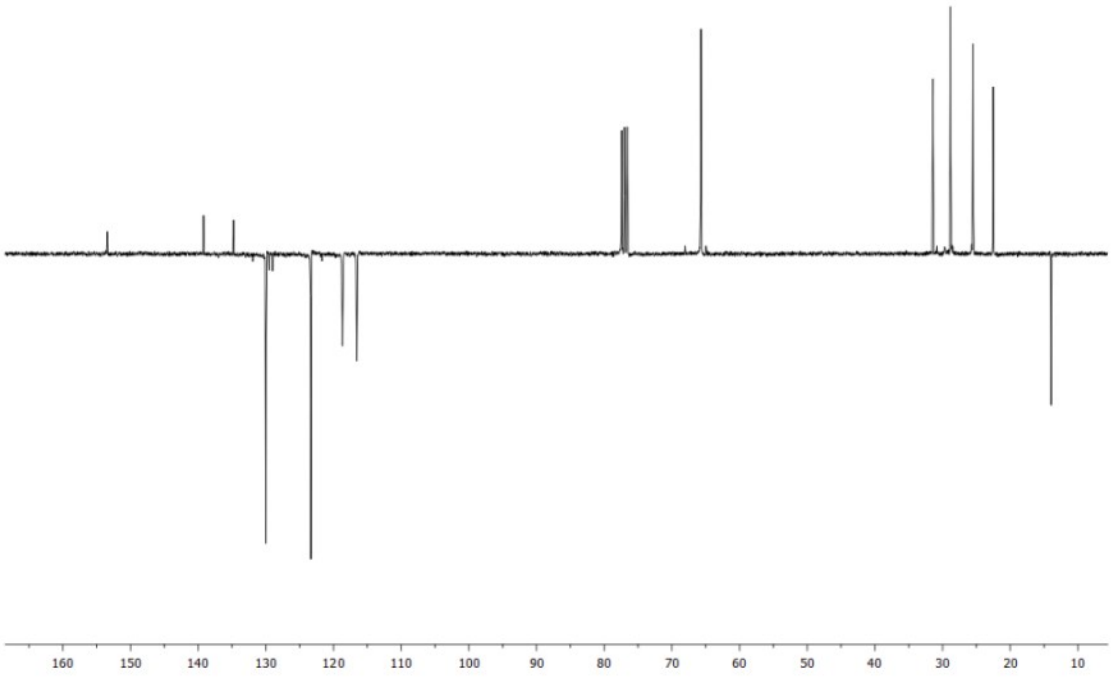


- Hexyl (3-chlorophenyl)carbamate (**2g**)

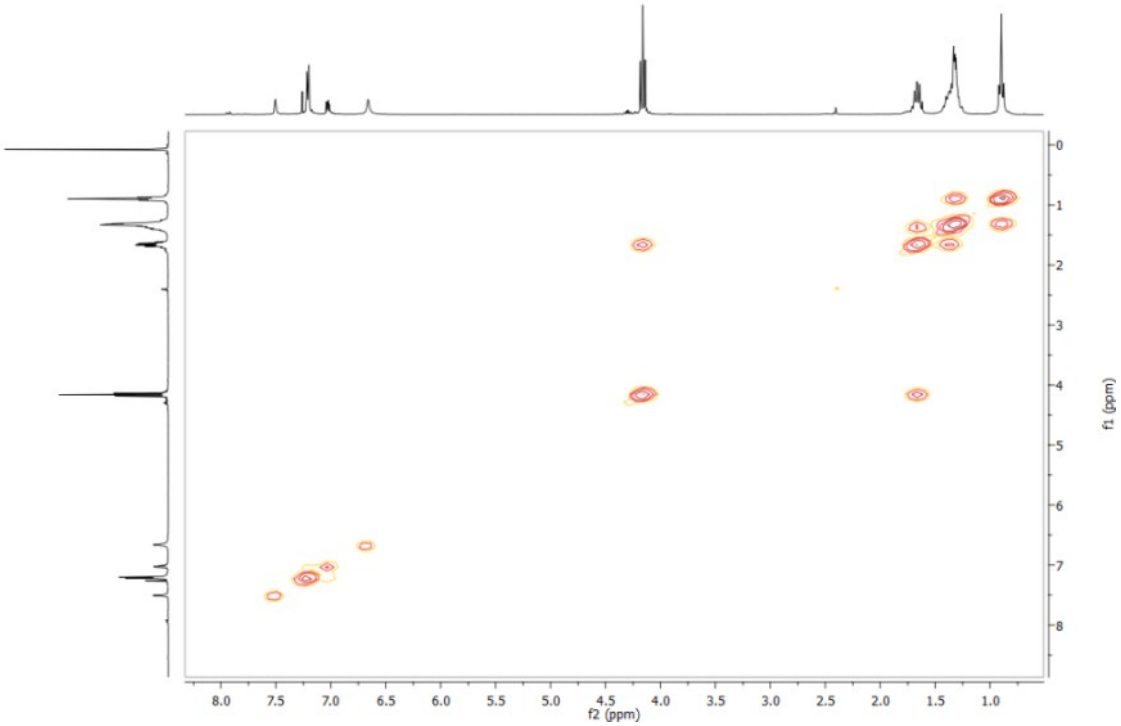
^{1}H NMR



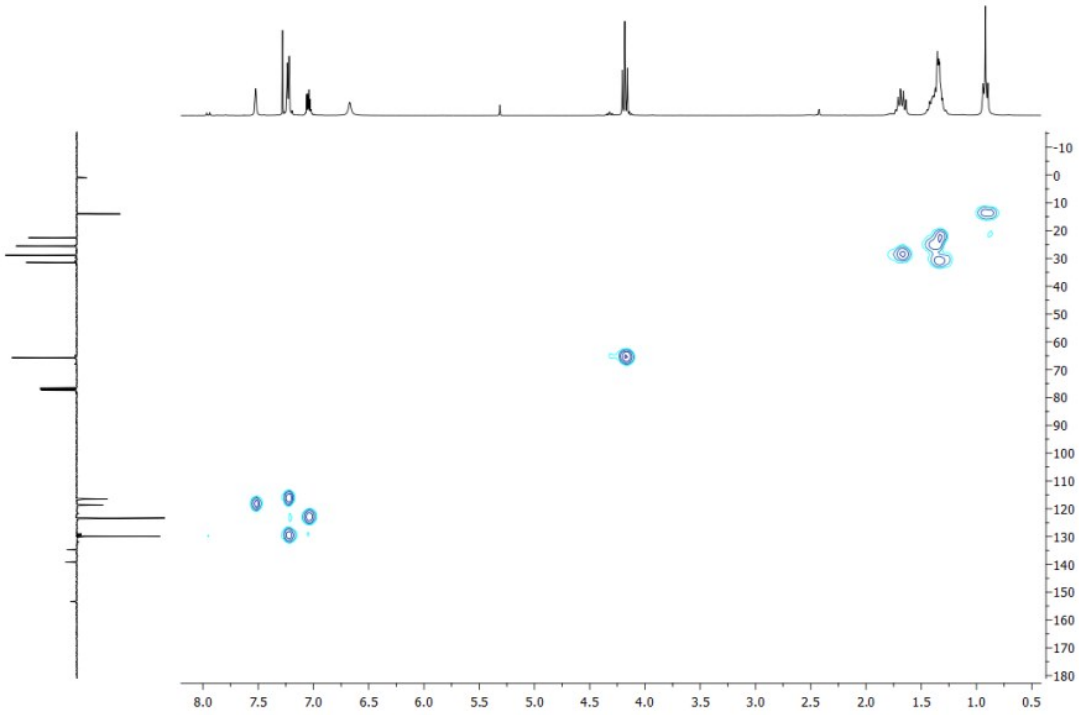
^{13}C NMR (APT)



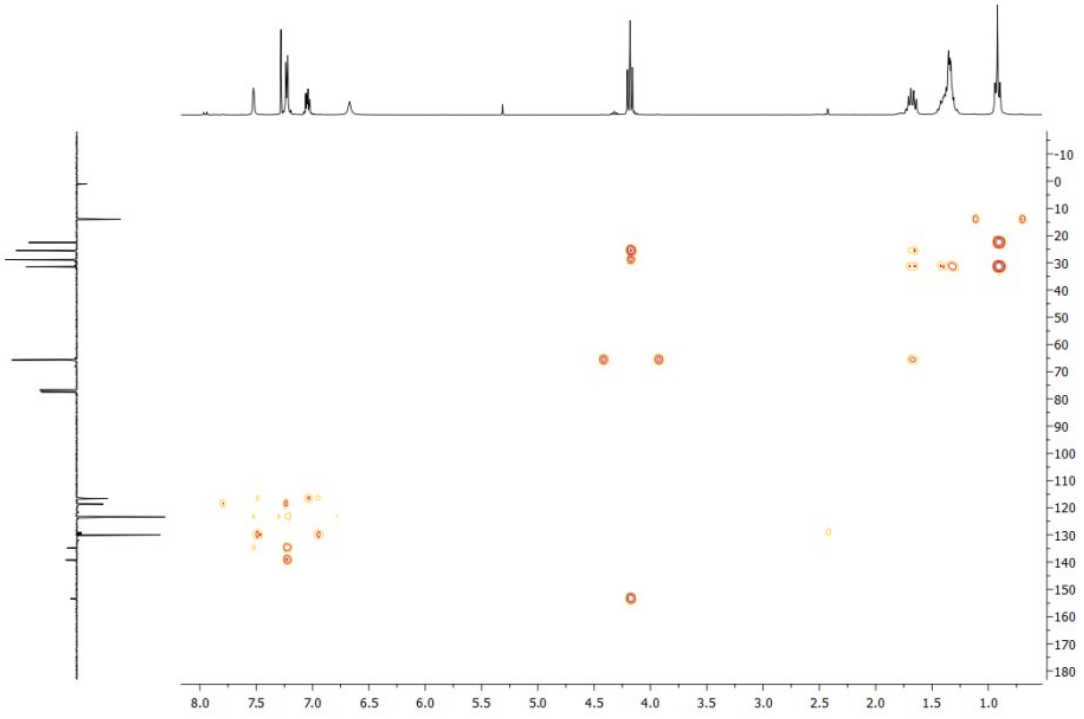
^{1}H-^{1}H COSY NMR



^{1}H-^{13}C HSQC NMR

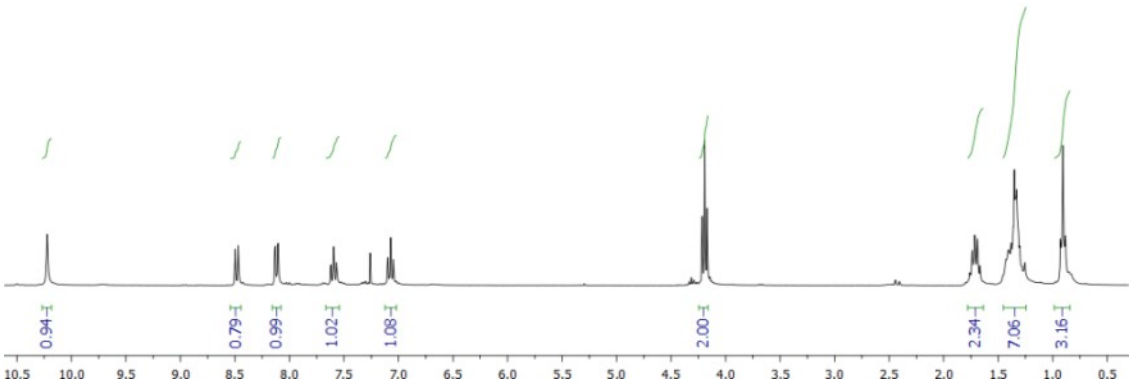


^{1}H-^{13}C HMBC NMR

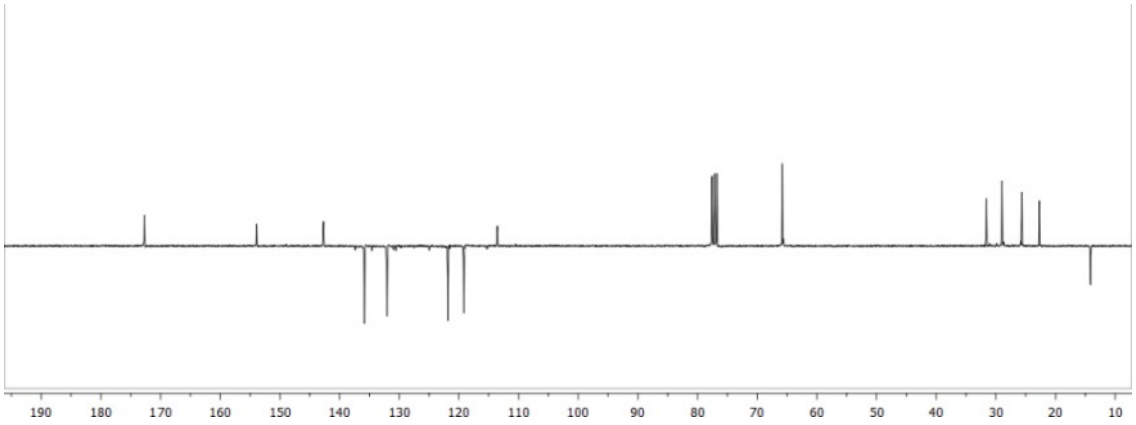


- 2-(((Hexyloxy)carbonyl)amino)benzoic acid (**2h**)

