Cp*Rh(III)/Bicyclic Olefin Co-catalyzed C–H Bond Amidation by Intramolecular Amide Transfer

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1. General information

The reactions were performed under an argon atmosphere in oven-dried glassware, unless otherwise noted. Further, the reaction temperatures are reported corresponding to the oil bath temperature. Dry solvents were bought and stored over molecular sieves in an argon atmosphere.

Commercially available chemicals were obtained from Aldrich Chemical Co, Alfa Aesar, ABCR, TCI Europe, Acros Organics and were used as received.

The analytical thin layer chromatography (TLC) was performed on Polygram SIL G/UV254 plates. The flash chromatography was performed on Merck silica gel (40-63 mesh) by standard techniques eluting with solvents as indicated. The solvents used for columns, were on technical grade and distilled once.

On a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600, the ^{1}H and ^{13}C-NMR spectra were recorded in solvents as indicated. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm).

On a BrukerDaltonicsMicroTof the ESI mass spectra were recorded.

Furthermore, no attempts were made to optimize yields for substrate synthesis.

2. Synthesis of the starting materials

2.1 General procedure for the synthesis of *N*-phenoxyacetamides 1

Method A:[1]

O-mesitylsulfonylhydroxylamine (MSH) was prepared according to the literature.[2]

Phenols (1.5 equiv) was dissolved in methanol (0.7 M), and then potassium *tert*-butoxide (1.5 equiv) was added. The mixture was allowed to stir for 0.5 h under argon atmosphere. Then methanol was removed under vacuum, and DMF was added into the residue (1.3 M). Then the freshly prepared *O*-mesitylsulfonylhydroxylamine (1.0 equiv, 0.9 M in DMF) was added under ice cooling. The mixture was allowed to stir for 2.0 h, diluted with ethylacetate, and washed with brine. The aqueous layer was extracted with EtOAc. Ethylacetate was then removed under reduce pressure to afford the corresponding *N*-aryloxyamine. Na_2CO_3 (1.5 equiv) and H_2O/EtOAc (v/v 1/2, 1.0 M) was next added to the reaction flask. The resulting solution was kept under ice followed by dropwise addition of acyl chloride (1.2 equiv). After stirring at 0 ºC for 2 h, the reaction was quenched with sat. $NaHCO_3$ and diluted with EtOAc. The organic phase was washed twice with sat. $NaHCO_3$, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to provide the desired product.

Method B:[3]

A mixture of *N*-hydroxyphthalimide (1.0 equiv), arylboronic acid (2.0 equiv), CuCl (1.0equiv), freshly activated 4Å molecular sieves (250mg/mmol) and pyridine (1.1 equiv.) were dissolved in 1,2-dichloroethane (0.25 M) and stirred at room temperature under air. After 48-120 hours, the reaction mixture turned green. Silica gel was added to the flask and the solvent was evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel to afford desired *N*-aryloxyphthalimides. The product was directly used for the next step.

Hydrazine monohydrate (4.00 equiv., 51%-64%) was added to the solution of *N*-aryloxyphthalimide (1.0 equiv) in DCM (0.25 M). The reaction was stirred at room temperature overnight. $MgSO_4$ was added to the mixture and the suspension was stirred for additional 10 minutes. The precipitate was filtered off and washed with DCM followed by EtOAc. The filtrate was concentrated and the resulting oil was directly used without further purification.

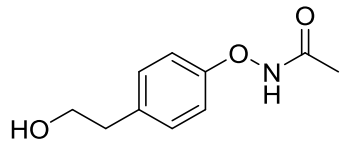
N-aryloxyamine (1.0 equiv.) was dissolved in EtOAc/H_2O (0.3 M, 2:1) followed by the addition of Na_2CO_3 (1.2 equiv.). The resulting solution was cooled to 0 °C and acetylchloride (1.10 equiv.) was added dropwise to the mixture. After stirring at room temperature overnight

the reaction was quenched with saturated $NaHCO_3$ and extracted with EtOAc. The organic phase was washed three times with saturated $NaHCO_3$ and dried over $MgSO_4$, followed by filtration. The solvent was evaporated under reduced pressure. The crude product was purified by recrystallization from EtOAc/pentane to afford the desired *N*-aryloxyacetamide.

Compounds **1m**-**1s** were synthesized according to method A and compounds **1a**-**1l** were synthesized according to method B.

Analytical data for the new compounds:

N-(4-(2-hydroxyethyl)phenoxy)acetamide (**1o**)



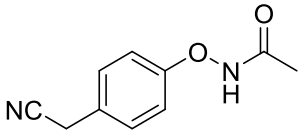
Chemical Formula: $C_{10}H_{13}NO_3$
Exact Mass: 195,0895
Molecular Weight: 195,2180

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.14 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 4.59 (t, *J* = 4.9 Hz, 1H), 3.55 (q, *J* = 7.0 Hz, 2H), 2.73 – 2.62 (m, 2H), 1.89 (s, 3H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6) δ 167.0, 157.9, 133.3, 129.7, 112.6, 62.3, 38.1, 19.4 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 218.0788; found 218.0793.

N-(4-(isocyanomethyl)phenoxy)acetamide (**1p**)



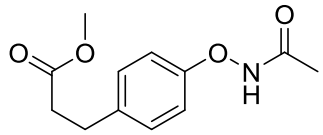
Chemical Formula: $C_{10}H_{10}N_2O_2$
Exact Mass: 190,0742
Molecular Weight: 190,2020

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 3.96 (s, 2H), 1.91 (s, 3H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6) δ 167.2, 159.0, 129.2, 124.9, 119.4, 113.3, 21.5, 19.4 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 213.0634; found 213.0640.

methyl 3-(4-(acetamidooxy)phenyl)propanoate (**1q**)



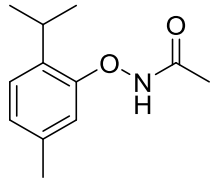
Chemical Formula: $C_{12}H_{15}NO_4$
Exact Mass: 237,1001
Molecular Weight: 237,2550

^{1}H NMR (600 MHz, Methanol-d_4) δ 7.16 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.63 (s, 3H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.01 (s, 3H) ppm.

^{13}C NMR (151 MHz, Methanol-d_4) δ 165.5, 161.0, 150.0, 127.0, 120.9, 104.8, 42.5, 27.3, 21.6, 9.8 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 260.0893; found 260.0905.

N-(2-isopropyl-5-methylphenoxy)acetamide (**1r**)



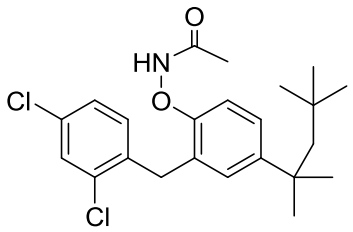
Chemical Formula: $C_{12}H_{17}NO_2$
Exact Mass: 207,1259
Molecular Weight: 207,2730

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.09 (d, J = 7.7 Hz, 1H), 6.85 – 6.75 (m, 2H), 3.25 – 3.18 (m, 1H), 2.24 (s, 3H), 1.91 (s, 3H), 1.17 (d, J = 6.9 Hz, 6H) ppm.

^{13}C NMR (126 MHz, DMSO-d_6) δ 167.1, 156.3, 135.9, 131.0, 125.7, 122.8, 112.3, 26.0, 22.5, 20.9, 19.5 ppm.

HR-MS (ESI) Expected for [M + Na+] = 230.1151; found 230.1153.

N-(2-(2,4-dichlorobenzyl)-4-(2,4,4-trimethylpentan-2-yl)phenoxy)acetamide (**1s**)



Chemical Formula: $C_{23}H_{29}Cl_2NO_2$
Exact Mass: 421,1575
Molecular Weight: 422,3900

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.63 (s, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.33 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.21 (d, *J* = 9.6 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.07 (s, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 4.03 (s, 2H), 1.88 (s, 3H), 1.62 (s, 2H), 1.24 (s, 6H), 0.62 (s, 9H) ppm.

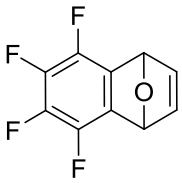
^{13}C NMR (75 MHz, DMSO-d_6) δ 167.1, 155.0, 143.2, 137.0, 134.1, 132.0, 131.5, 128.5, 128.3, 127.2, 125.3, 123.4, 111.6, 56.2, 37.6, 32.4, 32.0, 31.6, 31.5, 19.4 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 444.1468; found 444.1525.

2.2 General procedure for the synthesis of olefins 2

Bicyclic alkene **2a,**[4] **2c,**[5] **2d,**[6] **2e**[7] are known compounds and were prepared according to the methods given in the cited references without any optimization of the reaction conditions.

7-oxa-(tetrafluorobenzo)-norbornadiene **2e**[7]



^{1}H NMR (600 MHz, Methylene Chloride-d_2) δ 7.09 (s, 2H), 6.02 (s, 2H) ppm.

^{13}C NMR (151 MHz, Methylene Chloride-d_2, ^{19}F-decoupled) δ 143.24, 141.60, 139.16, 131.33, 80.74 ppm.

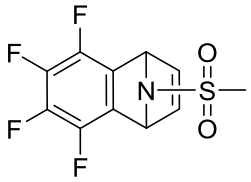
^{19}F NMR (564 MHz, Methylene Chloride-d_2) δ -143.81 – -143.95 (m), -158.49 – -158.62 (m) ppm.

Bicyclic alkene **2b** was prepared according to the following procedure:[8]

A flame dried flask was flushed with argon and cooled to -78 ^{o}C. This reaction vessel was charged with ether (20 mL), ^{n}BuLi (5.5 mL, 1.6 M in hexane, 1.1 equiv) and then pentafluorobenzene (840 mg, 5.0 mmol, 1.0 equiv). A solution of *N*-trimethylsilylpyrrole (2.08 g, 15.0 mmol, 3.0 equiv) in ether (10 mL) was added with stirring and the reaction mixture was allowed to room temperature over two hours. Water was added and the aqueous layer was extracted with ether. The combined organic extracts were dried over anhydrous sodium sulfate, the drying agent separated by filtration. The filtrate was concentrated and the resulting oil was directly used without further purification.

The resulting oil was dissolved in DCM (20 mL) followed by the addition of NEt_3 (0.83 mL, 6.0 mmol, 1.2 equiv). The solution was cooled to 0 ^{o}C and methanesulfonyl chloride (0.46 mL, 6.0 mmol, 1.2 equiv) was added slowly. After stirring at room temperature for 2.0 h, the reaction was quenched with saturated $NaHCO_3$ and extracted with EtOAc. The organic phase was washed three times with saturated $NaHCO_3$ and dried over $MgSO_4$, followed by filtration.

The solvent was evaporated under reduced pressure. The crude reaction mixture was purified by silica gel flash chromatography directly.



Chemical Formula: $C_{11}H_7F_4NO_2S$
Exact Mass: 293.0134
Molecular Weight: 293.2356

White solid, 40% yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.12 (t, *J* = 1.3 Hz, 2H), 5.79 (s, 2H), 2.78 (s, 3H) ppm.

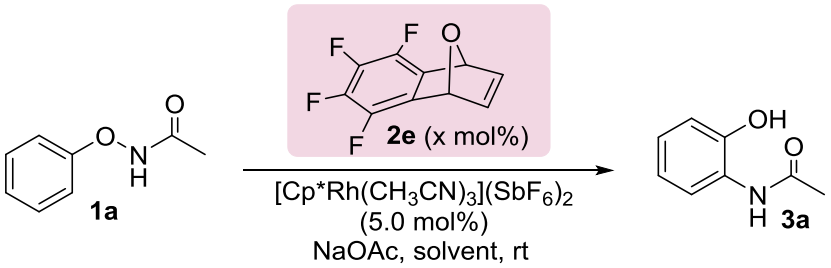
^{13}C NMR (151 MHz, Chloroform-*d*, ^{19}F-decoupled) δ 143.0, 141.6, 139.1, 129.4, 65.0, 41.4 ppm.

^{19}F NMR (564 MHz, Chloroform-*d*) δ -141.84 – -142.02 (m), -155.86 – -156.12 (m) ppm.

HR-MS (ESI) Expected for [M + Na^+] = 316.0026; found 316.0045.

3. Catalysis reactions

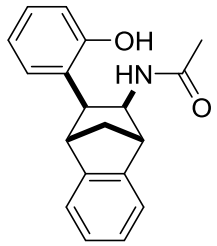
3.1 Optimization reactions[a]



Entry	Solvent	2e (x mol%)	Yield(%)[b]
1	CH_2Cl_2	20	94 (87)[c]
2	THF	20	0
3	MeOH	20	0
4	CH_3CN	20	0
5	toluene	20	89
6	DMF	20	0
7	CH_2Cl_2	10	52
8	CH_2Cl_2	5	26

[a] Reaction conditions: **1a** (0.1 mmol), **2e** (x mol%), [Cp*Rh(CH_3CN)$_3$](SbF_6)$_2$ (5.0 mol%), NaOAc (0.05 mmol, 50 mol%), in a solvent (0.25 mL) for 12 h at room temperature. [b]NMR yield. [c]Isolated yield for 0.2 mmol scale reaction.

N-(3-(2-hydroxyphenyl)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-yl)acetamide



Chemical Formula: $C_{19}H_{19}NO_2$
Exact Mass: 293,1416
Molecular Weight: 293,3660

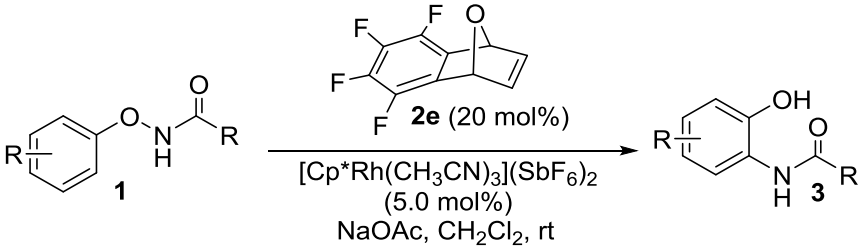
^{1}H NMR (300 MHz, DMSO-d_6) δ 9.12 (s, 1H), 7.32 – 7.25 (m, 1H), 7.22 (d, *J* = 5.9 Hz, 2H), 7.13 – 6.99 (m, 3H), 6.83 (t, *J* = 7.1 Hz, 1H), 6.75 – 6.65 (m, 2H), 4.22 (t, *J* = 8.9 Hz, 1H), 3.49 (s, 1H), 3.09 – 3.05 (m, 2H), 2.34 (d, *J* = 9.5 Hz, 1H), 1.85 (d, *J* = 6.5 Hz, 1H), 1.51 (s, 3H) ppm.

^{13}C NMR (75 MHz, DMSO-d_6) δ 168.0, 155.8, 150.2, 146.4, 127.1, 127.0, 126.6, 126.1, 125.6, 121.8, 120.4, 118.7, 114.2, 52.3, 50.3, 46.1, 45.6, 43.6, 22.7 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 316.1308; found 316.1304.

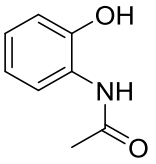
Decomposition of **2e** under the catalytic conditions: a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. **2e** (21.6 mg, 0.1 mmol, 1.0 equiv.), NaOAc (4.1 mg, 0.05 mmol, 0.5 equiv.), and $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (4.2 mg, 0.005 mmol, 5.0 mol%) were added to the tube under argon. Then, dichloromethane (0.5 mL) was added to the tube. The Schlenk tube was sealed and stirred for 4.0 h at room temperature. 1,3,5-trimethoxybenzene (0.1 mmol) was added as the internal standard, and the mixture was filtered. The crude ^{1}H-NMR showed that 74% of **2e** was left. The same reaction was carried out for 12.0 h, and the ^{1}H-NMR showed that 64% of **2e** was left. Some complex signals appeared in the aromatic region in the crude ^{1}H-NMR. On the other hand, GC-MS or ESI-MS of the reaction mixtures did not show useful information for these new compounds. These results indicated that **2e** partly decomposed to some undefined compounds under standard reaction conditions.

3.2 General procedure for the Cp*Rh(III)/Olefin co-catalyzed C-H amidation of aryloxyacetamide 1



A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. The aryloxyacetamide **1** (0.2 mmol, 1.0 equiv), NaOAc (8.2 mg, 0.10 mmol, 0.5 equiv), **2e** (8.6 mg, 0.04 mmol, 20 mmol%) and $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8.4 mg, 0.01 mmol, 5.0 mol%) were added to the tube under argon. Then, dichloromethane (0.5 mL) was added to the tube. The Schlenk tube was sealed and stirred for 12 h (16 h for **3a**–**3l**) at room temperature. The crude reaction mixture was purified by silica gel flash chromatography directly. The reaction time was not optimized.

N-(2-hydroxyphenyl)acetamide (**3a**)[8]



Chemical Formula: $C_8H_9NO_2$
Exact Mass: 151,0633
Molecular Weight: 151,1650

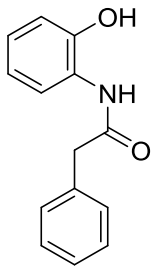
White solid, 26.2 mg, 87%.

^{1}H NMR (300 MHz, Methanol-d_4) δ 7.58 (dd, J = 8.0, 1.6 Hz, 1H), 7.00 (ddd, J = 8.0, 7.3, 1.6 Hz, 1H), 6.89 – 6.75 (m, 2H), 2.17 (s, 3H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 172.2, 149.7, 127.1, 126.8, 124.0, 120.6, 117.2, 23.4 ppm.

HR-MS (ESI) Expected for $[M + Na^+]$ = 174.0525; found 174.0531.

***N*-(2-hydroxyphenyl)-2-phenylacetamide (3b)**[9]



Chemical Formula: $C_{14}H_{13}NO_2$
Exact Mass: 227,0946
Molecular Weight: 227,2630

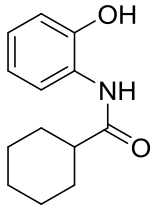
White solid, 32.8 mg, 72%.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.79 (s, 1H), 9.33 (s, 1H), 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.38 – 7.28 (m, 4H), 7.27 – 7.19 (m, 1H), 6.97 – 6.81 (m, 2H), 6.74 (td, *J* = 7.6, 1.7 Hz, 1H), 3.74 (s, 2H) ppm.

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.5, 147.6, 136.1, 129.2, 128.3, 126.5, 126.3, 124.5, 121.9, 118.9, 115.5, 42.9 ppm.

HR-MS (ESI) Expected for [M + Na^+] =250.0838; found 250.0846.

***N*-(2-hydroxyphenyl)cyclohexanecarboxamide (3c)**[9]



Chemical Formula: $C_{13}H_{17}NO_2$
Exact Mass: 219,1259
Molecular Weight: 219,2840

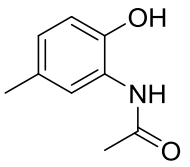
Brown solid, 35.0mg, 80%.

^{1}H NMR (300 MHz, Methanol-d_4) δ 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.03 – 6.94 (m, 1H), 6.90 – 6.75 (m, 2H), 2.46 (tt, *J* = 11.7, 3.5 Hz, 1H), 1.97 – 1.70 (m, 5H), 1.61 – 1.19 (m, 5H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 176.6, 148.2, 125.9, 125.2, 122.2, 119.3, 115.9, 45.4, 29.4, 25.5, 25.3 ppm.

HR-MS (ESI) Expected for [M + H^+] = 220.1332; found 220.1338.

***N*-(2-hydroxy-5-methylphenyl)acetamide (3e)**[8]



Chemical Formula: $C_9H_{11}NO_2$
Exact Mass: 165,0790
Molecular Weight: 165,1920

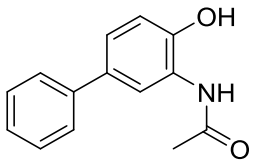
White solid, 22.8 mg, 69%.

^{1}H NMR (300 MHz, Methanol-d_4) δ 7.37 (d, J = 2.1 Hz, 1H), 6.81 (dd, J = 8.4, 2.1 Hz, 1H), 6.74 (d, J = 8.2 Hz, 1H), 2.23 (s, 3H), 2.16 (s, 3H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 172.2, 147.4, 130.0, 127.3, 126.7, 124.4, 117.2, 23.4, 20.7 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 188.0682; found 188.0690.

***N*-(4-hydroxy-[1,1'-biphenyl]-3-yl)acetamide (3f)**[8]



Chemical Formula: $C_{14}H_{13}NO_2$
Exact Mass: 227,0946
Molecular Weight: 227,2630

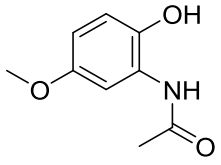
White solid, 28.5 mg, 63%.

^{1}H NMR (300 MHz, Methanol-d_4) δ 7.93 (d, J = 2.3 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.42 – 7.31 (m, 2H), 7.26 (ddd, J = 8.2, 2.3, 1.2 Hz, 2H), 6.93 (d, J = 8.4 Hz, 1H), 2.20 (s, 3H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 172.3, 149.2, 142.1, 134.1, 129.7, 127.6, 127.5, 127.4, 125.2, 122.4, 117.5, 23.6 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 250.0838; found 250.0835.

***N*-(2-hydroxy-5-methoxyphenyl)acetamide (3g)**[8]



Chemical Formula: $C_9H_{11}NO_3$
Exact Mass: 181.0739
Molecular Weight: 181.1910

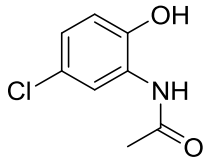
White solid, 28.5 mg, 63%.

^{1}H NMR (300 MHz, Methanol-d_4) δ 7.31 (d, J = 3.0 Hz, 1H), 6.77 (d, J = 8.8 Hz, 1H), 6.58 (dd, J = 8.8, 3.0 Hz, 1H), 3.71 (s, 3H), 2.16 (s, 3H) ppm.

^{13}C NMR (126 MHz, Methanol-d_4) δ 172.10, 154.33, 143.15, 127.72, 117.52, 111.73, 109.37, 56.14, 23.57 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 204.0631; found 204.0624.

N-(5-chloro-2-hydroxyphenyl)acetamide (3h)[8]



Chemical Formula: $C_8H_8ClNO_2$
Exact Mass: 185,0244
Molecular Weight: 185,6070

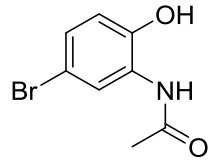
White solid, 26.5 mg, 71%.

^{1}H NMR (300 MHz, Methanol-d_4) δ 7.84 (d, J = 2.6 Hz, 1H), 6.94 (dd, J = 8.6, 2.5 Hz, 1H), 6.80 (d, J = 8.6 Hz, 1H), 2.17 (s, 3H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 172.1, 147.9, 128.4, 125.6, 124.9, 122.9, 117.4, 23.7 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 208.0147; found 208.0146.

N-(5-bromo-2-hydroxyphenyl)acetamide (3i)[10]



Chemical Formula: $C_8H_8BrNO_2$
Exact Mass: 228,9738
Molecular Weight: 230,0610

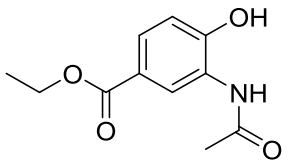
White solid, 31.7 mg, 69%.

^{1}H NMR (300 MHz, Methanol-d_4) δ 7.98 (d, J = 2.5 Hz, 1H), 7.08 (dd, J = 8.6, 2.5 Hz, 1H), 6.76 (d, J = 8.6 Hz, 1H), 2.17 (s, 3H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 172.1, 148.4, 128.8, 128.7, 125.8, 117.9, 111.8, 23.7 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 251.9642; found 251.9641.

Ethyl 3-acetamido-4-hydroxybenzoate (3j)[8]



Chemical Formula: $C_{11}H_{13}NO_4$
Exact Mass: 223,0845
Molecular Weight: 223,2280

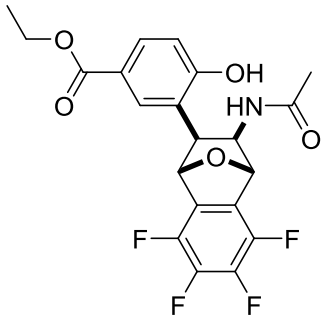
White solid, 11.2 mg, 25%

^{1}H NMR (300 MHz, Methanol-d_4) δ 8.42 (d, J = 2.2 Hz, 1H), 7.69 (dd, J = 8.5, 2.1 Hz, 1H), 6.90 (d, J = 8.5 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.19 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 170.9, 166.6, 152.8, 127.0, 125.7, 124.0, 121.2, 114.9, 60.4, 22.1, 13.2 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 246.0742; found 246.0749.

The reaction with 100 mol% of **2e**: a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. **1j** (22.3 mg, 0.1 mmol, 1.0 equiv.), **2e** (21.6 mg, 0.1 mmol, 1.0 equiv.), NaOAc (4.1 mg, 0.05 mmol, 0.5 equiv), and $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (4.2 mg, 0.005 mmol, 5.0 mol%) were added to the tube under argon. Then, dichloromethane (0.5 mL) was added to the tube. The Schlenk tube was sealed and stirred for 12.0 h at room temperature. 1,3,5-trimethoxybenzene (0.1 mmol) was added as the internal standard, and the mixture was filtered. The crude ^{1}H-NMR showed that the desired product **3j** in 47% yield and the corresponding olefin carboamidation product in 30% yield.

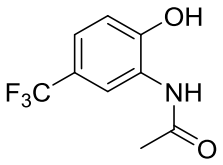


Chemical Formula: $C_{21}H_{17}F_4NO_5$
Exact Mass: 439.1043
Molecular Weight: 439.3626

White solid. **^{1}H NMR** (600 MHz, Methanol-d_4) δ 8.09 (d, J = 1.9 Hz, 1H), 7.81 (dd, J = 8.5, 2.1 Hz, 1H), 6.80 (d, J = 8.5 Hz, 1H), 5.88 (s, 1H), 5.55 (s, 1H), 4.56 (d, J = 7.7 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.75 (d, J = 7.7 Hz, 1H), 1.56 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, Methanol-d_4, the carbons in C_6F_4 did not list) δ 172.4, 168.5, 161.8, 131.5,

131.3, 125.5, 122.4, 115.4, 82.7, 82.3, 61.8, 54.7, 44.1, 22.1, 14.7 ppm. **^{19}F NMR** (564 MHz, Methanol-d_4) δ -144.34 (t, *J* = 20.0 Hz), -145.10 (t, *J* = 20.2 Hz), -157.52 – -157.66 (m), -158.24 – -158.43 (m) ppm. **HR-MS (ESI)** Expected for [M + Na^+] = 462.0935; found 462.0941.

***N*-(2-hydroxy-5-(trifluoromethyl)phenyl)acetamide (3k)**



Chemical Formula: $C_9H_8F_3NO_2$
Exact Mass: 219.0507
Molecular Weight: 219.1632

Yellow solid, 4 mg, 0.02 mmol, 9%

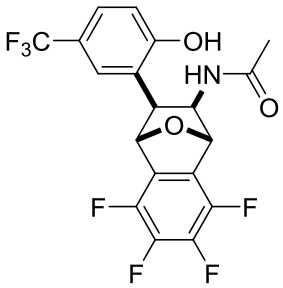
^{1}H NMR (300 MHz, Methanol-d_4) 8.20 (d, *J* = 2.2 Hz, 1H), 7.26 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 2.19 (s, 3H) ppm.

^{13}C NMR (151 MHz, Methanol-d_4, ^{19}F-decoupled) δ 172.3, 152.1, 127.8, 125.9, 123.1, 122.4, 120.2, 116.4, 23.7 ppm.

^{19}F NMR (282 MHz, Methanol-d_4) δ -62.97 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 242.0399; found 242.0398.

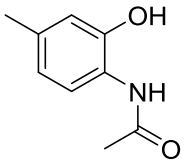
The reaction with 100 mol% of **2e**: a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. **1k** (22.0 mg, 0.1 mmol, 1.0 equiv.), **2e** (21.6 mg, 0.1 mmol, 1.0 equiv.), NaOAc (4.1 mg, 0.05 mmol, 0.5 equiv), and $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (4.2 mg, 0.005 mmol, 5.0 mol%) were added to the tube under argon. Then, dichloromethane (0.5 mL) was added to the tube. The Schlenk tube was sealed and stirred for 12.0 h at room temperature. 1,3,5-trimethoxybenzene (0.1 mmol) was added as the internal standard, and the mixture was filtered. The crude ^{1}H-NMR showed that the desired product **3k** in 28% yield and the corresponding olefin carboamidation product in 26% yield.



Chemical Formula: $C_{19}H_{12}F_7NO_3$
Exact Mass: 435.0705
Molecular Weight: 435.2978

White solid. **^{1}H NMR** (500 MHz, Methanol-d_4) δ 7.65 (s, 1H), 7.40 (d, J = 10.7 Hz, 1H), 6.86 (d, J = 8.6 Hz, 1H), 5.80 (s, 1H), 5.58 (s, 1H), 4.51 (d, J = 7.6 Hz, 1H), 3.82 (d, J = 7.5 Hz, 1H), 1.55 (s, 3H) ppm. ^{13}C NMR (126 MHz, Methanol-d_4, the carbons in C_6F_4 did not list) δ 172.3, 160.2, 127.2, 127.1, 127.1, 127.1, 126.4, 126.4, 126.4, 126.3, 125.2, 122.7, 122.4, 122.1, 121.9, 115.8, 82.6, 82.4, 55.0, 44.1, 22.0 ppm. **^{19}F NMR** (470 MHz, Methanol-d_4) δ -62.54, -144.35 (t, J = 20.1 Hz), -145.06 (t, J = 20.2 Hz), -157.16 – -157.79 (m), -158.04 – -158.51 (m) ppm. **HR-MS (ESI)** Expected for [M + Na^+] = 458,0598; found 458.0614.

***N*-(2-hydroxy-4-methylphenyl)acetamide (3l)**[11]



Chemical Formula: $C_9H_{11}NO_2$
Exact Mass: 165,0790
Molecular Weight: 165,1920

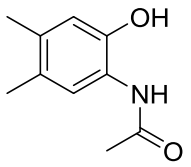
White solid, 22.5 mg, 68%.

^{1}H NMR (300 MHz, Methanol-d_4) δ 7.38 (d, J = 8.1 Hz, 1H), 6.69 (d, J = 1.9 Hz, 1H), 6.62 (ddd, J = 8.1, 1.9, 0.8 Hz, 1H), 2.24 (s, 3H), 2.15 (s, 3H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 172.2, 149.7, 137.1, 124.4, 124.0, 121.2, 118.0, 23.3, 21.0 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 188.0682; found 188.0686.

***N*-(2-hydroxy-4,5-dimethylphenyl)acetamide (3m)**



Chemical Formula: $C_{10}H_{13}NO_2$
Exact Mass: 179,0946
Molecular Weight: 179,2190

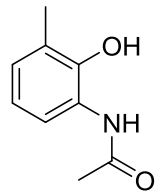
White solid, 30.2 mg, 84%.

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.20 (s, 1H), 6.65 (s, 1H), 2.16 – 2.14 (m, 9H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 172.2, 147.7, 135.5, 128.5, 125.1, 124.3, 118.9, 23.2, 19.4, 19.0 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 202.0838; found 202.0846.

***N*-(2-hydroxy-3-methylphenyl)acetamide (3n)**



Chemical Formula: $C_9H_{11}NO_2$
Exact Mass: 165,0790
Molecular Weight: 165,1920

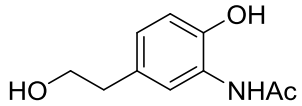
Brown solid, 27.7 mg, 84%.

^{1}H NMR (300 MHz, Methanol-d_4) δ 7.05 (dd, J = 8.0, 1.6 Hz, 1H), 6.96 (ddd, J = 7.5, 1.7, 0.9 Hz, 1H), 6.73 (t, J = 7.7 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 3H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 172.8, 148.6, 128.9, 128.5, 127.0, 122.1, 120.7, 23.0, 16.6 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 188.0682; found 188.0685.

***N*-(2-hydroxy-5-(2-hydroxyethyl)phenyl)acetamide (3o)**



Chemical Formula: $C_{10}H_{13}NO_3$
Exact Mass: 195,0895
Molecular Weight: 195,2180

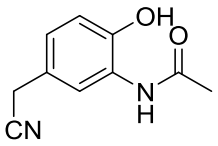
White solid, 26.9 mg, 69%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (s, 1H), 7.49 (s, 1H), 6.69 – 6.73 (m, 2H), 3.52 (t, J = 7.2 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 2.08 (s, 3H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 146.2, 129.7, 126.1, 125.1, 122.7, 115.8, 62.5, 38.5, 23.6 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 218.0788; found 218.0787.

***N*-(5-(cyanomethyl)-2-hydroxyphenyl)acetamide (3p)**



Chemical Formula: $C_{10}H_{10}N_2O_2$
Exact Mass: 190,0742
Molecular Weight: 190,2020

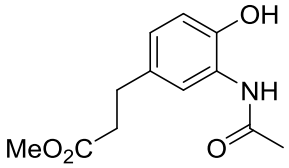
White solid, 34.2 mg, 90%.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.91 (s, 1H), 9.29 (s, 1H), 7.78 (s, 1H), 6.91 – 6.83 (m, 2H), 3.88 (s, 2H), 2.09 (s, 3H) ppm.

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.0, 147.1, 126.8, 124.0, 121.7, 121.3, 119.6, 115.9, 23.7, 21.8 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 213.0634; found 213.0624.

methyl 3-(3-acetamido-4-hydroxyphenyl)propanoate (3q)



Chemical Formula: $C_{12}H_{15}NO_4$
Exact Mass: 237,1001
Molecular Weight: 237,2550

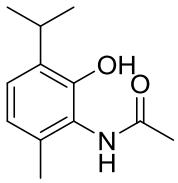
White solid, 37.0 mg, 78%.

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.45 (d, J = 2.1 Hz, 1H), 6.85 (dd, J = 8.2, 2.2 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 3.64 (s, 3H), 2.81 (t, J = 7.6 Hz, 2H), 2.58 (t, J = 7.6 Hz, 2H), 2.16 (s, 3H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 175.2, 172.2, 148.0, 133.1, 127.0, 126.5, 123.6, 117.3, 52.0, 36.9, 31.3, 23.5.

HR-MS (ESI) Expected for [M + Na^+] = 260.0893; found 260.0895.

***N*-(2-hydroxy-3-isopropyl-6-methylphenyl)acetamide (3r)**



Chemical Formula: $C_{12}H_{17}NO_2$
Exact Mass: 207,1259
Molecular Weight: 207,2730

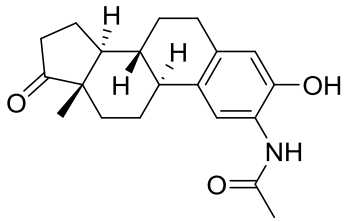
White solid, 26.1 mg, 63%.

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.15 (s, 1H), 8.30 (s, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 3.21 (dt, J = 13.6, 6.7 Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 1.14 (d, J = 6.9 Hz, 6H) ppm.

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.8, 149.5, 133.4, 132.2, 124.0, 123.5, 120.5, 26.5, 22.9, 22.6, 17.8 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 230.1151; found 230.1166.