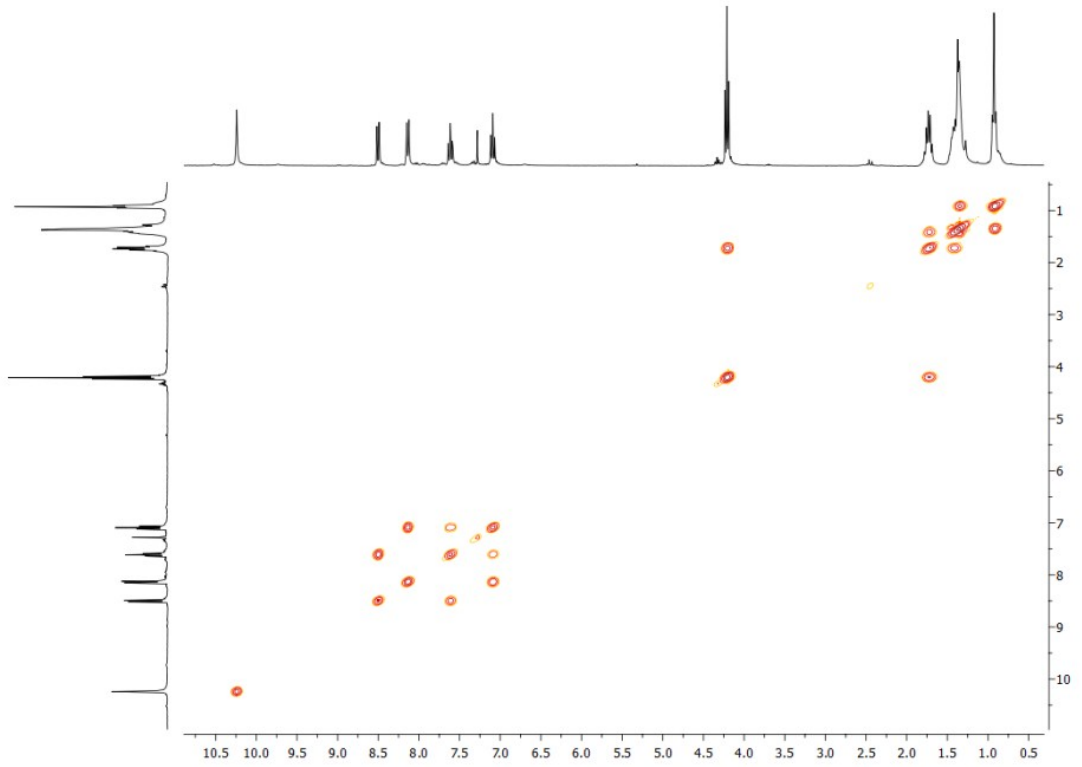
^{1}H NMR



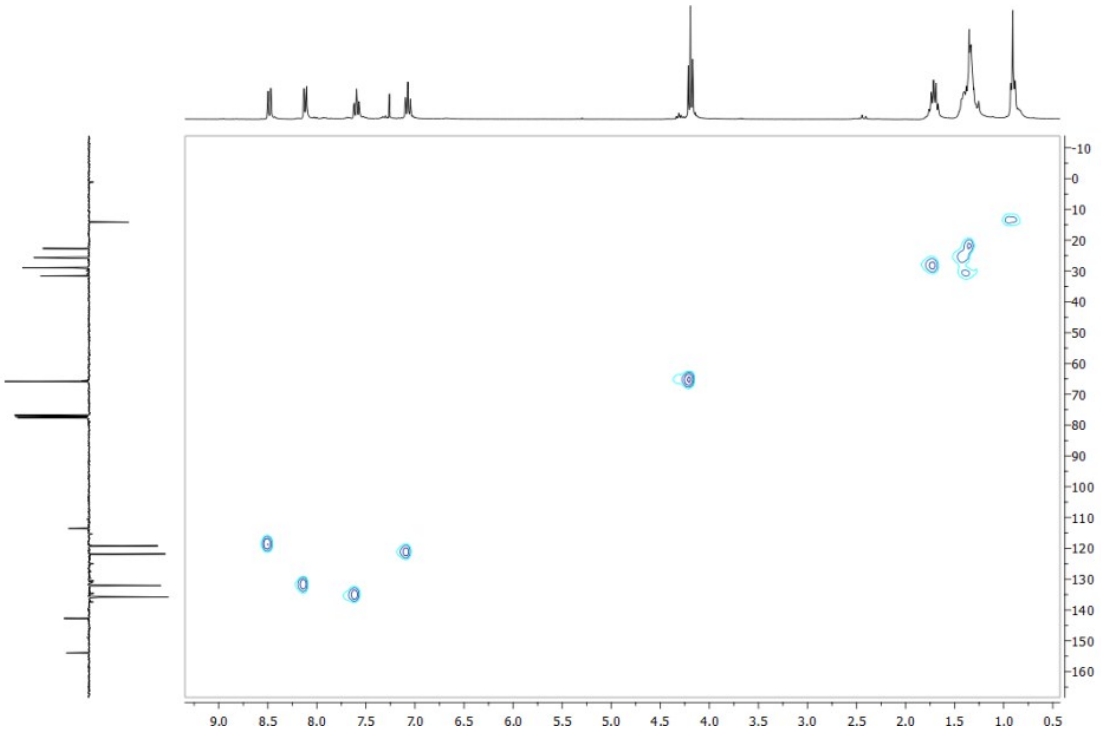
^{13}C NMR (APT)



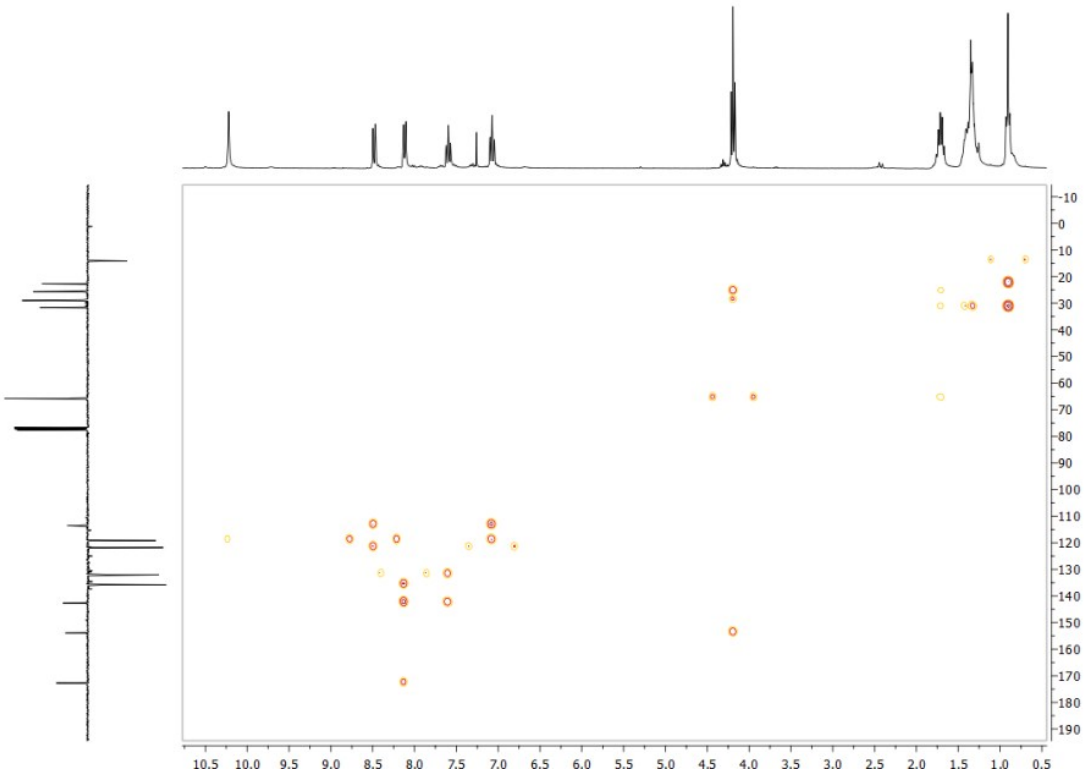
^{1}H-^{1}H COSY NMR



^{1}H-^{13}C HSQC NMR

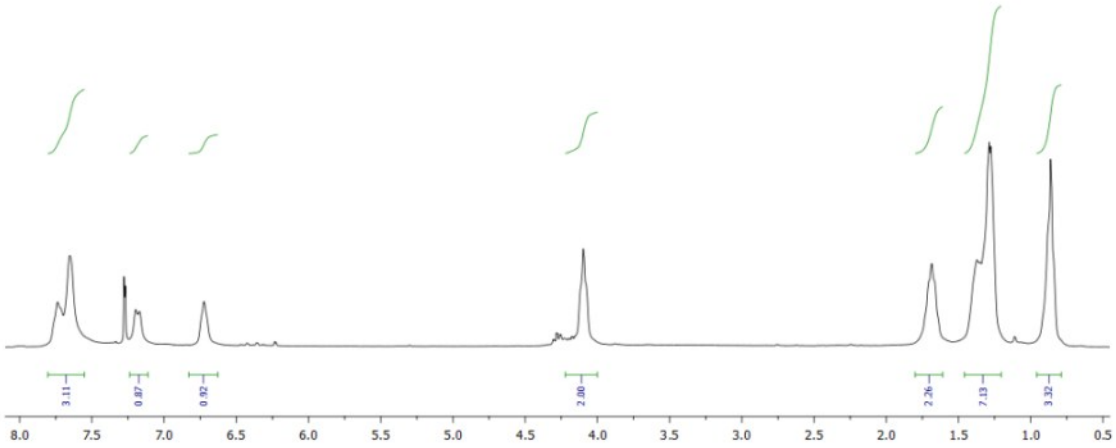


^{1}H-^{13}C HMBC NMR

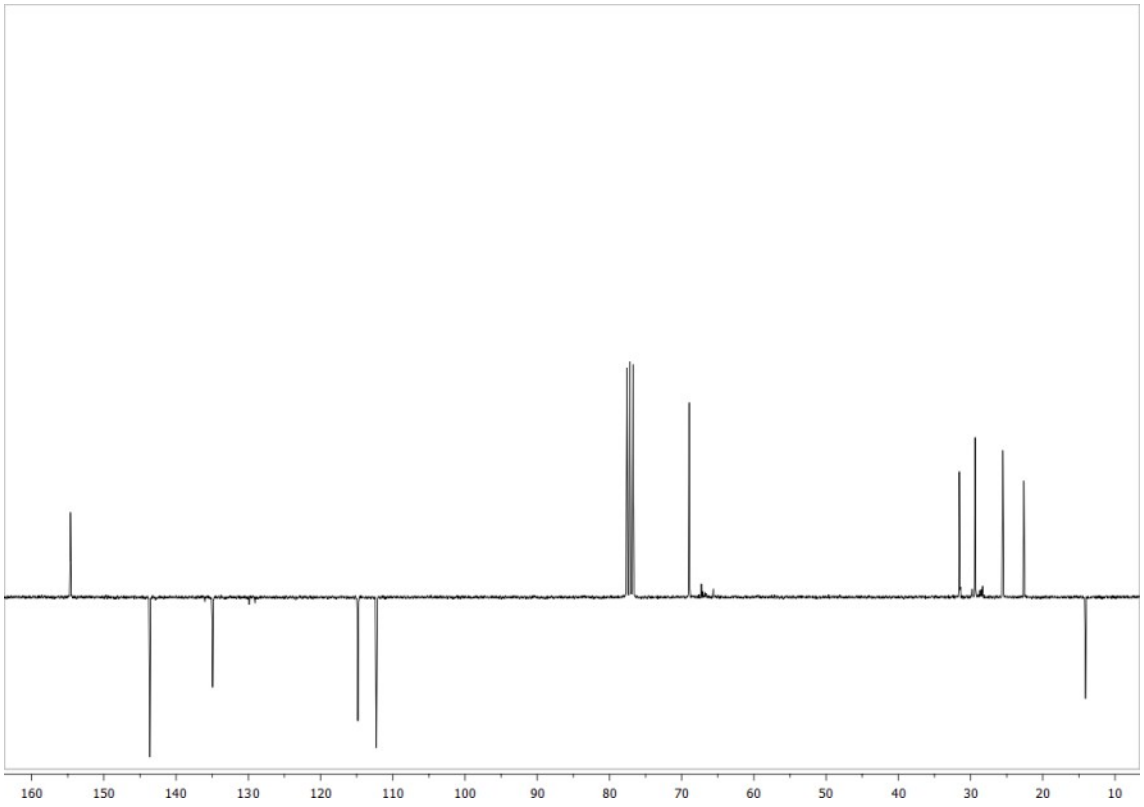


- Hexyl pyridin-2-ylcarbamate (**2i**)

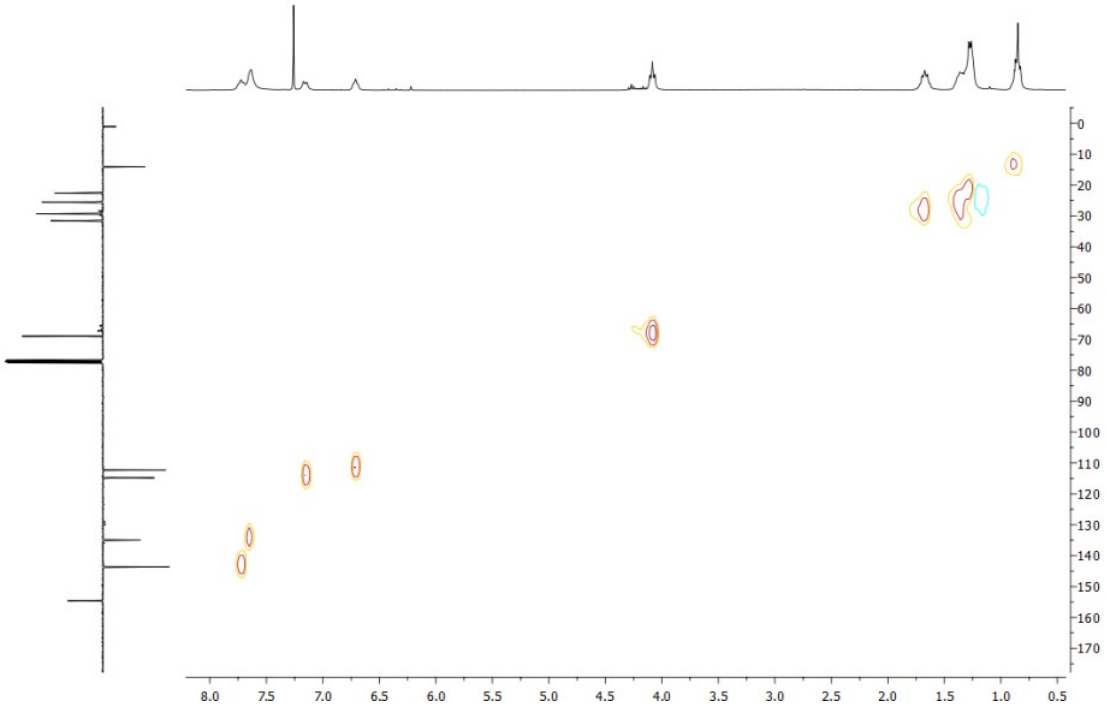
^{1}H NMR



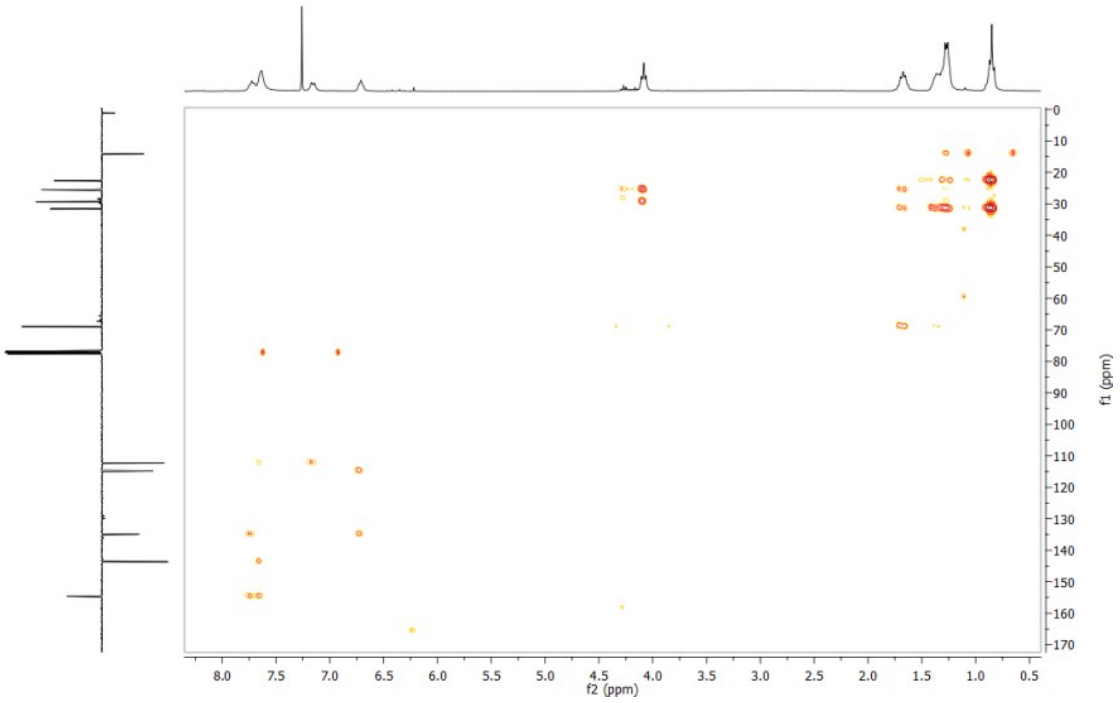
^{13}C NMR (APT)



^{1}H-^{13}C HSQC NMR

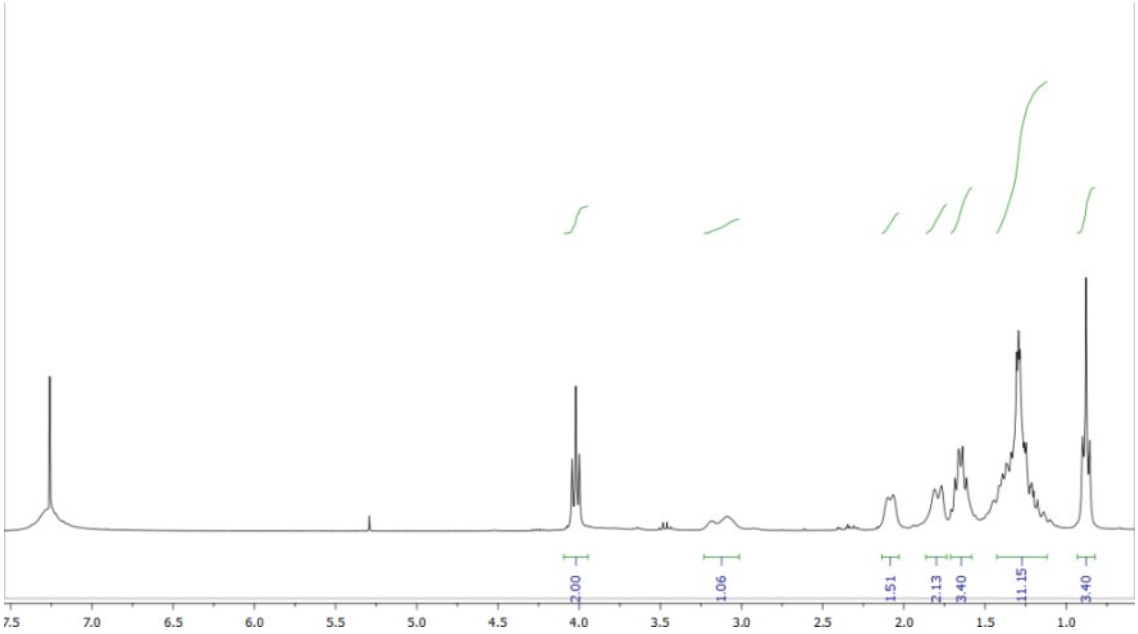


^{1}H-^{13}C HMBC NMR

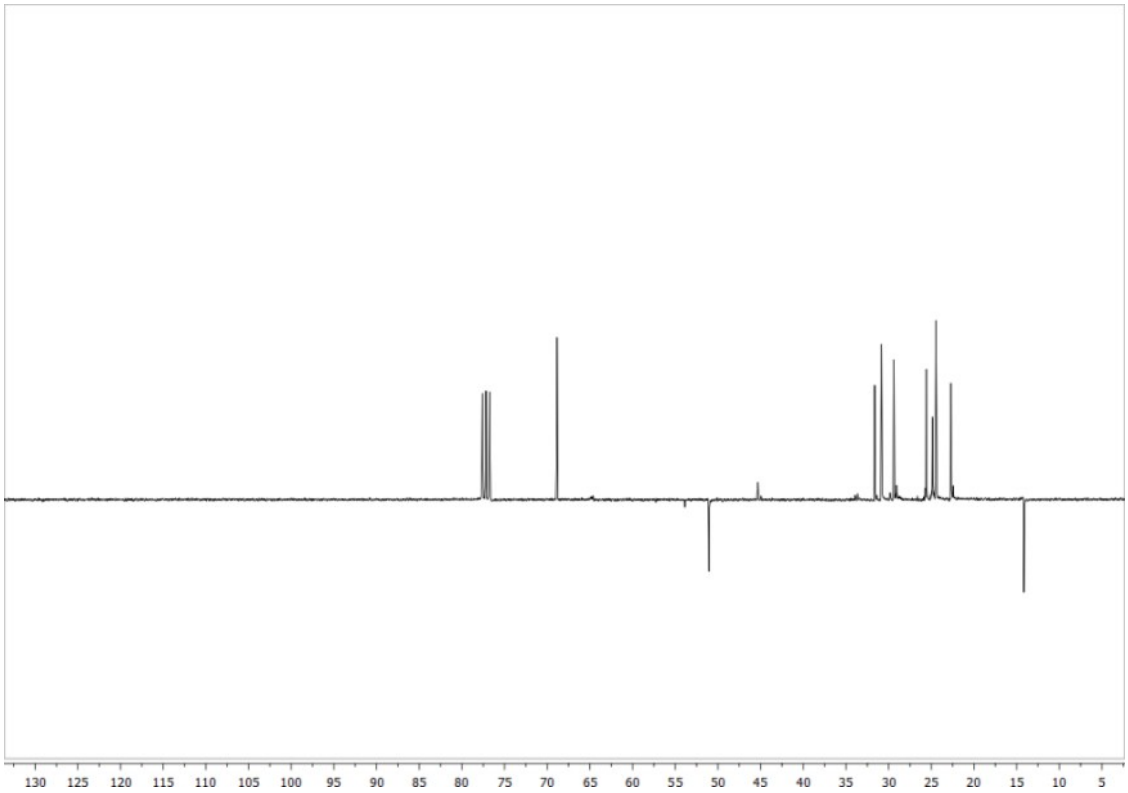


- Hexyl (cyclohexyl)carbamate (**2j**)

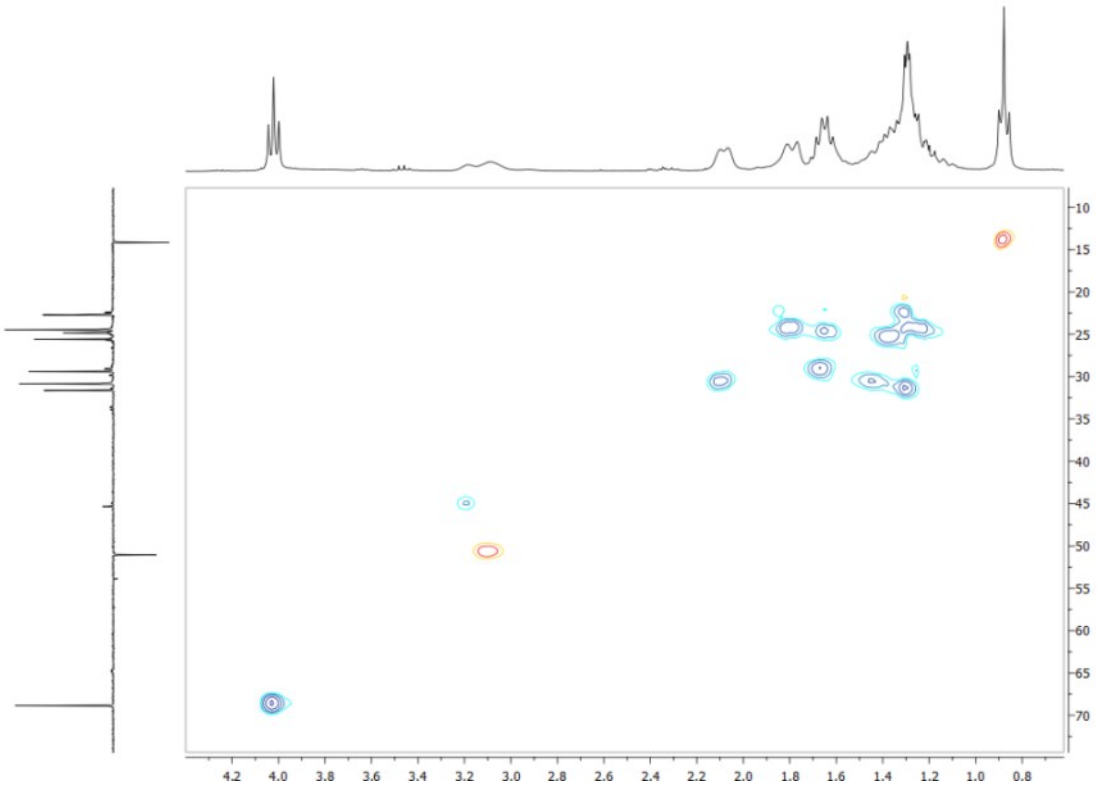
^{1}H NMR



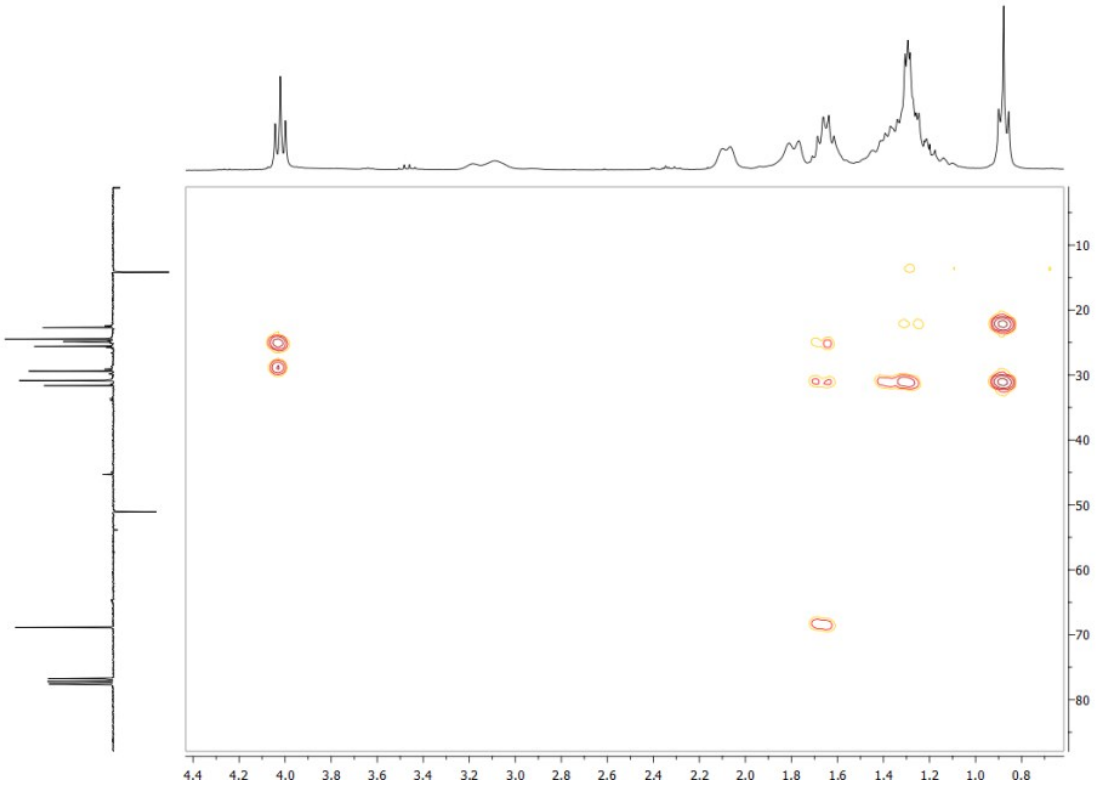
^{13}C NMR (APT)