***N*-((8R,9S,13S,14S)-3-hydroxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)acetamide (3s)**



Chemical Formula: $C_{20}H_{25}NO_3$
Exact Mass: 327,1834
Molecular Weight: 327,4240

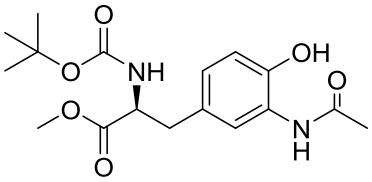
White solid, 33.4 mg, 51%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.47 (s, 1H), 9.32 (s, 1H), 7.49 (s, 1H), 6.54 (s, 1H), 2.77 – 2.68 (m, 2H), 2.43 (dd, J = 18.8, 8.1 Hz, 1H), 2.27 – 2.10 (m, 3H), 2.06 (s, 3H), 1.97 – 1.87 (m, 2H), 1.75 (d, J = 10.5 Hz, 1H), 1.60 – 1.43 (m, 3H), 1.38 – 1.29 (m, 3H), 0.82 (s, 3H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) δ 219.7, 169.0, 146.0, 132.7, 130.0, 124.0, 119.5, 115.9, 49.6, 47.3, 43.5, 37.9, 35.4, 31.3, 28.5, 26.2, 25.7, 23.5, 21.2, 13.5 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 350.1727; found 350.1730.

methyl (*S*)-3-(3-acetamido-4-hydroxyphenyl)-2-((tert-butoxycarbonyl)amino)propanoate (3t)



Chemical Formula: $C_{17}H_{24}N_2O_6$
Exact Mass: 352,1634
Molecular Weight: 352,3870

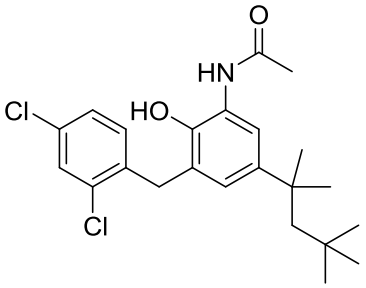
White solid, 42.3 mg, 60%.

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.60 (s, 1H), 9.28 (s, 1H), 7.52 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 9.1 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 4.24 – 3.85 (m, 1H), 3.59 (s, 3H), 2.89 – 2.78 (m, 1H), 2.75 – 2.70 (m, 1H), 2.08 (s, 3H), 1.33 (s, 9H) ppm.

^{13}C NMR (126 MHz, DMSO-d_6) δ 172.6, 168.9, 155.3, 146.5, 127.8, 126.1, 125.2, 122.7, 115.7, 78.3, 55.6, 51.7, 36.0, 28.1, 23.6 ppm.

HR-MS (ESI) Expected for [M + Na^+] = 375.1527; found 375.1550.

***N*-(3-(2,4-dichlorobenzyl)-2-hydroxy-5-(2,4,4-trimethylpentan-2-yl)phenyl)acetamide (3u)**



Chemical Formula: $C_{23}H_{29}Cl_2NO_2$
Exact Mass: 421,1575
Molecular Weight: 422,3900

White solid, 38.0 mg, 45%.

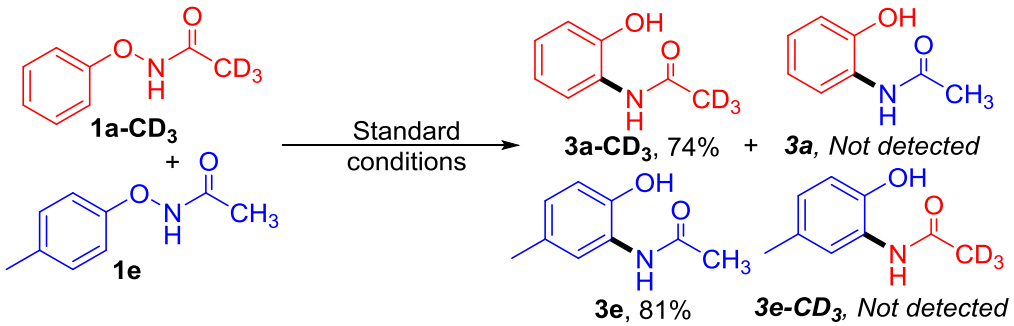
^{1}H NMR (300 MHz, Methanol-d_4) δ 7.43 (d, *J* = 2.1 Hz, 1H), 7.19 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 2.3 Hz, 1H), 4.06 (s, 2H), 2.20 (s, 3H), 1.65 (s, 2H), 1.27 (s, 6H), 0.67 (s, 9H) ppm.

^{13}C NMR (75 MHz, Methanol-d_4) δ 173.0, 146.2, 142.6, 139.0, 135.9, 133.4, 133.1, 129.8, 129.1, 128.0, 127.1, 126.7, 120.8, 57.8, 38.8, 34.3, 33.1, 32.3, 22.9 ppm (One carbon is missing because of overlapping).

HR-MS (ESI) Expected for [M + Na^+] = 444.1468; found 444.1461.

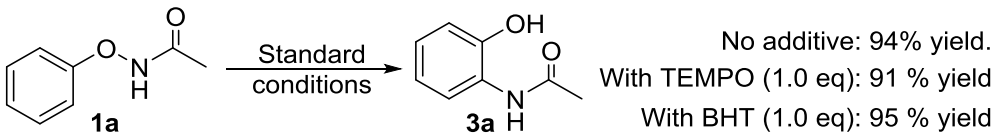
4. Mechanistic investigations

4.1 The cross-over experiment



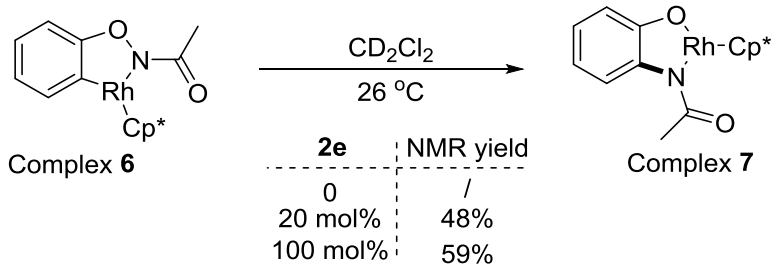
A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. The aryloxyacetamide **1a-CD3** (15.4 mg, 0.10 mmol, 0.50 equiv), **1e** (16.5 mg, 0.10 mmol, 0.50 equiv), **2e** (8.6 mg, 0.04 mmol, 20 mmol%), and $[Cp^*Rh(CH_3CN)_3](SbF6)_2$ (8.4 mg, 0.01 mmol, 5.0 mol%) were added to the tube under argon. Then, dichloromethane (0.5 mL) was added to the tube. The Schlenk tube was sealed and stirred for 12 h at room temperature. 1,3,5-trimethoxybenzene (0.1 mmol) was added as the internal standard, and the mixture was filtered. The resulting ESI-MS of the crude reaction mixture does not indicate the formation of **3e-CD3** or **3a**, whereas **3e** and **3a-CD3** were obtained. The crude ^{1}H-NMR showed that the NMR yields for these two products (74% for **3a-CD3** and 81% for **3e**).

4.2 The effect of radical scavengers



A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. *N*-(phenoxy)acetamide **1a** (15.1 mg, 0.1 mmol), NaOAc (4.1 mg, 0.05 mmol, 0.5 equiv), **2e** (4.3 mg, 0.02 mmol, 20 mmol%), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (4.2 mg, 0.005 mmol, 5.0 mol%) and additives (TEMPO or BHT, 0.1 mmol, 1.0 equiv) were added to the tube under argon. Then, dichloromethane (0.5 mL) was added to the tube. The Schlenk tube was sealed and stirred for 12 h at room temperature. After the reaction, 1,3,5-trimethoxybenzene (0.1 mmol) was added as the internal standard, and the mixture was filtered. The yield was determined by ^{1}H-NMR.

4.3 The studies of the reactions between the Rhodium complex 6 and 2e

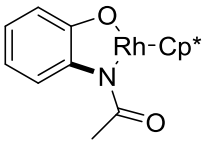


Rhodium complex **6** was prepared according to the reported procedure[12]

Complex **6** (19.3 mg, 0.05 mmol, 1.0 equiv) and olefin **2e** (10.8 mg, 0.05 mmol, 1.0 equiv) were added into a NMR tube under air. Then 0.5 mL CD_2Cl_2 was added followed by the addition of CH_2Br_2 (8.7 mg, 0.05 mmol, 1.0 equiv) as the internal standard. The NMR tube was measured at 5.0 h at 26 °C, and the NMR yield of complex **7** was 59%, along with 65% of **2e** left.

The same reaction was also carried out with catalytic amount of **2e** (2.16 mg, 0.01 mmol, 20 mol%). And 48% of the complex **7** was detected without any olefin **2e** at 5.0 h.

The synthesis of complex **7**: To a Schlenk tube were added complex **6** (77.4 mg, 0.2 mmol), olefin **2e** (43.2 mg, 0.2 mmol) and CH_2Cl_2 (2 mL) under a stream of argon. The solution was stirred for 6.0 h and then the solvent was removed in vacuo. Complex **7** (brown solid, 28 mg, 36% yield) was obtained by recrystallization from CH_2Cl_2 and ether at -20 °C for 48h. Suitable crystals for diffraction study were grown from the solution of **7** with mixed solvents of CH_2Cl_2 and ether at -20°C and the X-ray structure showed a dimer of complex **7**.

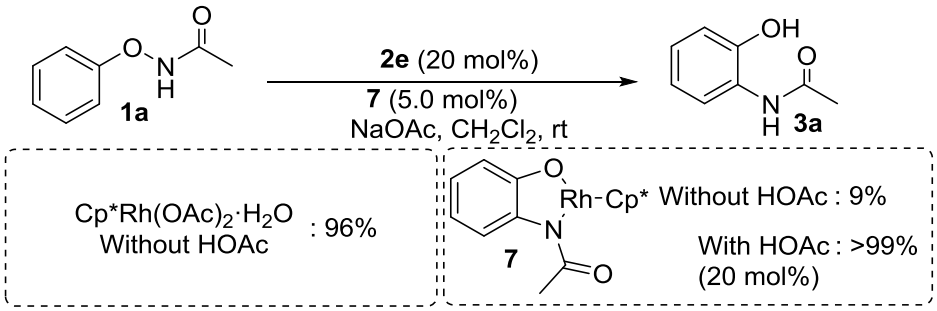


^{1}H NMR (600 MHz, Methylene Chloride-d_2) δ 8.08 (d, J = 7.7 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.68 (t, J = 7.3 Hz, 1H), 6.64 (t, J = 7.4 Hz, 1H), 2.47 (s, 3H), 0.97 (s, 15H) ppm.

^{13}C NMR (151 MHz, Methylene Chloride-d_2) δ 173.22, 165.30, 148.25, 125.10, 120.78, 119.31, 117.32, 91.92, 91.87, 28.72, 7.87 ppm.

HR-MS (ESI) Expected for [M + H^+] = 388.0778; found 388.0776.

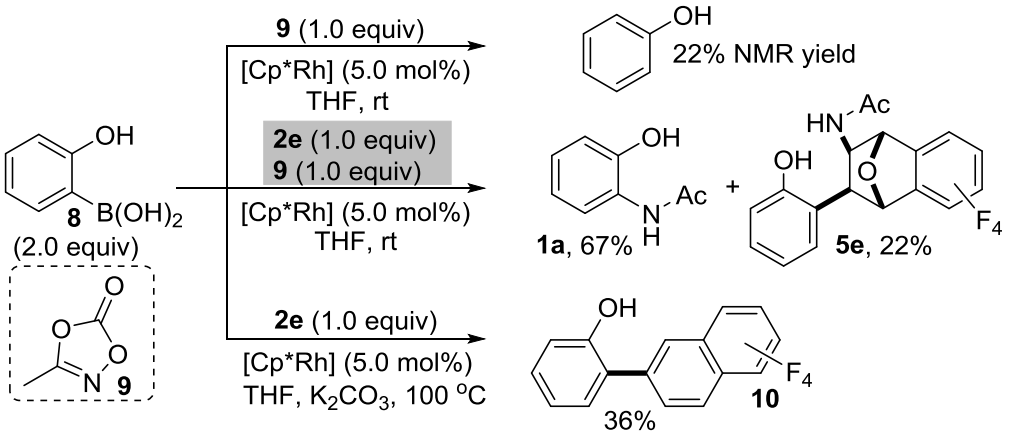
4.4 The regeneration of active catalyst from complex 7



A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. *N*-(phenoxy)acetamide **1a** (15.1 mg, 0.1 mmol), NaOAc (4.1 mg, 0.05 mmol, 0.5 equiv), **2e** (4.3 mg, 0.02 mmol, 20 mmol%), the complex **7** (1.9 mg, 0.005 mmol, 5.0 mol%) and additives [with or without (HOAc, 1 μL, 20 mol%)] were added to the tube under argon. Then, dichloromethane (0.5 mL) was added to the tube. The Schlenk tube was sealed and stirred for 12 h at room temperature. After the reaction, 1,3,5-trimethoxybenzene (0.1 mmol) was added as the internal standard, and the mixture was filtered. The solvent was removed in vacuo and the yield was determined by ^{1}H-NMR.

The reaction was also carried out using Cp*Rh(OAc)$_2$·H$_2$O (5.0 mol%) as the catalyst without the addition of HOAc.

4.5 The studies of intermolecular amidation of (2-hydroxyphenyl)boronic acid 8

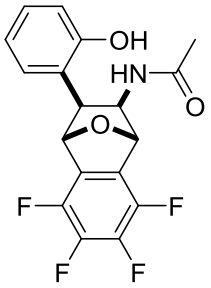


(a) A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. (2-hydroxyphenyl)boronic acid **8** (27.6 mg, 0.2 mmol, 2.0 equiv), **9** (10 mg, 0.1 mmol, 1.0 equiv) and Cp*Rh(OAc)$_2$·H$_2$O (1.87 mg, 0.005 mmol, 5.0 mol%) were added. Then, THF (0.5 mL) was added to the tube under argon. The Schlenk tube was sealed and stirred for 12 h at room temperature. After the reaction, 1,3,5-trimethoxybenzene (0.1 mmol) was added as the internal standard, and the mixture was filtered. The solvent was

removed in vacuo and the yield was determined by ^{1}H-NMR. Only 20% of the phenol was detected.

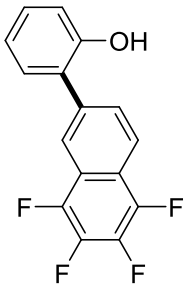
(b) A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. (2-hydroxyphenyl)boronic acid **8** (27.6 mg, 0.2 mmol, 2.0 equiv), **9** (10.1 mg, 0.1 mmol, 1.0 equiv), **2e** (21.6 mg, 0.1 mmol, 1.0 equiv) and Cp*Rh(OAc)$_2$·H$_2$O (1.87 mg, 0.005 mmol, 5.0 mol%) were added. Then, THF (0.5 mL) was added to the tube under argon. The Schlenk tube was sealed and stirred for 12 h at room temperature. After the reaction, 1,3,5-trimethoxybenzene (0.1 mmol) was added as the internal standard, and the mixture was filtered. The solvent was removed in vacuo and the yield was determined by ^{1}H-NMR. 67% of **1a**, 22% of **5e** and 43% of **2e** were detected.

(c) A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was dried under vacuum. (2-hydroxyphenyl)boronic acid **8** (27.6 mg, 0.2 mmol, 2.0 equiv), **2e** (21.6 mg, 0.1 mmol, 1.0 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv) and Cp*Rh(OAc)$_2$·H$_2$O (1.87 mg, 0.005 mmol, 5.0 mol%) were added. Then, THF (0.5 mL) was added to the tube under argon. The Schlenk tube was sealed and stirred for 12 h at 100 ^{o}C. After the reaction, 1,3,5-trimethoxybenzene (0.1 mmol) was added as the internal standard, and the mixture was filtered. The solvent was removed in vacuo and the yield was determined by ^{1}H-NMR. 36% of **6e** was detected.



Chemical Formula: $C_{18}H_{13}F_4NO_3$
Exact Mass: 367,0832
Molecular Weight: 367,2996

White solid. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.29 (s, 1H), 7.32 (dd, J = 7.7, 1.5 Hz, 1H), 7.10 (d, J = 9.2 Hz, 1H), 7.06 (td, J = 7.9, 1.6 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H), 5.89 (s, 1H), 5.54 (s, 1H), 4.61 – 4.24 (m, 1H), 3.61 (d, J = 7.8 Hz, 1H), 1.46 (s, 3H) ppm.**^{13}C NMR** (151 MHz, DMSO-d_6, ^{19}F-decoupled) δ 168.4, 155.3, 140.1, 139.3, 139.1, 139.1, 129.0, 128.5, 127.6, 126.0, 123.7, 118.7, 114.5, 81.2, 80.8, 52.4, 41.8, 22.2 ppm.**^{19}F NMR** (564 MHz, DMSO-d_6) δ-141.75 (t),-142.78 (m),-155.63 (m),-156.37(m) ppm. **HR-MS (ESI)** Expected for [M + Na$^+$] = 390.0724; found 390.0740.



Chemical Formula: $C_{16}H_8F_4O$
Exact Mass: 292.0511
Molecular Weight: 292.2326

White solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 5.07 (s, 1H) ppm.**^{13}C NMR** (151 MHz, Chloroform-*d*, ^{19}F-decoupled) δ 152.6, 142.4, 142.3, 138.3, 138.1, 137.1, 130.8, 130.0, 129.2, 127.2, 121.6, 120.9, 120.1, 120.0, 118.8, 116.4 ppm. **^{19}F NMR** (564 MHz, Chloroform-*d*) δ -150.29 (t, *J* = 16.9 Hz), -150.40 (t, *J* = 17.0 Hz), -158.36 (t, *J* = 18.3 Hz), -158.71 (t, *J* = 18.4 Hz) ppm. **HR-MS (ESI)** Expected for $[M-H]^-$ = 291.0439; found 291.0432.

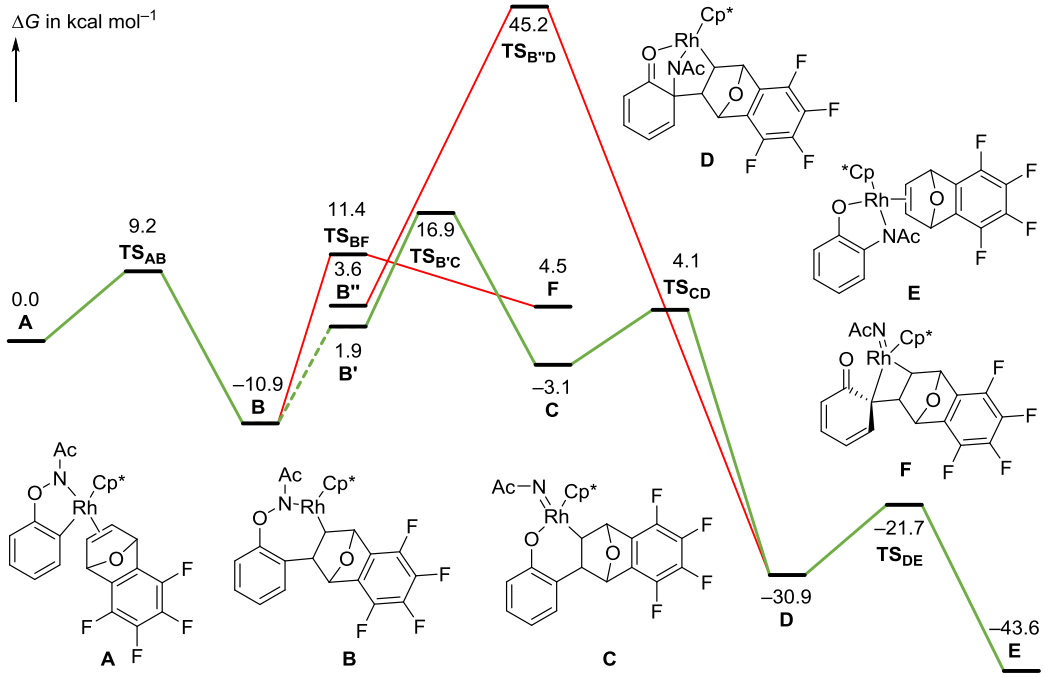
5. Computational Details

All computations[13] were carried out with the Gaussian 09 suite. The geometries of all stationary points were optimized using the M06 hybrid functional with the Lanl2DZ effective core potential and associated basis set for rhodium and the 6-31G(d) basis for all other atoms. All intermediates have been confirmed by the absence of negative eigenvalues in the frequency analysis at the same level. All transition states have been characterized by their imaginary eigenvector vibration. Single point computations were performed using the SDD effective core potential and associated basis set on rhodium as implemented in Gaussian 09 and the 6-311++G(d,p) basis on all other atoms, as well as the SMD model of solvation with all presets for dichloromethane. The computational methods were chosen to allow comparison with previous computational analyses of reactions involving [Cp*Rh] and *N*-phenoxyacetamide at this level.[14,15] No symmetrical or internal coordinate constraints have been applied. Only relevant structures are included; regioisomers and conformers of higher energy are not shown but have been accounted for in all cases. The reported free energies in kcal mol^{-1} are the sum of the single point electronic energies and the free energy corrections from the frequency analysis at the level of the optimization. Optimized structures are visualized using CYLview and selected molecular orbitals obtained from the single points are visualized using Chemissian, natural population analysis was performed with the NBO 3.1 module within Gaussian at the level of the single points.[13]

5.1 Full discussion of the computational results

Previous computational analyses have shown that the Cp*Rh(OAc)$_2$-mediated C–H activation of phenoxyacetamide (**1a**) proceeds with free enthalpies of activation of about 16–20 kcal mol^{-1}.[14,16–18] From the experimental evidence, it can safely be assumed that the intramolecular amidation proceeds from the metalacycle **6** and does not require additional additives such as acid. Thus, we limited the computational study to begin with the olefin-coordinated rhodacycle **A**. In the most favorable pathway (Scheme S1), the rhodacycle generated from C–H activation adds to the exo face of the olefin with a low free energy of activation of 9.2 kcal mol^{-1} (**TS$_{AB}$**). It has been noted previously that carbometalation of norbornadiene derivatives occurs at the exo face of the olefin.[19,20] In accordance with this, we found barriers for the addition to the exo face to be ca. 10 kcal mol^{-1} lower than addition

to the endo face. Consequently, we limit the discussion of all consecutive steps to isomers resulting from exo addition. The seven-membered rhodacycle **B** resulting from olefin insertion has a large number (~15) of isomers with varying Rh–arene distances and varying orientations of the ONAc moiety, spanning about 16 kcal mol^{-1}. Several low transition states exist between the conformers and most of these structures will be populated to varying degrees. Oxidative addition of Rh into the N–O bond then occurs from one of the higher energy conformers[15,17] of the seven-membered metalacycle (**B'**) with a barrier of $\Delta G^{\ddagger}$ = 15.0 kcal mol^{-1} ($\mathbf{TS_{B'C}}$) forming what is formally a Rh(V) nitrenoid species (**C**). While a transition state exists for an alternative N–O cleavage from the most stable conformer of **B**, this step generating the spirocyclic, dearomatized nitrenoid **F** has a higher barrier ($\Delta G^{\ddagger}$ = 22.3 kcal mol^{-1}, $\mathbf{TS_{BF}}$) and is endergonic by 15.4 kcal mol^{-1} and thus likely not competitive under the reaction conditions. After N–O cleavage, a nitrenoid addition to the *ortho* carbon has a low free energy barrier of 7.2 kcal mol^{-1} ($\mathbf{TS_{CD}}$), generating another spirocyclic, dearomatized intermediate **D**. An alternative concerted process generating this intermediate directly from an isomer of **B** without the formation of a Rh(V) intermediate was located with a very high barrier of $\Delta G^{\ddagger}$ = 41.6 kcal mol^{-1} ($\mathbf{TS_{B"D}}$), clearly disfavored in comparison to the stepwise process. The olefin elimination from **D** ($\Delta G^{\ddagger}$ = 9.2 kcal mol^{-1}, $\mathbf{TS_{DE}}$) resembles a group transfer reaction and restores aromaticity, generating the product–Rh complex **E** (corresponding to isolated complex **7** with the olefin) from which the final product can be released by protonation. No pathway was found for an olefin release from **C** prior to nitrenoid addition.



Scheme S1. Free energy profile of the *ortho* amidation process.

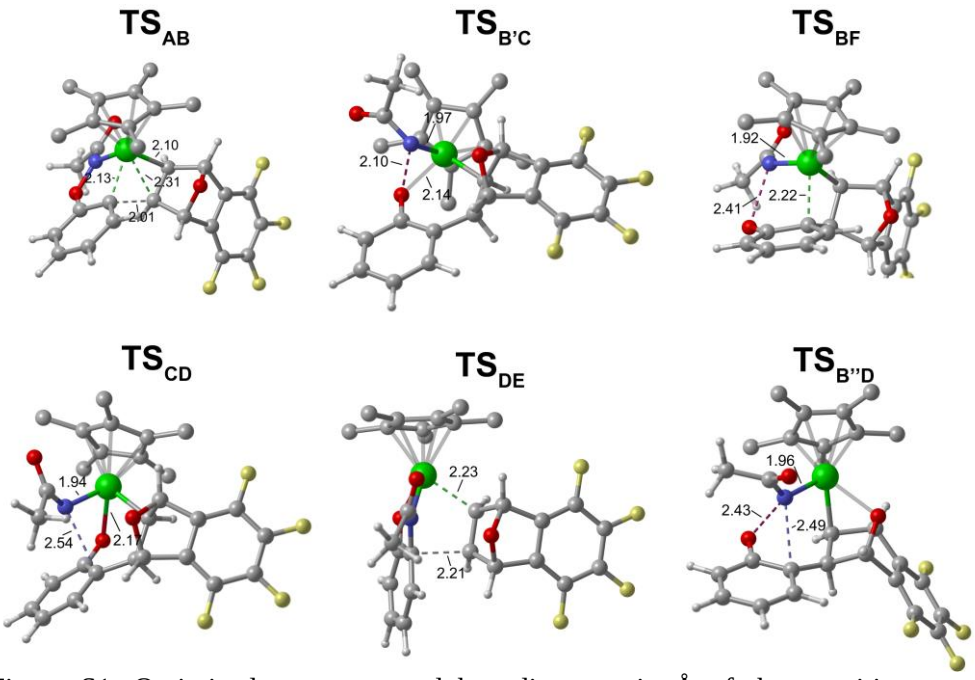


Figure S1. Optimized structures and key distances in Å of the transition states along the *ortho* amidation pathway. Cp* hydrogen atoms have been omitted for clarity.

Computed electronic and geometric parameters are in line with the interpretation of **C** as a Rh(V) nitrenoid. The Rh–N bond distance of 1.87 Å and Wiberg bond index of 1.12 both indicate a double bond character. This is further substantiated by the molecular orbitals with HOMO–48 (E = –12.929 eV) being Rh–N σ-bonding, HOMO–12 (E = –8.800 eV) being Rh–N π-bonding (Figure S2) and the LUMO (E = –3.240 eV) being Rh–N π*-antibonding (Figure S3). The NBO charge of Rh is 0.336, that of N is –0.340. Both the bond distance and NBO charges are very similar to previously analyzed Rh nitrenoid species.[14,18,21]

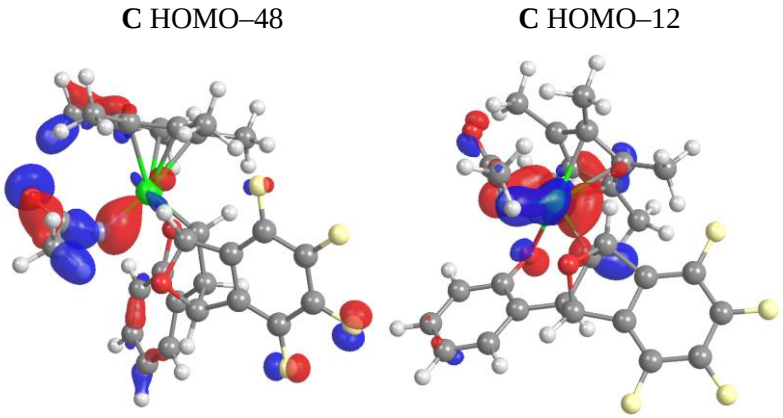


Figure S2. Kohn–Sham orbital plots (isodensity value: 0.05 au) of Rh–N bonding orbitals for **C**.

The aromatic nitrenoid addition is a novel mechanistic step in this catalytic system and crucial for the success of this reaction. Frontier molecular orbital analysis reveals the electronic nature of this reaction (Figure S3).[18] The HOMO in **C** corresponds to a π bonding orbital of the phenyl moiety while the LUMO represents the π* antibonding orbital of the Rh nitrenoid. In the HOMO of transition state **TS$_{CD}$**, both the phenyl π- and the nitrenoid π*-orbitals are present with a bonding interaction between N and the *ortho* C, a signature for electrophilic attack by the nitrenoid to the nucleophilic arene moiety. Presumably, the concomitant reduction of Rh is a driving force of this process.

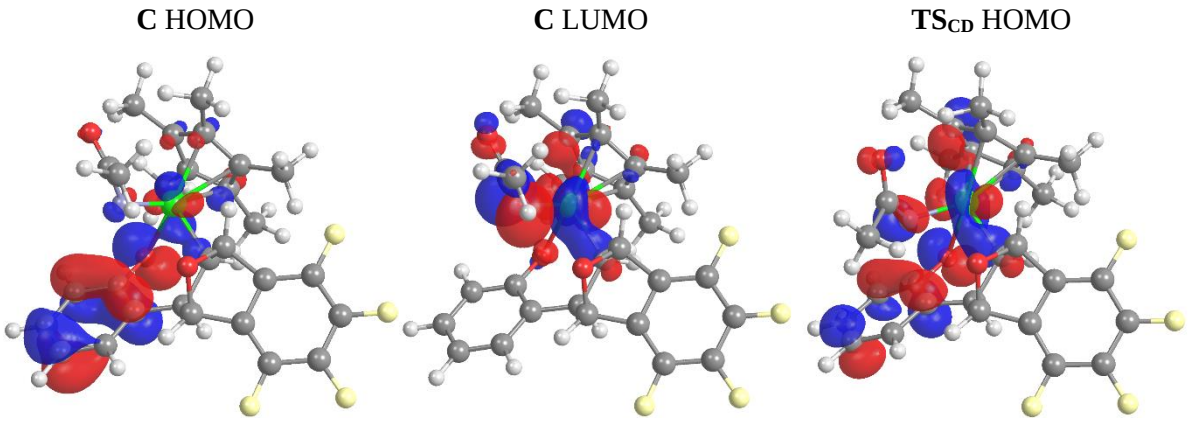
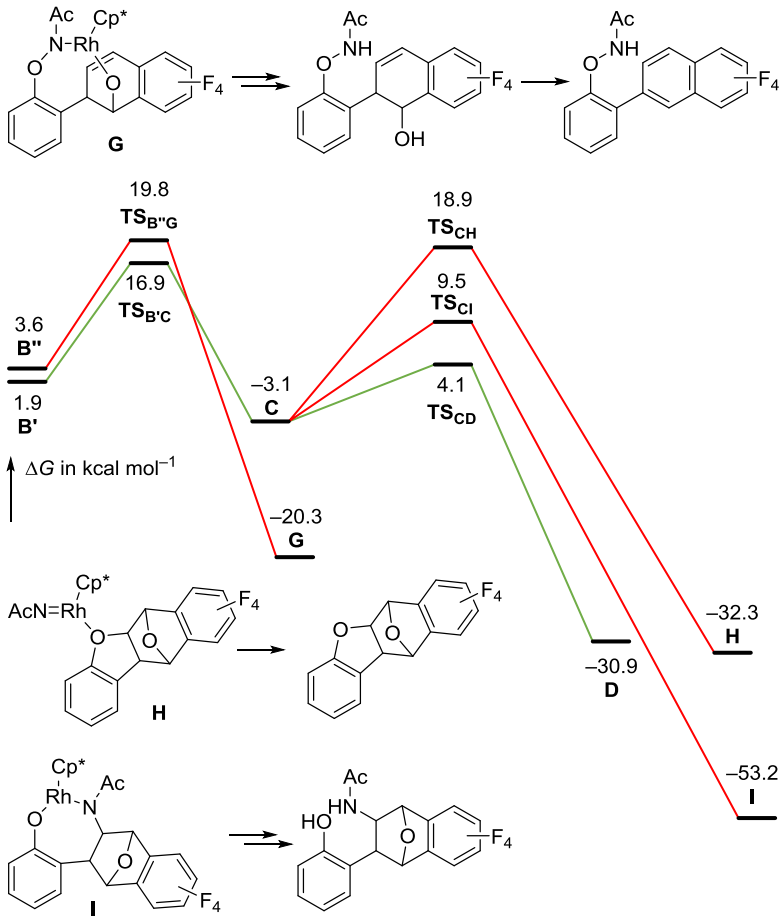


Figure S3. Kohn–Sham orbital plots (isodensity value: 0.04 au) of frontier orbitals for **C** and $\mathbf{TS_{CD}}$.

According to previous reports and observed side products,[3,5,20] a number of different processes can potentially take place in this system. In order to understand the factors responsible for the high selectivity for *ortho* amidation, some of these alternatives were studied (Scheme S2).



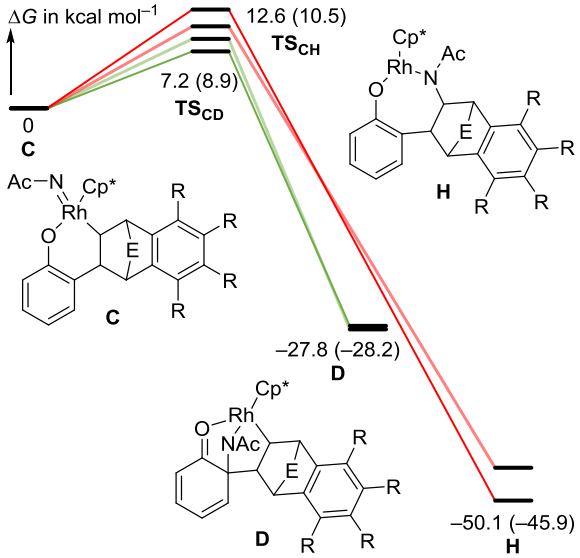
Scheme S2. Comparison of alternative modes of reaction (red) with the *ortho* amidation (green).

Firstly, the olefin insertion product **B** might undergo β-O-elimination, eventually leading to dihydronaphthylated or naphthylated products. The lowest free energy barrier for this elimination is 16.2 kcal mol^{-1} ($\mathbf{TS_{B''G}}$, cf. $\Delta G^{\ddagger}$ = 15.0 kcal mol^{-1} for N–O oxidative addition, $\mathbf{TS_{B'C}}$) and occurs from a different higher-energy conformer **B''**. While this is a feasible barrier, the facility of N–O cleavage of the oxyacetamide DG outcompetes β-O-elimination of the strained olefin.

Besides amidation, it can be imagined that reductive elimination of the phenoxide and alkyl ligands might occur from **C**, forming a potential tetrahydrodibenzofuran product. This pathway was evaluated

and found to have a potentially feasible free energy of activation of 22.0 kcal mol^{-1} (**TS$_{CH}$**). Nevertheless, reaction of the nitrenoid moiety as the most reactive part of the complex far outcompetes the reductive elimination in this system.

The nitrenoid moiety in the key intermediate **C** can react with two different carbon atoms. In previous reports, addition of a nitrenoid derived from an oxidizing DG to an organorhodium nucleophile generated by olefin or alkyne insertion has been observed in what is overall a carboamidation of the reaction partner.[3,20a] The corresponding migratory nitrenoid insertion into the Rh–C bond in **C** can take place with a barrier of $\Delta G^{\ddagger}$ = 12.6 kcal mol^{-1} (**TS$_{CI}$**). The difference to the *ortho* nitrenoid addition (**TS$_{CD}$**: $\Delta G^{\ddagger}$ = 7.2 kcal mol^{-1}) corresponds to the very high site selectivity obtained in the experiments. As observed during the optimization of this reaction, in the presence of one equivalent of benzonorbornadiene **2d**, roughly equal amounts of olefin carboamidation and *ortho* amidation products are formed. Comparing the computed barriers of both amidation pathways for both of the olefins **2d** and **2e** (Scheme S3), the same trend is found with distinctly closer barriers for both pathways with the carbocyclic olefin compared to the heterocyclic olefin ($\Delta\Delta G^{\ddagger}$ = 1.6 vs. 5.4 kcal mol^{-1}). Structural and electronic features of the Rh nitrenoids **C** derived from **2d** and **2e** were analyzed to rationalize this difference (Figure S4). Natural population analysis reveals that the nitrogen is slightly more electron rich in **C$_{2d}$** (–0.376 vs. –0.340 in **C$_{2e}$**). While most key nuclear distances are nearly identical, the N–C distance to the *ortho* carbon is shorter in **C$_{2e}$** by 0.12 Å. The dihedral angle between the former olefin carbons and Rh–N is smaller in **C$_{2e}$** by 8.7°, also indicating an incline of the nitrenoid moiety towards the arene in **C$_{2e}$**. Presumably, the bridging part of the bicyclic olefins hinders the more common migratory nitrenoid insertion by steric repulsion with the methyl group on the NAc moiety, instead forcing the nitrenoid to add to the arene. Both, dispersive stabilization in carbocycle **2d**, and electrostatic repulsion in heterocycle **2e** might alter the degree of hindrance and explain the observed difference in selectivity.



Scheme S3. Comparison of amidation pathways with olefins **2d** and **2e**. Green: *ortho* addition **C**–**D**, red: migratory nitrenoid insertion **C**–**H**; darker lines: **2e** (E = O, R = F), brighter lines and numbers in brackets: **2d** (E = CH_2, R = H).

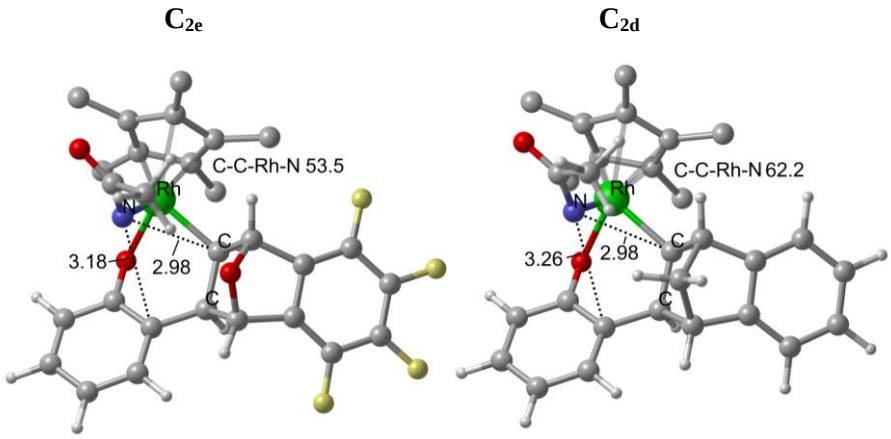
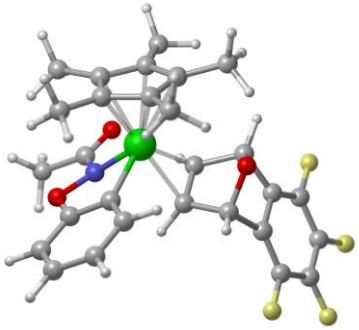


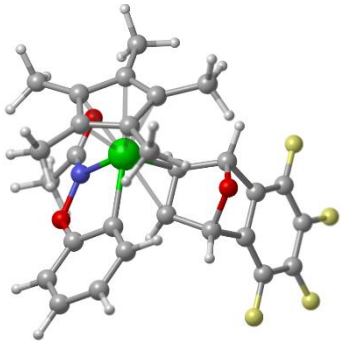
Figure S4. Optimized structures of the Rh nitrenoid intermediates **C** derived from olefins **2e** and **2d** with key N–C distances in Å and the dihedral angle C–C–Rh–N (atoms indicated).

5.2 Minimum energy structures of the relevant intermediates and transition states.

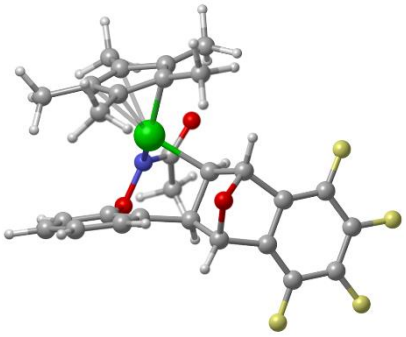
A



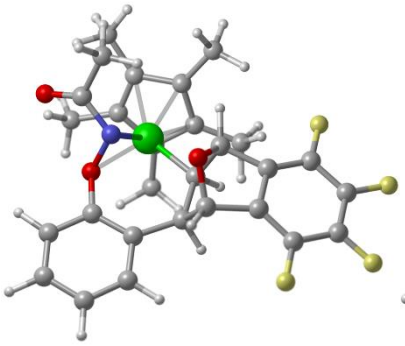
TS_{AB}



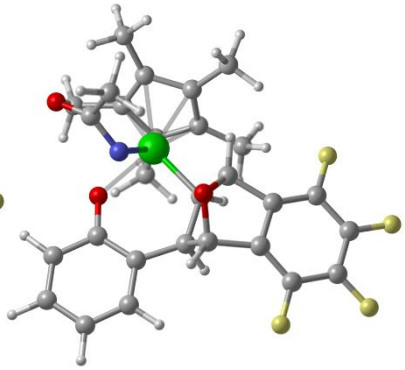
B



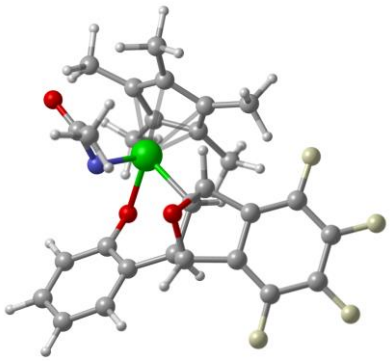
B'



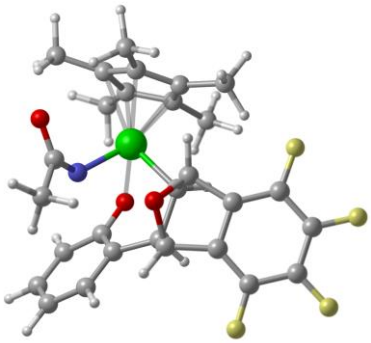
$TS_{B'C}$



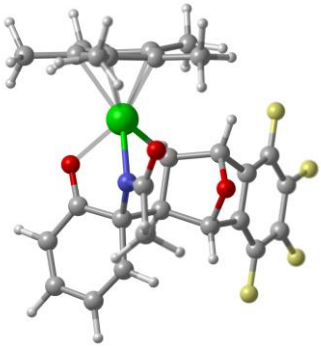
C



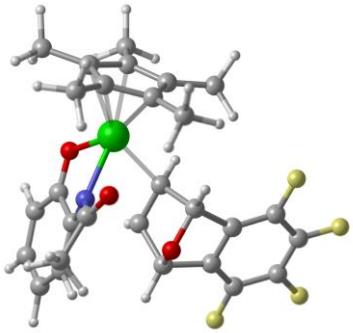
TS_{CD}



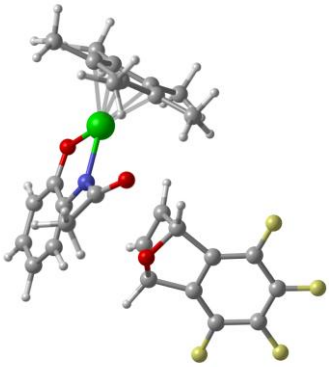
D



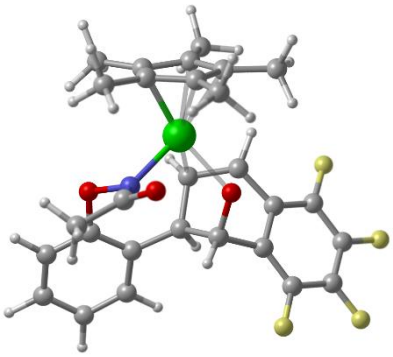
TS_{DE}



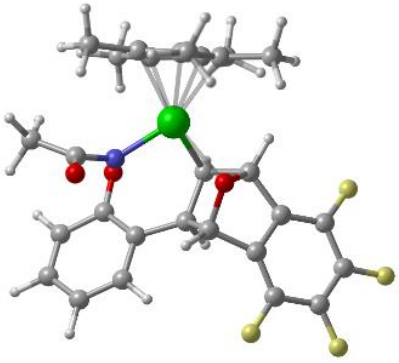
E



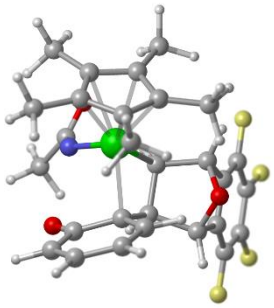
B''



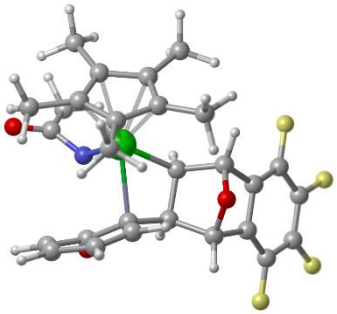
$TS_{B''D}$



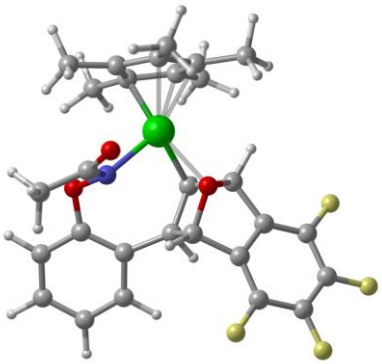
TS_{BF}



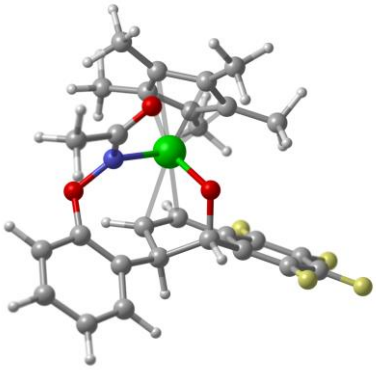
F



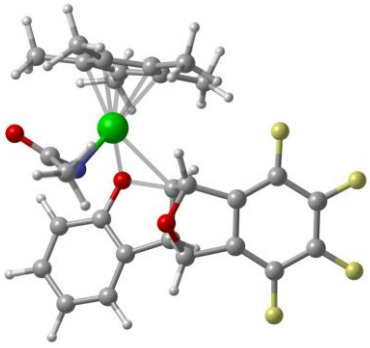
$TS_{B''S}$



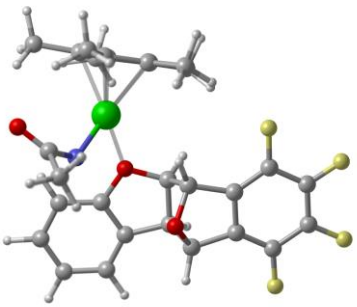
S



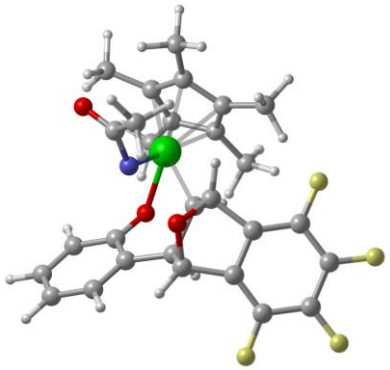
TS_{CH}



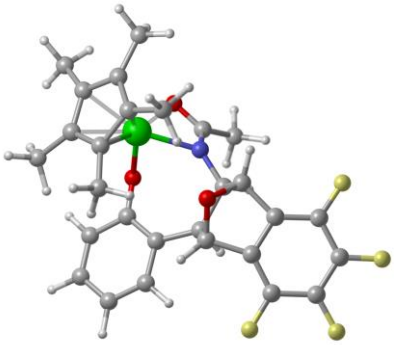
H



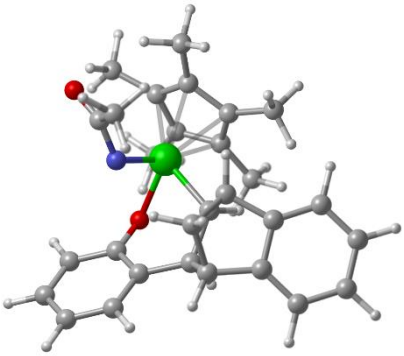
TS_{CI}



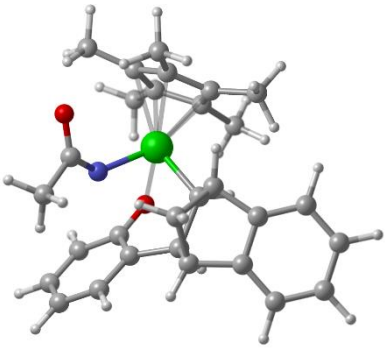
I



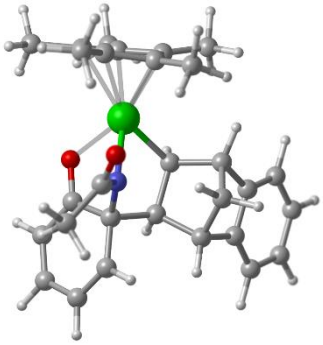
C_{2d}



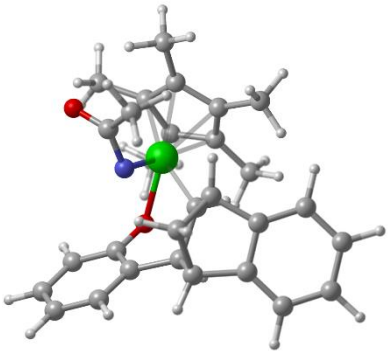
TS_{CD-2d}



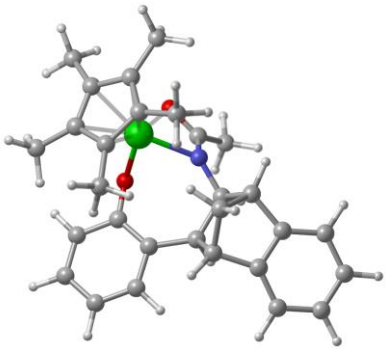
D_{2d}



TS_{CI-2d}



I_{2d}



5.3 Cartesian coordinates of minimum energy structures in .xyz format

The comment line contains the structure name, energies in Hartree of both the method used for optimization (E_DZ) and for the single points (E_TZ) and the number of imaginary frequencies (NIMAG).

```
63
A E_DZ = -1870.778107 E_TZ = -1872.309494 NIMAG = 0
C   1.772207 -1.248504 -0.651552
C   1.604883  0.844829 -1.062362
C   0.843868 -0.736741  0.452641
C   0.769772 -1.207970  1.431593
C   0.738328  0.632553  0.173034
C   0.622354  1.410477  0.921432
C   1.729985 -2.301862 -0.935952
C   1.383683  1.696445 -1.709112
C   3.039746  0.681211 -0.568504
C   3.147680 -0.688601 -0.295985
C  -1.653612  1.733658 -0.186338
C  -2.229487  2.186021  1.004174
Rh -1.535645  2.617121 -1.250145
O  -2.735610  3.478200  1.116461
N  -2.039019  3.917516 -1.154672
C  -1.065244  2.289249 -2.179819
O  -2.644499  4.336726  0.025476
C  -3.185946  3.796441  2.055193
C  -1.954999  4.597274 -2.001131
C  -3.038639  5.348172  0.108597
C  -1.242275 -0.289747 -0.130510
C  -2.351166  1.347010  2.065226
C  -1.518244  0.203249  1.870539
C  -1.521629 -0.638359  2.926588
C  -0.977874 -1.748695  2.859025
C  -2.191187 -0.166197  4.195355
C  -1.823686  0.816982  4.508407
C  -3.273809 -0.066173  4.042333
O  -1.998244 -0.907384  4.975211
C  -2.196590 -0.822570 -2.130475
C  -1.420401 -1.960007 -1.755549
C  -3.208591 -0.635992 -1.123023
C  -1.916392 -2.471481 -0.508459
F  -3.034816 -1.667420 -0.136312
F  -0.416993 -2.608577 -2.640892
F  -0.935961 -3.093665 -3.481162
F   0.289471 -1.884730 -3.059910
F   0.149612 -3.390381 -2.122302
C  -2.054308 -0.083406 -3.414853
H  -2.506589  0.913637 -3.362407
H  -0.995803  0.038377 -3.682324
H  -2.542630 -0.623895 -4.239936
C  -1.418192 -3.653986  0.249730
H  -1.273267 -3.392255  1.306601
H  -2.122669 -4.496153  0.189449
H  -0.454186 -4.003933 -0.139398
C  -3.881047 -1.875155  1.069474
H  -4.735200 -2.525355  0.830249
H  -3.304952 -2.348986  1.872843
H  -4.281075 -0.927252  1.450907
C  -4.328934  0.345807 -1.155026
H  -5.217768 -0.096998 -1.627421
H  -4.611559  0.663819 -0.143776
H  -4.063626  1.251843 -1.712064
O   1.439370 -0.395680 -1.751882
C   4.300887 -1.213957  0.223835
C   5.382256 -0.355639  0.461559
C   5.274838  1.000619  0.194043
C   4.084001  1.531732 -0.319458
F   4.436076 -2.508593  0.497533
F   4.012350  2.838619 -0.557376
F   6.311069  1.795698  0.419502
F   6.520282 -0.840985  0.937179
63
B E_DZ = -1870.797527 E_TZ = -1872.327086 NIMAG = 0
C   1.399974 -0.590391 -1.238127
C   1.765523  1.511950 -1.038640
C   0.581438 -0.265430  0.017187
C   0.891589 -0.859544  0.883507
C   0.796066  1.259576  0.135888
C   1.236091  1.560824  1.097645
C   1.120185 -1.472705 -1.817713
C   1.804195  2.532029 -1.431618
C   3.083417  0.873017 -0.674828
C   2.852090 -0.497968 -0.815140
C  -0.542735  1.972057 -0.033256
C  -1.362920  2.212232  1.095109
Rh -0.943965  2.556059 -1.250428
O  -2.457578  3.071925  1.030174
N  -2.047297  3.392565 -1.323579
C  -0.367857  2.338246 -2.148229
O  -2.787865  3.676021 -0.173885
C  -3.041137  3.228093  1.934963
C  -2.323927  3.839300 -2.277136
C  -3.643782  4.347115 -0.225553
C  -1.505997 -0.303359 -0.036941
C  -1.098816  1.590350  2.275638
C  -1.238641  0.166780  2.025309
C  -0.614960 -0.582812  2.962606
C  -0.572631 -1.813190  2.840097
C  -0.015643  0.114639  4.159031
C   0.820705  0.755360  3.849732
C  -0.743386  0.765356  4.656411
O   0.344704 -0.647309  4.854901
C  -2.919613 -0.637910 -1.715714
C  -1.992926 -1.722681 -1.673600
C  -3.737876 -0.652636 -0.517917
C  -2.122461 -2.331553 -0.378306
F  -3.239294 -1.676478  0.310195
F  -1.146526 -2.173339 -2.812965
F  -1.758337 -2.685225 -3.570377
F  -0.646252 -1.331949 -3.310801
F  -0.376513 -2.884341 -2.491423
C  -3.111024  0.283146 -2.867223
H  -3.431441  1.279984 -2.538720
H  -2.186608  0.400690 -3.446342
H  -3.884721 -0.107326 -3.545357
C  -1.381751 -3.512269  0.138594
H  -1.090350 -3.349069  1.183838
H  -1.997388 -4.422526  0.081884
H  -0.464777 -3.690668 -0.437161
C  -3.691301 -2.042730  1.678060
H  -4.359662 -2.915536  1.641228
H  -2.828892 -2.291021  2.309361
H  -4.231374 -1.218953  2.158274
C  -4.831494  0.312070 -0.218134
H  -5.749206  0.076851 -0.777246
H  -5.081394  0.309760  0.849436
H  -4.541002  1.339725 -0.480009
O   1.277029  0.599600 -2.031414
C   3.827039 -1.409559 -0.489653
C   5.065425 -0.939668 -0.045835
C   5.293127  0.423949  0.095733
C   4.285392  1.343023 -0.206200
F   3.635320 -2.722869 -0.597129
F   6.040005 -1.794516  0.232978
F   6.479515  0.848988  0.509935
F   4.524343  2.643024 -0.044421
63
B' E_DZ = -1870.778129 E_TZ = -1872.308073 NIMAG = 0
C   0.054447  5.099586 -0.955237
C   0.748450  3.905338 -0.835444
C   0.127907  2.697923 -0.484454
C  -1.249085  2.758764 -0.270476
C  -1.964814  3.947768 -0.382037
C  -1.317636  5.124124 -0.725339
C   1.665242  1.537387 -1.297772
C   0.584881  6.009025 -1.231077
O   1.823781  3.889696 -1.025872
Rh  0.521797  0.045297 -0.215994
C  -3.033983  3.911657 -0.183313
C  -1.879665  6.051854 -0.811568
C   1.041021  1.495295 -0.391235
O  -2.041936  1.656541  0.019280
N  -1.501931 -0.453890 -0.218983
C   0.924565 -0.568354 -1.032338
O   1.197348 -0.354005  1.123904
C   0.694214 -1.117551  1.723623
C   1.988147  1.602925  0.857502
C   2.201048  2.618492  1.201814
C   2.651228 -0.592458  0.778275
C   1.281515  0.869565  1.841663
```

C -1.658877 1.041584 1.283788
C -2.806685 0.785640 2.014340
C -3.961781 1.047454 1.709607
C -2.438291 0.131929 3.326764
C -3.033264 -0.778452 3.466650
C -1.369553 -0.099012 3.395785
C -2.699970 0.817740 4.141251
C -2.158524 -1.601749 -1.968286
C -1.190035 -2.358410 -1.245767
F -3.354247 -1.485552 -1.139318
C -1.721512 -2.576924 0.076335
F -3.103034 -2.108882 0.088493
C -1.065574 -3.358467 1.160947
F -1.409081 -4.403854 1.159822
F 0.025888 -3.373582 1.047132
F -1.293294 -2.939345 2.150059
C 0.118106 -2.860684 -1.749029
H 0.905763 -2.816753 -0.984446
H 0.031381 -3.910140 -2.064027
H 0.468481 -2.287319 -2.615807
C -4.604805 -0.752595 -1.484692
H -4.516991 -0.223568 -2.439986
H -5.458244 -1.441373 -1.565093
H -4.845695 -0.012369 -0.709078
C -4.075567 -2.221131 1.209239
H -4.941016 -2.828160 0.906973
H -3.629651 -2.703699 2.087084
H -4.460633 -1.234200 1.512818
C -2.040654 -1.112118 -3.369384
H -0.992397 -1.009777 -3.673358
H -2.528317 -1.800233 -4.075714
H -2.511871 -0.128726 -3.488965
C 3.170310 0.691731 0.595373
C 4.448111 0.866457 0.123178
C 5.234066 -0.260654 -0.132895
F 4.963132 2.074969 -0.097083
C 4.711515 -1.538119 0.038321
F 6.487007 -0.118998 -0.547706
C 3.397756 -1.704314 0.480089
F 5.473118 -2.595216 -0.213432
F 2.891914 -2.940112 0.588188
63
B" E_DZ = -1870.772522 E_TZ = -1872.303383 NIMAG = 0
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C -0.329153 -0.202319 -1.088755
C -0.334211 -0.336842 -2.176285
C -0.994870 1.081275 -0.581093
C -1.963117 1.123837 -1.105176
C -0.746694 -2.279964 -0.330341
C -1.127462 1.258248 1.711274
C -2.752968 0.041851 0.727863
C -0.473961 2.486852 -0.806076
C 0.831314 2.989880 -0.686350
Rh -1.438500 3.411262 -1.240976
O 1.140411 4.308839 -1.022950
N -1.151524 4.728999 -1.564086
C -2.468129 3.063343 -1.340321
O 0.160122 5.179111 -1.468203
C 2.175606 4.625038 -0.903126
C -1.946350 5.393217 -1.896892
C 0.417431 6.206122 -1.721126
C 1.451126 -0.668994 -0.035603
C 1.909990 2.265936 -0.266165
C 1.555430 1.260226 0.654449
C 2.014761 1.506689 1.913000
C 2.004999 0.616213 2.762910
C 2.495417 2.905993 2.226567
C 2.663599 2.972990 3.304804
C 3.432724 3.123363 1.698066
O 1.770776 3.668422 1.915365
C 3.014321 -2.131743 0.823489
C 2.157660 -2.792527 -0.159449
C 3.666997 -1.070022 0.186037
F 2.325772 -2.157042 -1.413247
C 3.182905 -1.008491 -1.193359
F 1.339250 -3.998928 0.145226
C 1.982943 -4.868649 0.342368
F 0.724231 -3.846843 1.043623
F 0.671996 -4.265916 -0.682971
F 3.082991 -2.517087 2.258925
H 3.652758 -1.788590 2.843629
H 2.078482 -2.557079 2.701523
H 3.546468 -3.506874 2.384904
C 1.729690 -2.567097 -2.714992
H 1.619729 -1.712360 -3.392795
H 2.364128 -3.307593 -3.222796
H 0.736326 -3.017338 -2.591377
C 3.664737 -0.058297 -2.232381
H 4.627864 -0.380140 -2.656231
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H 3.793468 0.947698 -1.815624
C 4.606617 -0.091476 0.798161
H 4.529058 0.884494 0.302510
H 4.383424 0.061507 1.860737
H 5.648051 -0.429960 0.703645
O -0.639302 -0.672024 1.044077
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F -6.004531 -2.070199 -0.575840
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F -6.339679 0.122217 0.957670
F -4.215198 1.561829 1.805702
63
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C -0.469113 0.077361 -0.297464
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C -0.985324 1.543688 -0.433848
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C -0.726229 -1.194933 1.557446
C -2.195814 2.570226 1.185170
C -2.655821 -0.600525 0.589050
C -0.014417 2.700175 -0.464139
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H -6.308537 -1.922159 -1.702838
H -5.592591 0.423320 -1.269141

6. Crystallographic data

X-Ray diffraction: Data sets for compounds **6** and **7** were collected with a D8 Venture CMOS diffractometer. Data sets for compound **3t** were collected with an APEX II CCD diffractometer. Programs used: data collection: APEX2 V2014.5-0;[22] cell refinement: SAINT V8.34A;[22] data reduction: SAINT V8.34A;[22] absorption correction, SADABS V2014/2;[22] structure solution SHELXT-2014;[23] structure refinement SHELXL-2014.[23] *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: For compound **3t** one disordered over two positions *t*Bu group was found in the asymmetrical unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. Moreover, a badly disordered pentane molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE[24] was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule.

X-ray crystal structure analysis of 3t: A colorless needle-like specimen of $C_{17}H_{24}N_2O_6$, approximate dimensions 0.040 mm x 0.040 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1411 frames were collected. The total exposure time was 26.39 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 19509 reflections to a maximum θ angle of 66.75° (0.84 Å resolution), of which 3762 were independent (average redundancy 5.186, completeness = 99.6%, R_{int} = 12.14%, R_{sig} = 11.74%) and 2805 (74.56%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 13.7749(14) Å, $\underline{b}$ = 21.091(2) Å, $\underline{c}$ = 7.3456(7) Å, volume = 2134.1(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 1863 reflections above 20 σ(I) with 7.665° < 2θ < 131.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.829. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8510 and 0.9730. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12$, with Z = 4 for the formula unit, $C_{17}H_{24}N_2O_6$. The final anisotropic full-matrix least-squares refinement on F^2 with 275 variables converged at R1 = 5.21%, for the observed data and wR2 = 13.59% for all data. The goodness-of-fit was 1.043. The largest peak in the final difference electron density synthesis was 0.212 $e^-/Å^3$ and the largest hole was -0.217 $e^-/Å^3$ with an RMS deviation of 0.053 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.097 g/cm^3 and F(000), 752 e^-.

X-ray crystal structure analysis of 6: A dark red plate-like specimen of $C_{18}H_{22}NO_2Rh$, approximate dimensions 0.071 mm x 0.164 mm x 0.243 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 4.00 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 14670 reflections to a maximum θ angle of 27.52° (0.77 Å resolution), of which 3708 were independent (average redundancy 3.956, completeness = 99.4%, R_{int} = 4.45%, R_{sig} = 3.67%) and 3067 (82.71%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 12.4920(6) Å, $\underline{b}$ = 8.7630(4) Å, $\underline{c}$ = 15.2416(6) Å, β = 103.801(2)°, volume = 1620.29(13) $Å^3$, are based upon the refinement of the XYZ-centroids of 9033 reflections above 20 σ(I) with 5.504° < 2θ < 50.77°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.905. The

calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7830 and 0.9290. The final anisotropic full-matrix least-squares refinement on F^2 with 205 variables converged at R1 = 2.64%, for the observed data and wR2 = 5.37% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 0.613 $e^-/Å^3$ and the largest hole was -0.642 $e^-/Å^3$ with an RMS deviation of 0.094 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.588 g/cm^3 and F(000), 792 e^-.

X-ray crystal structure analysis of 7: A red prism-like specimen of $C_{36}H_{44}N_2O_4Rh_2$, approximate dimensions 0.166 mm x 0.213 mm x 0.245 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 295 frames were collected. The total exposure time was 3.69 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 17324 reflections to a maximum θ angle of 27.55° (0.77 Å resolution), of which 3595 were independent (average redundancy 4.819, completeness = 98.7%, R_{int} = 2.97%, R_{sig} = 2.23%) and 3263 (90.76%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.9285(5) Å, b = 14.9350(6) Å, c = 10.6506(5) Å, β = 90.570(2)°, volume = 1579.22(13) $Å^3$, are based upon the refinement of the XYZ-centroids of 9942 reflections above 20 σ(I) with 6.263° < 2θ < 55.09°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.905. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7760 and 0.8400. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 2 for the formula unit, $C_{36}H_{44}N_2O_4Rh_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 205 variables converged at R1 = 2.36%, for the observed data and wR2 = 5.99% for all data. The goodness-of-fit was 1.141. The largest peak in the final difference electron density synthesis was 0.505 $e^-/Å^3$ and the largest hole was -0.629 $e^-/Å^3$ with an RMS deviation of 0.081 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.629 g/cm^3 and F(000), 792 e^-.

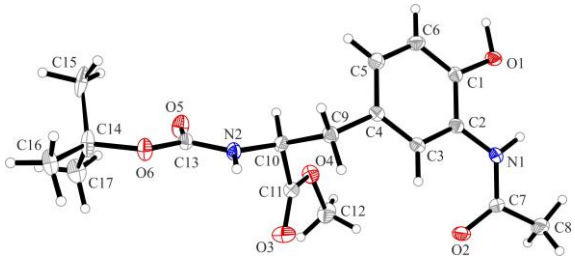


Figure S5. Crystal structure of compound **3t**.
(Thermals ellipsoids are shown with 30% probability.)

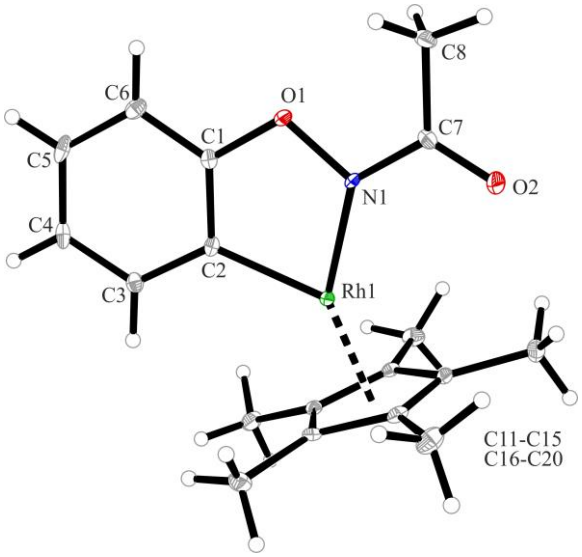


Figure S6. Crystal structure of compound **6**.
(Thermals ellipsoids are shown with 30% probability.)

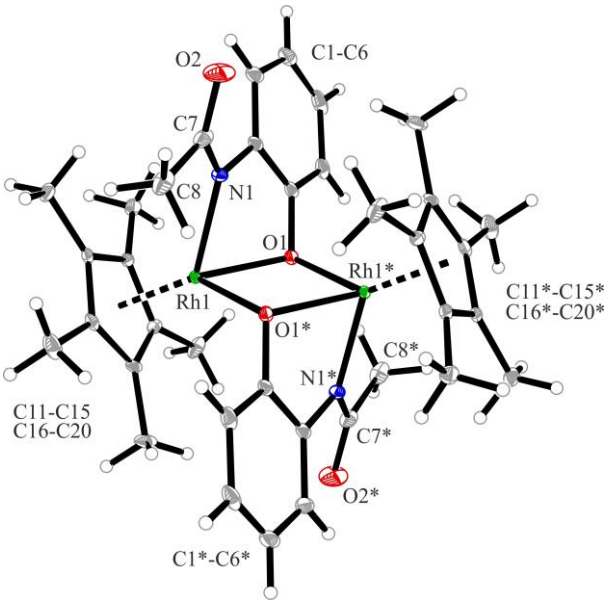


Figure S7. Crystal structure of compound **7**.
(Thermals ellipsoids are shown with 30% probability.)

7. Literature

(1) Li, B.; Lan, J.; Wu, D.; You, J. *Angew. Chem. Int. Ed.* **2015**, *54*, 14008.

(2) Bernardes,G. J. L.; Chalker,J. M.; Errey,J. C.; Davis,B. G. *J. Am. Chem. Soc.* **2008**, *130*, 5052.

(3) Liu, G.; Shen,Y.; Zhou,Z.; Lu,X. *Angew. Chem. Int. Ed.* **2013**, *52*, 6033.

(4) Yang,Q.; Choy,P. Y.; Fan,B.; Kwong,F. Y. *Adv. Synth. Cat.* **2015**, *357*, 2345.

(5) Gandeepan, P.; Rajamalli, P.; Cheng, C.-H. *Angew. Chem. Int. Ed.* **2016**, *55*, 4308.

(6) Coe, J. W.; Wirtz, M. C.; Bashore, C. G.; Candler, J. *Org. Lett.* **2004**, *6*, 1589.

(7) McKee, M.; Haner, J.; Carlson, E.; Tam, William, *Synthesis* **2014**, *46*, 1518.

(8) Li, K.-L.; Du, Z.-B.; Guo, C.-C.; Chen, Q.-Y. *J. Org. Chem.* **2009**, *74*, 3286.

(9) Matsushita, H.; Lee, S.-H.; Joung, M.; Clapham, B.; Janda, K. D. *Tetrahedron Lett.* **2004**, *45*, 313.

(10) Armitage, M.; Bret, G.; Choudary, B. M.; Kingswood, M.; Loft, M.; Moore, S.; Smith, S.; Urquhart, W. J. *Org. Process Res. Dev.* **2012**, *16*, 1626.

(11) Seth, K.; Nautiyal, M.; Purohit, P.; Parikh, N.; Chakraborti, A. K. *Chem. Commun.* **2015**, *51*, 191.

(12) (a) Wu, Q.; Chen, Y.; Yan, D.; Zhang, M.; Lu, Y.; Sun, W.-Y.; Zhao, J. *Chem. Sci.* **2017**,*8*, 169. (b) Wang, X.; Lerchen, A.; Gensch, T.; Knecht, T.; Daniliuc, C. G.; Glorius, F. *Angew. Chem. Int. Ed.* **2017**, *56*, 1381.