^{1}H-^{13}C HSQC NMR

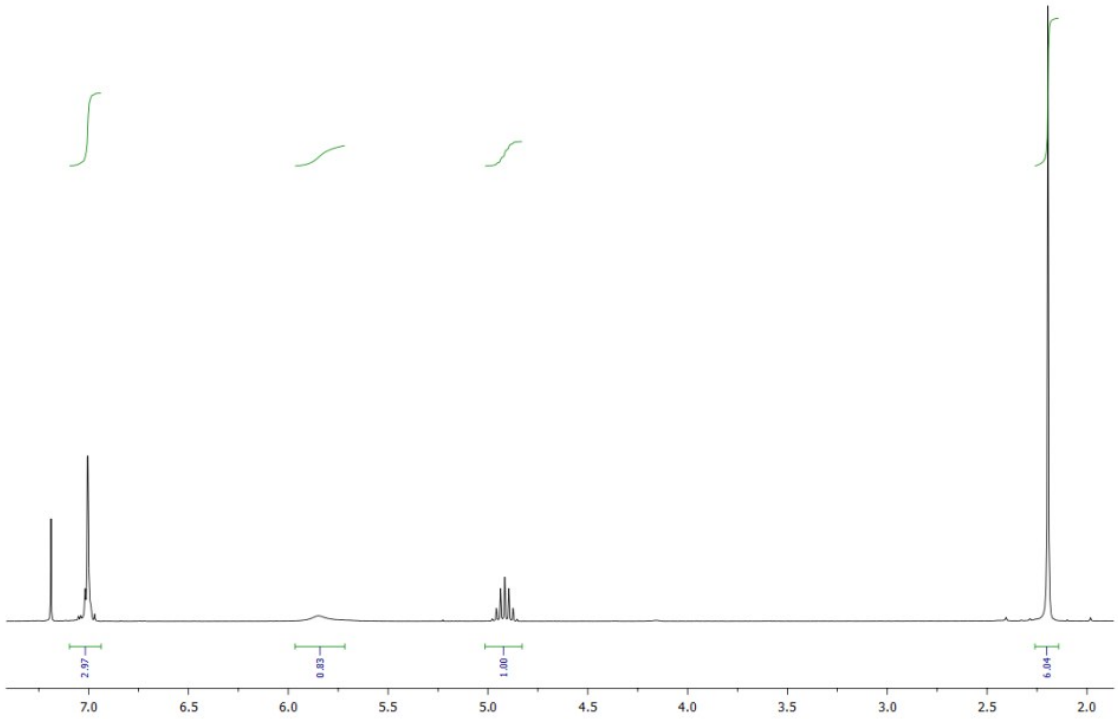


^{1}H-^{13}C HMBC NMR

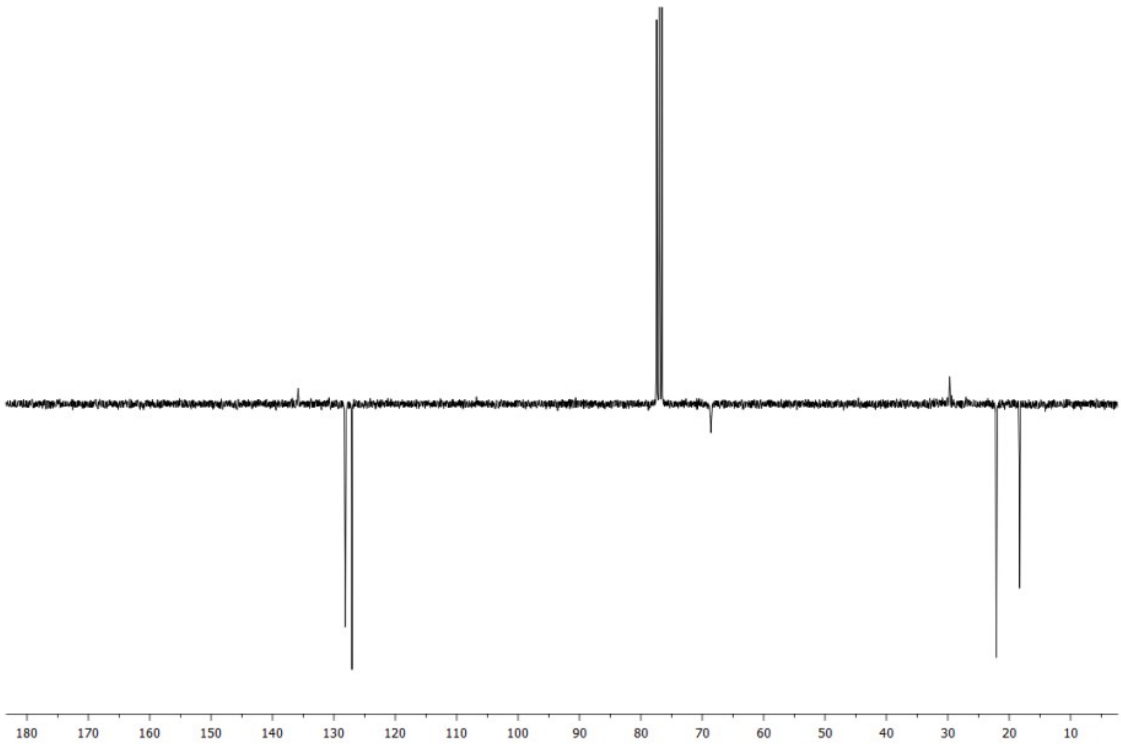


- Isopropyl (2,6-dimethylphenyl)carbamate (**3d**)

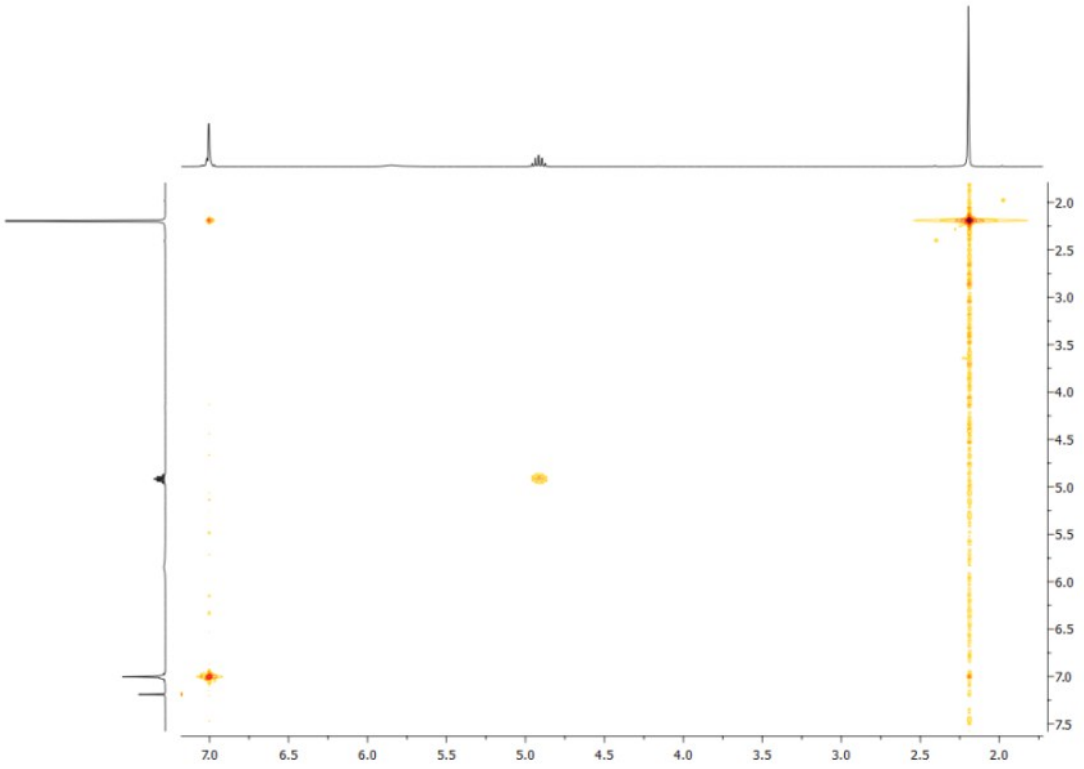
^{1}H NMR



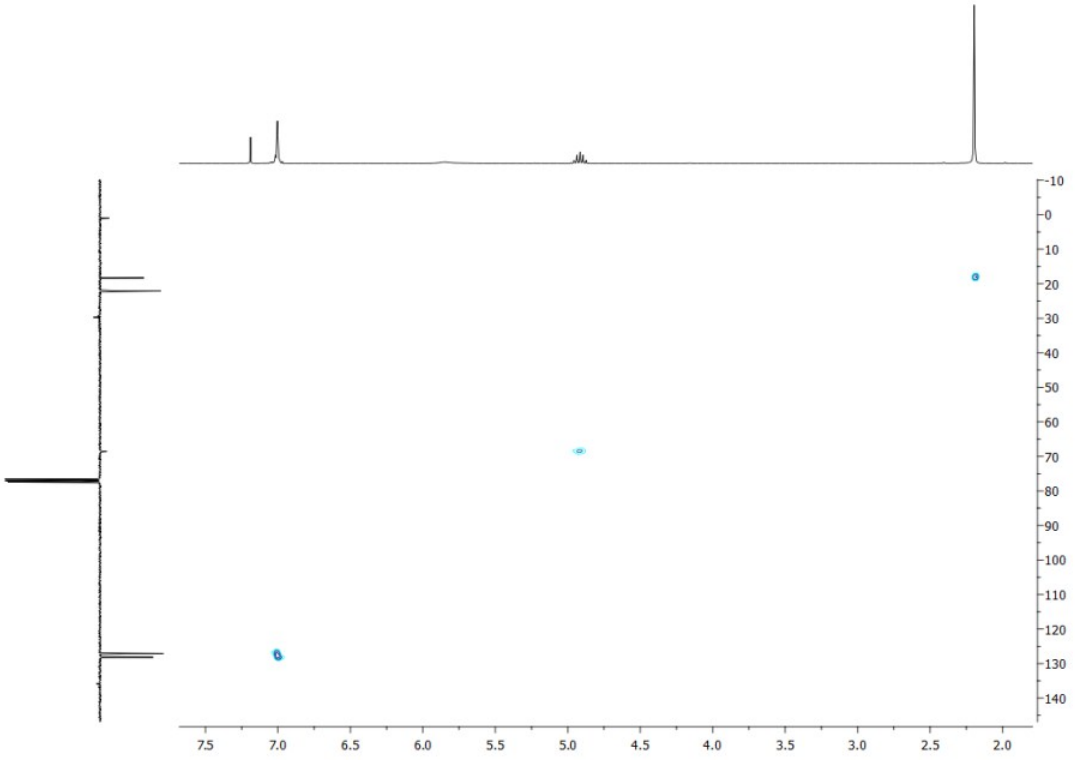
^{13}C NMR (APT)