(13) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision D.01;

Gaussian, Inc.: Wallingford, CT, 2013. (b) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215. (c) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (d) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866. (e) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. *Theor. Chem. Acc.* **1990**, *77*, 123. (f) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378. (g) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (h) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 2257. (i) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.* **1973**, *28*, 213. (j) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (k) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111. (l) Roy, L. E.; Hay, P. J.; Martin, R. L. *J. Chem. Theory Comput.* **2008**, *4*, 1029. Visualization of computed structures using: (m) Legault, C. Y. *CYLView, 1.0b*; Université de Sherbrooke, Canada, 2009; http://www.cylview.org. Visualization of molecular orbitals using: (n) Leonid, S. *Chemissian 4.43*, 2016; http://www.chemissian.com. (o) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold., F. NBO Version 3.1.

(14) Yang, Y. F.; Houk, K. N.; Wu, Y. D. *J. Am. Chem. Soc.* **2016**, *138*, 6861–6868.

(15) Chen, J.; Guo, W.; Xia, Y. *J. Org. Chem.* **2016**, *81*, 2635–2638.

(16) Guo, W.; Xia, Y. *J. Org. Chem.* **2015**, *80*, 8113–8121.

(17) Li, J.; Qiu, Z. *J. Org. Chem.* **2015**, *80*, 10686–10693.

(18) Qiu, Z.; Deng, J.; Zhang, Z.; Wu, C.; Li, J.; Liao, X. *Dalt. Trans.* **2016**, *45*, 8118–8126.

(19) Lautens, M.; Fagnou, K.; Hiebert, S.; *Acc. Chem. Res*. **2003**, *36*, 48.

(20) (a) Hu, Z.; Tong, X.; Liu, G. *Org. Lett.* **2016**, *18*, 1702. (b) Shen, Y.; Liu, G.; Zhou, Z.; Lu, X. *Org. Lett.* **2013**, *15*, 3366. (c) Zhou, Z.; Liu, G.; Chen, Y.; Lu, X. *Org. Lett.* **2015**, *17*, 5874. (d) Qi, Z.; Li, X. Angew. Chem. Int. Ed. 2013, 52, 8995. (e) Dong, W.; Parthasarathy, K.; Cheng, Y.; Pan, F.; Bolm, C. Chem. Eur. J. 2014, 20, 15732. (f) Li, D. Y.; Jiang, L. L.; Chen, S.; Huang, Z. L.; Dang, L.; Wu, X. Y.; Liu, P. N. Org. Lett. 2016, 18, 5134.

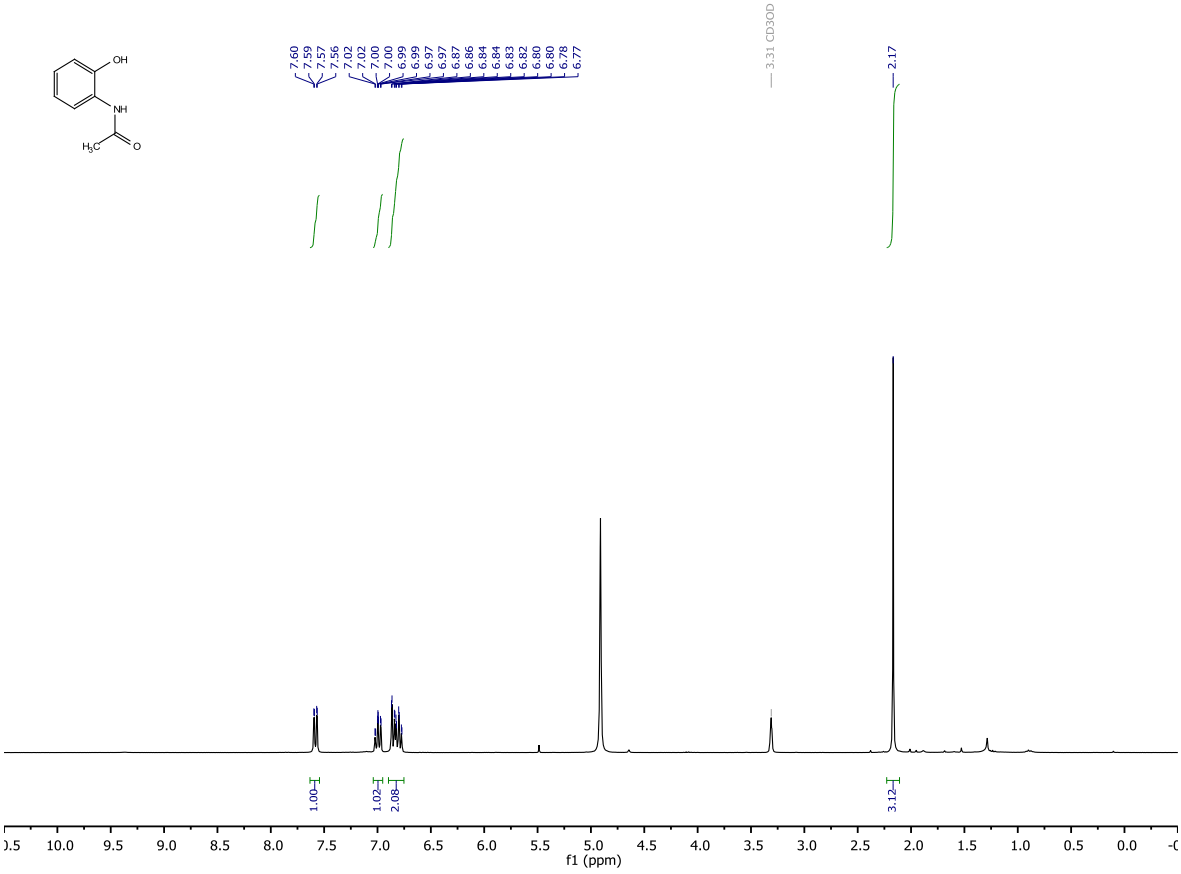
(21) (a) Park, S. H.; Kwak, J.; Shin, K.; Ryu, J.; Park, Y.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 2492–2502. (2) Figg, T. M.; Park, S.; Park, J.; Chang, S.; Musaev, D. G. *Organometallics* **2014**, *33*, 4076–4085. (3) Park, Y.; Heo, J.; Baik, M.-H.; Chang, S. *J. Am. Chem. Soc.* **2016**, *138*, 14020–14029.

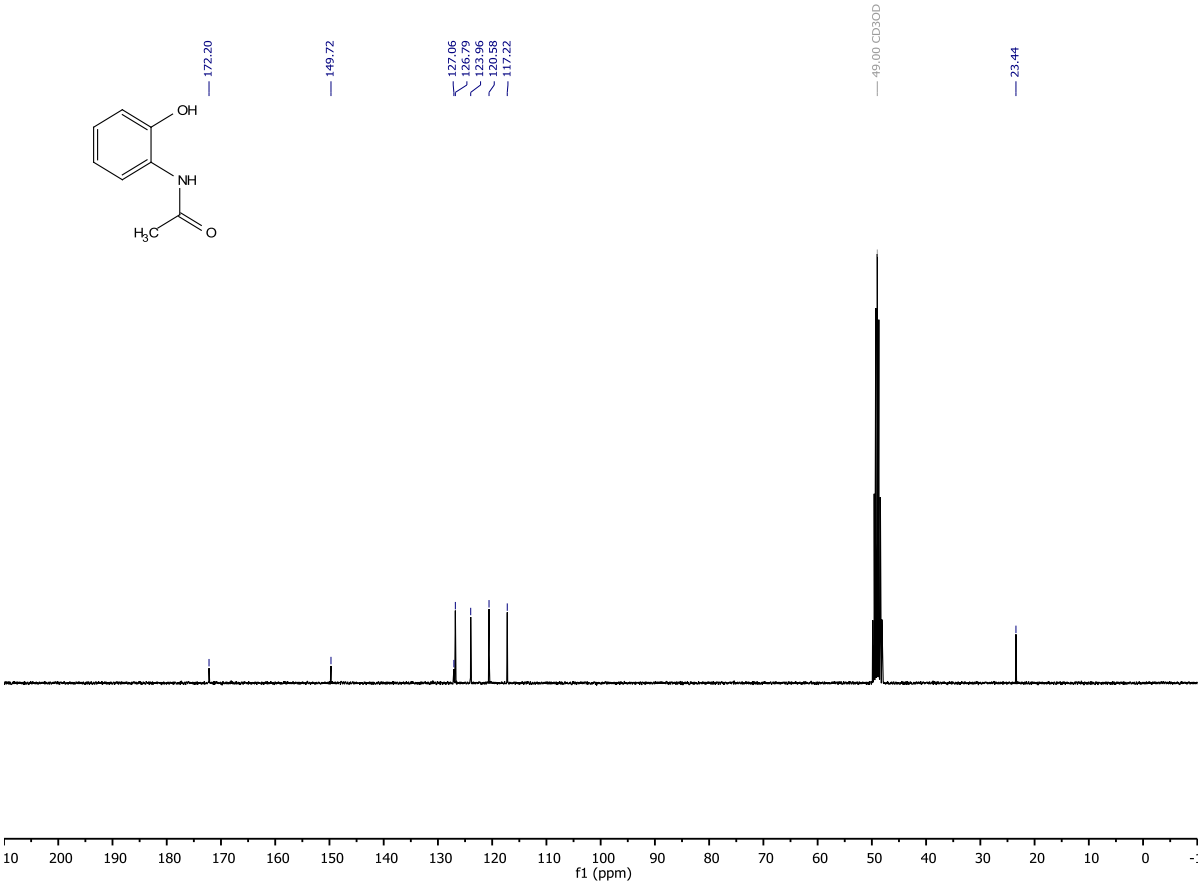
(22) *APEX2* (**2014**), *SAINT* (**2013**) and *SADABS* (**2014**), Bruker AXS Inc., Madison, Wisconsin, USA.

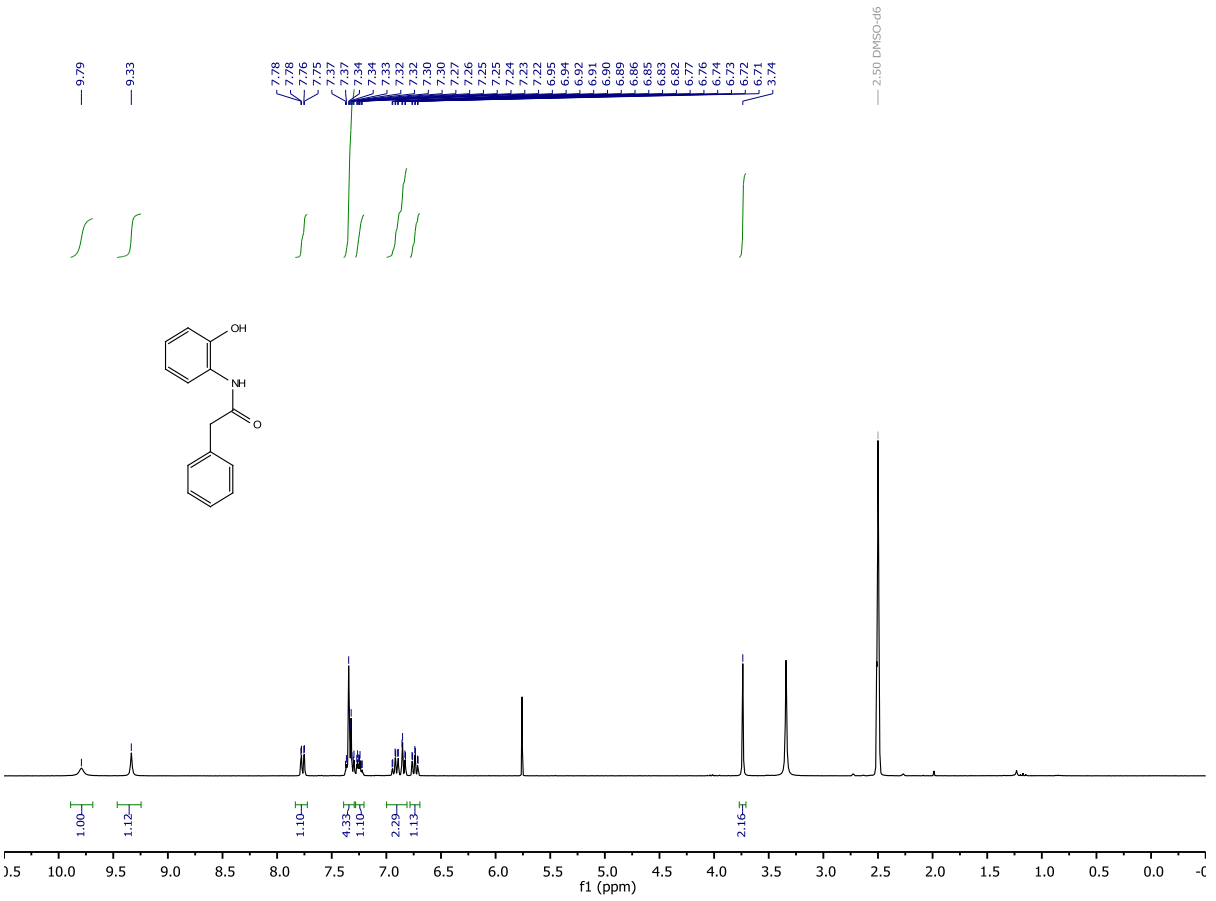
(23) *SHELX* software: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.

(24) Spek, A.L. *Acta Cryst*. **2015**, *C71*, 9–18.

8. NMR Spectra



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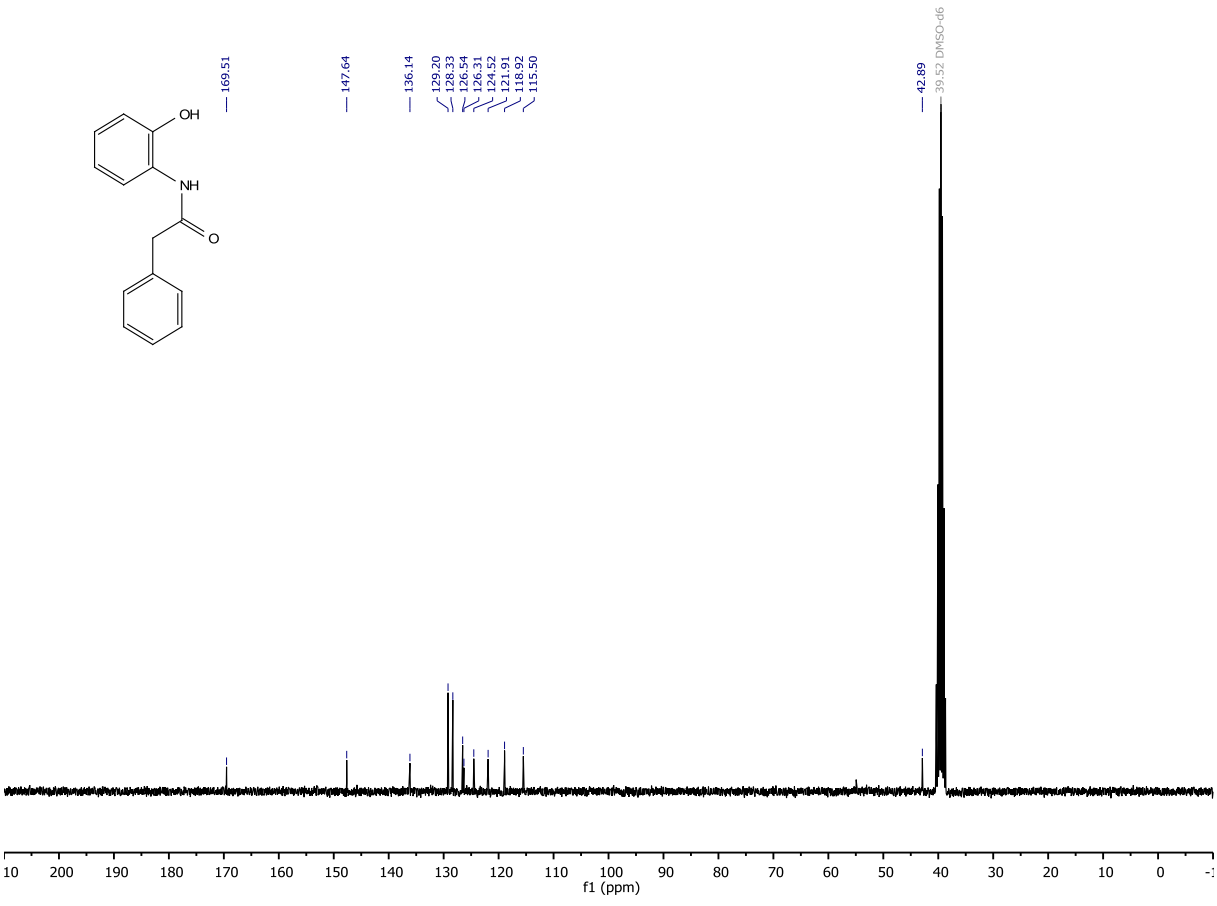
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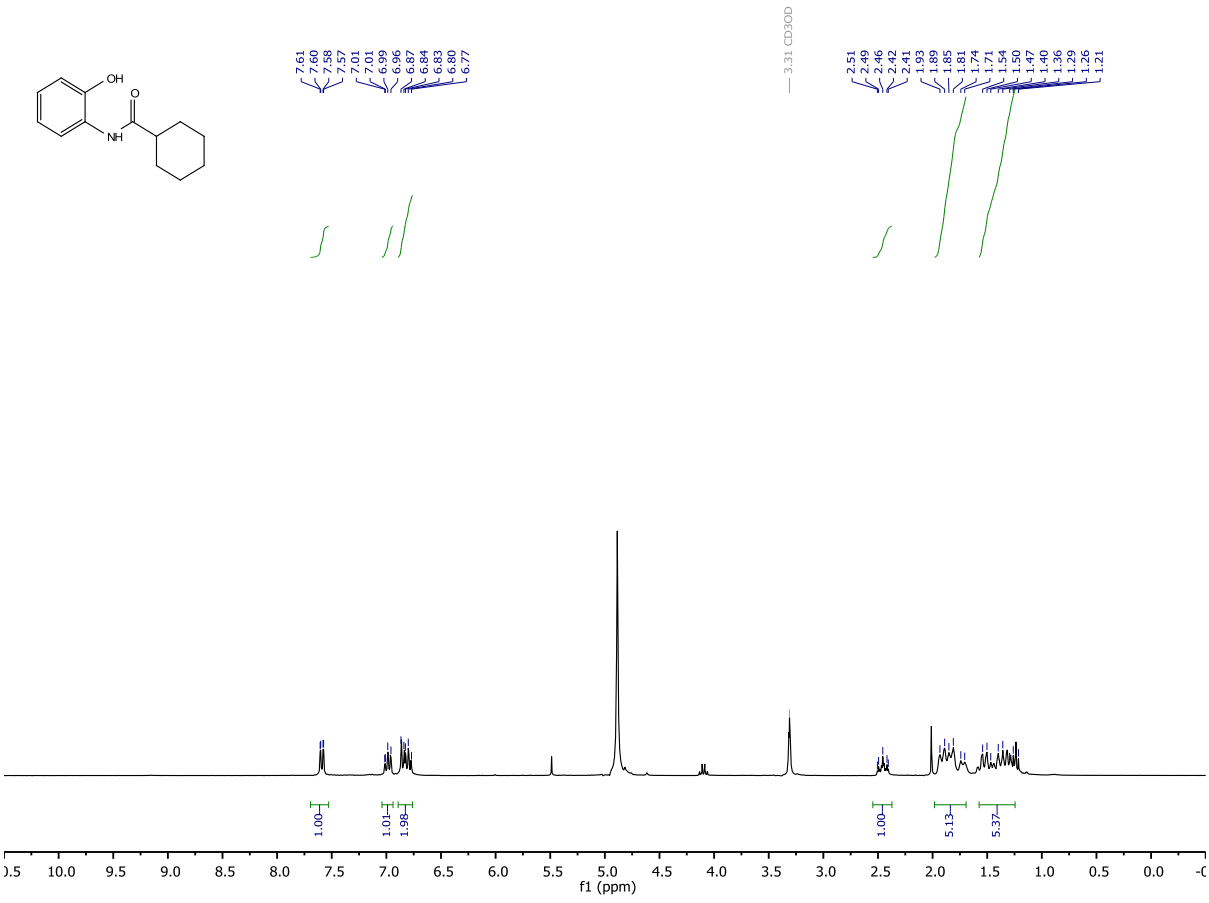
NH
O
f1 (ppm)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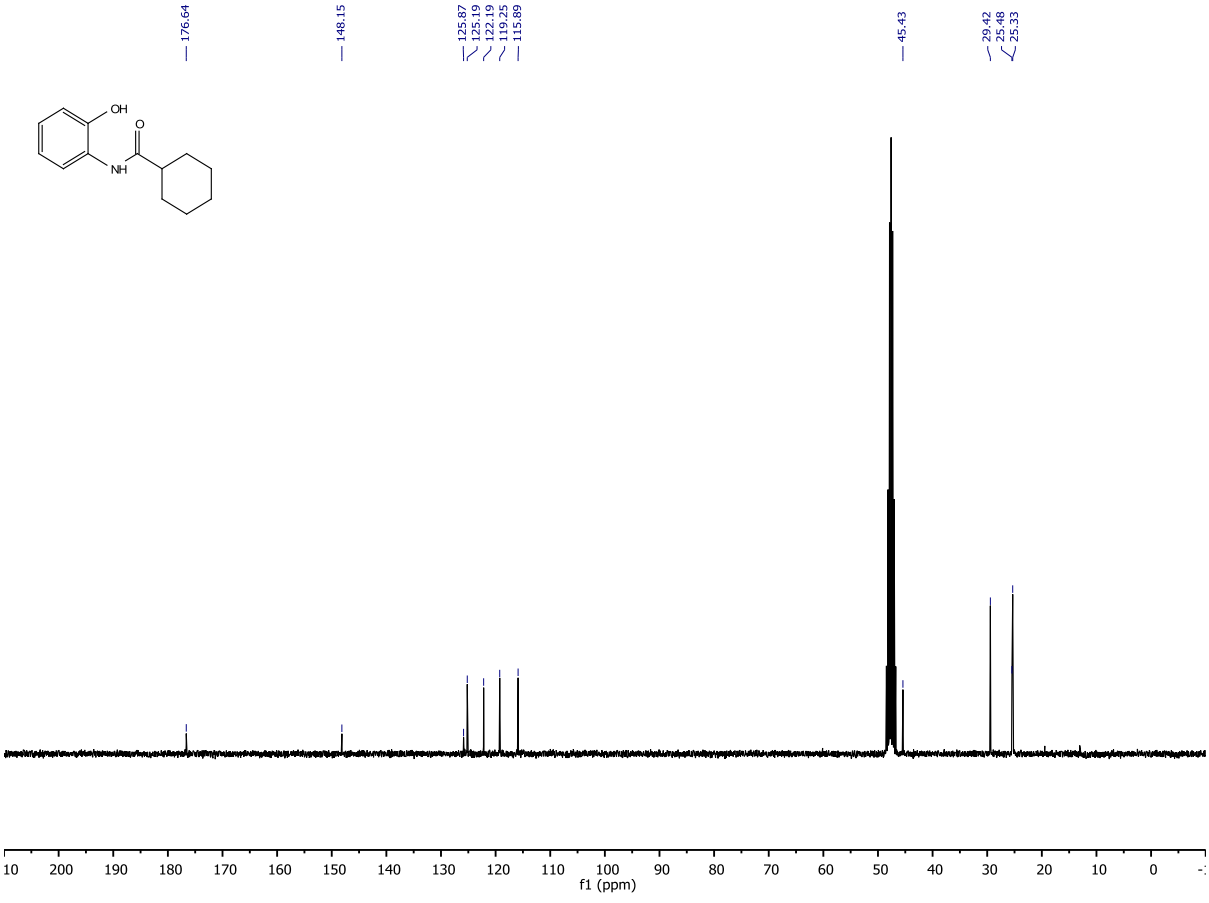
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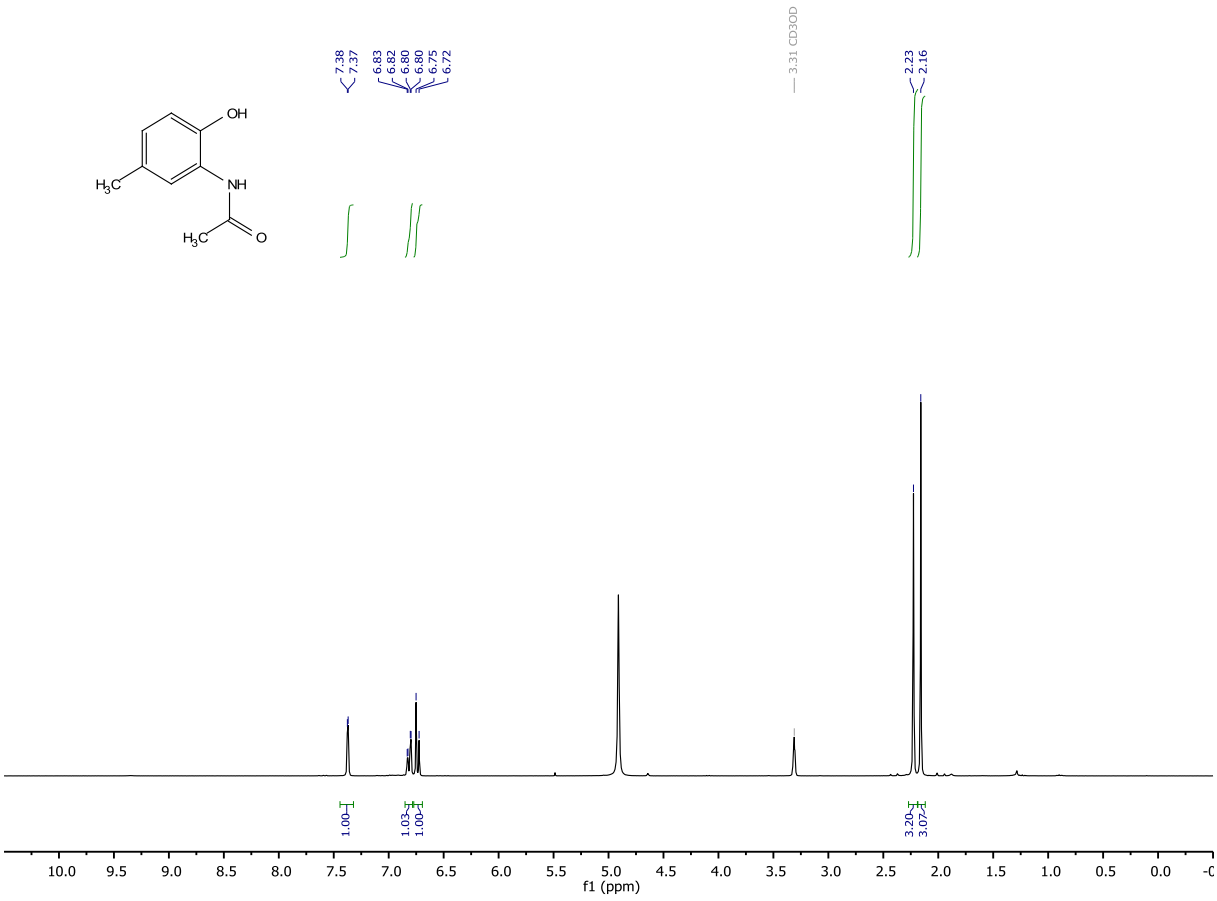
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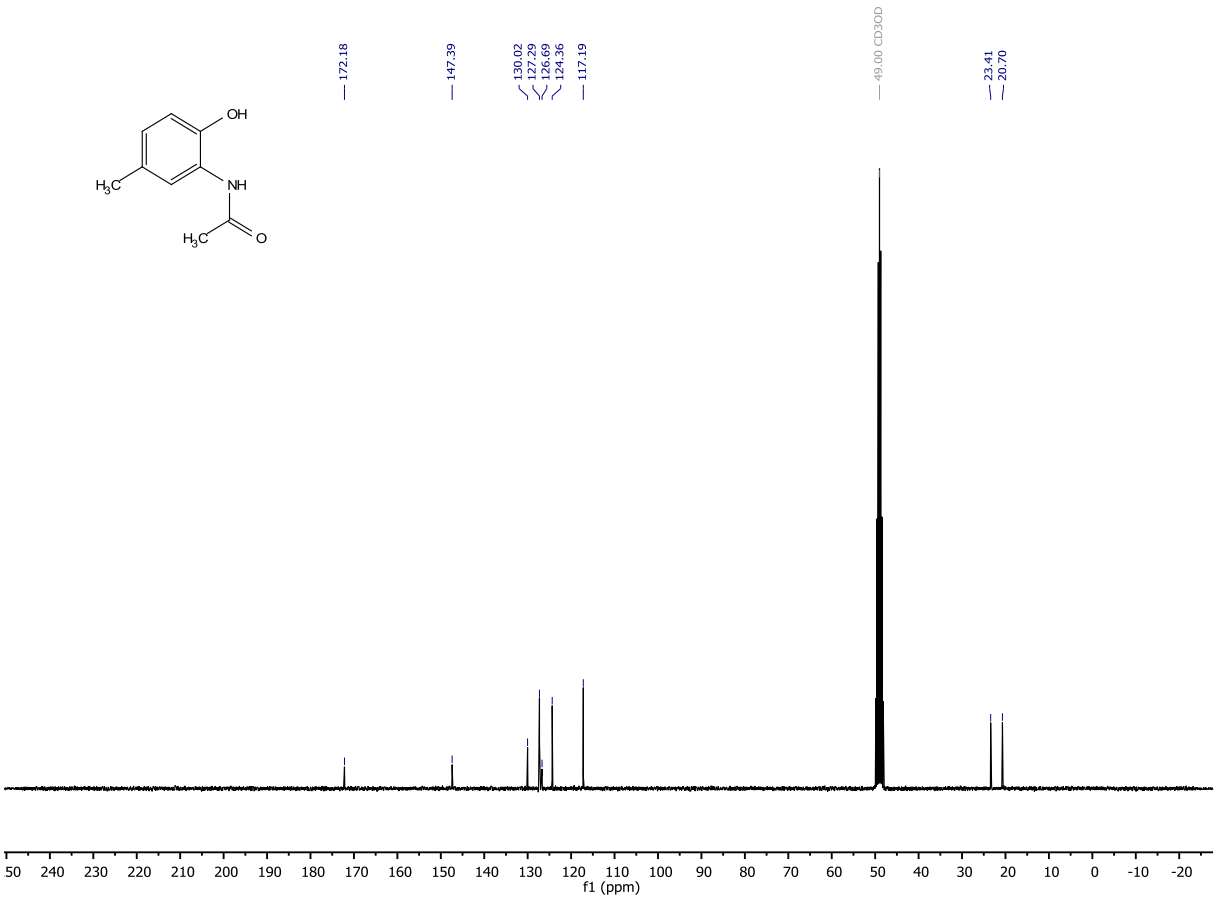
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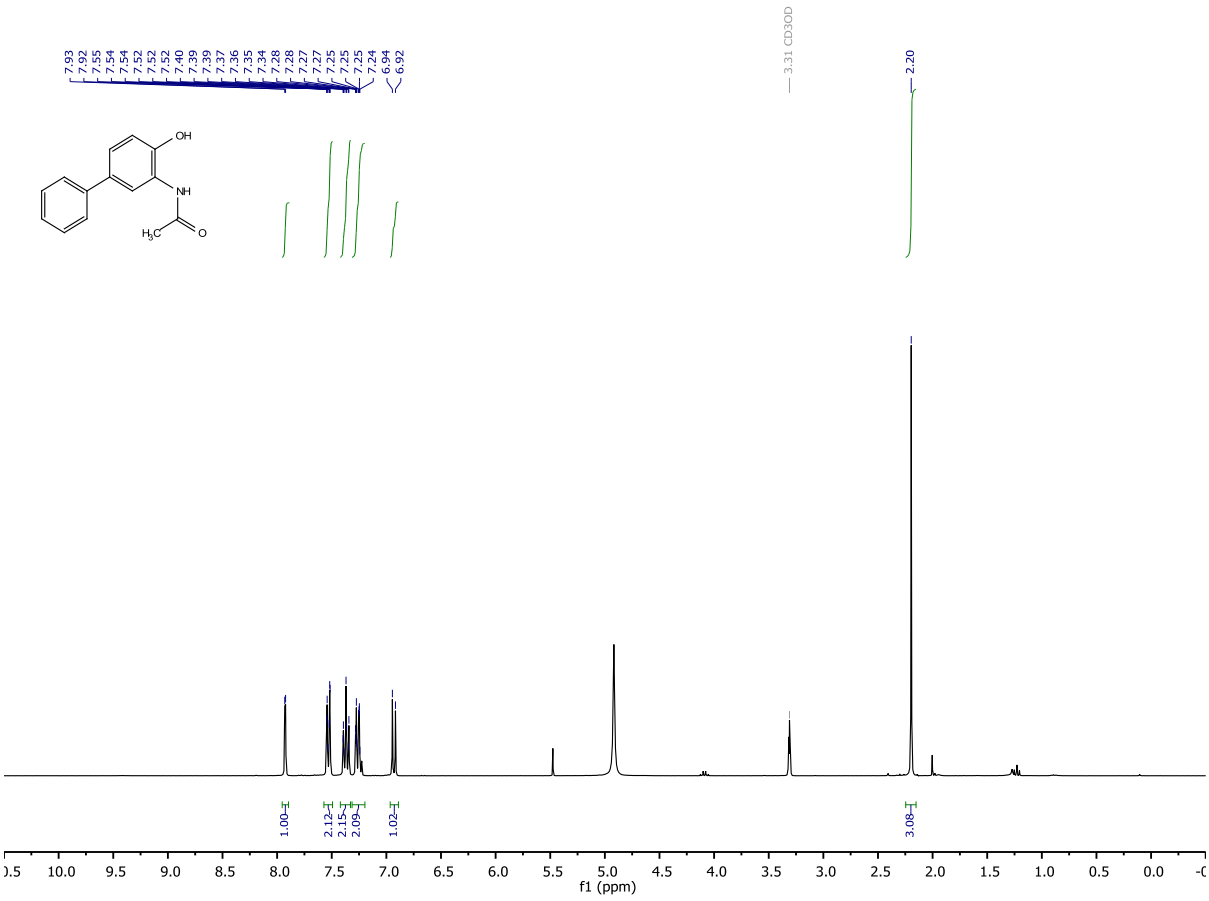
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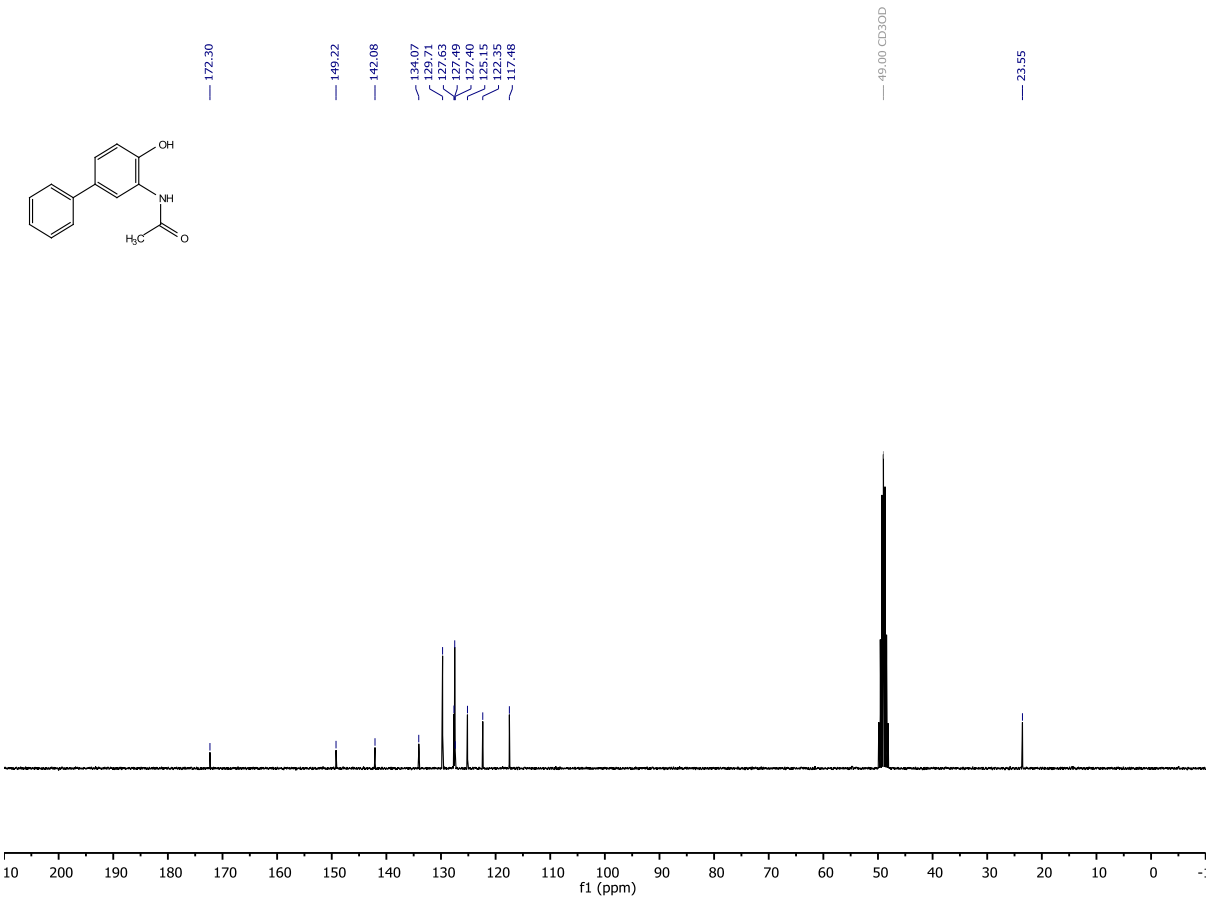
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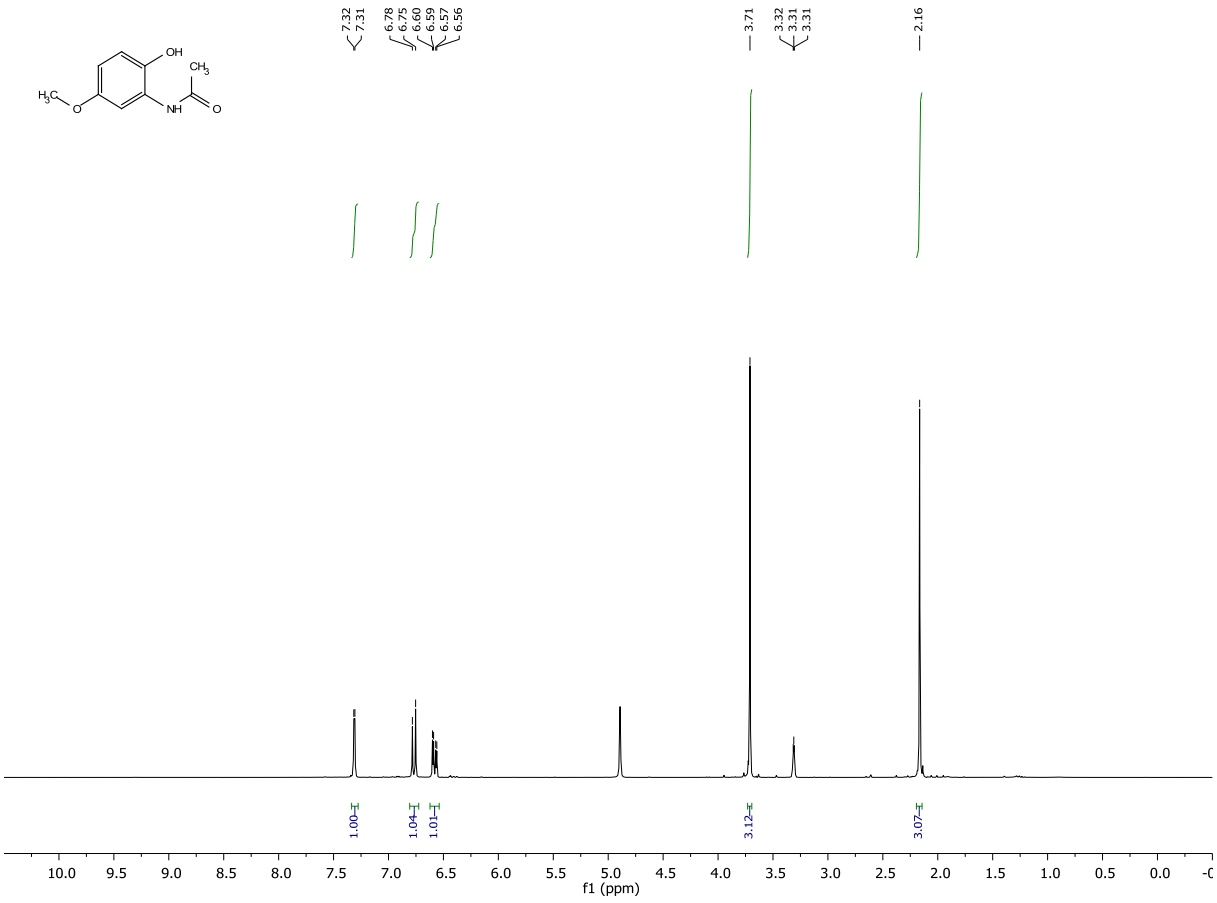
f1 (ppm)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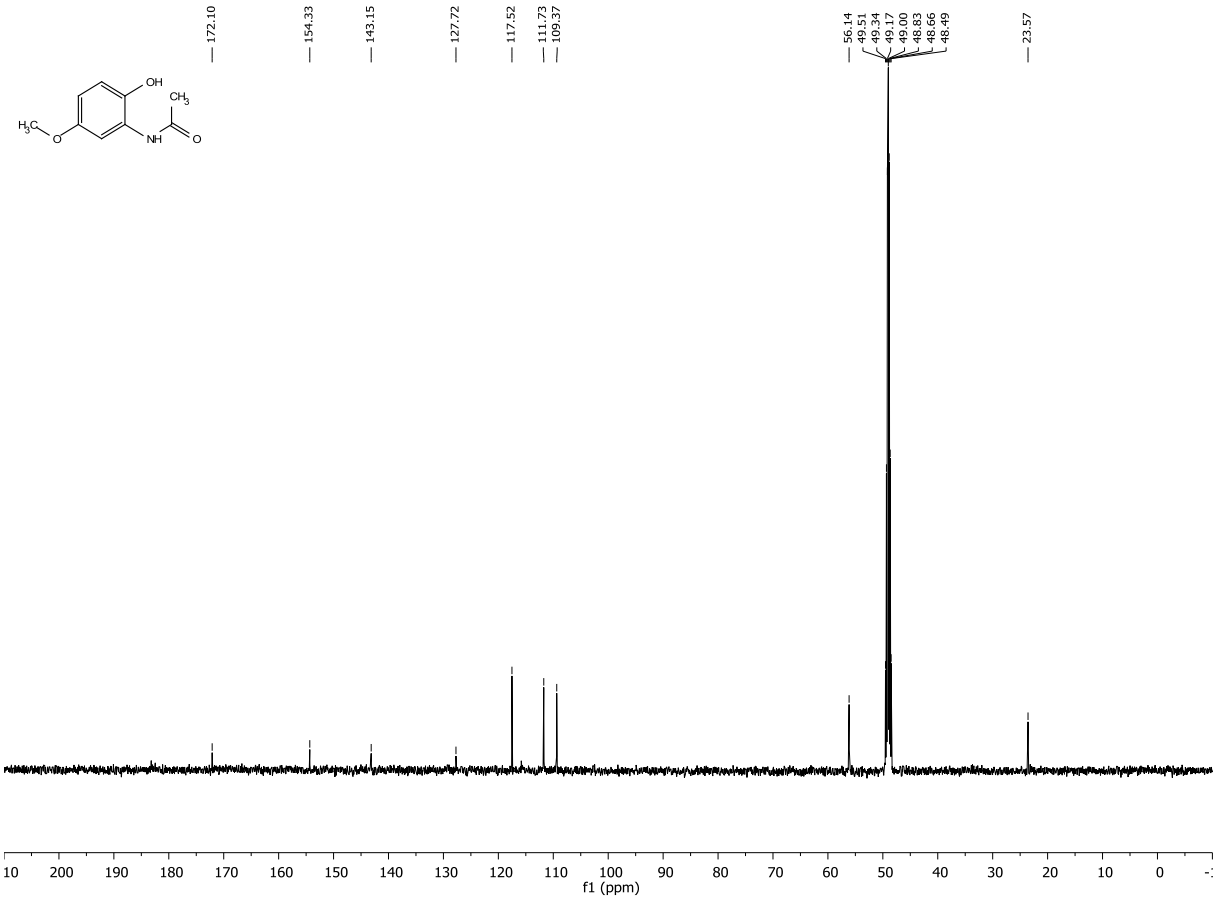
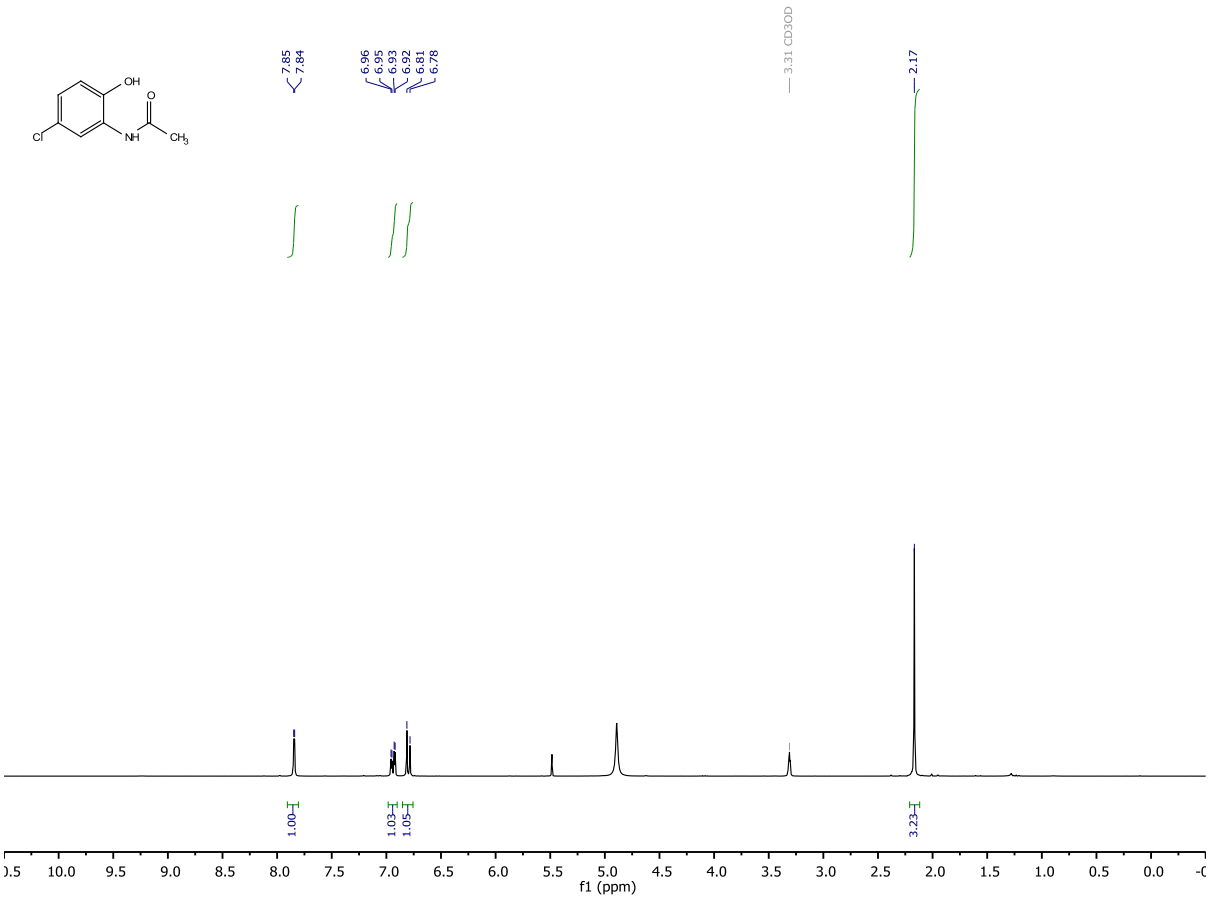
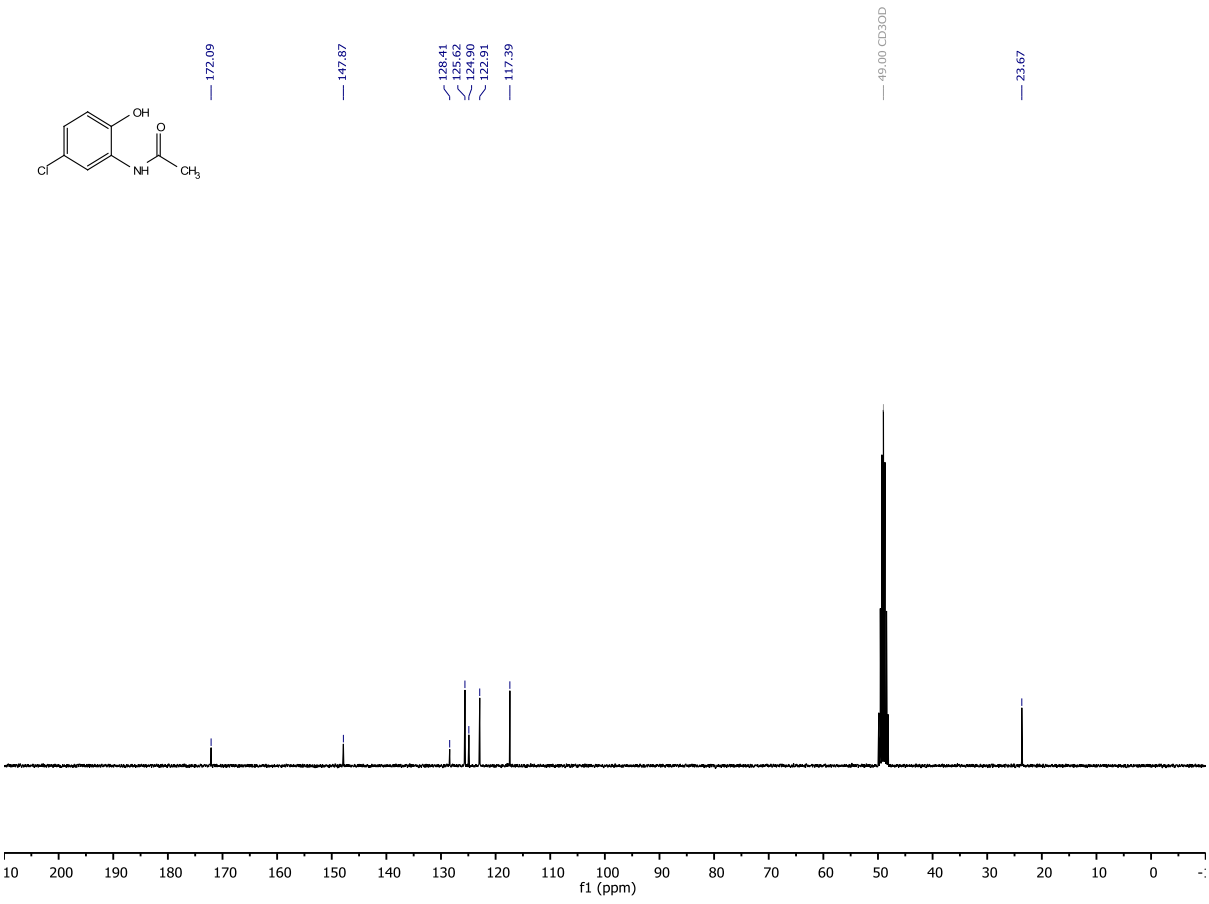
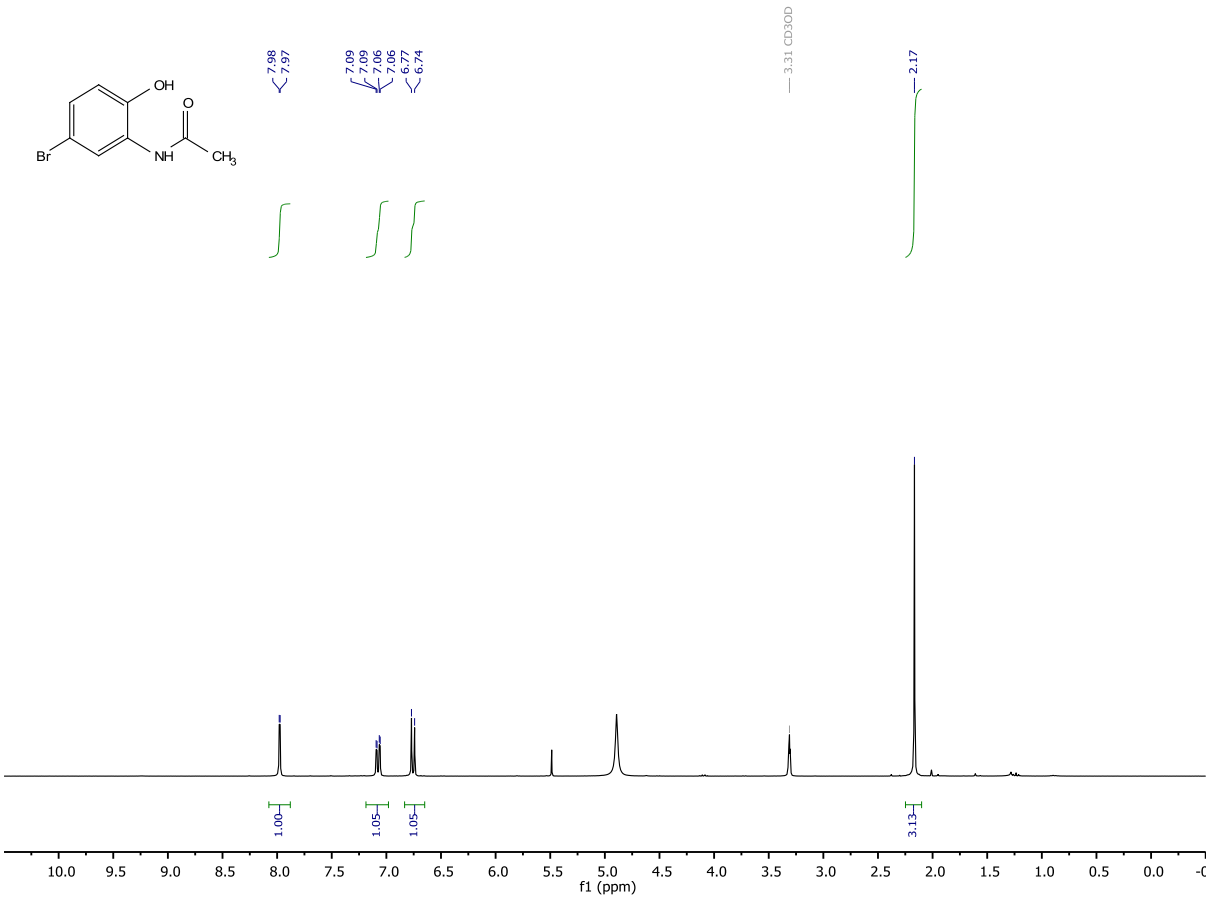
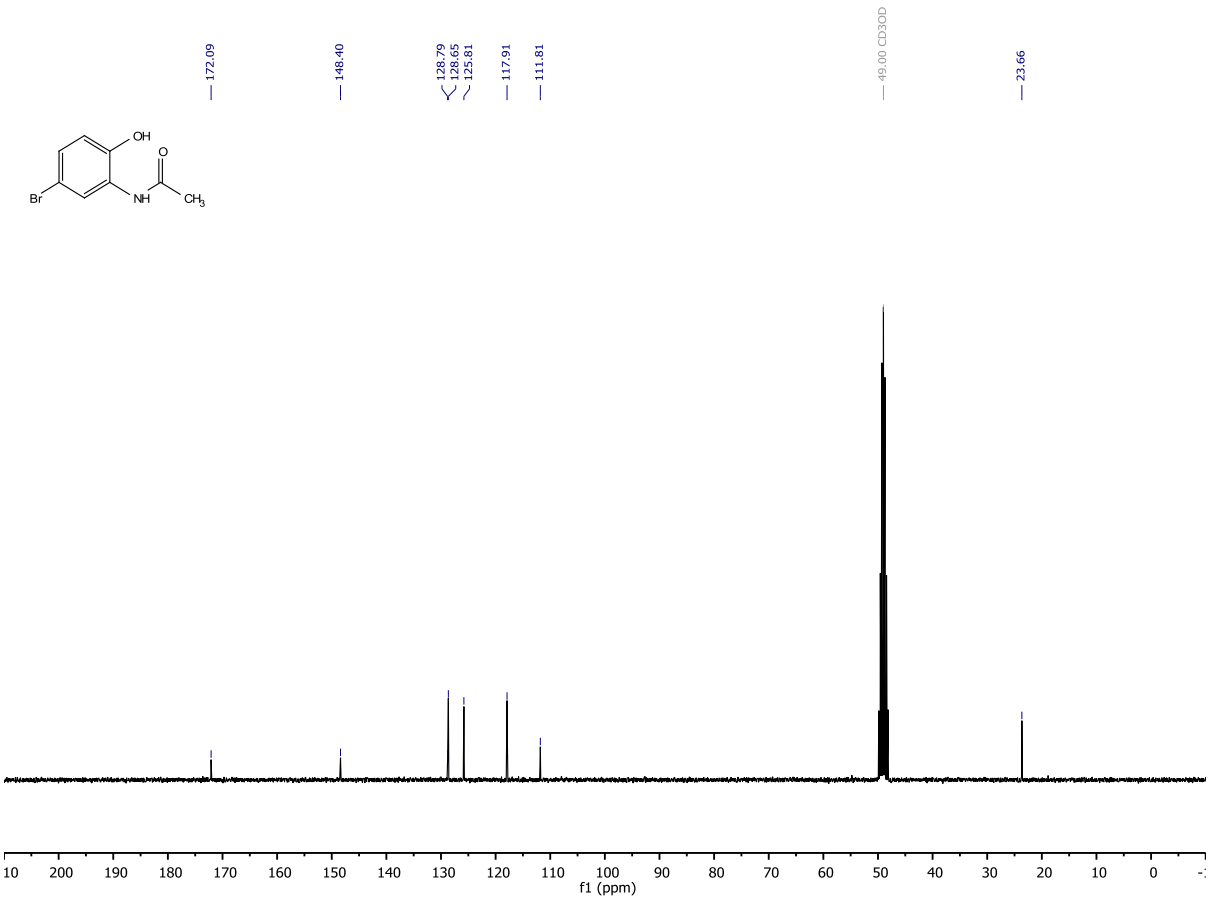
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

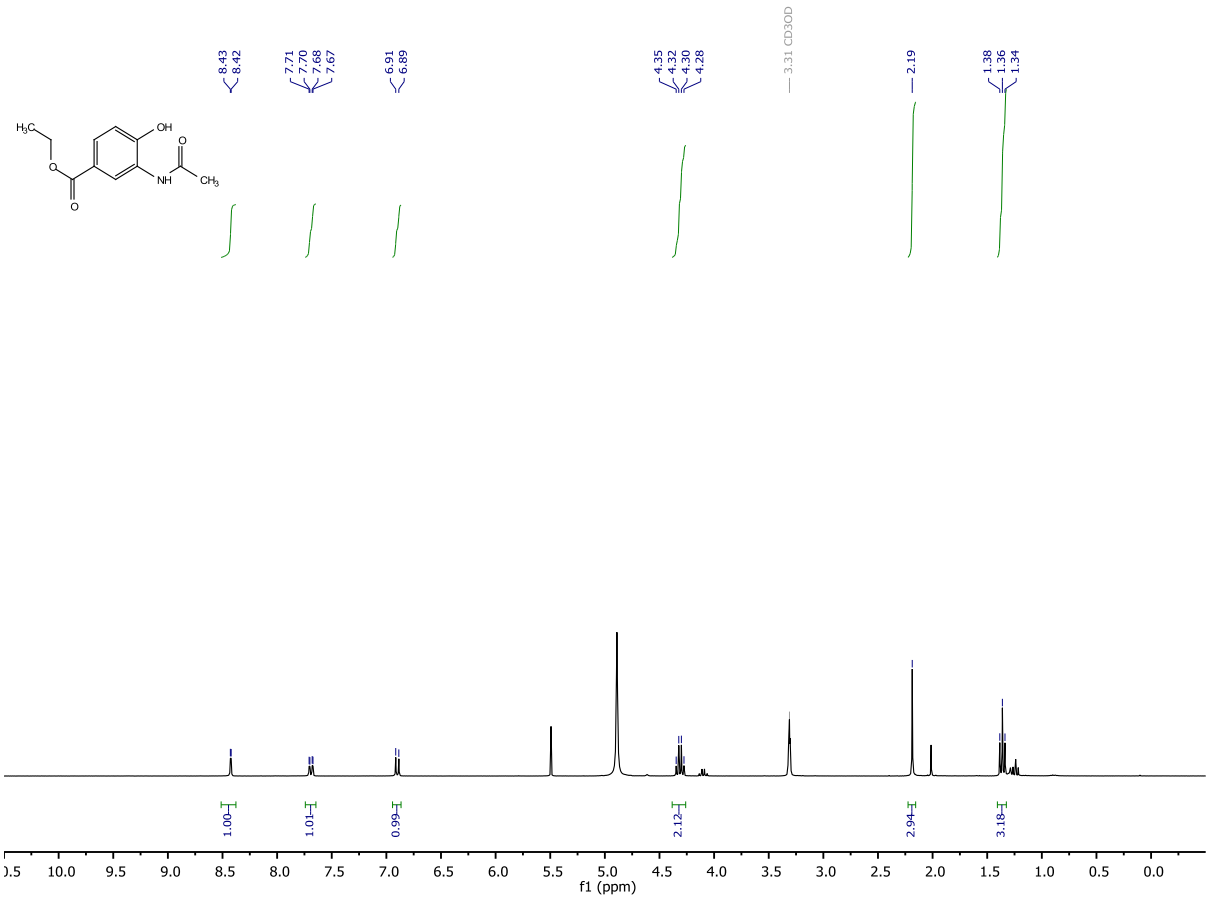

172.10
154.33
143.15
127.72
117.52
111.73
109.37
56.14
49.51
49.34
49.17
49.00
48.83
48.66
48.49
23.57
OH
CH3
H3C
O
NH
O
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

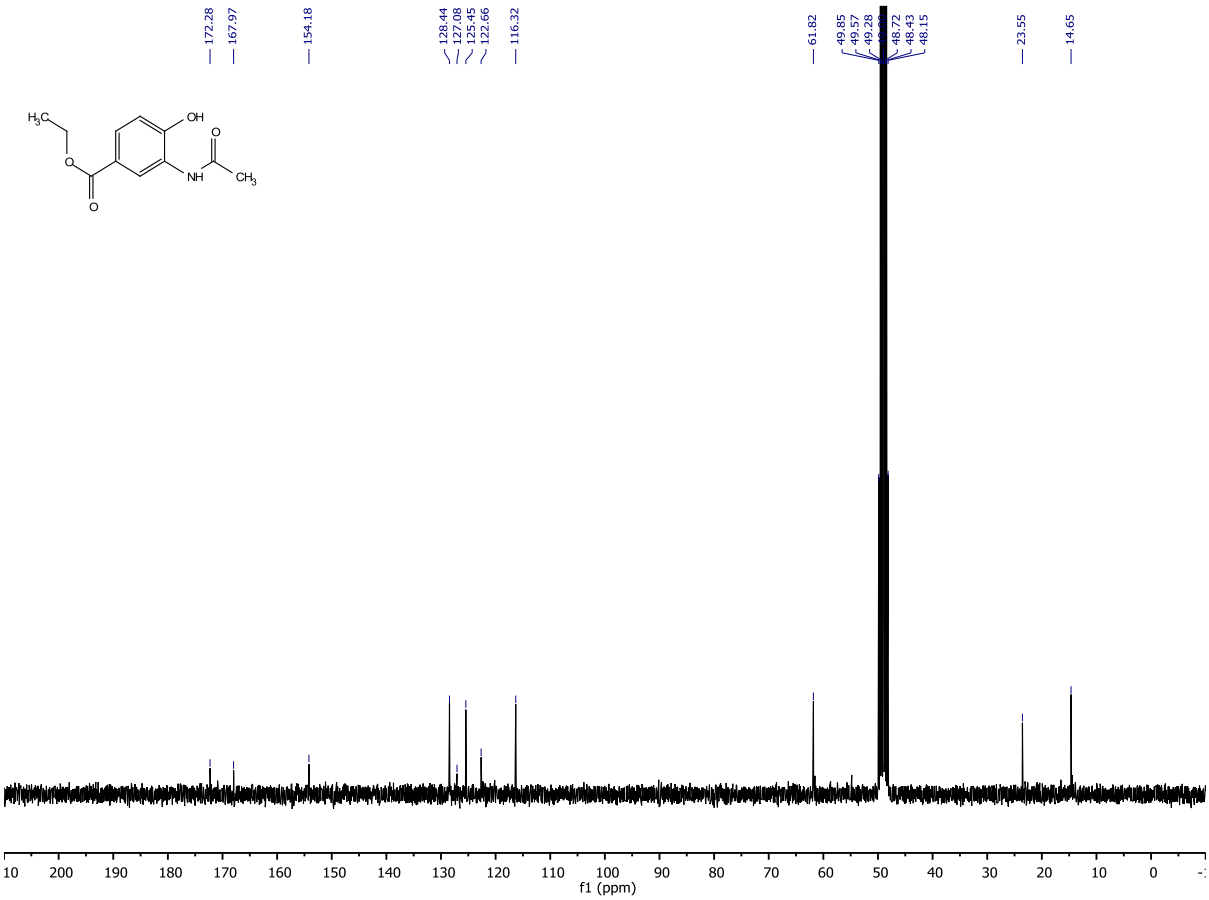

OH
O
Cl
NH
CH3
7.85
7.84
6.96
6.95
6.93
6.92
6.81
6.78
3.31 CD3OD
2.17
1.00
1.03
1.05
3.23
f1 (ppm)

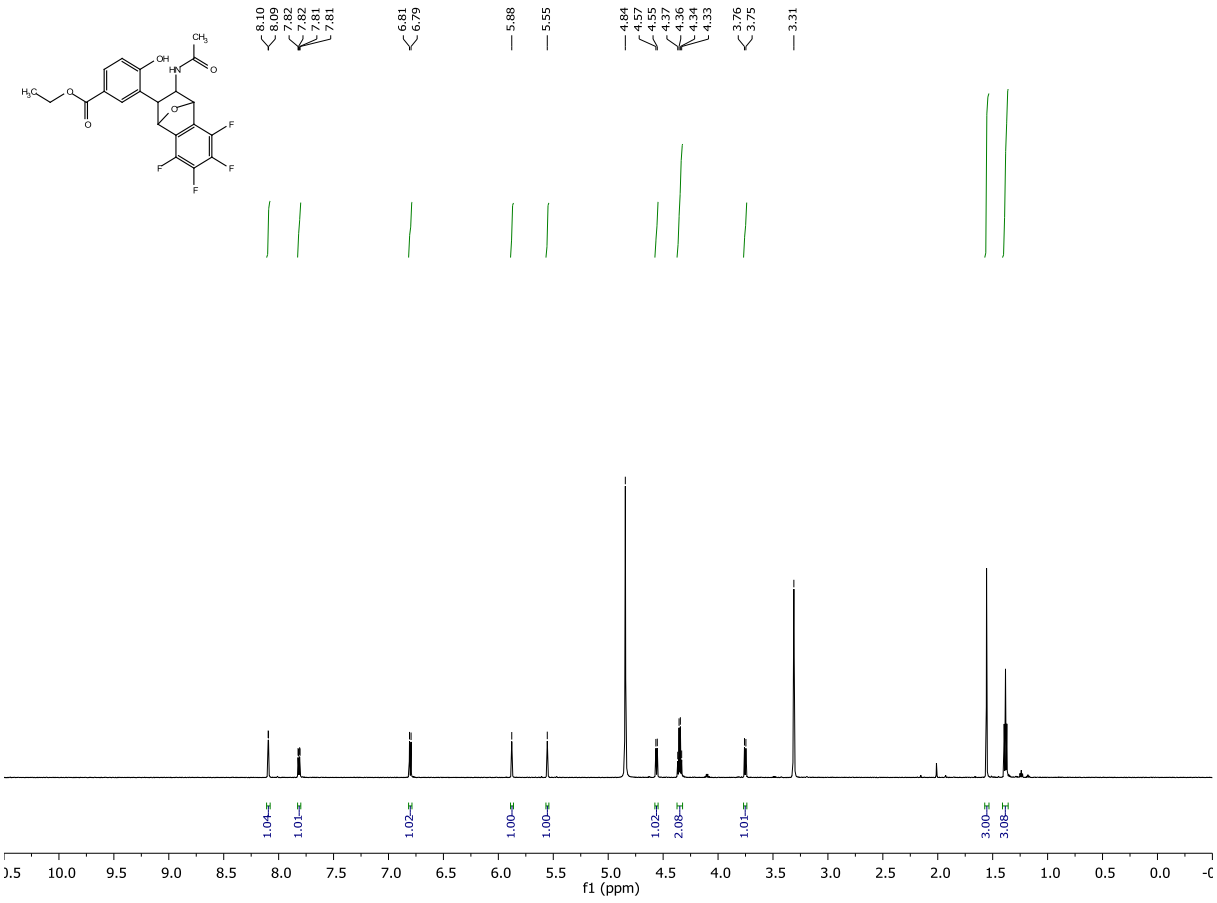

OH
O
Cl
NH
CH3
172.09
147.87
128.41
125.62
124.90
122.91
117.39
49.00 CD3OD
23.67
f1 (ppm)