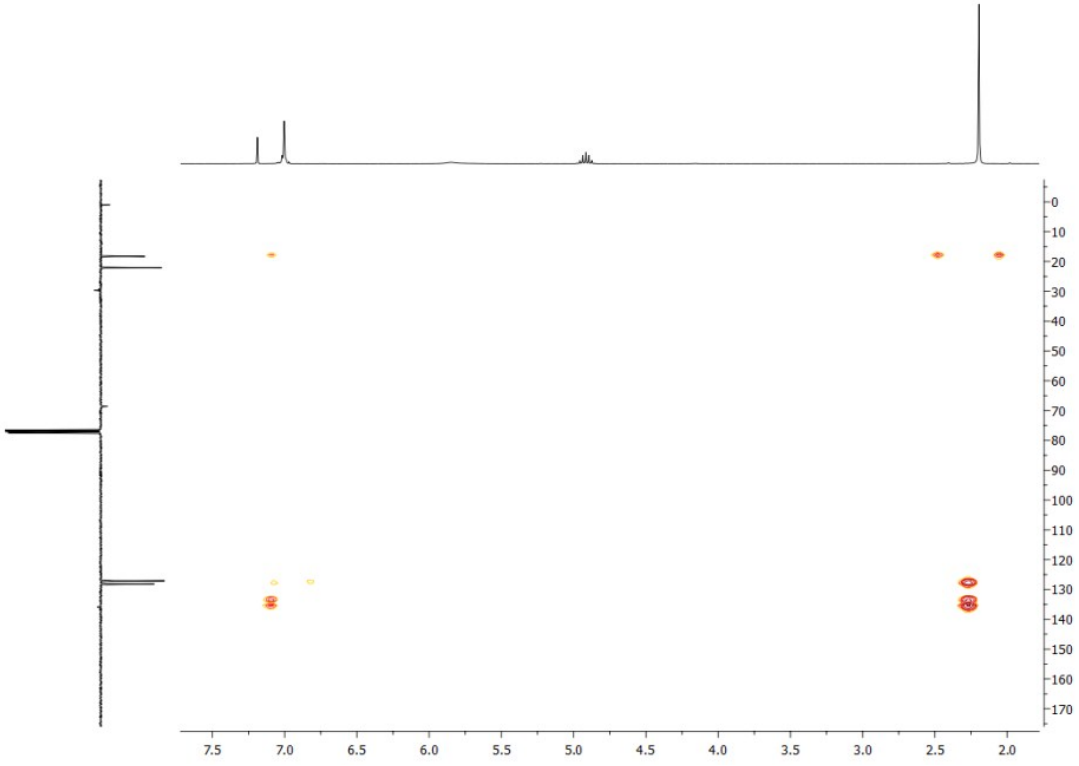
^{1}H-^{1}H COSY NMR



^{1}H-^{13}C HSQC NMR

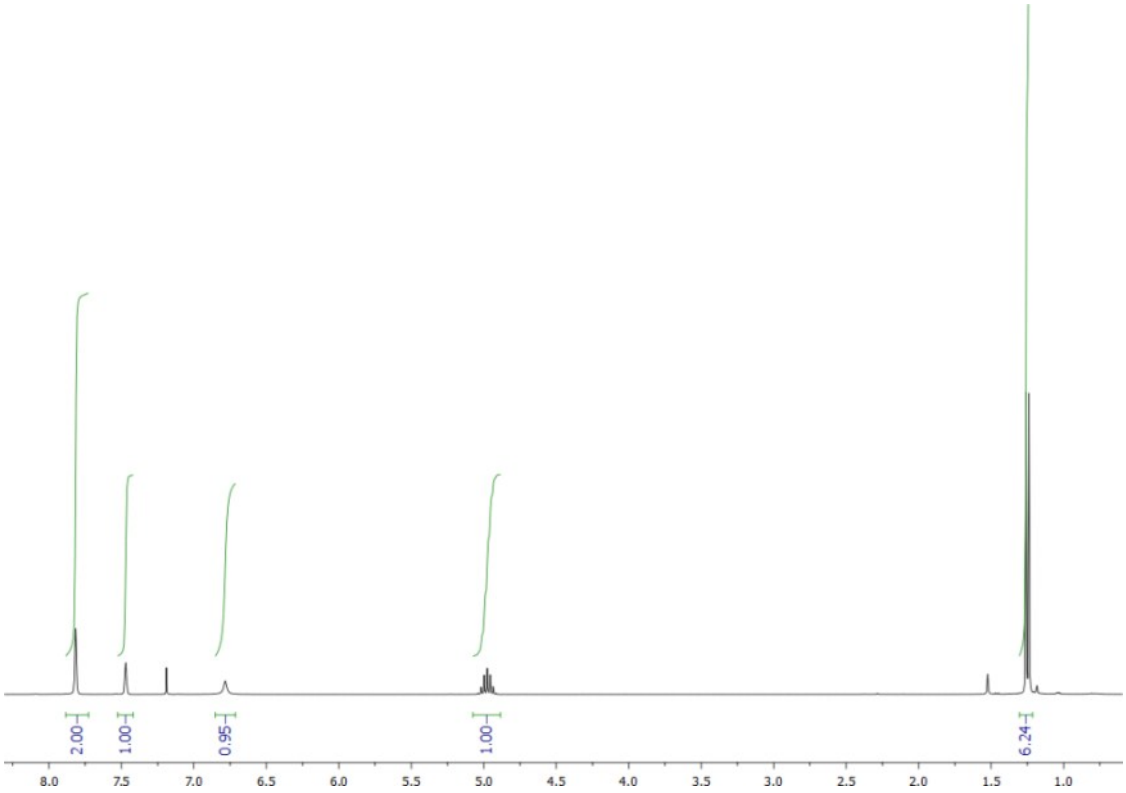


^{1}H-^{13}C HMBC NMR

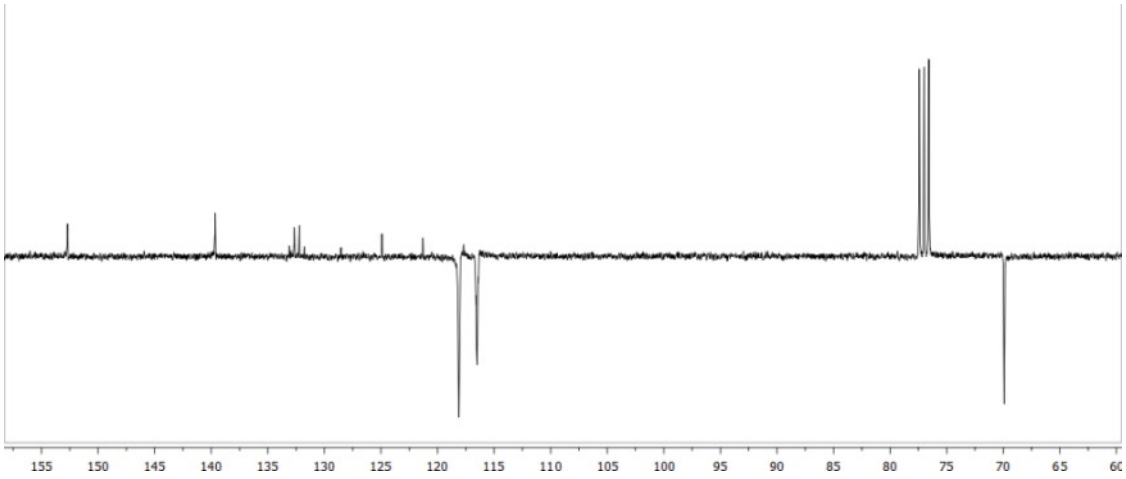


- Isopropyl (3,5-bis(trifluoromethyl)phenyl)carbamate (**3g**)

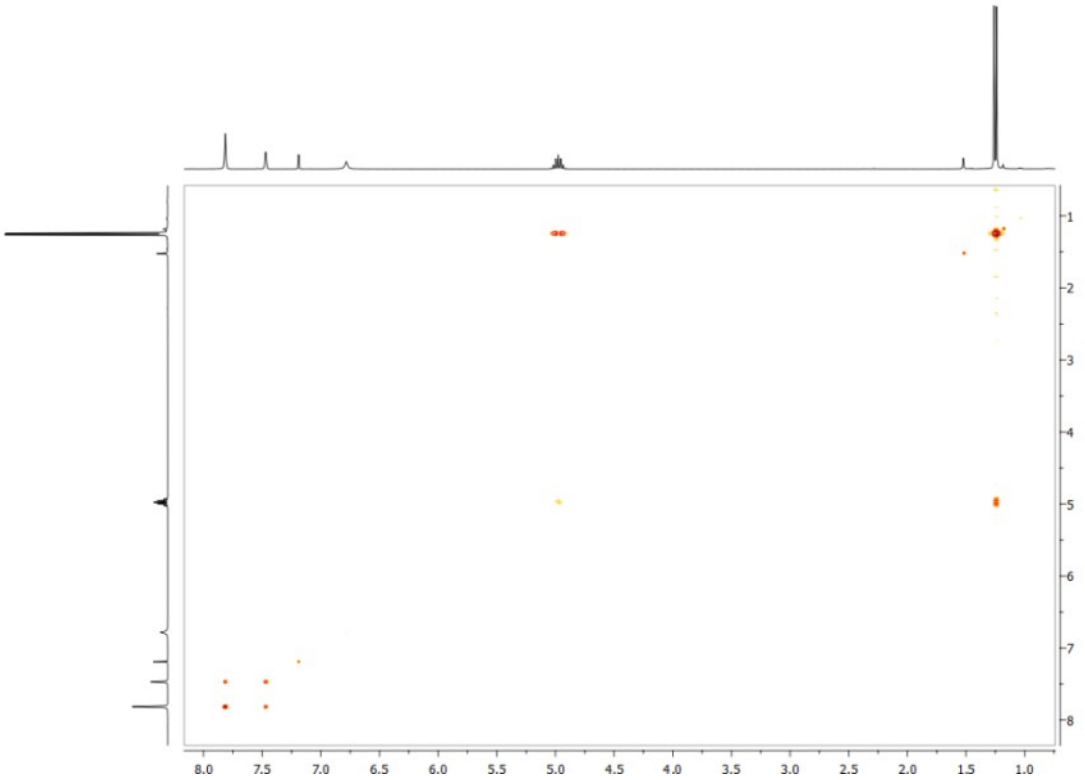
^{1}H NMR



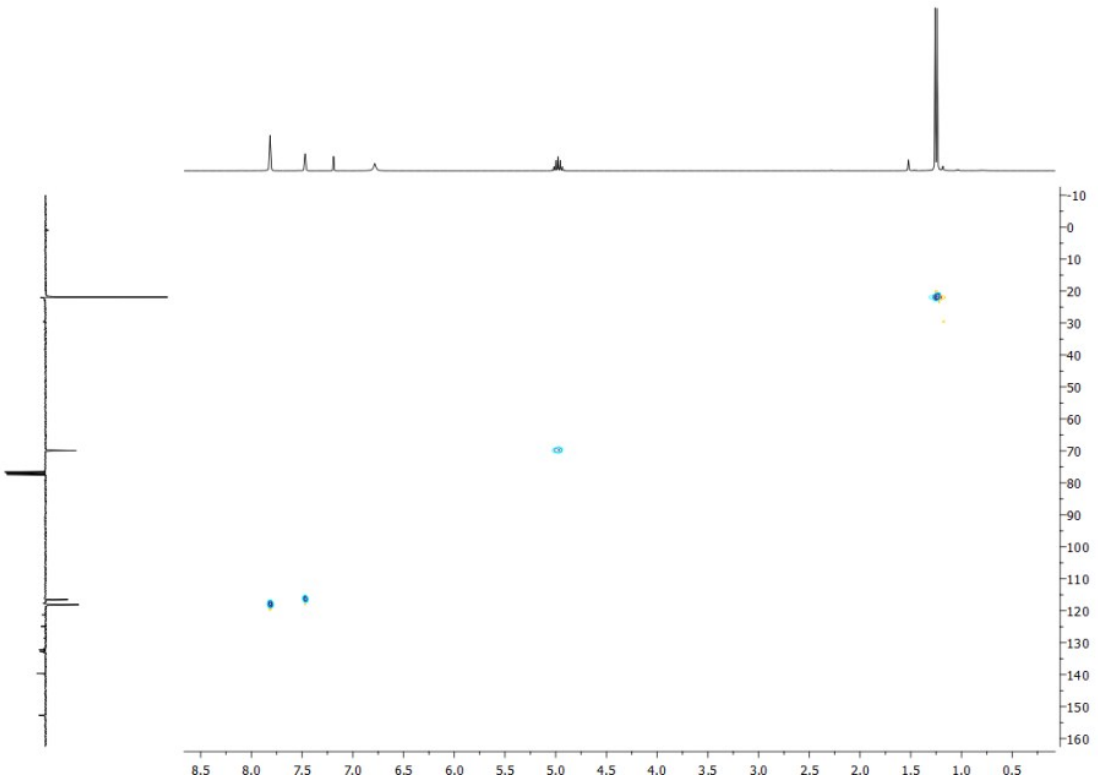
^{13}C NMR (APT)