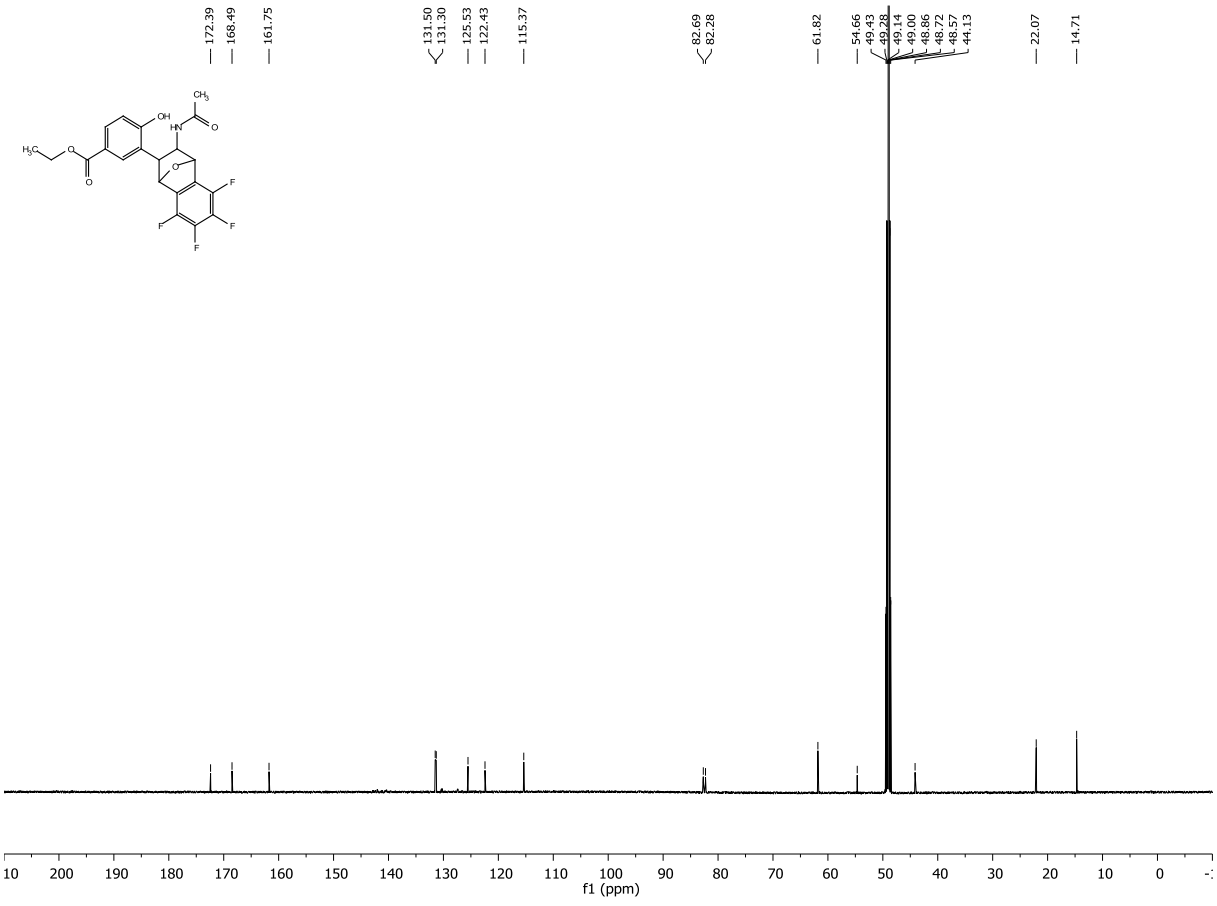

OH
O
Br
NH
CH3
7.98
7.97
7.09
7.09
7.06
7.06
6.77
6.74
3.31 CD3OD
2.17
1.00
1.05
1.05
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

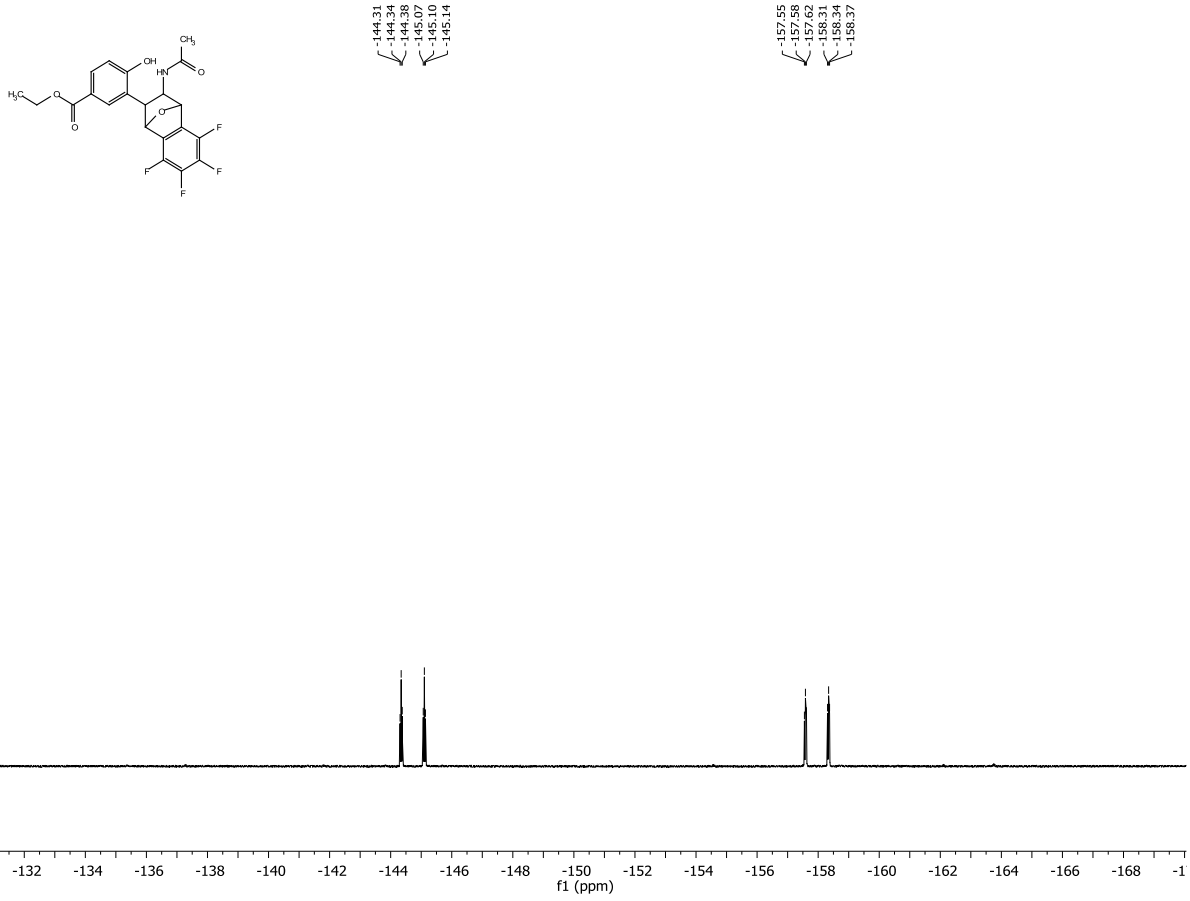

OH
O
Br
NH
CH3
172.09
148.40
128.79
128.65
125.81
117.91
111.81
49.00 CD3OD
23.66
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

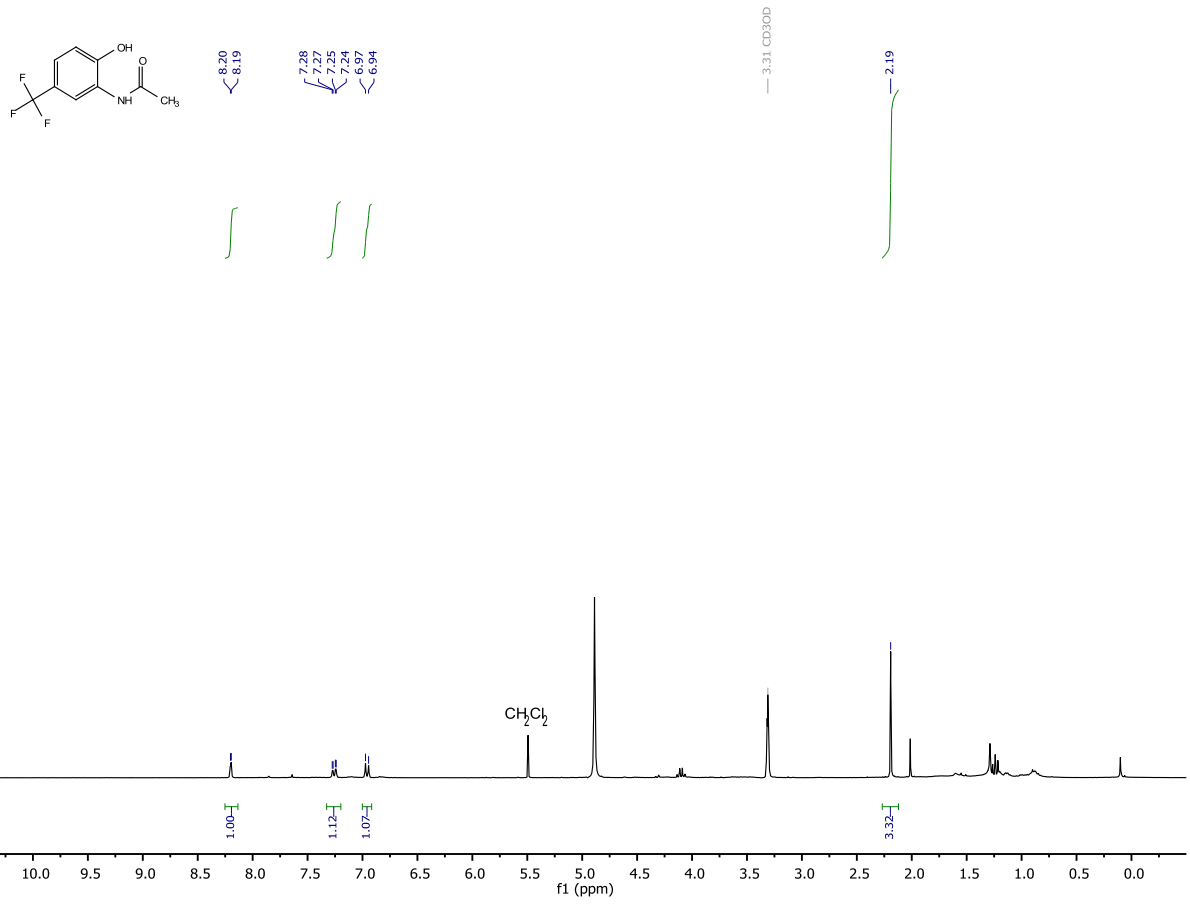

8.43
8.42
7.71
7.70
7.68
7.67
6.91
6.89
4.35
4.32
4.30
4.28
3.31 CD3OD
2.19
1.38
1.36
1.34
OH
O
NH
CH3
1.00
1.01
0.99
2.12
2.94
3.18
f1 (ppm)

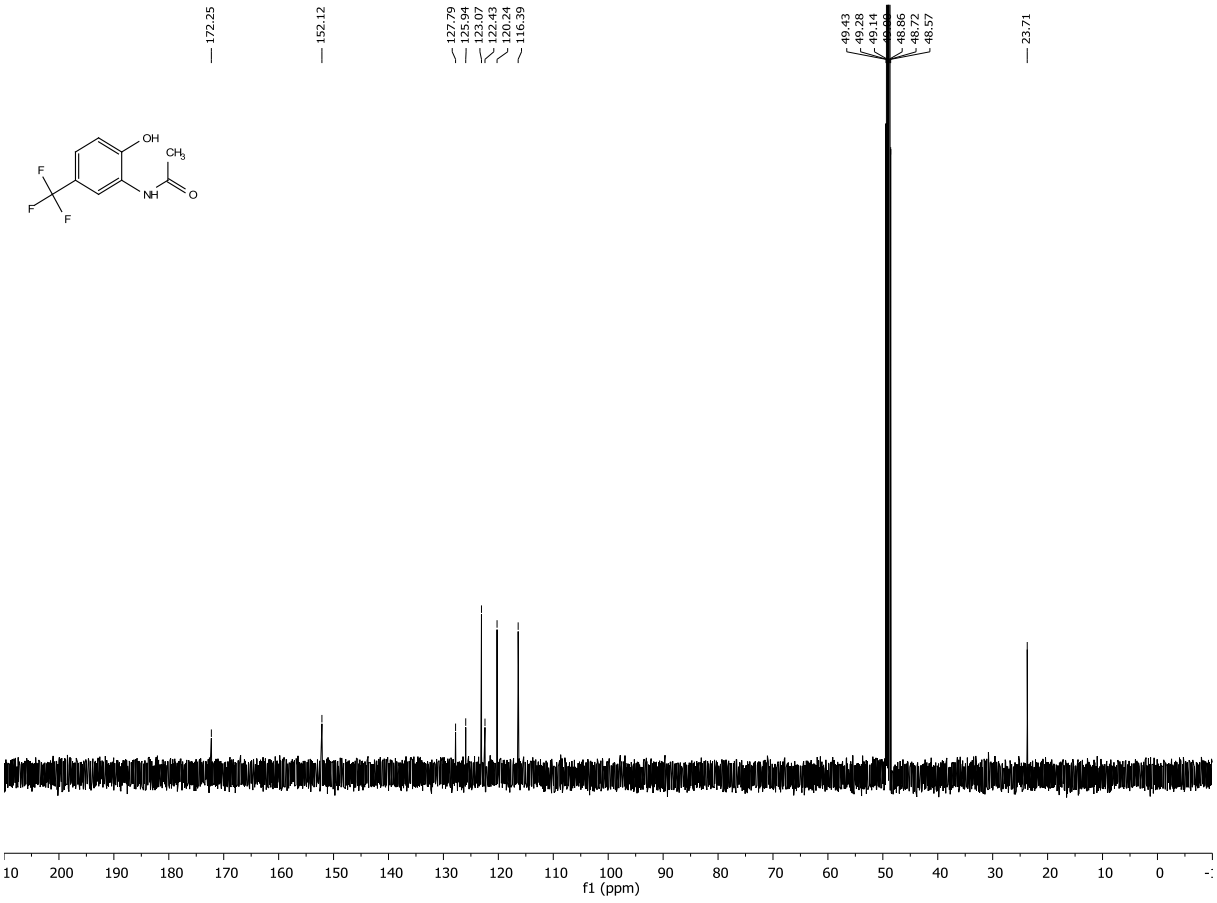

172.28
167.97
154.18
128.44
127.08
125.45
122.66
116.32
61.82
49.85
49.57
49.28
48.72
48.43
48.15
23.55
14.65
OH
O
NH
CH3
f1 (ppm)

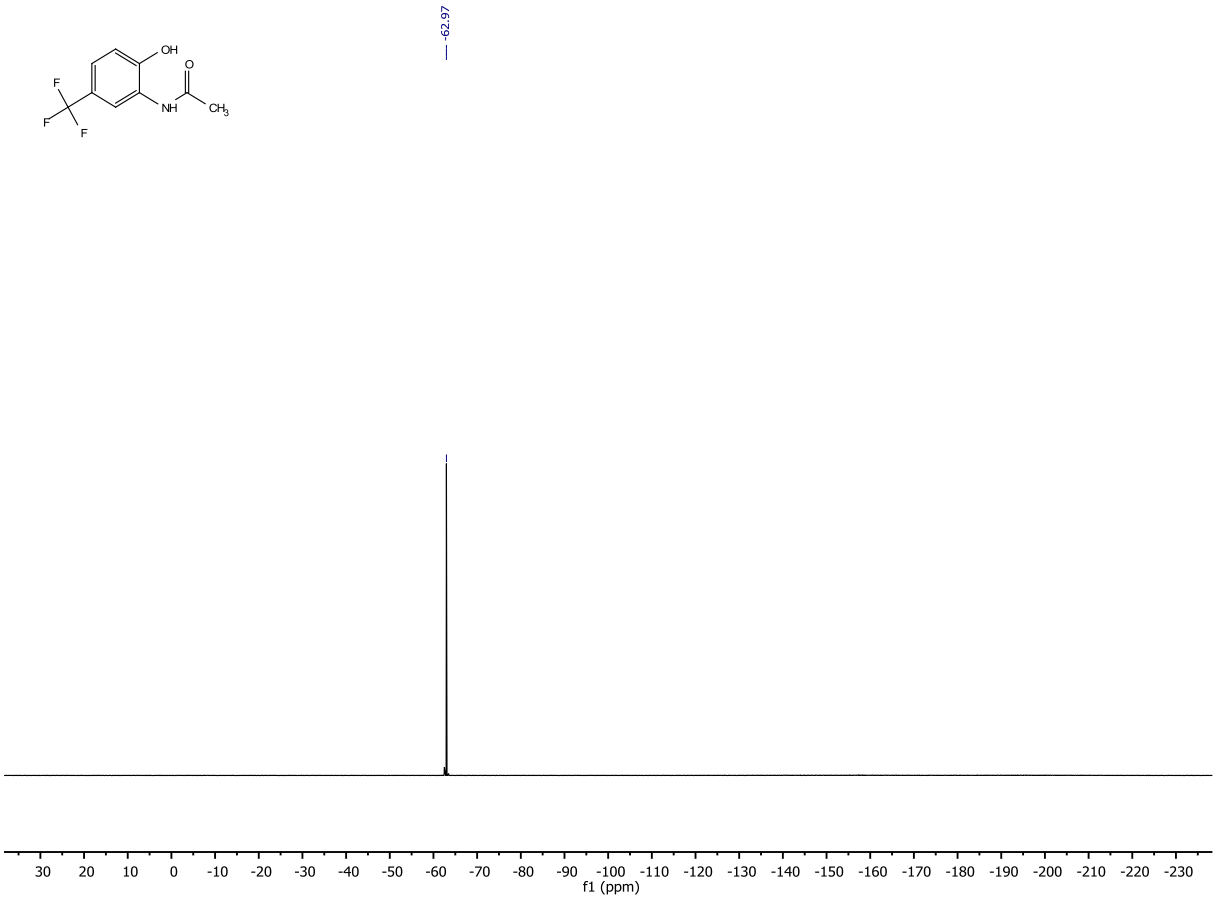

8.10
8.09
7.82
7.82
7.81
7.81
6.81
6.79
5.88
5.55
4.84
4.57
4.55
4.37
4.36
4.34
4.33
3.76
3.75
3.31
1.04
1.01
1.02
1.00
1.00
1.02
2.08
1.01
3.00
3.08
f1 (ppm)

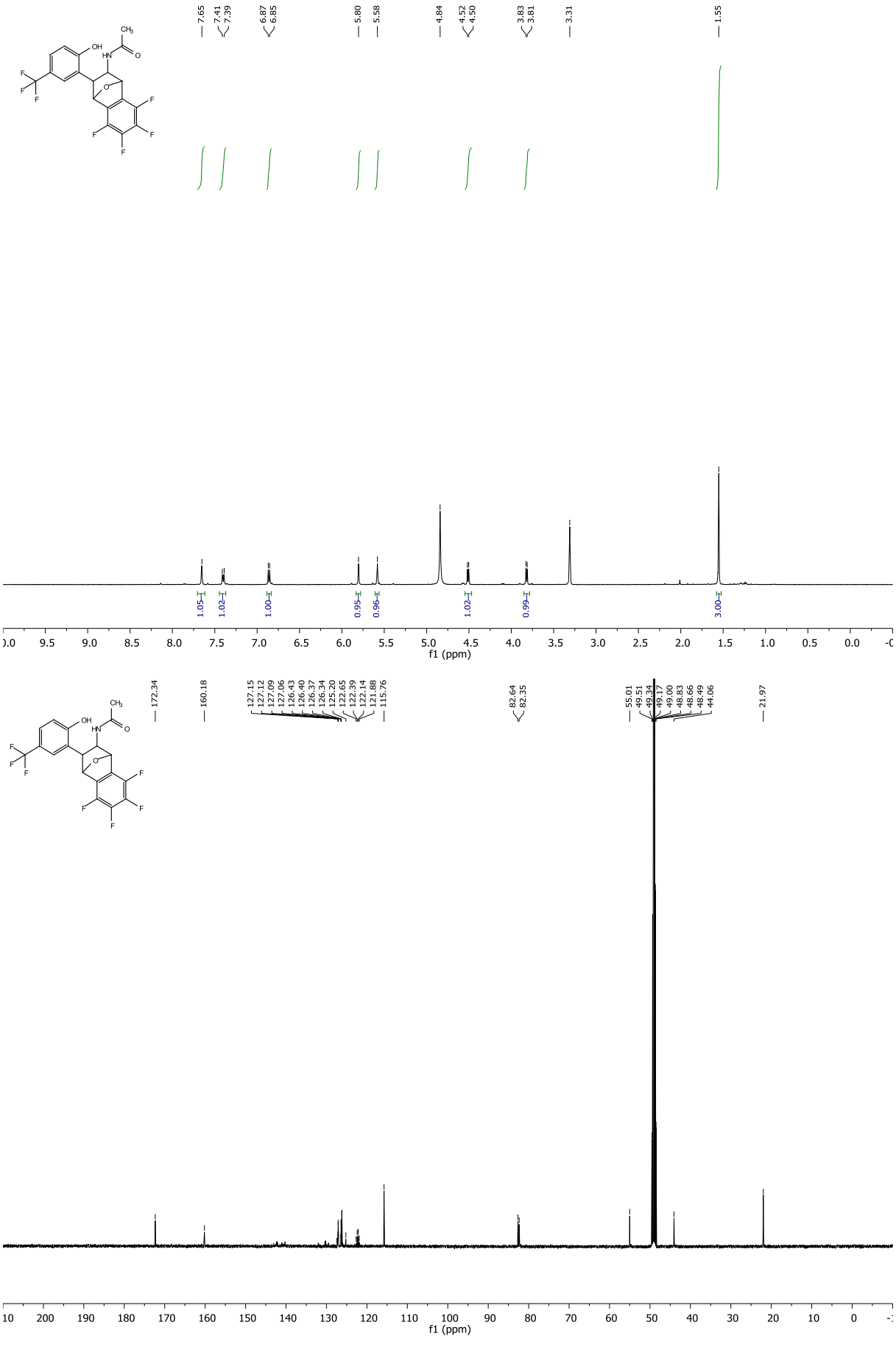

172.39
168.49
161.75
131.50
131.30
125.53
122.43
115.37
82.69
82.28
61.82
54.66
49.43
49.28
49.14
49.00
48.86
48.72
48.57
44.13
22.07
14.71
f1 (ppm)

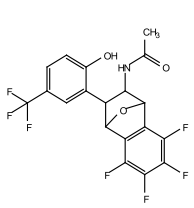

-144.31
-144.34
-144.38
-145.07
-145.10
-145.14
-157.55
-157.58
-157.62
-158.31
-158.34
-158.37
f1 (ppm)


8.20
8.19
7.28
7.27
7.25
7.24
6.97
6.94
3.31 CD3OD
2.19
CH2Cl2
1.00
1.12
1.07
3.32
f1 (ppm)


172.25
152.12
127.79
125.94
123.07
122.43
120.24
116.39
49.43
49.28
49.14
48.86
48.72
48.57
23.71
OH
CH3
F
F
F
NH
O
f1 (ppm)


-62.97
OH
O
F
F
F
NH
CH3
f1 (ppm)


7.65
7.41
7.39
6.87
6.85
5.80
5.58
4.84
4.52
4.50
3.83
3.81
3.31
1.55
1.05
1.02
1.00
0.95
0.96
1.02
0.99
3.00
f1 (ppm)
172.34
160.18
127.15
127.12
127.09
127.06
126.43
126.40
126.37
126.34
125.20
122.65
122.39
122.14
121.88
115.76
82.64
82.35
55.01
49.51
49.34
49.17
49.00
48.83
48.66
48.49
44.06
21.97
f1 (ppm)


CH3
OH
HN
O
F
F
F
O
F
F
F
F

-62.54


-144.31
-144.35
-144.40
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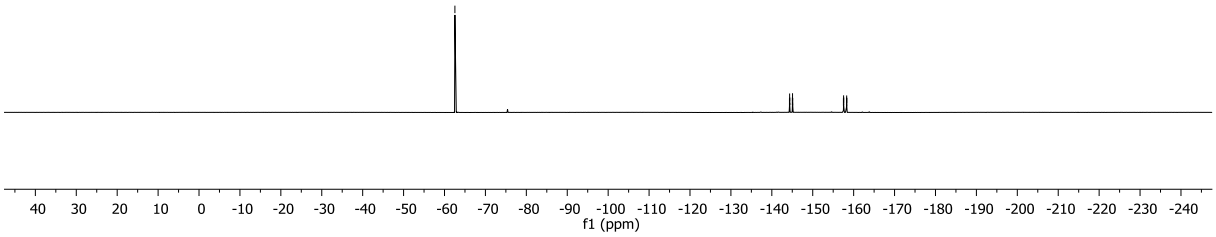
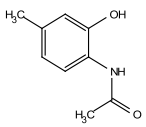
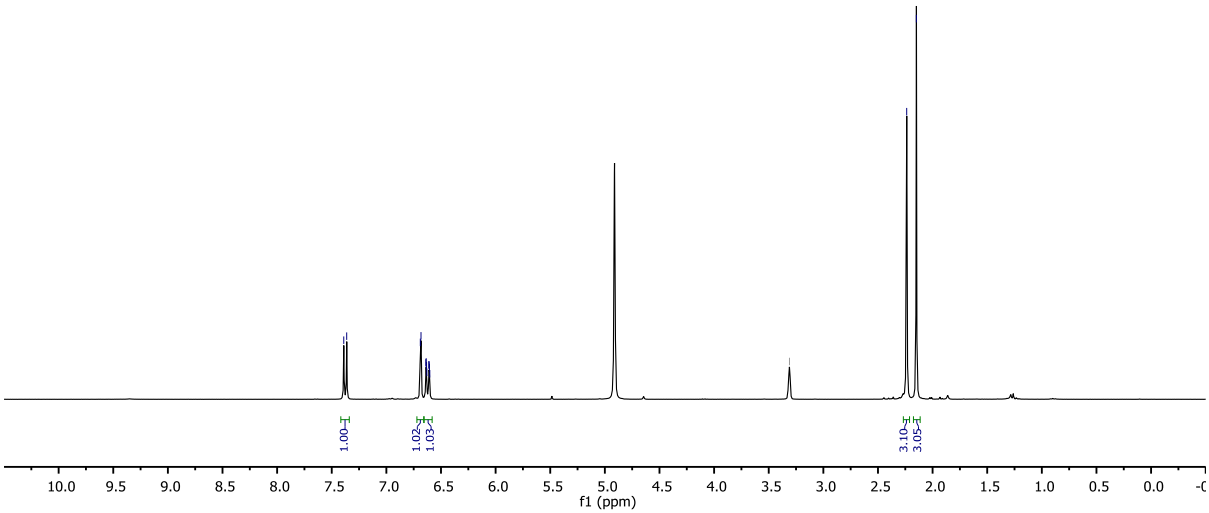
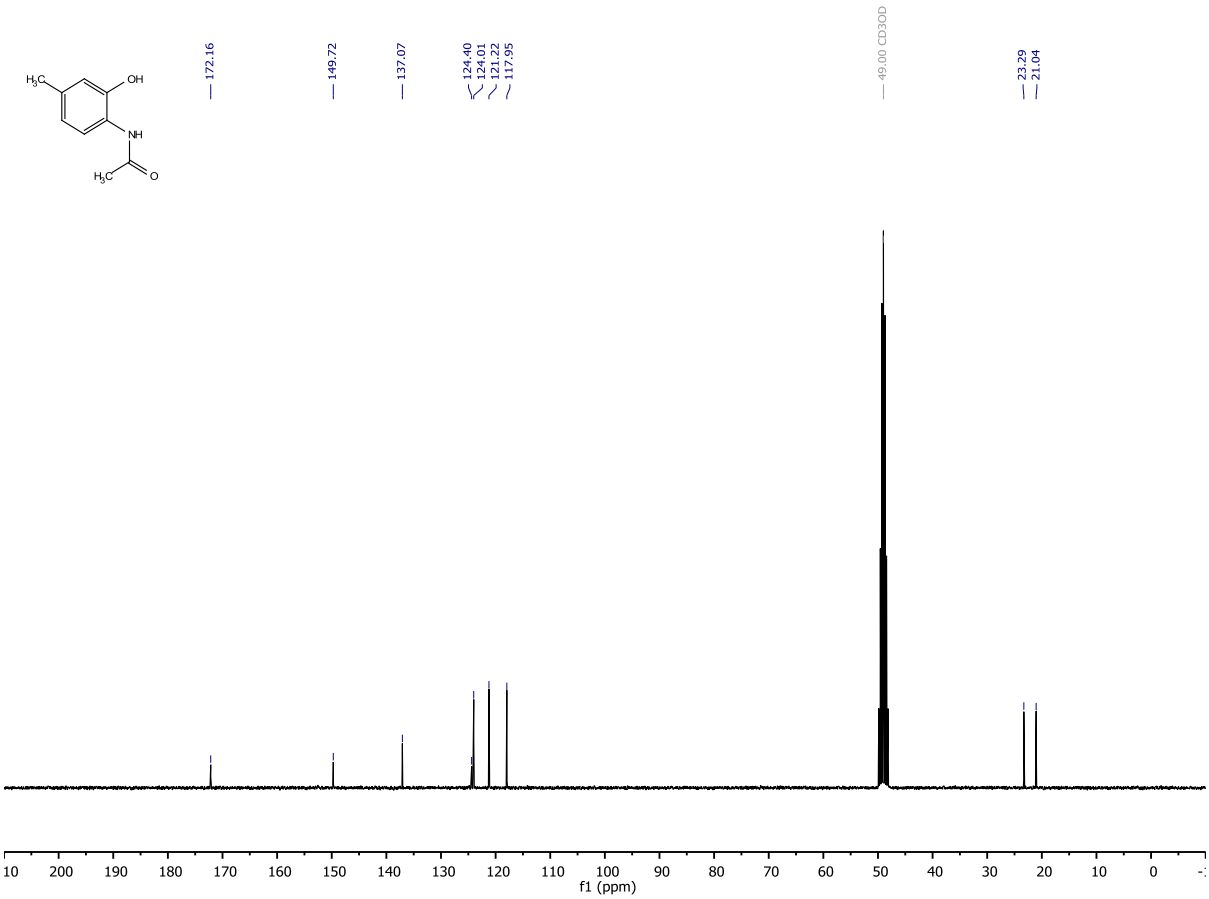
-157.54
-157.58
-158.26
-158.30
-158.34