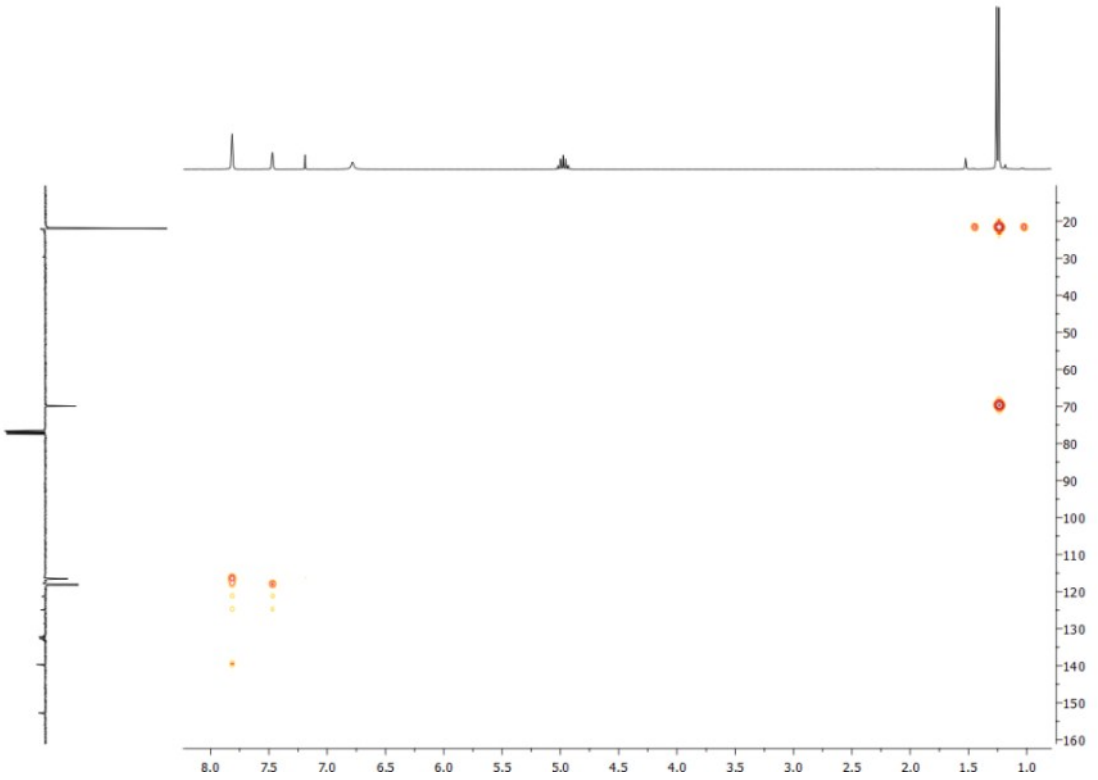
^{1}H-^{1}H COSY NMR



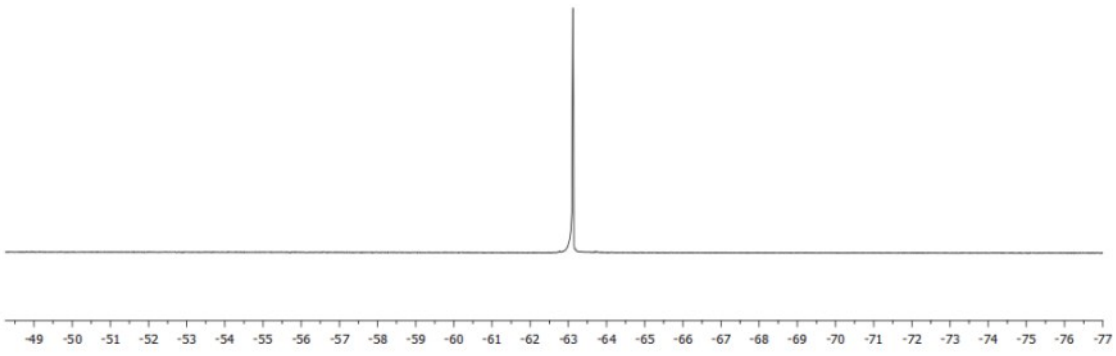
^{1}H-^{13}C HSQC NMR



^{1}H-^{13}C HMBC NMR

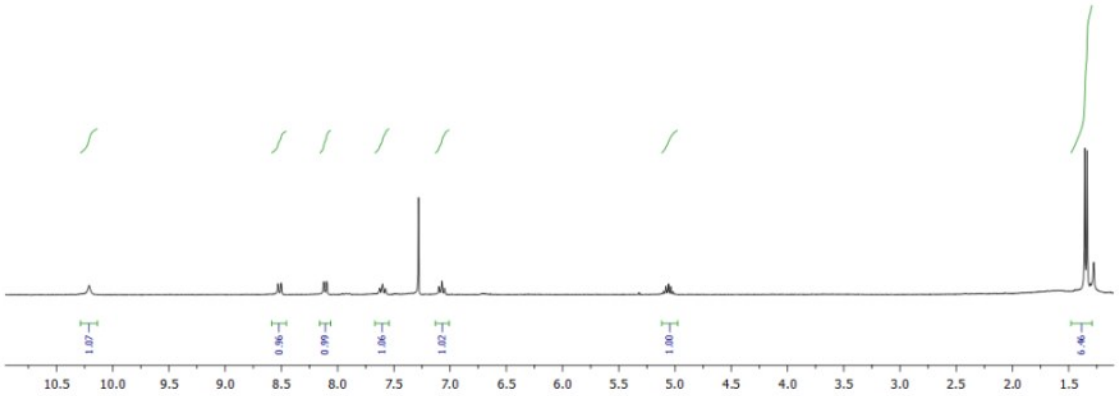


^{19}F NMR

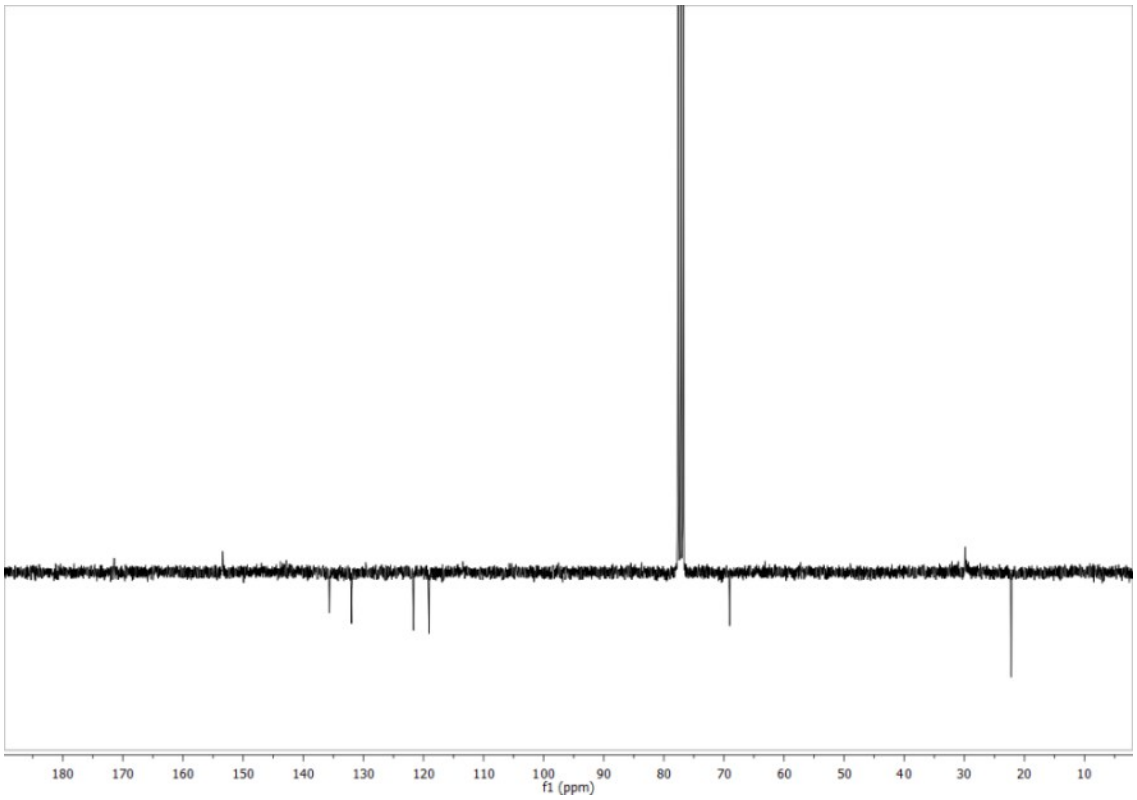


- 2-(((Isopropyloxy)carbonyl)amino)benzoic acid **(3h)**

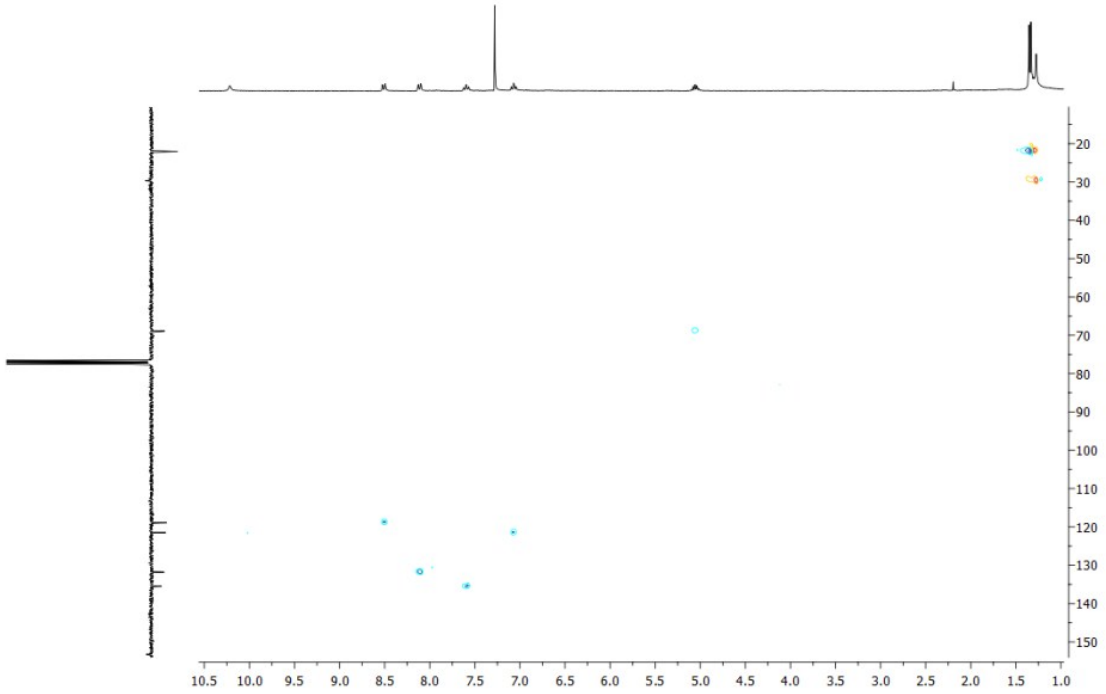
^{1}H NMR



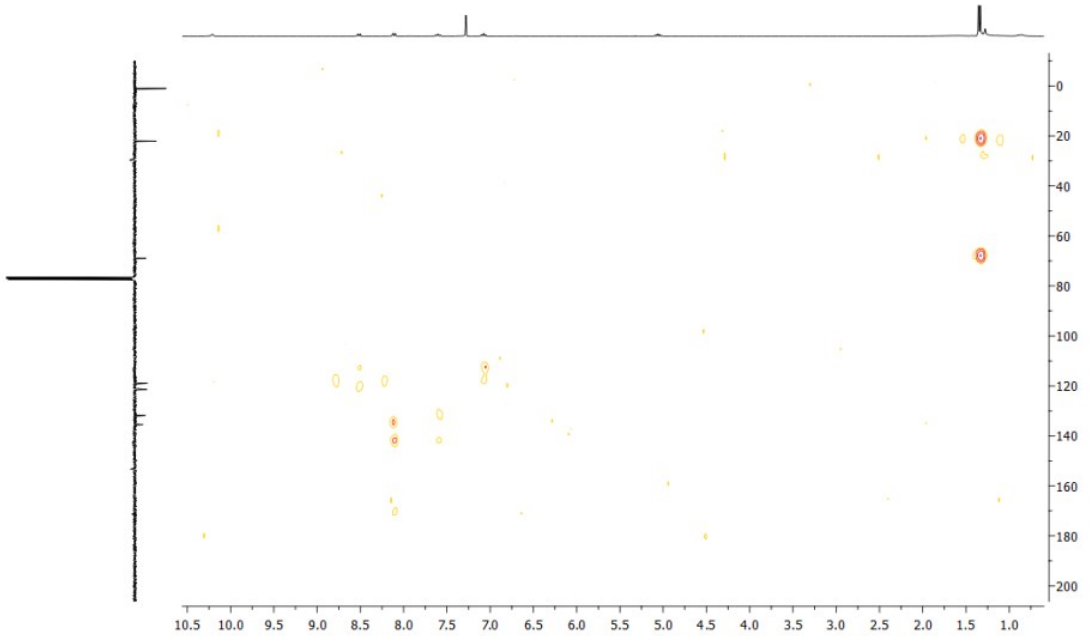
^{13}C NMR (APT)



^{1}H-^{13}C HSQC NMR



^{1}H-^{13}C HMBC NMR



DFT Calculations

Computational Methods.

All DFT theoretical calculations were carried out using Gaussian09 program package, D.01 revision.[8] The B3LYP method,[9] including the D3 dispersion correction scheme developed by Grimme with Becke Johnson dumping, has been used for both energies and gradient calculations.[10] All atoms were treated with the def2-SVP basis set[11] together with the corresponding core potential for Rh for geometry optimizations. Energies were further refined by single point calculations using the def2-TZVP basis set. All calculations included solvent corrections using the PCM[12] approach for toluene (ε= 2.3741) as implemented in G09. The "ultrafine" grid was employed in all calculations. All reported energies are Gibbs free energies in an standard state 1M calculated at 373.15 K[13] and including Grimme correction to improve entropy calculation of low-lying vibrational frequencies.[14] The nature of the stationary points was confirmed by analytical frequency analysis, and transition states were characterized by a single imaginary frequency corresponding to the expected motion of the atoms.

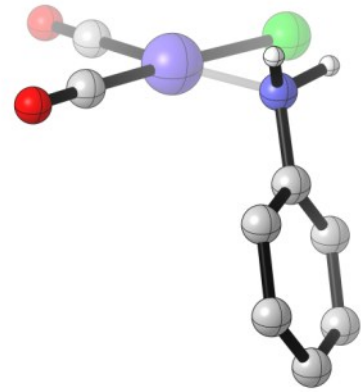
Table S1. Energetic values for all DFT calculated structures. Geometrical optimizations using the def2-SVP basis set and PCM correction in include the solvent (toluene), E(DZ). Single point energies using the def2-TZVP, E(TZ) basis set. Absolute Gibbs free energy in a 1M standard state calculated using frequencies obtained at the def2-SVP level and Grimme correction, G. Gibbs free energies are relative to **A** and isolated molecules, in kcal mol^{-1}.

	E(DZ)	E(TZ)	G	ΔG
A	-1084.72902	-1085.50055	-1085.41280	0.0
A'	-912.92898	-913.52564	-913.49901	5.2
B	-1859.24268	-1860.68517	-1860.57781	0.0
B'	-1687.44374	-1688.71398	-1688.66856	2.4
TSBC	-1859.20246	-1860.64961	-1860.54323	21.7
TSB'D	-1687.41795	-1688.68629	-1688.64338	18.2
C	-1275.49124	-1276.49164	-1276.35621	-16.2
TSCD	-1275.48586	-1276.48450	-1276.35256	-13.9
D	-1275.50222	-1276.50297	-1276.36677	-22.8
TSDE	-1275.48927	-1276.48621	-1276.35379	-14.7
E	-1275.49081	-1276.48751	-1276.35306	-14.2
F	-1312.33691	-1313.37697	-1313.26224	-10.8
TSFG	-1312.32493	-1313.36231	-1313.24472	0.2
G	-1425.62641	-1426.79443	-1426.67181	-29.9
TSGH	-1425.60201	-1426.76922	-1426.64907	-15.6
H	-910.51702	-911.11290	-911.13072	-77.9
prod	-515.15993	-515.73535	-515.61766	-78.2
HSO5	-774.47598	-775.16068	-775.16507	
RNH2	-287.42734	-287.74342	-287.66087	
ROH	-115.63714	-115.78070	-115.75534	
HSO4	-699.39889	-699.99616	-700.00279	
CO	-113.22611	-113.36350	-113.37921	
HSO4_H2O	-775.78662	-776.48049	-776.46745	
A''	-1571.78158	-1572.91364	-1572.91571	0.8
TSA''C1	-1571.73549	-1572.87116	-1572.87409	26.9
C1	-1571.78286	-1572.92099	-1572.92268	-3.6
TSAC2	-1084.63864	-1085.41641	-1085.33472	49.0
C2	-1084.65229	-1085.42599	-1085.34408	43.1
TSA'C3	-912.84130	-913.44641	-913.42545	51.3
C3	-912.86780	-913.46704	-913.44451	39.4

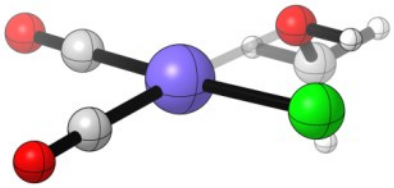
Table S2. Results for the total free energy barrier (in kcal/mol) and absolute electronic energies (DZ) and free energies (TZ) using other commonly employed DFT exchange-correlation functionals at the B3LYP-D3 optimized geometry.

	B3LYP-D3		M06		M06-L		B97D		wB97xD		BP86-D3	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
Energy Barrier	9.8	23.0	8.9	19.4	8	18.6	8	18.5	13.9	24.4	3.7	14.2
A	-1084.7290	-1085.4128	-1085.0389	-1084.9512	-1085.3991	-1085.3113	-1085.3423	-1085.2546	-1085.2404	-1085.1526	-1085.6202	-1085.5325
D	-1275.5022	-1276.3668	-1275.9062	-1275.7700	-1276.3550	-1276.2188	-1276.2227	-1276.0865	-1276.1601	-1276.0239	-1276.6328	-1276.4966
TSFG	-1312.3249	-1313.2447	-1312.7517	-1312.6341	-1313.2231	-1313.1055	-1313.0613	-1312.9437	-1313.0029	-1312.8854	-1313.5031	-1313.3855
HSO5	-774.4760	-775.1651	-774.9507	-774.9551	-775.0766	-775.0810	-774.9380	-774.9424	-775.0100	-775.0144	-775.2165	-775.2209
ROH	-115.6371	-115.7553	-115.7015	-115.6761	-115.7507	-115.7254	-115.7054	-115.6800	-115.7369	-115.7116	-115.7763	-115.7509
HSO4	-699.3989	-700.0028	-699.8251	-699.8317	-699.9236	-699.9303	-699.8149	-699.8215	-699.8745	-699.8811	-700.0418	-700.0484
CO	-113.2261	-113.3792	-113.3016	-113.3173	-113.3442	-113.3599	-113.2912	-113.3069	-113.3219	-113.3376	-113.3600	-113.3757
HSO4_H2O	-775.7866	-776.4675	-776.2670	-776.2540	-776.3869	-776.3739	-776.2548	-776.2418	-776.3313	-776.3182	-776.5256	-776.5125

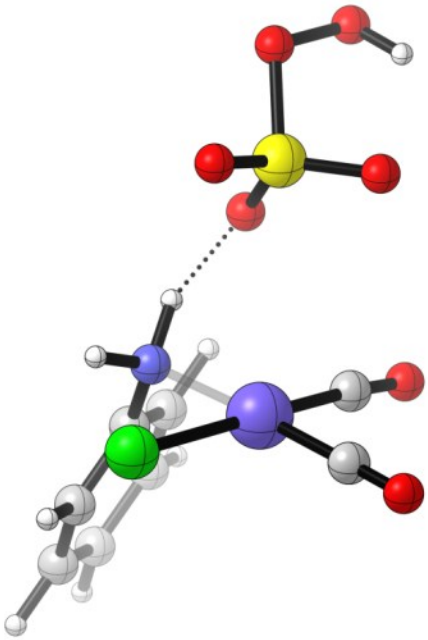
Figure S1. Geometrical representation for the DFT optimized structures.



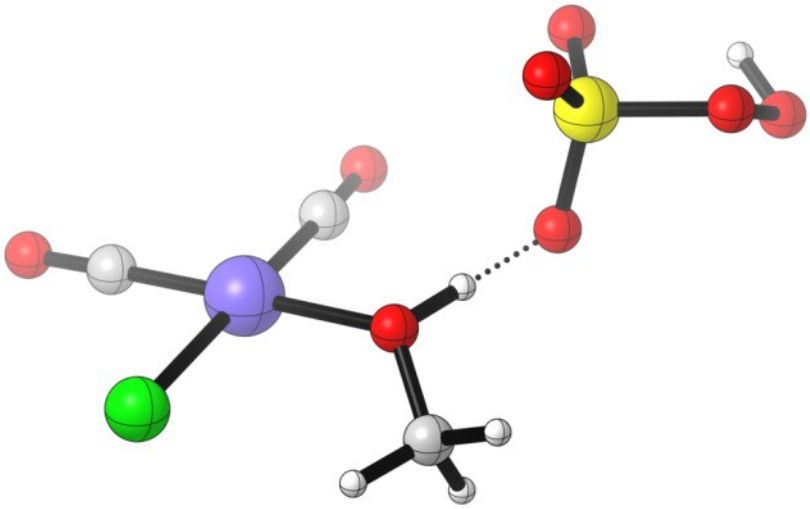
A



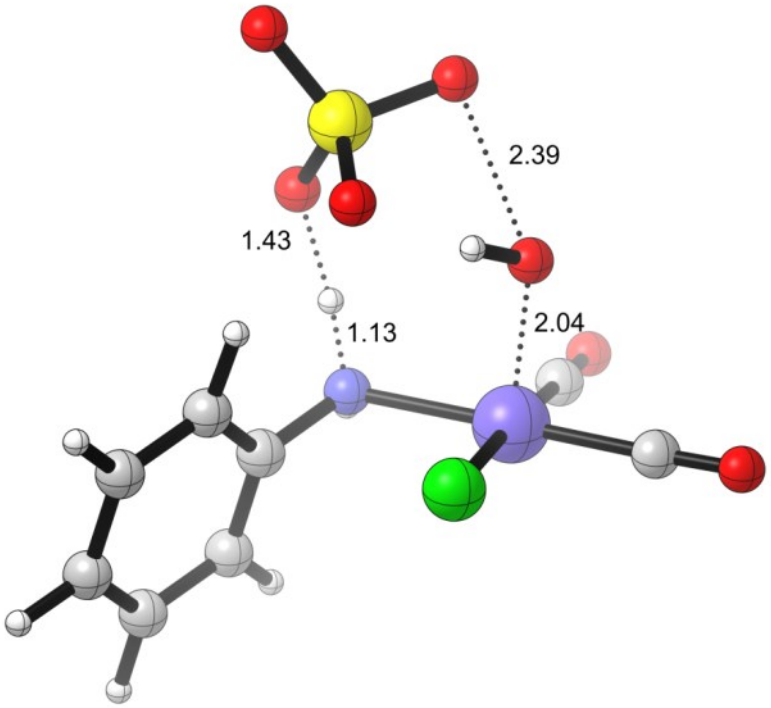
A'



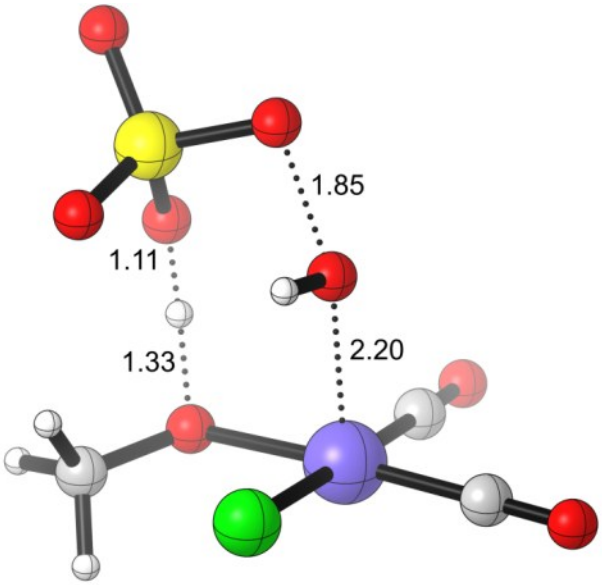
B



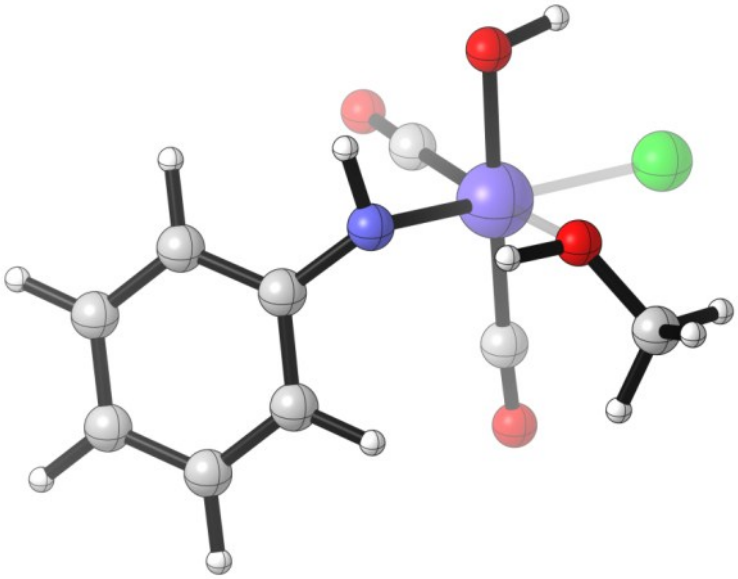
B’



TSBC



TSB'D



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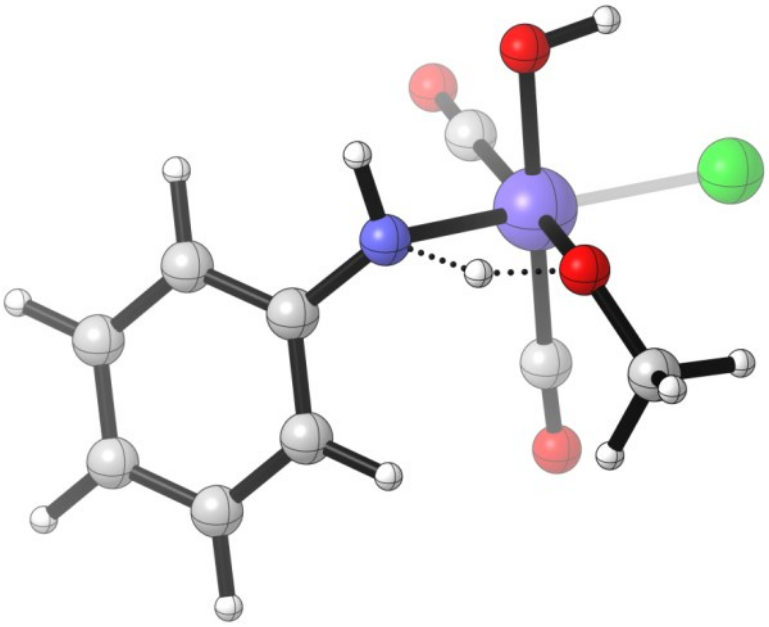
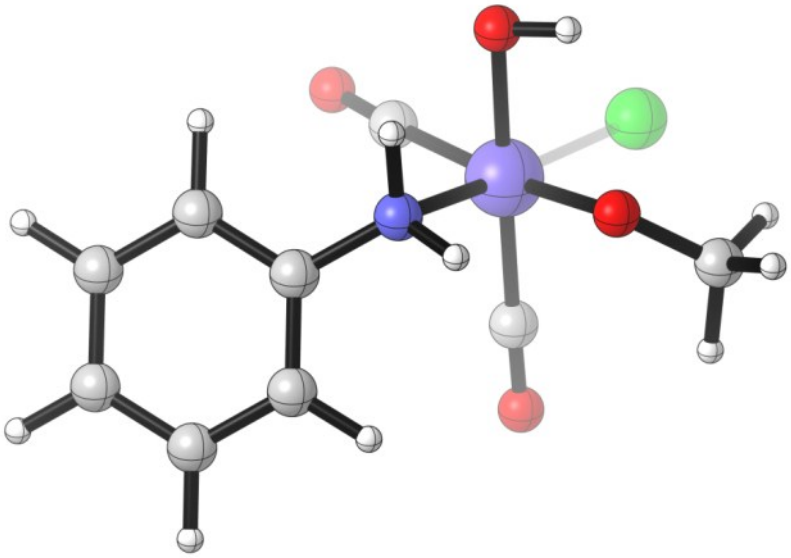
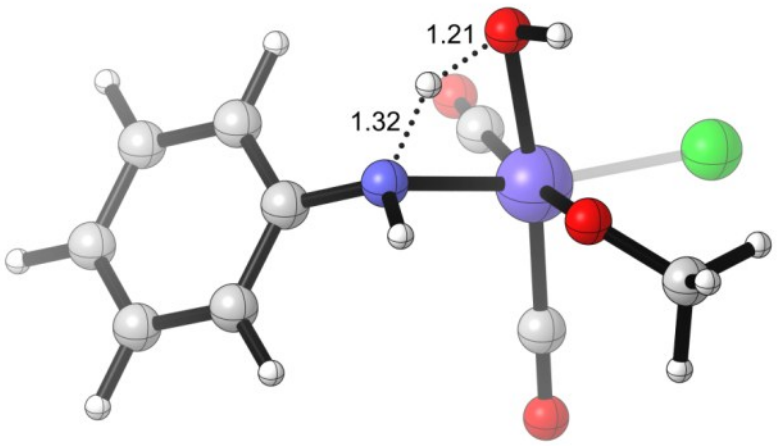


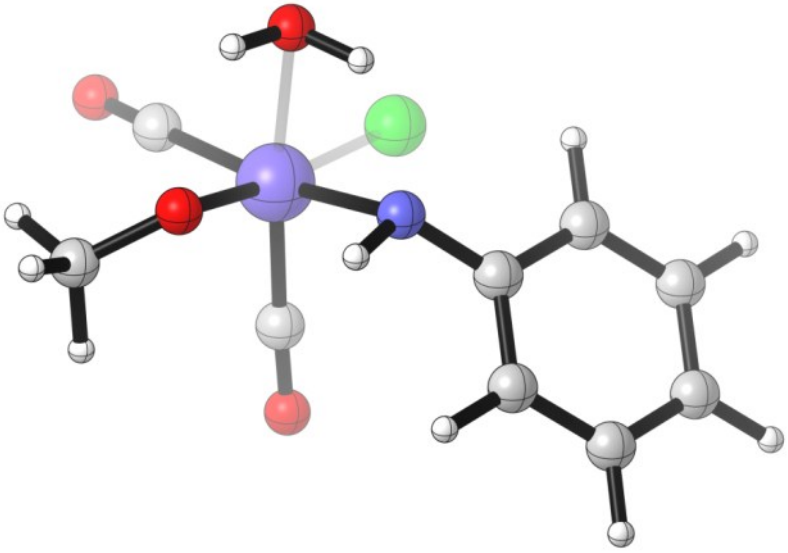
TSCD



D



TSDE



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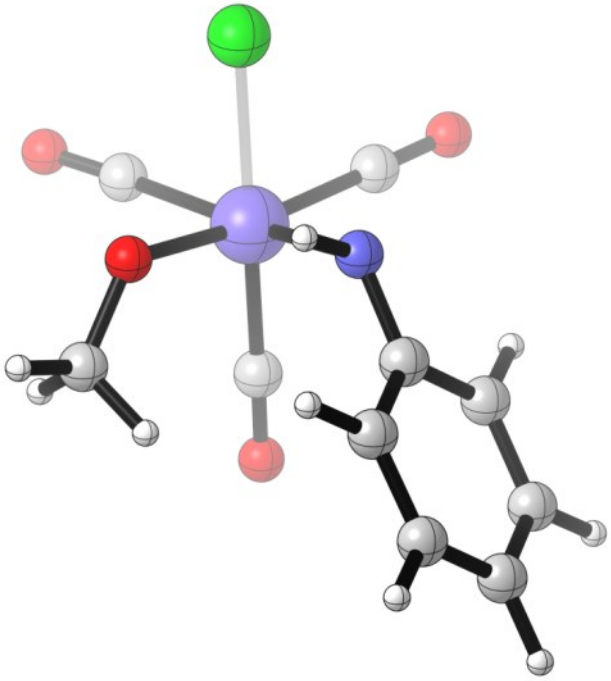
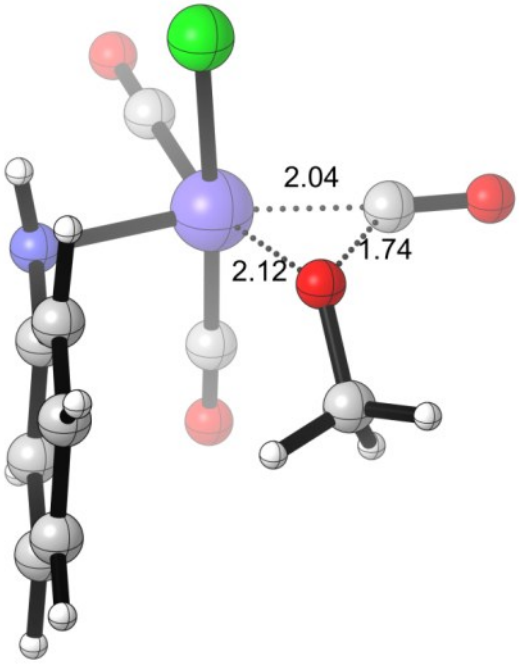
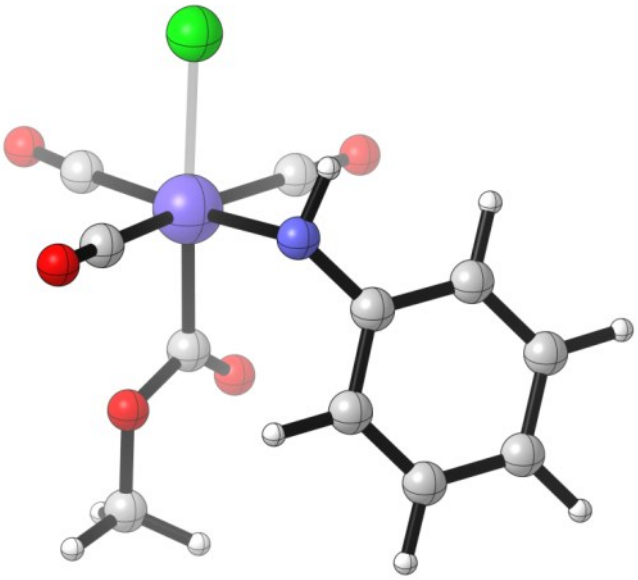