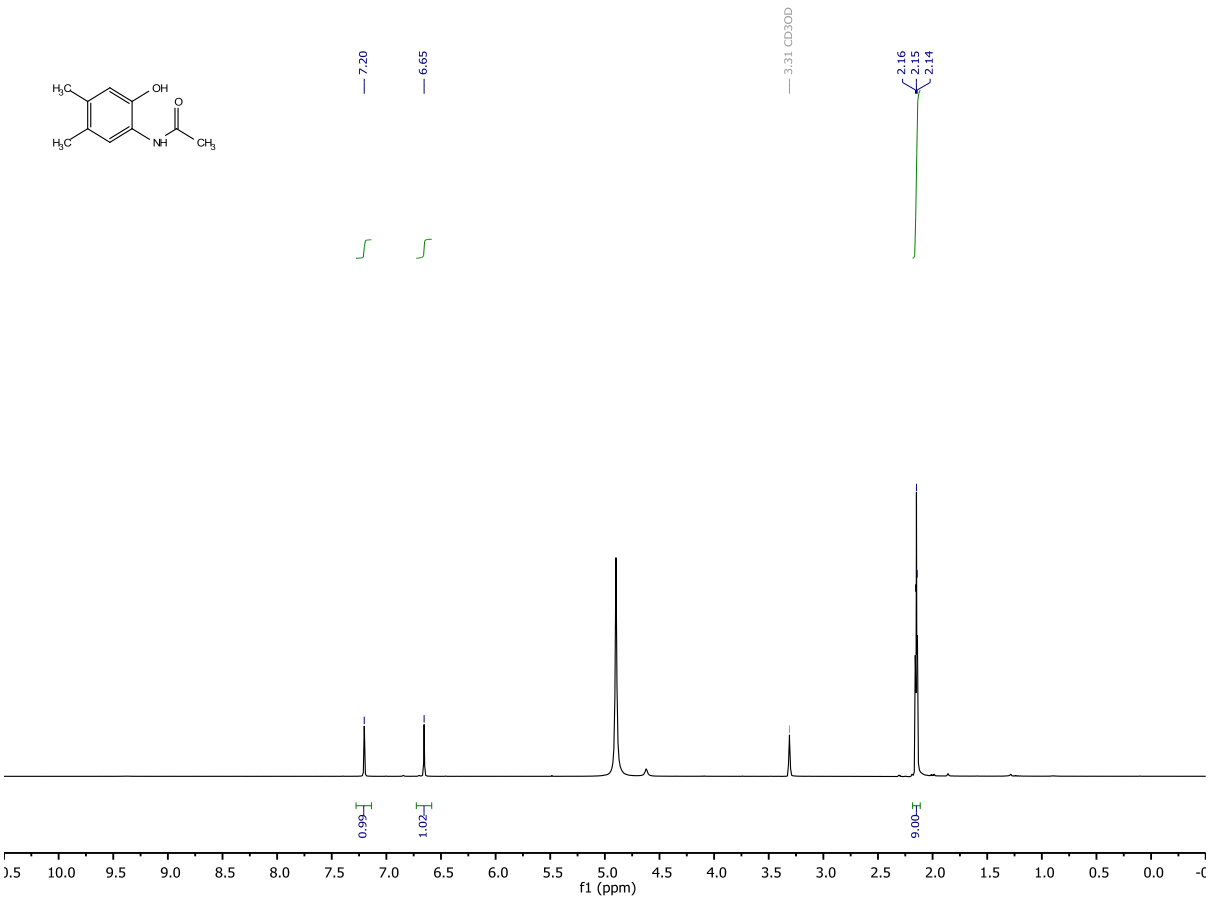

40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

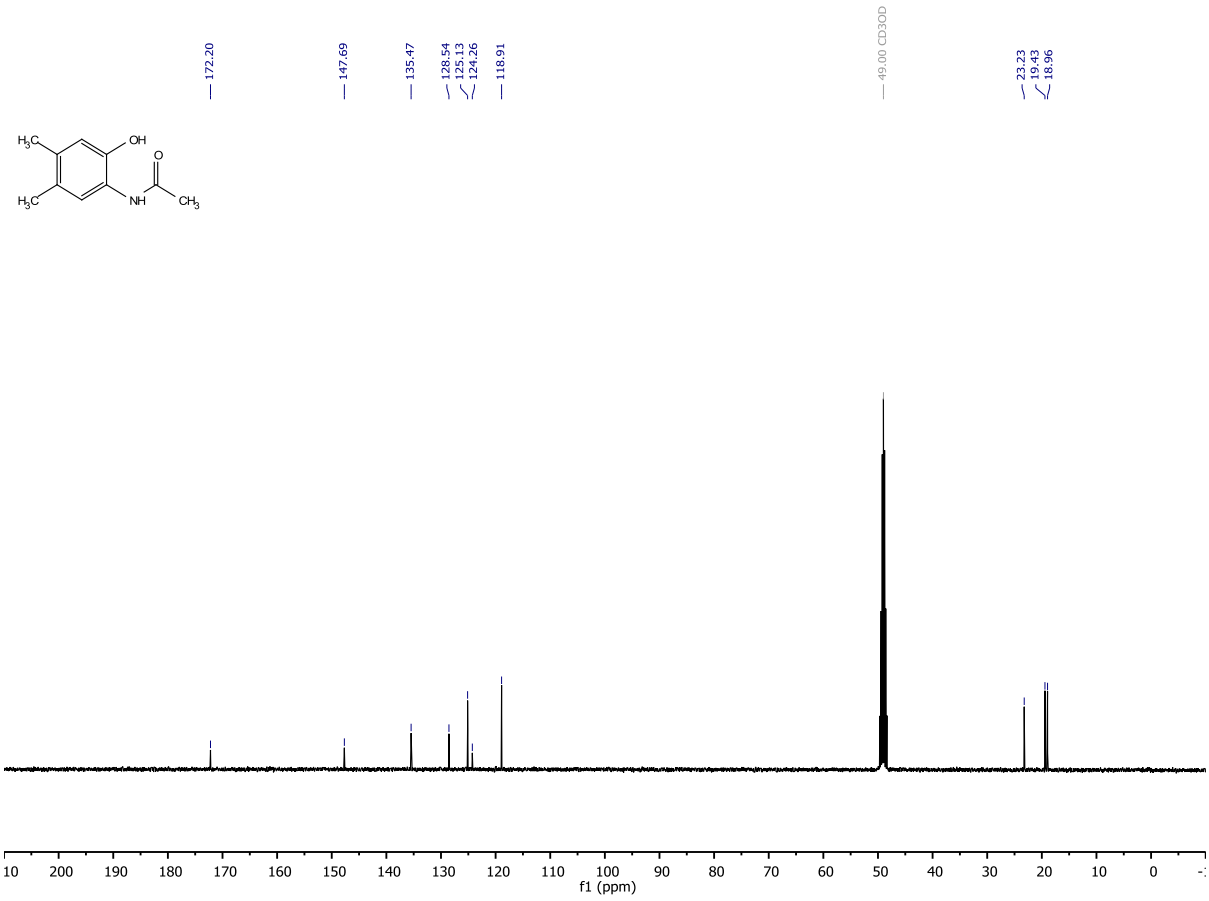

H3C
OH
NH
H3C
O

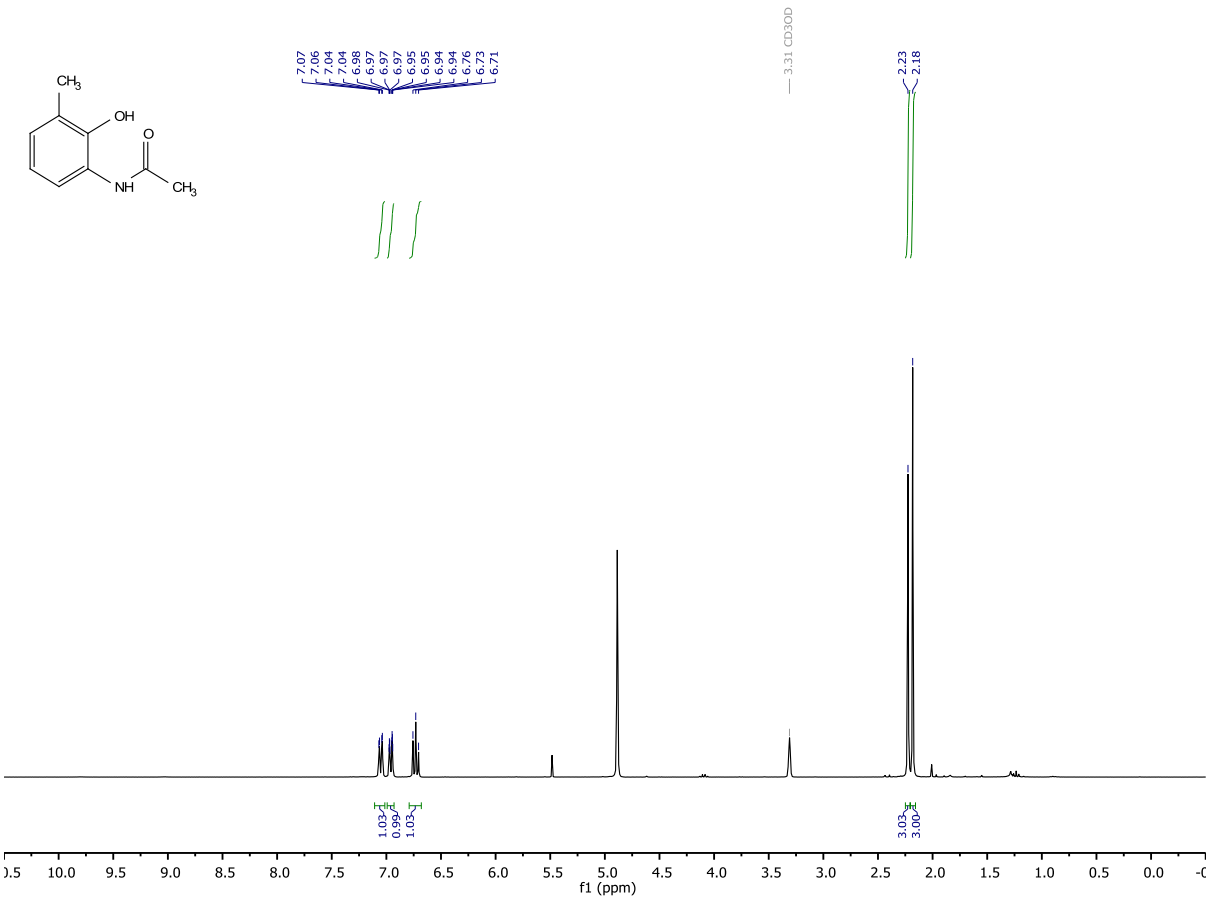

7.39
7.36
6.69
6.68
6.64
6.64
6.63
6.63
6.61
6.61
6.61
6.60
3.31 CD3OD
2.24
2.15

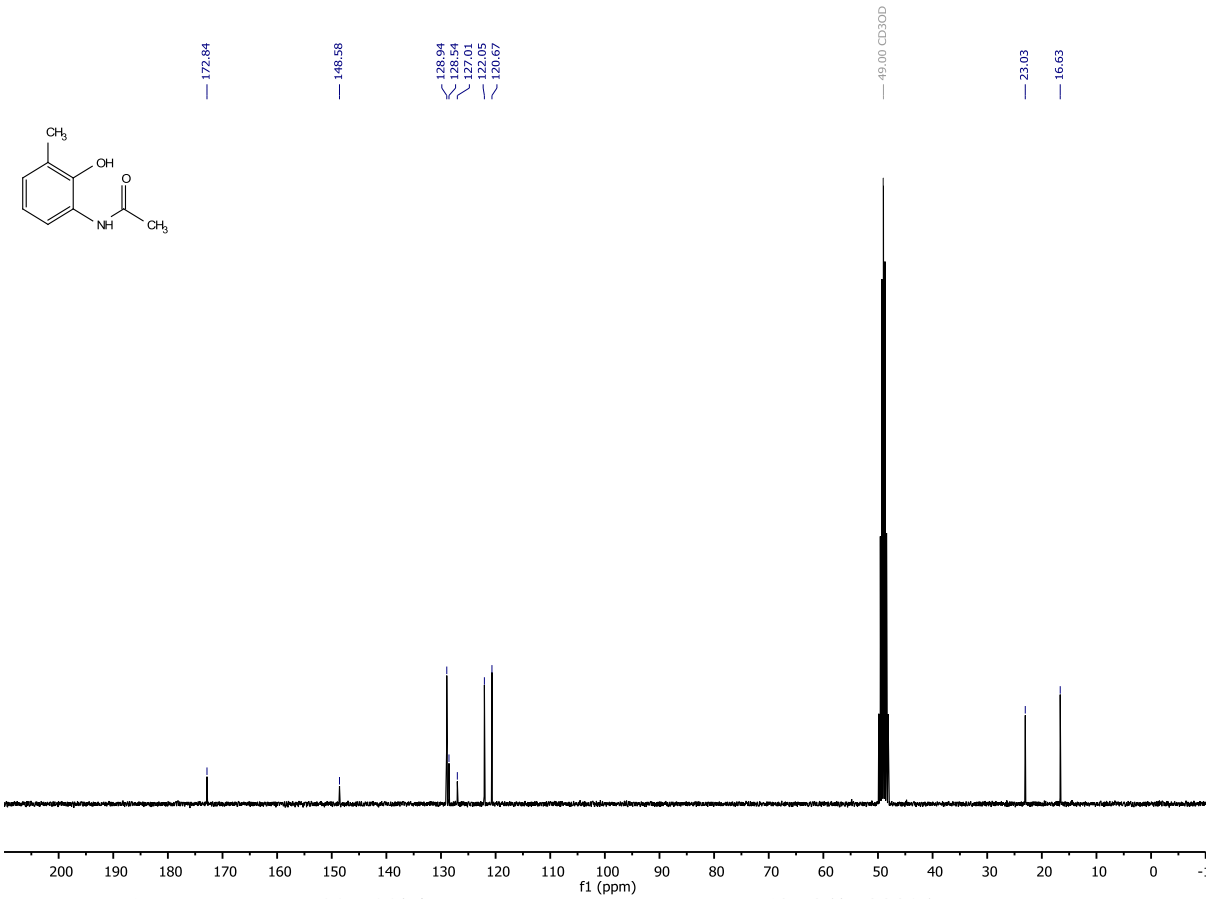

1.00
1.02
1.05
3.10
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.16
149.72
137.07
124.40
124.01
121.22
117.95
49.00 CD3OD
23.29
21.04
f1 (ppm)


7.20
6.65
3.31 CD3OD
2.16
2.15
2.14
0.99
1.02
9.00
f1 (ppm)


172.20
147.69
135.47
128.54
125.13
124.26
118.91
49.00 CD3OD
23.23
19.43
18.96
OH
O
NH
CH3
H3C
H3C
f1 (ppm)


7.07
7.06
7.04
7.04
6.98
6.97
6.97
6.97
6.95
6.95
6.94
6.94
6.76
6.73
6.71
3.31 CD3OD
2.23
2.18
CH3
OH
O
NH
CH3
1.03
0.99
1.03
3.03
3.00
f1 (ppm)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148.58
128.94
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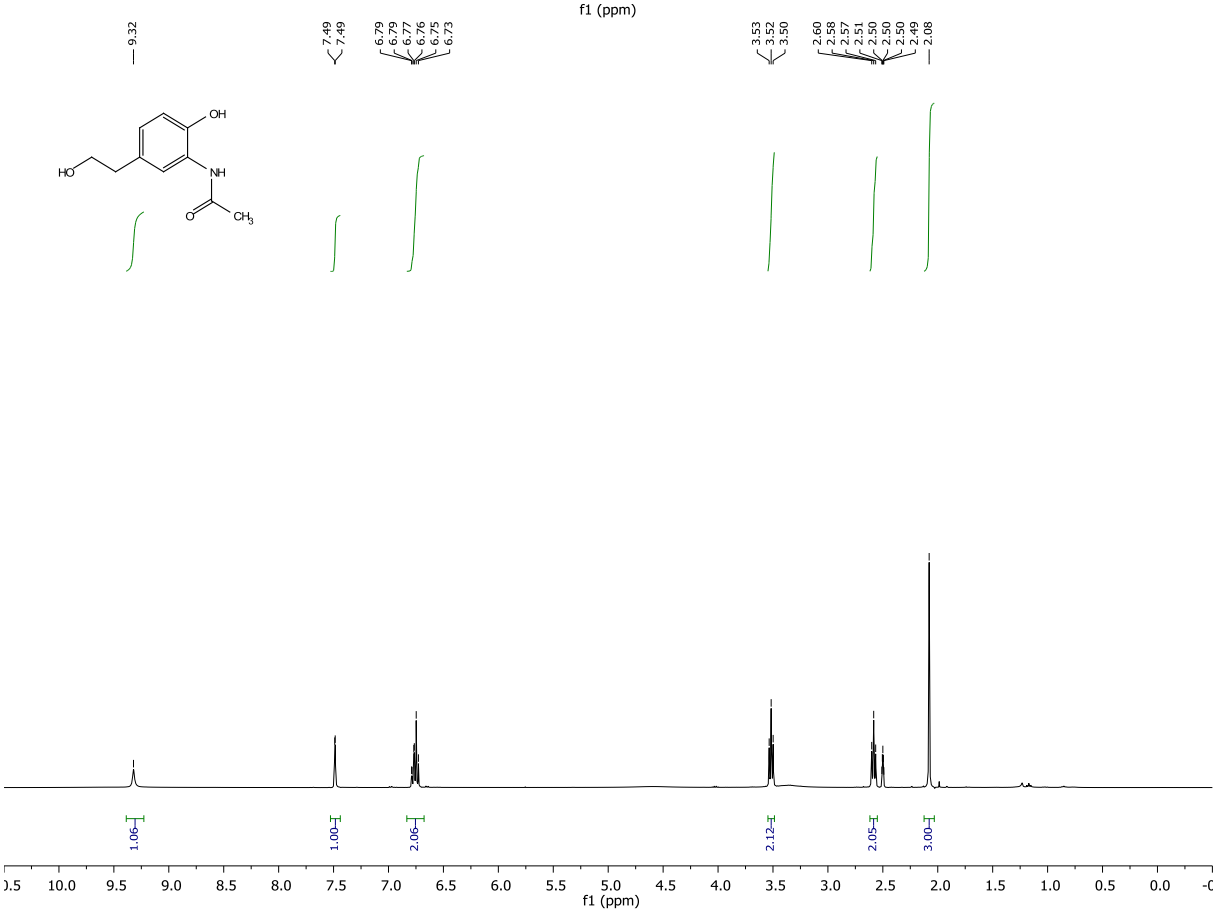
122.05
120.67
49.00 CD3OD
23.03
16.63
f1 (ppm)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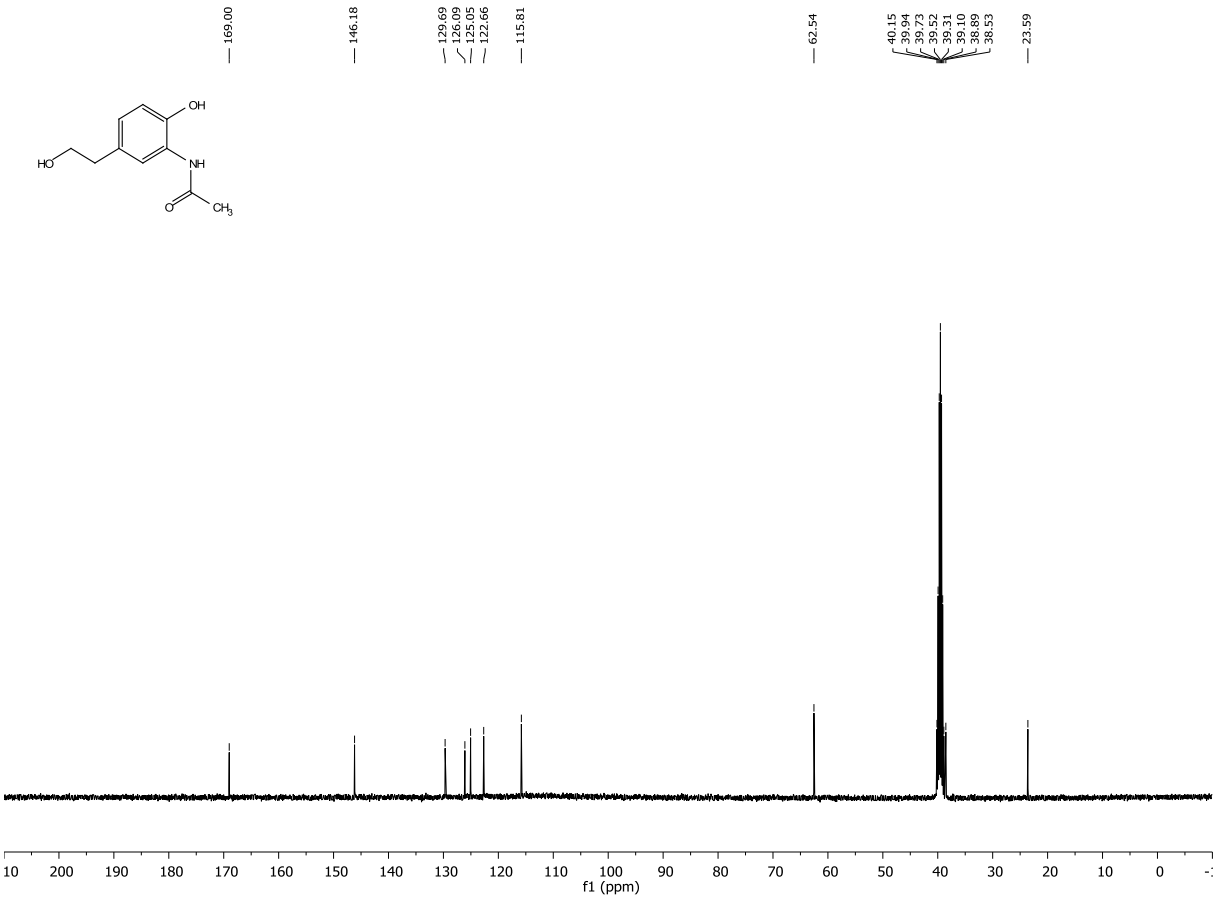
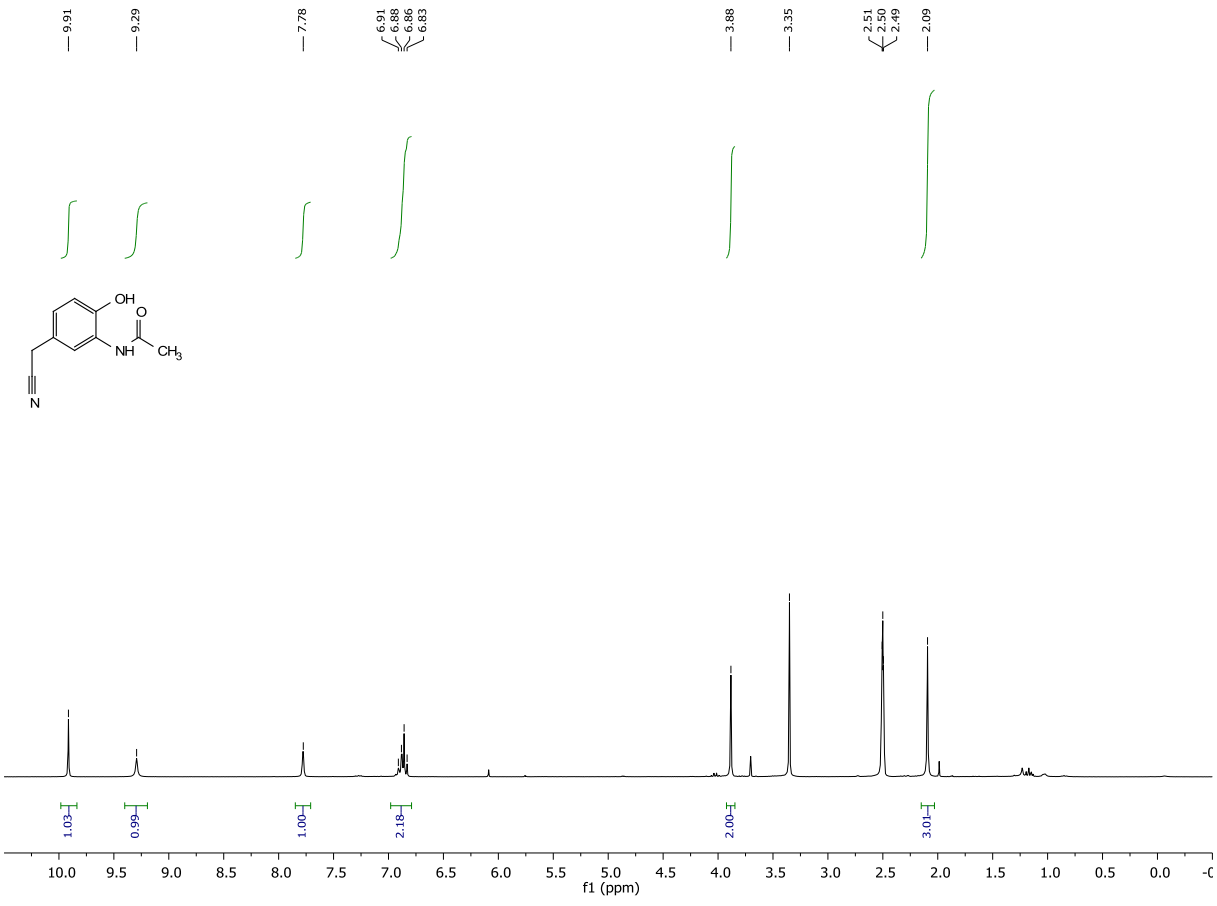
7.49
6.79
6.79
6.77
6.76
6.75
6.73
3.53
3.52
3.50
2.60
2.58
2.57
2.51
2.50
2.50
2.50
2.49
2.08
1.06
1.00
2.06
2.12
2.05
3.00
f1 (ppm)


169.00
146.18
129.69
126.09
125.05
122.66
115.81
62.54
40.15
39.94
39.73
39.52
39.31
39.10
38.89
38.53
23.59
OH
HO
NH
O
CH3
f1 (ppm)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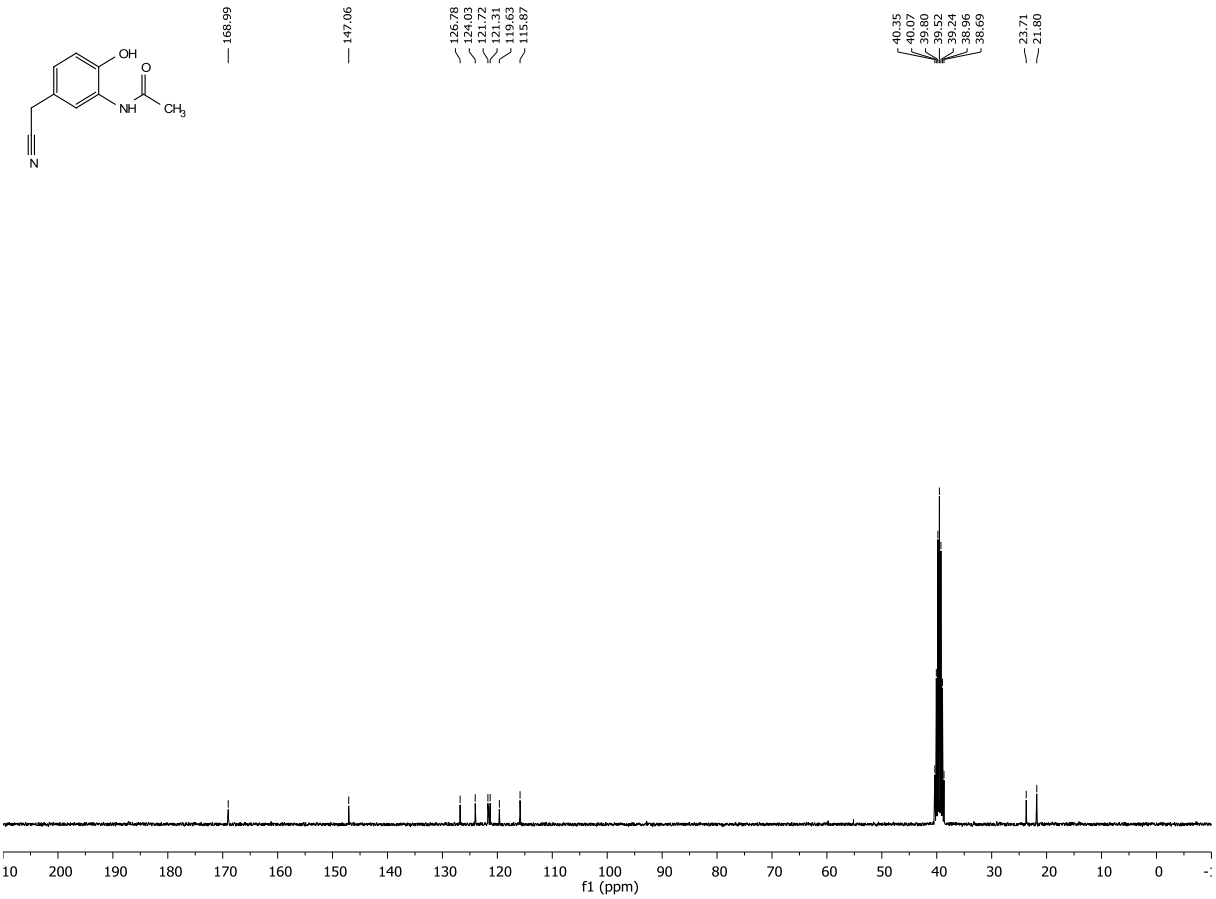
9.29
7.78
6.91
6.88
6.86
6.83
3.88
3.35
2.51
2.50
2.49
2.09
OH
O
NH
CH3
N
1.03
0.99
1.00
2.18
2.00
3.01
f1 (ppm)


OH
O
NH
CH3
N
168.99
147.06
126.78
124.03
121.72
121.31
119.63
115.87
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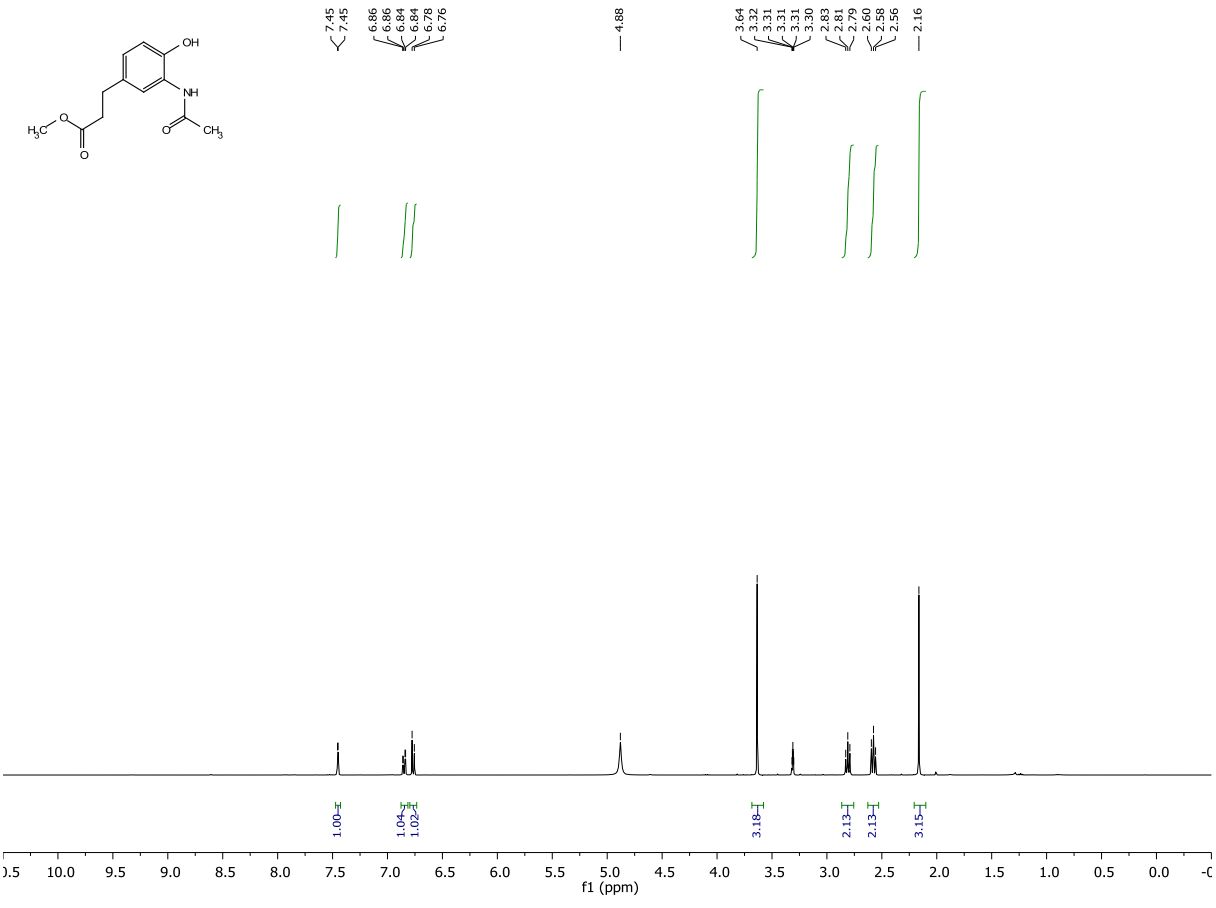
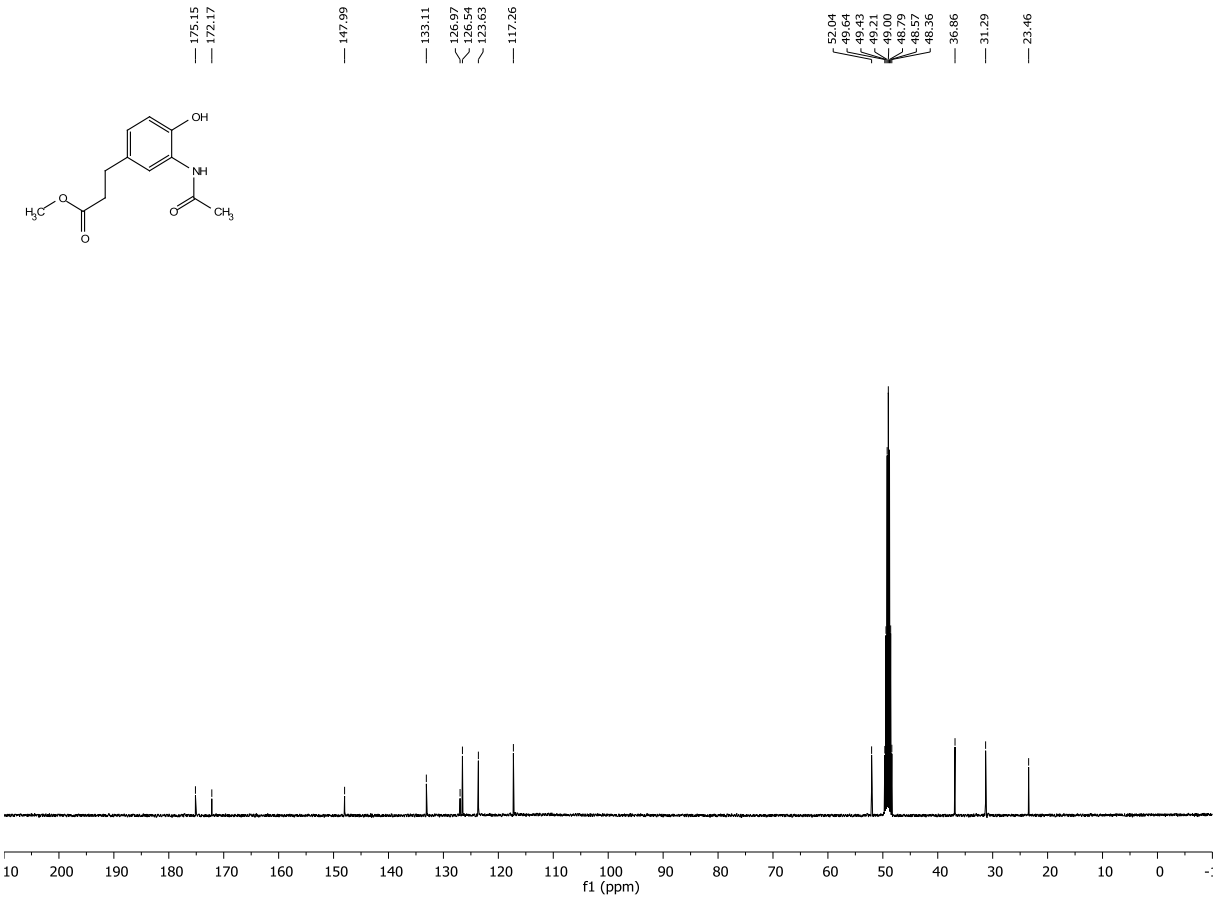
38.96
38.69
23.71
21.80
f1 (ppm)


OH
NH
O
CH3
H3C
O
O
7.45
7.45
6.86
6.86
6.84
6.84
6.78
6.76
4.88
3.64
3.32
3.31
3.31
3.31
3.30
2.83
2.81
2.79
2.60
2.58
2.56
2.16
1.00
1.04
1.02
3.18
2.13
2.13
3.15
f1 (ppm)