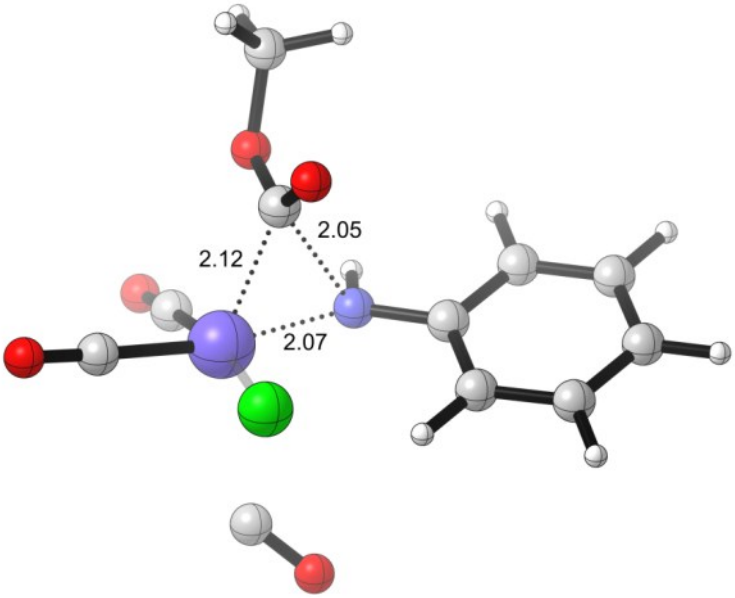
F



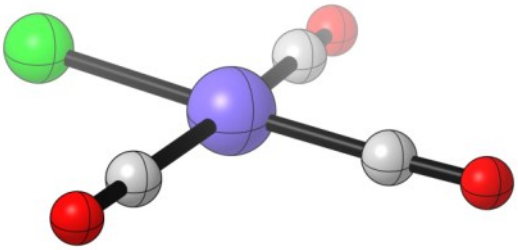
TSFG



G



TSGH



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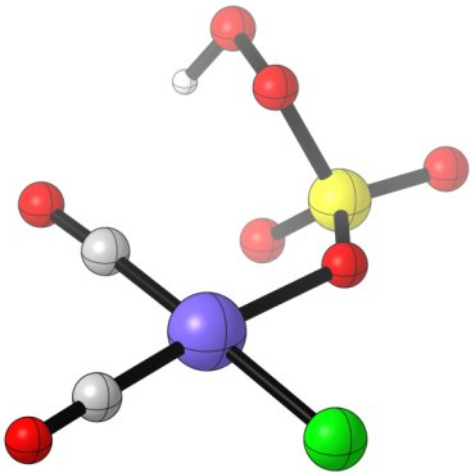
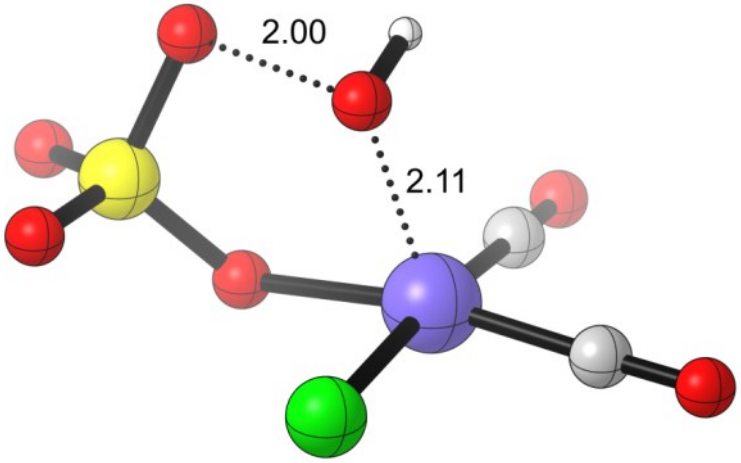
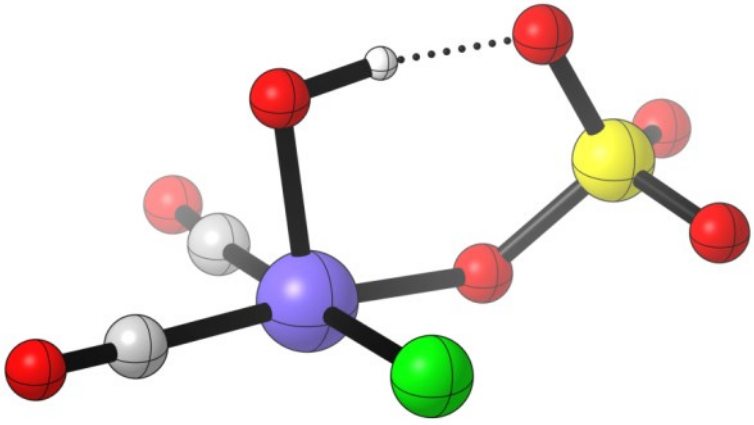


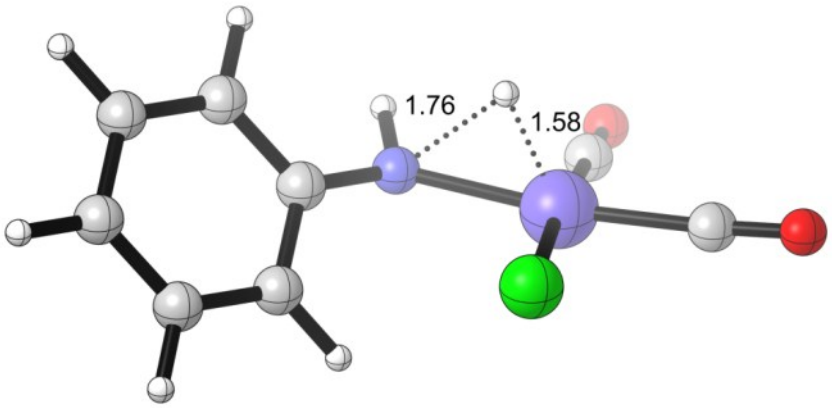
A''



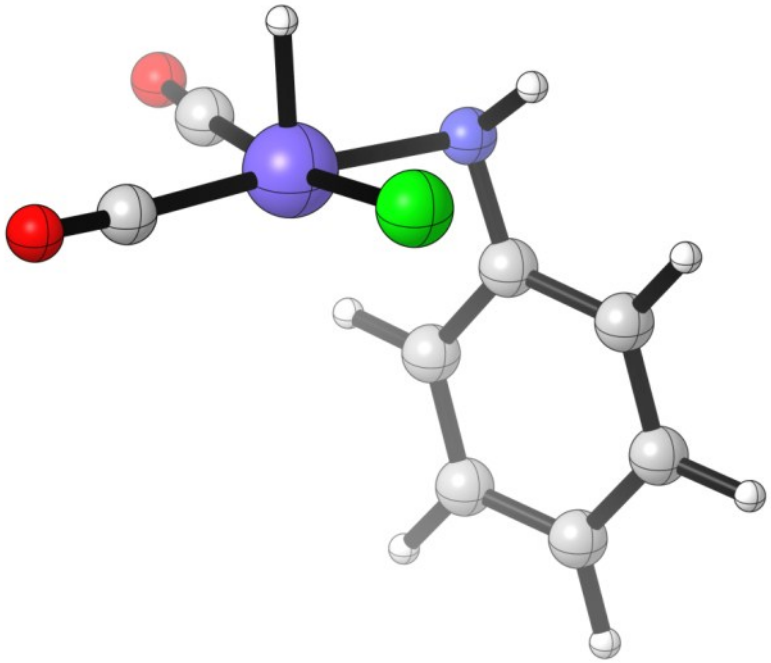
TSA''C1



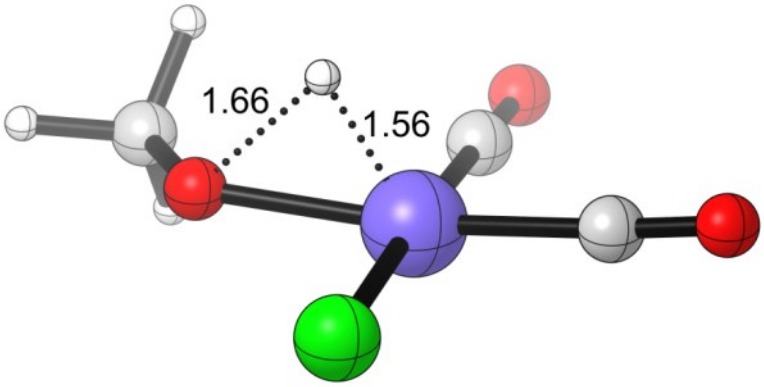
C1



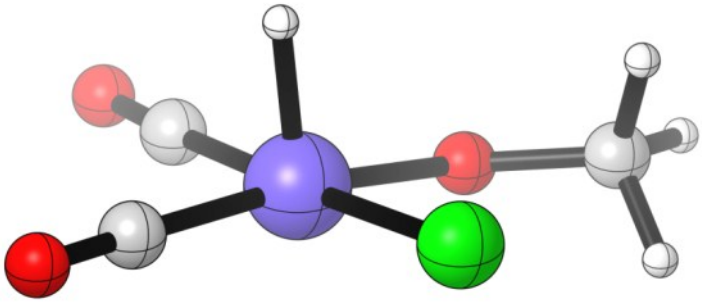
TSAC2



C2



TSA'C3



C3

Figure S2. DFT calculated Gibbs free energy profile (in kcal·mol^{-1}and relative to **A** and isolated molecules) for the alternative Rh(I) to Rh(III) transformations: direct oxidation (left), N-H oxidative addition (center), and O-H oxidative addition (right).

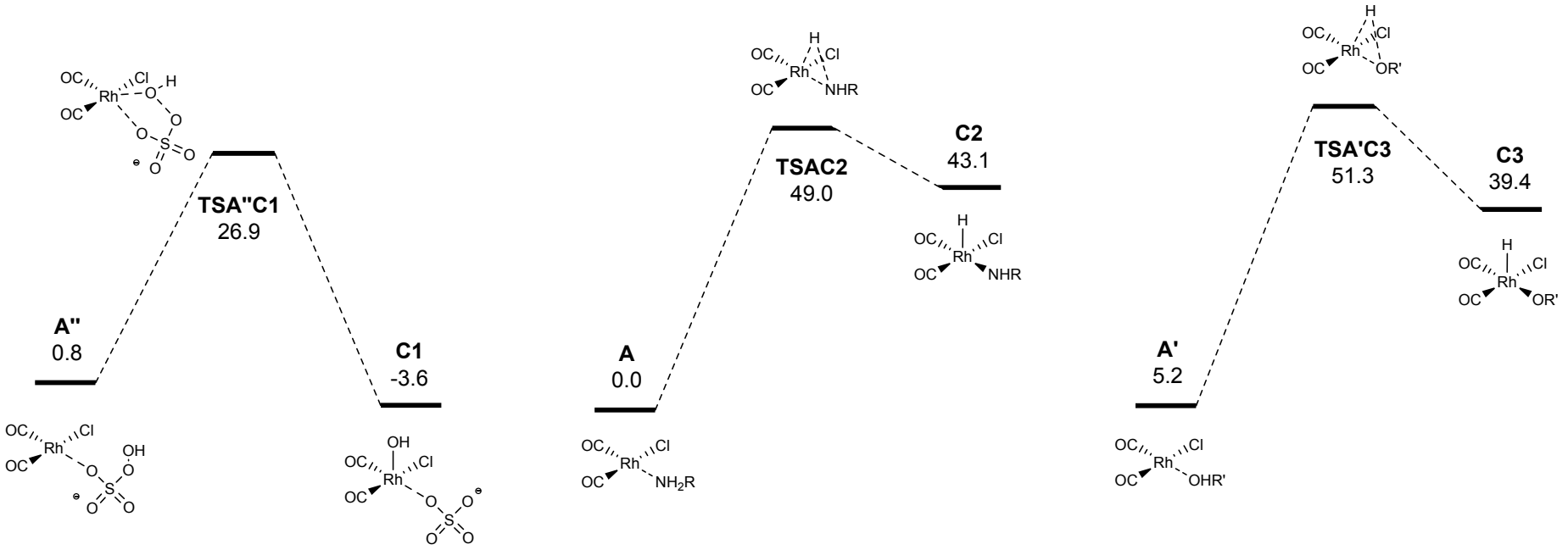


Table S3. Cartesian coordinates (in Å) for all calculated structures:

A
45 -1.141973 0.135988 -0.157879
6 -2.699363 0.305189 0.850765
6 -0.774460 1.957471 -0.083081
8 -3.661002 0.378765 1.463822
8 -0.518068 3.075178 -0.045313
17 -1.469266 -2.209161 -0.334781
7 0.629472 -0.280052 -1.334349
1 0.408859 -1.239875 -1.621148
1 0.688233 0.298403 -2.173211
6 1.847587 -0.229330 -0.567545
6 2.154672 -1.283586 0.300309
6 2.687214 0.884145 -0.656029
6 3.316264 -1.221071 1.070950
1 1.471228 -2.132015 0.374162
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1 1.990746 -0.184177 -1.313061
TSA'C3
1 -0.533426 -0.468359 1.280620
6 -1.223560 1.435738 -0.123628
8 -1.980082 2.288109 -0.149994
6 1.566666 1.190446 0.106290
8 2.473652 1.851984 0.288304
17 1.658253 -1.650088 -0.112940
45 0.053974 0.034852 -0.071153
8 -1.317999 -1.417321 0.174437
6 -2.705932 -1.190163 0.160659
1 -3.061470 -0.802509 -0.813033
1 -3.208732 -2.155856 0.343608
1 -3.043122 -0.488411 0.948754
C3
45 0.144304 0.069758 0.006308
6 1.492871 -1.302405 0.061861
8 2.244911 -2.154315 0.084742
17 -1.380281 -1.705548 -0.040161
6 1.354860 1.564605 -0.004655
8 2.052083 2.458049 -0.057746
6 -2.620094 1.178145 0.003018
1 0.292675 -0.005855 -1.501887
8 -1.253162 1.426223 0.184487
1 -3.036296 0.471659 0.744185
1 -3.153783 2.141983 0.101256

1	-2.847997	0.765700	-0.997879

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