175.15
172.17
147.99
133.11
126.97
126.54
123.63
117.26
52.04
49.64
49.43
49.21
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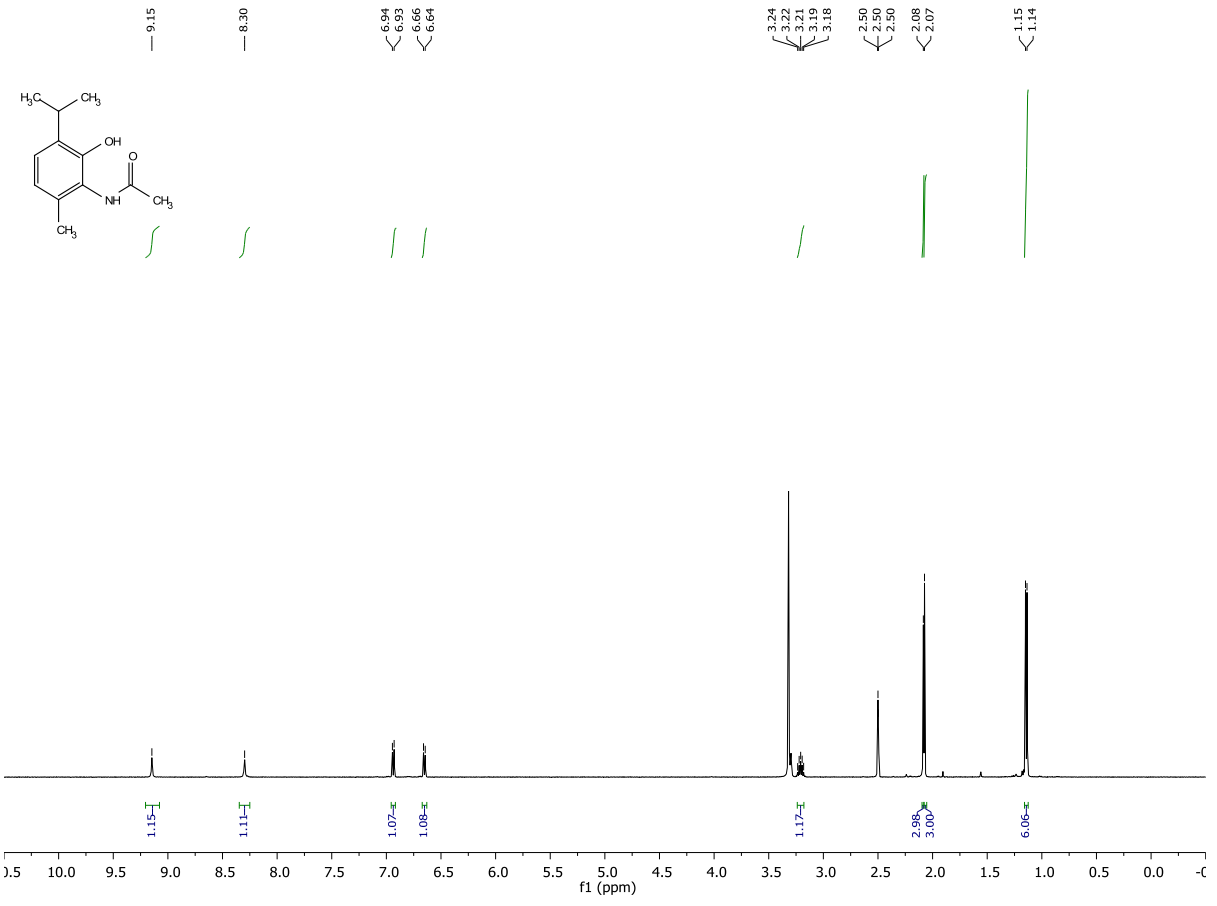
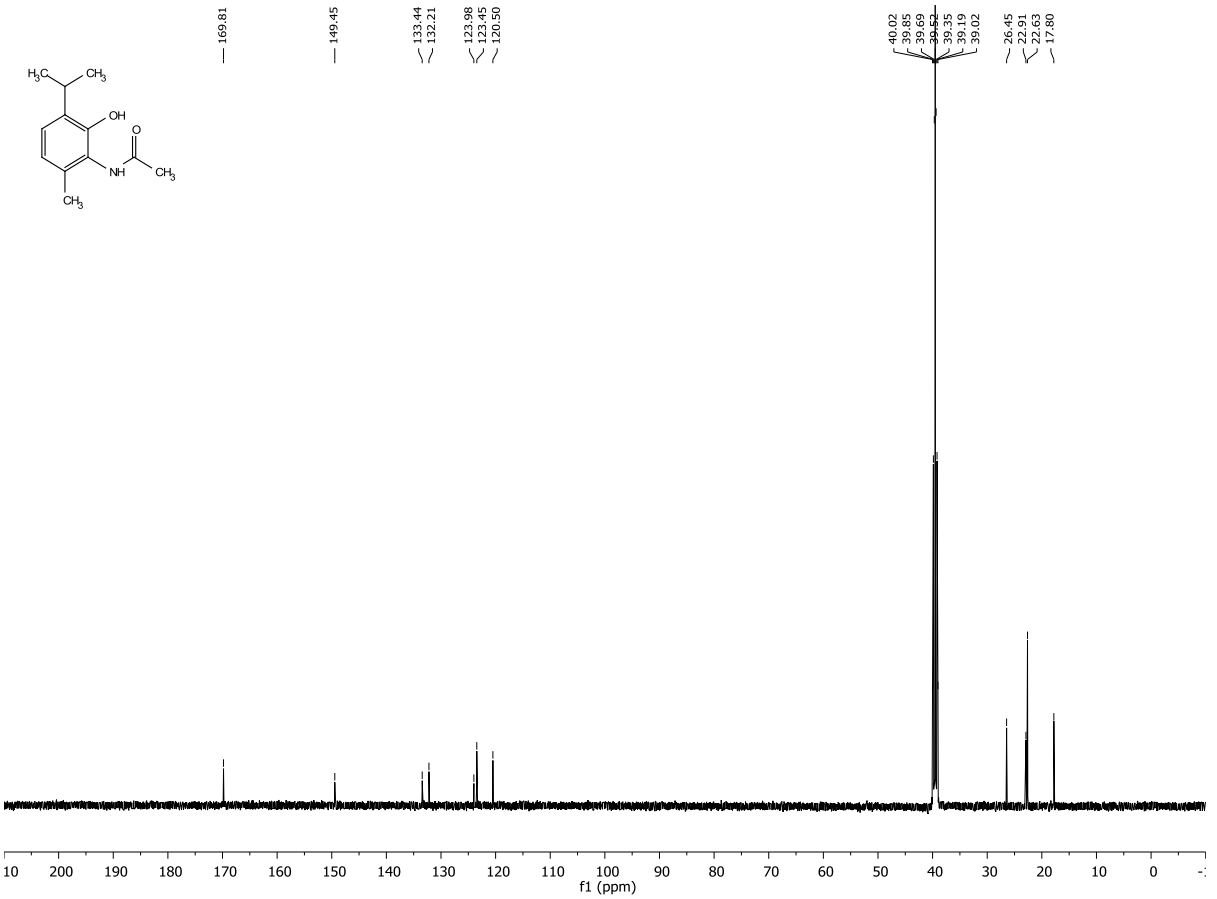
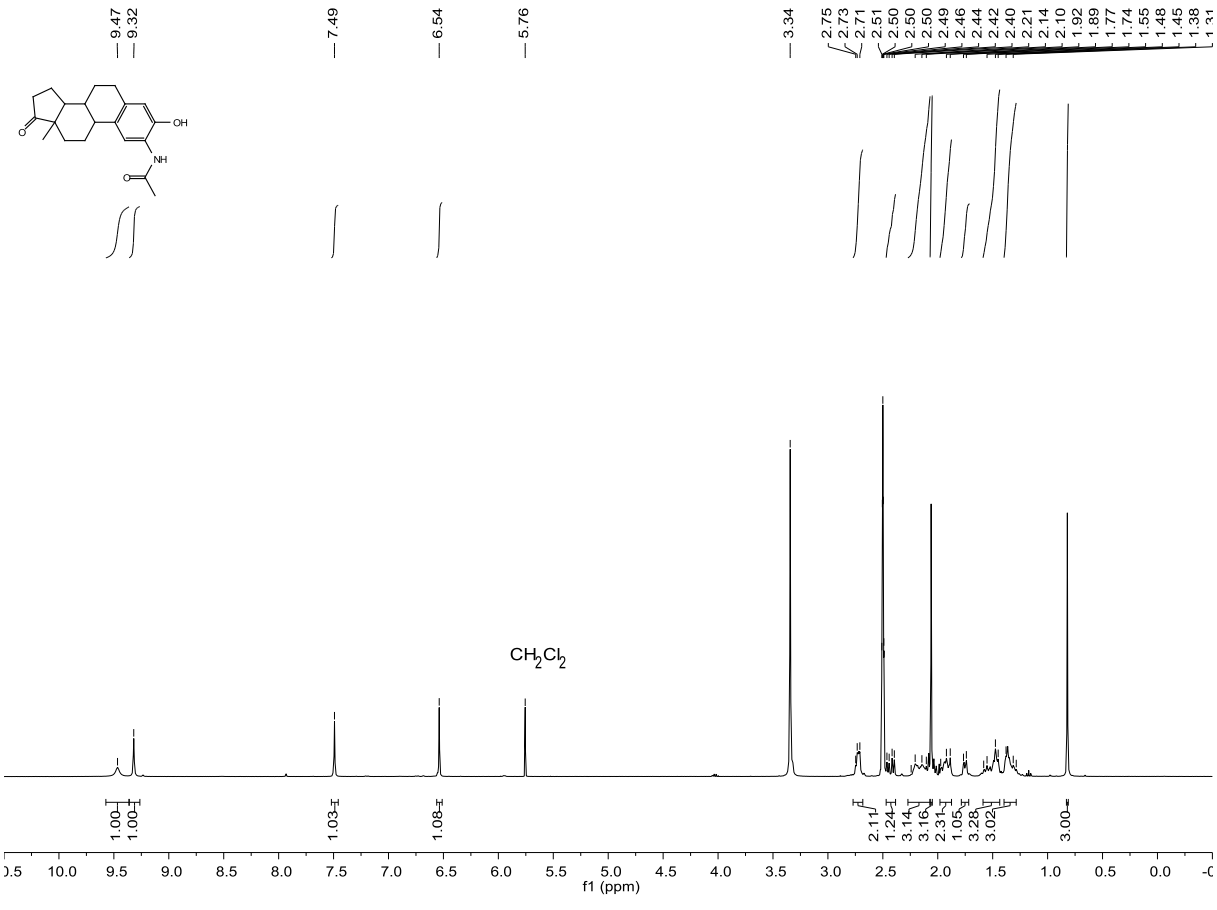
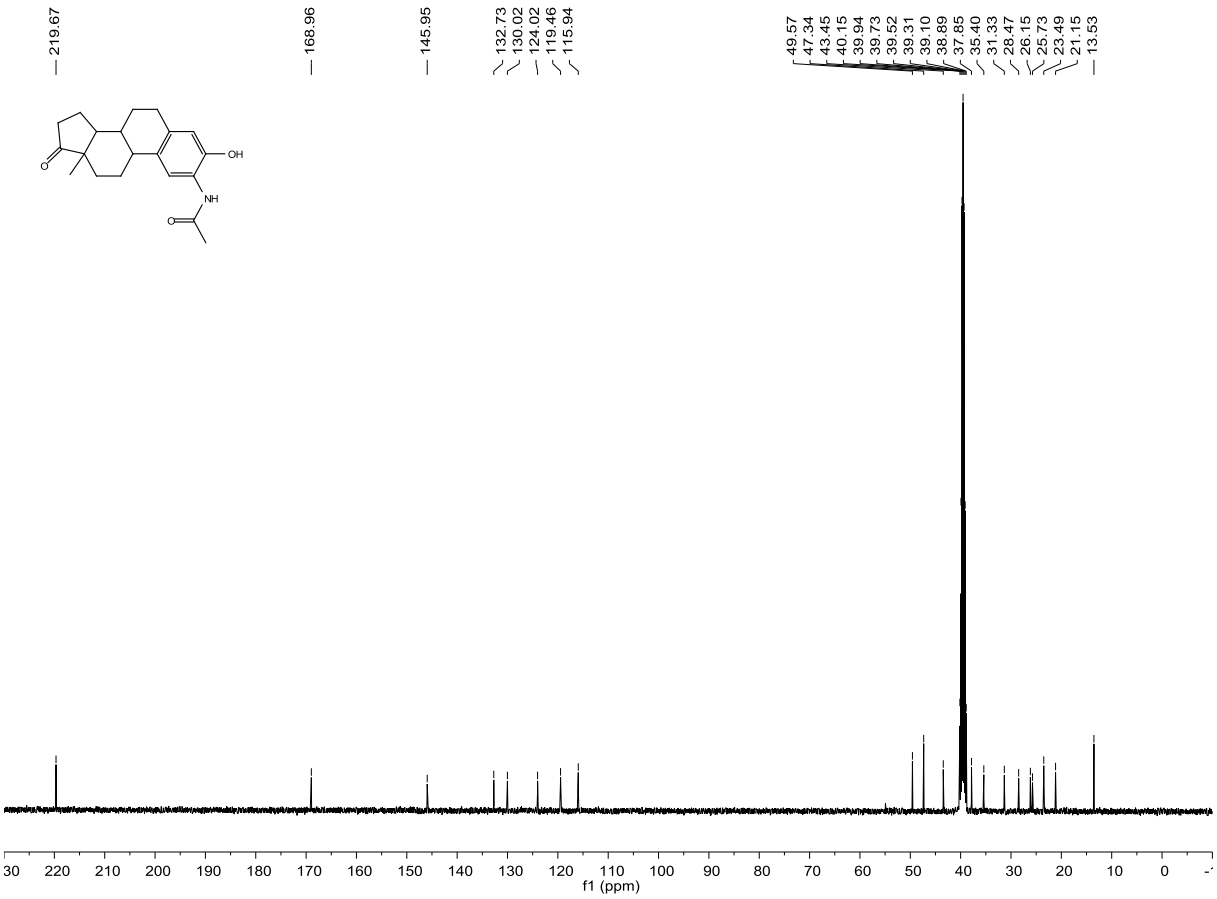
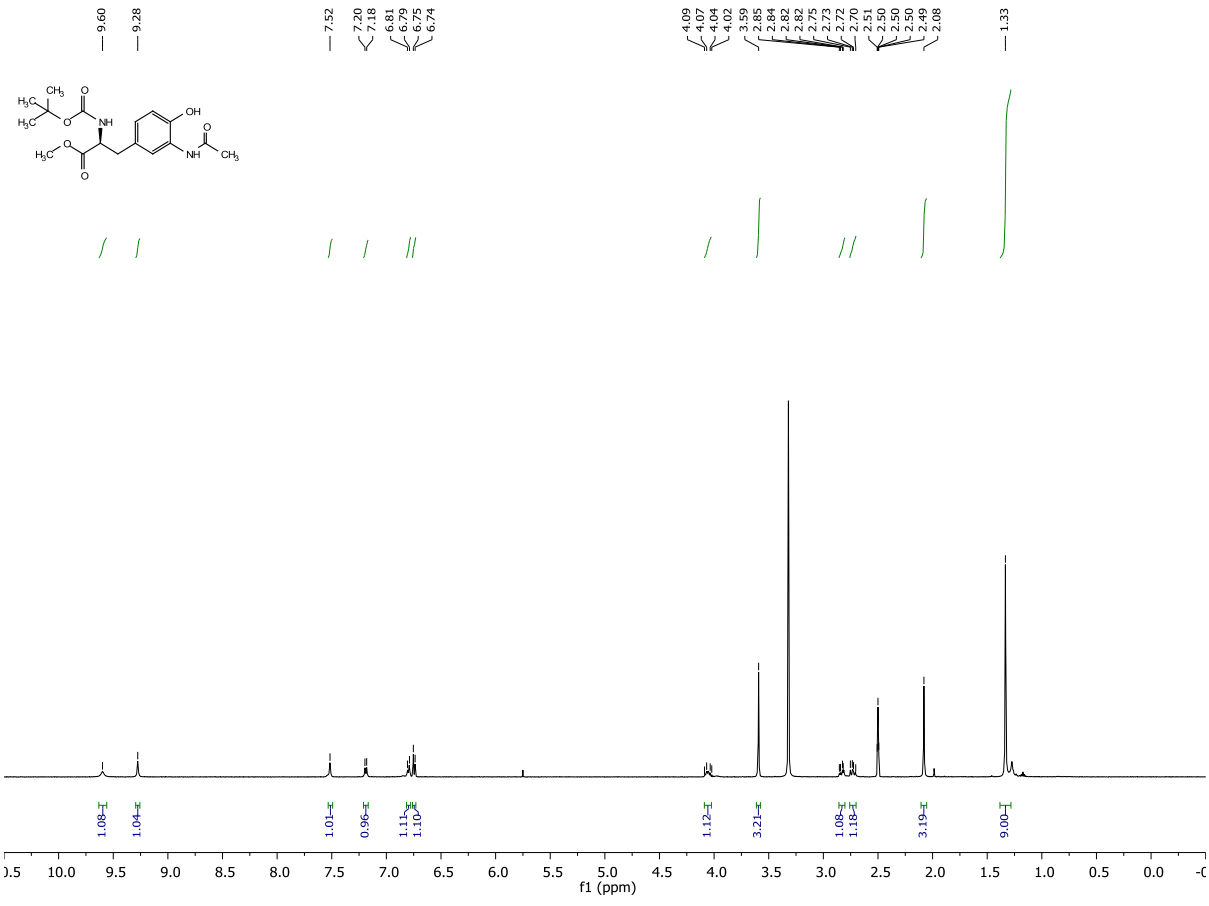
48.79
48.57
48.36
36.86
31.29
23.46
OH
NH
O
CH3
f1 (ppm)


9.15
8.30
6.94
6.93
6.66
6.64
3.24
3.22
3.21
3.19
3.18
2.50
2.50
2.50
2.08
2.07
1.15
1.14
H3C
CH3
OH
NH
CH3
1.15
1.11
1.07
1.08
1.17
2.98
3.00
6.06
f1 (ppm)


169.81
149.45
133.44
132.21
123.98
123.45
120.50
40.02
39.85
39.69
39.52
39.35
39.19
39.02
26.45
22.91
22.63
17.80
OH
O
NH
CH3
f1 (ppm)


9.47
9.32
7.49
6.54
5.76
3.34
2.75
2.73
2.71
2.51
2.50
2.50
2.50
2.49
2.46
2.44
2.42
2.40
2.21
2.14
2.10
1.92
1.89
1.77
1.74
1.55
1.48
1.45
1.38
OH
NH
O
CH2Cl2
1.00
1.00
1.03
1.08
2.11
1.24
3.14
3.16
2.31
1.05
3.28
3.02
3.00
f1 (ppm)


219.67
168.96
145.95
132.73
130.02
124.02
119.46
115.94
49.57
47.34
43.45
40.15
39.94
39.73
39.52
39.31
39.10
38.89
37.85
35.40
31.33
28.47
26.15
25.73
23.49
21.15
13.53
OH
NH
O
f1 (ppm)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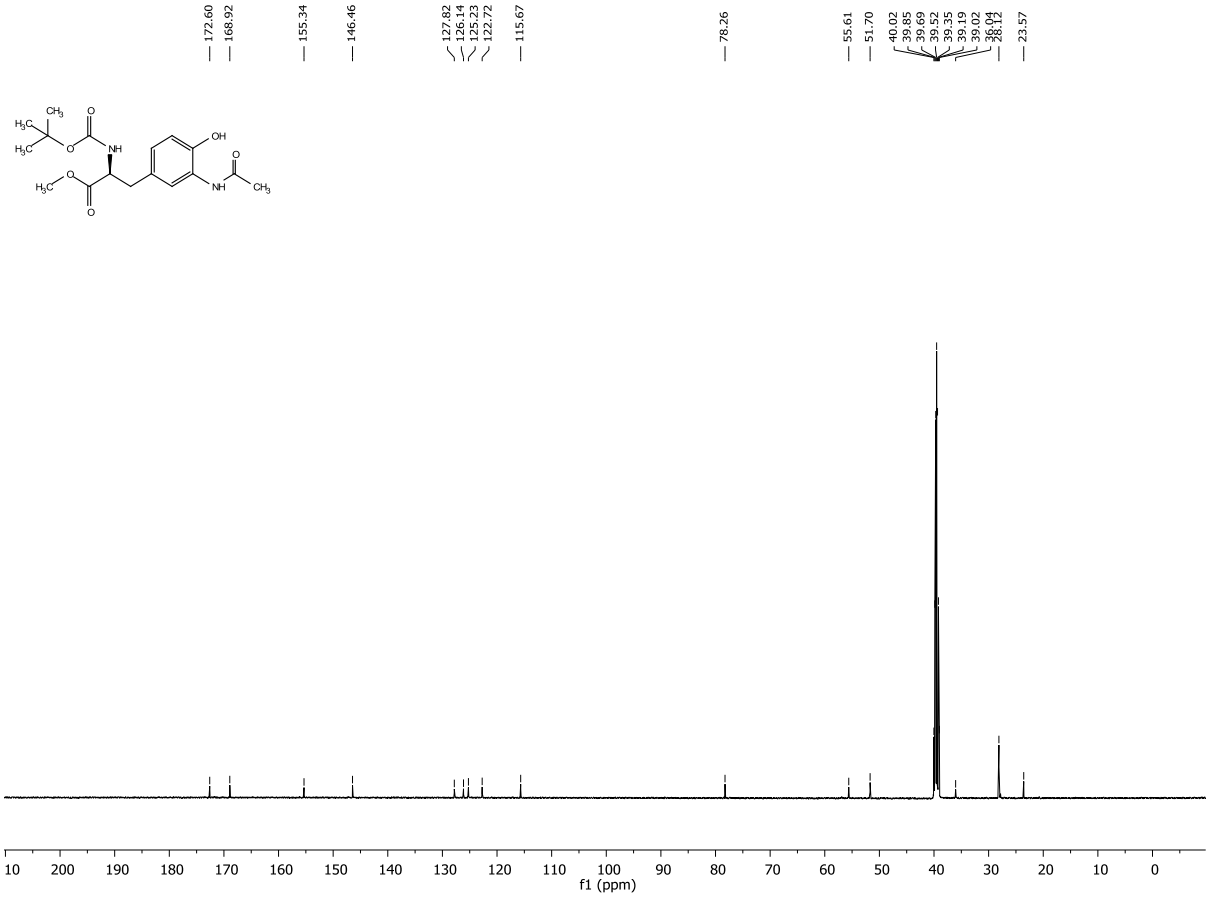
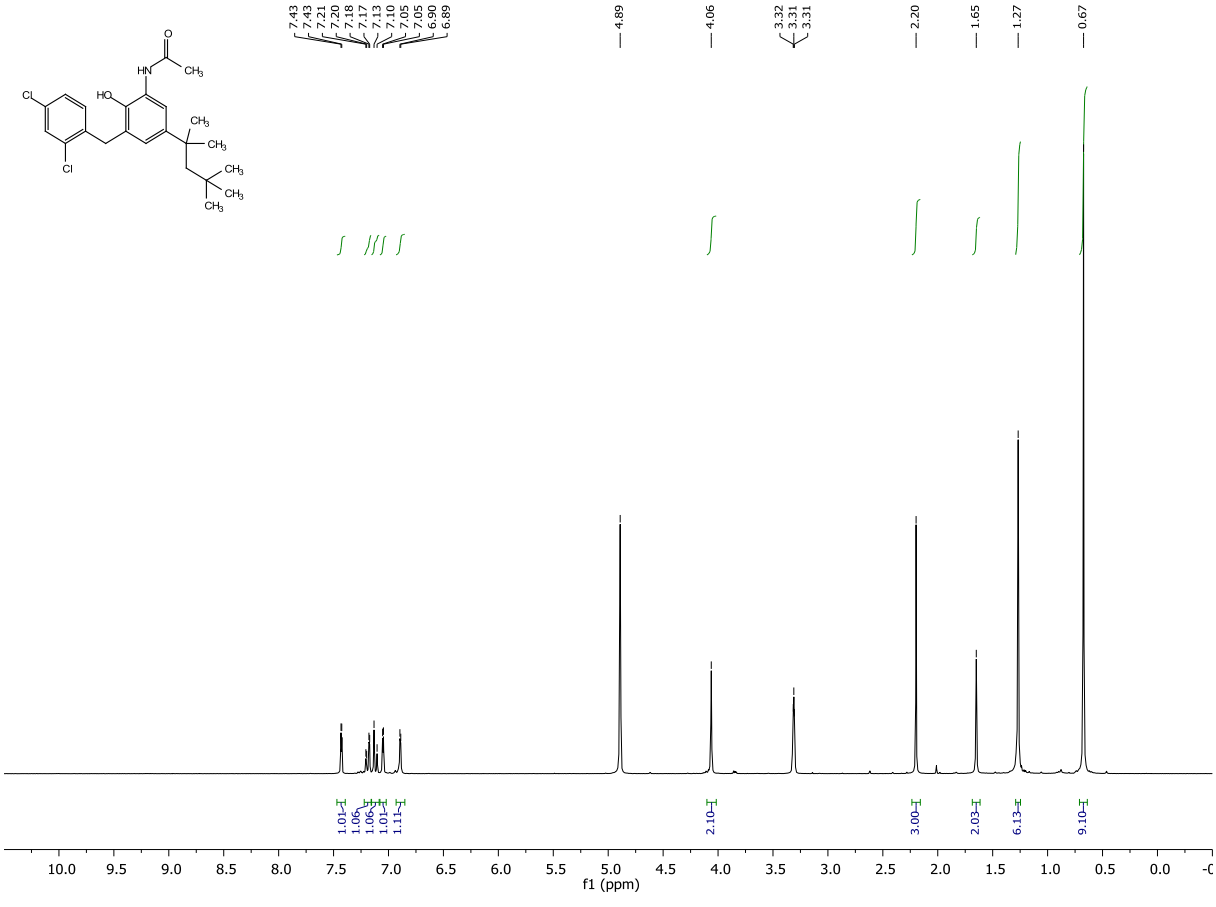
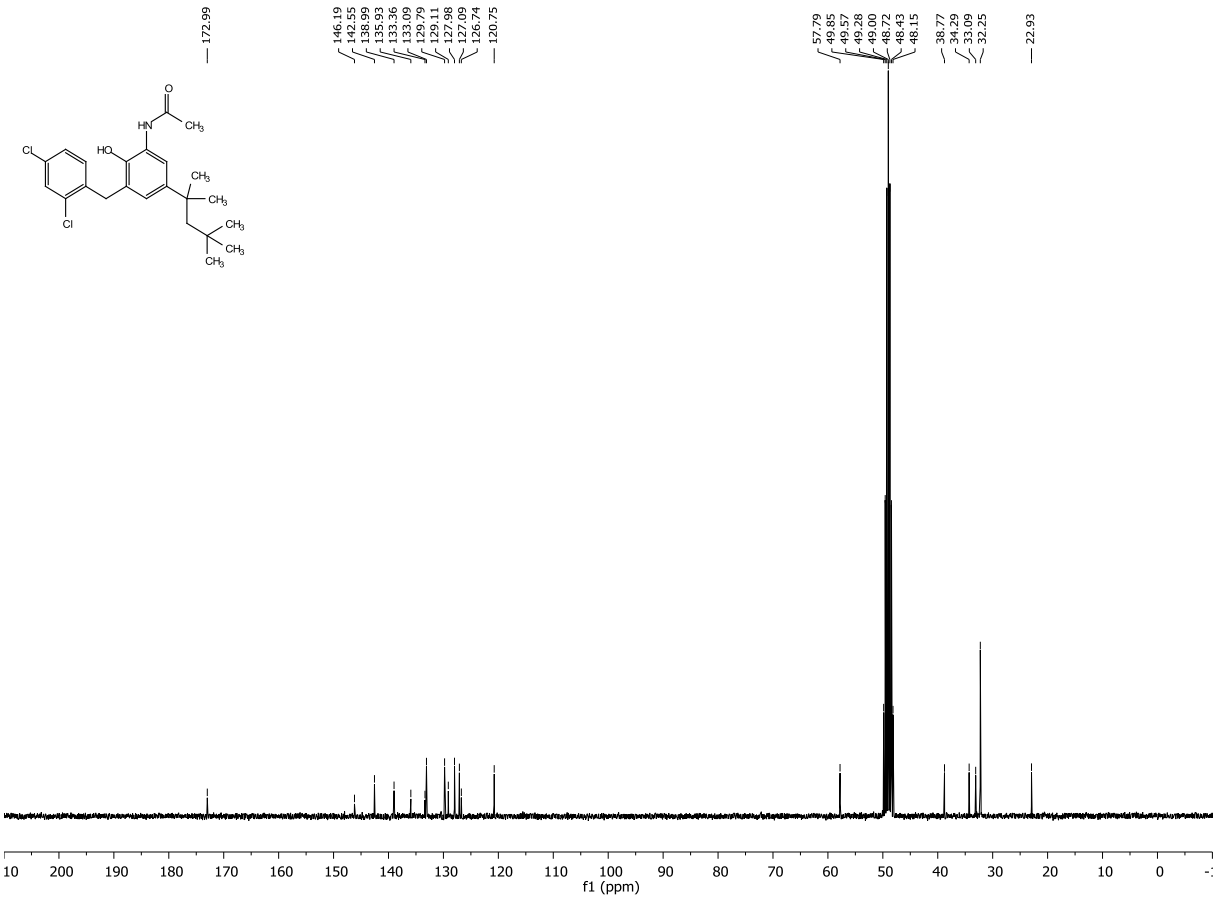
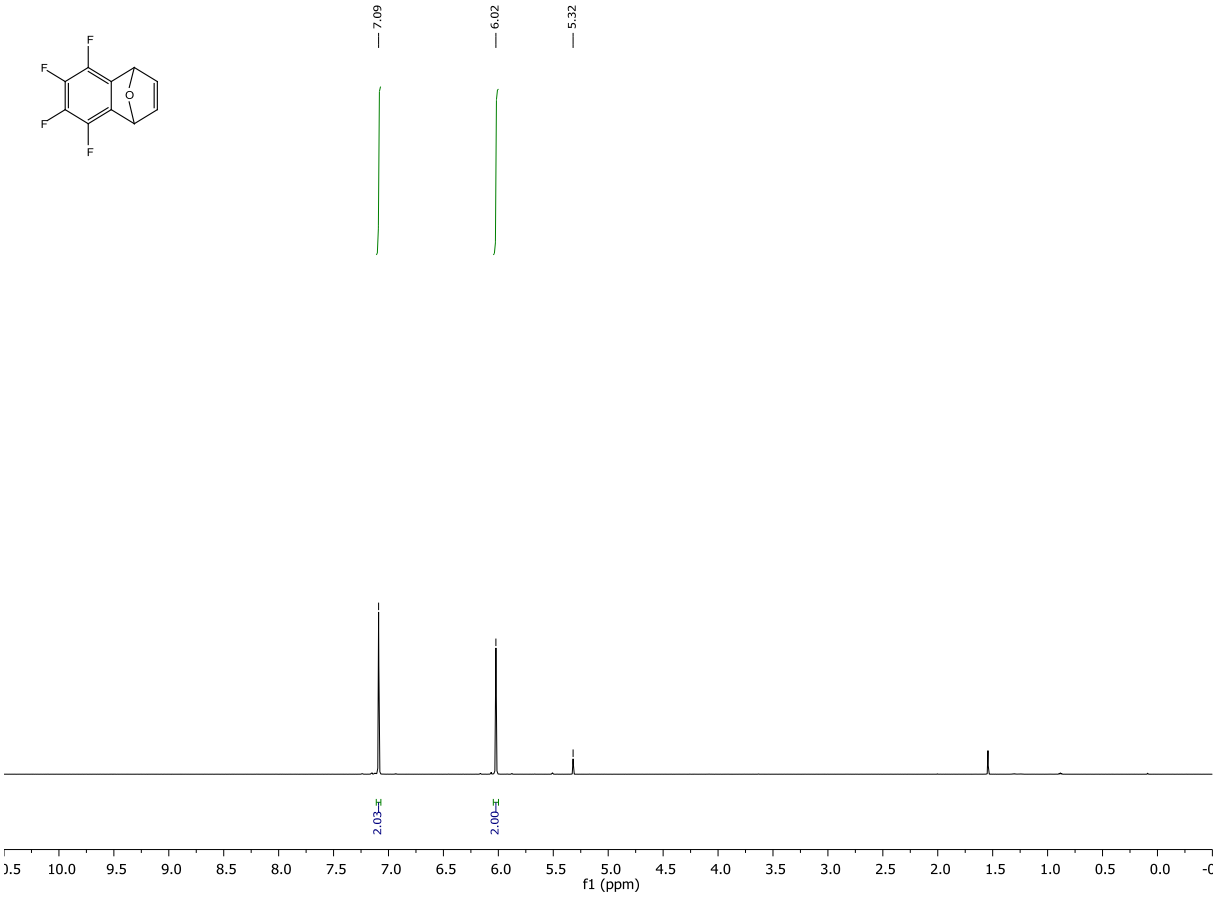
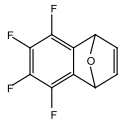
9.28
7.52
7.20
7.18
6.81
6.79
6.75
6.74
4.09
4.07
4.04
4.02
3.59
2.85
2.84
2.82
2.82
2.75
2.73
2.72
2.70
2.51
2.50
2.50
2.50
2.49
2.08
1.33
OH
NH
NH
1.08
1.04
1.01
0.96
1.11
1.10
1.12
3.21
1.08
1.18
3.19
9.00
f1 (ppm)


172.60
168.92
155.34
146.46
127.82
126.14
125.23
122.72
115.67
78.26
55.61
51.70
40.02
39.85
39.69
39.52
39.35
39.19
39.02
36.04
28.12
23.57
f1 (ppm)

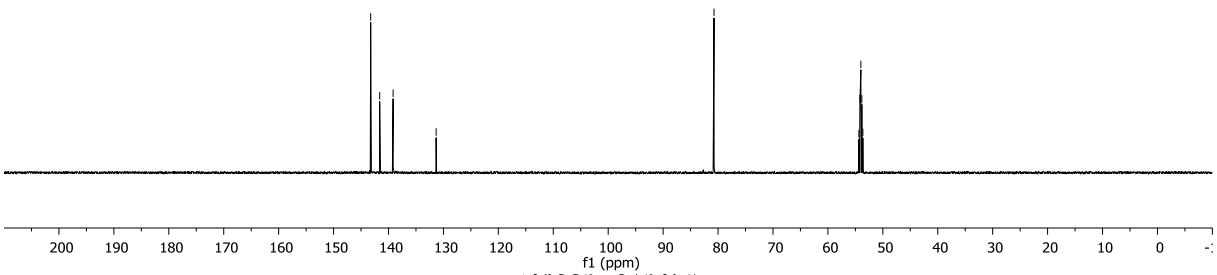

7.43
7.43
7.21
7.20
7.18
7.17
7.13
7.10
7.05
7.05
6.90
6.89
4.89
4.06
3.32
3.31
3.31
2.20
1.65
1.27
0.67
1.01
1.06
1.06
1.01
1.11
2.10
3.00
2.03
6.13
9.10
f1 (ppm)

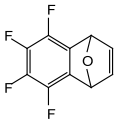

172.99
146.19
142.55
138.99
135.93
133.36
133.09
129.79
129.11
127.98
127.09
126.74
120.75
57.79
49.85
49.57
49.28
49.00
48.72
48.43
48.15
38.77
34.29
33.09
32.25
22.93
O
HN
CH3
HO
Cl
CH3
CH3
Cl
CH3
CH3
CH3
f1 (ppm)

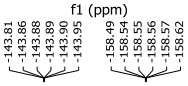

7.09
6.02
5.32
F
F
O
F
F
2.03
2.00
f1 (ppm)

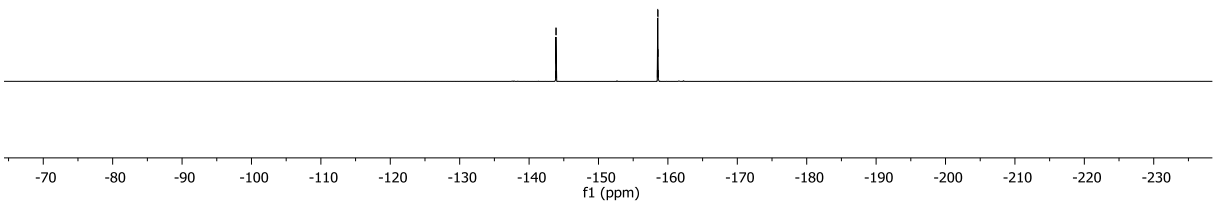

F
F
F
F
O

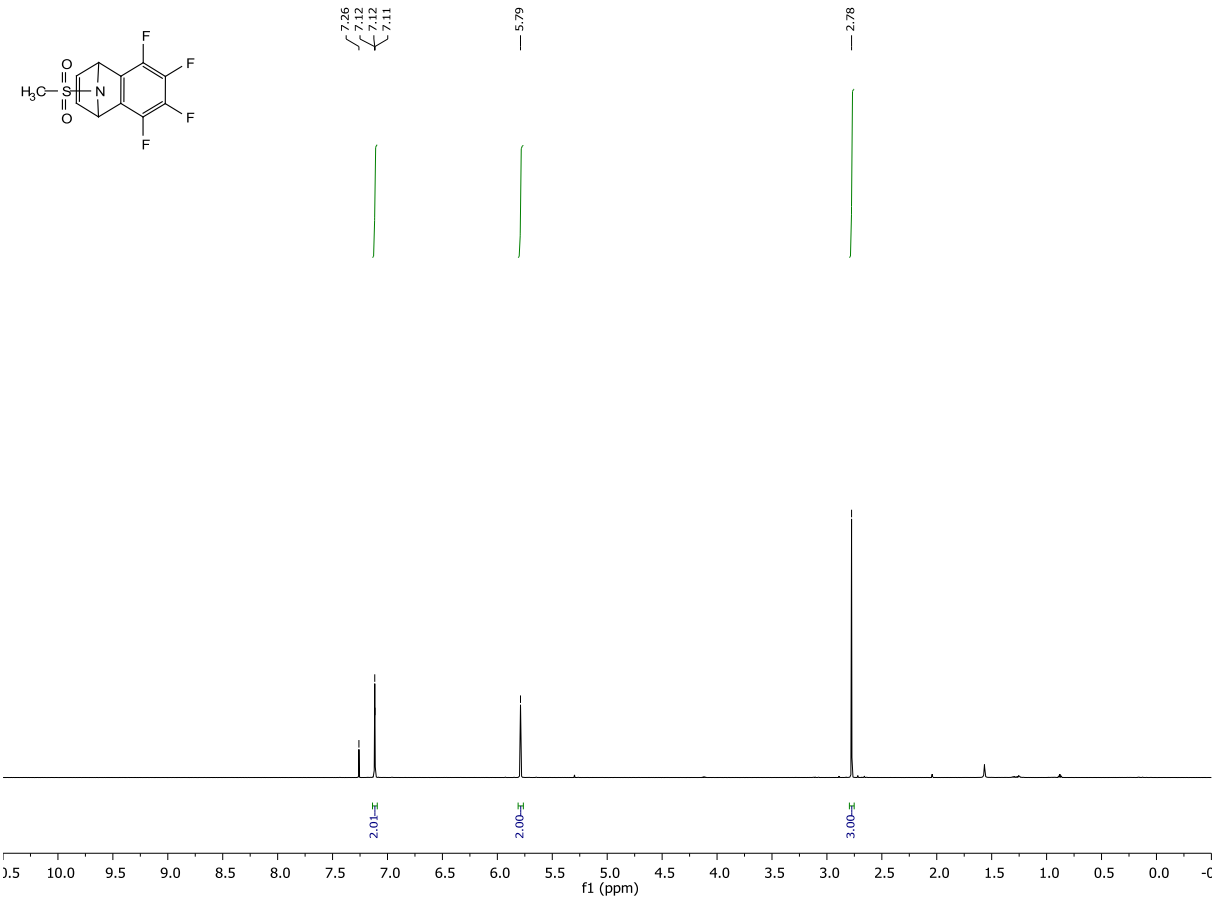

143.24
141.60
139.16
131.33
80.74
54.36
54.18
54.00
53.82
53.64

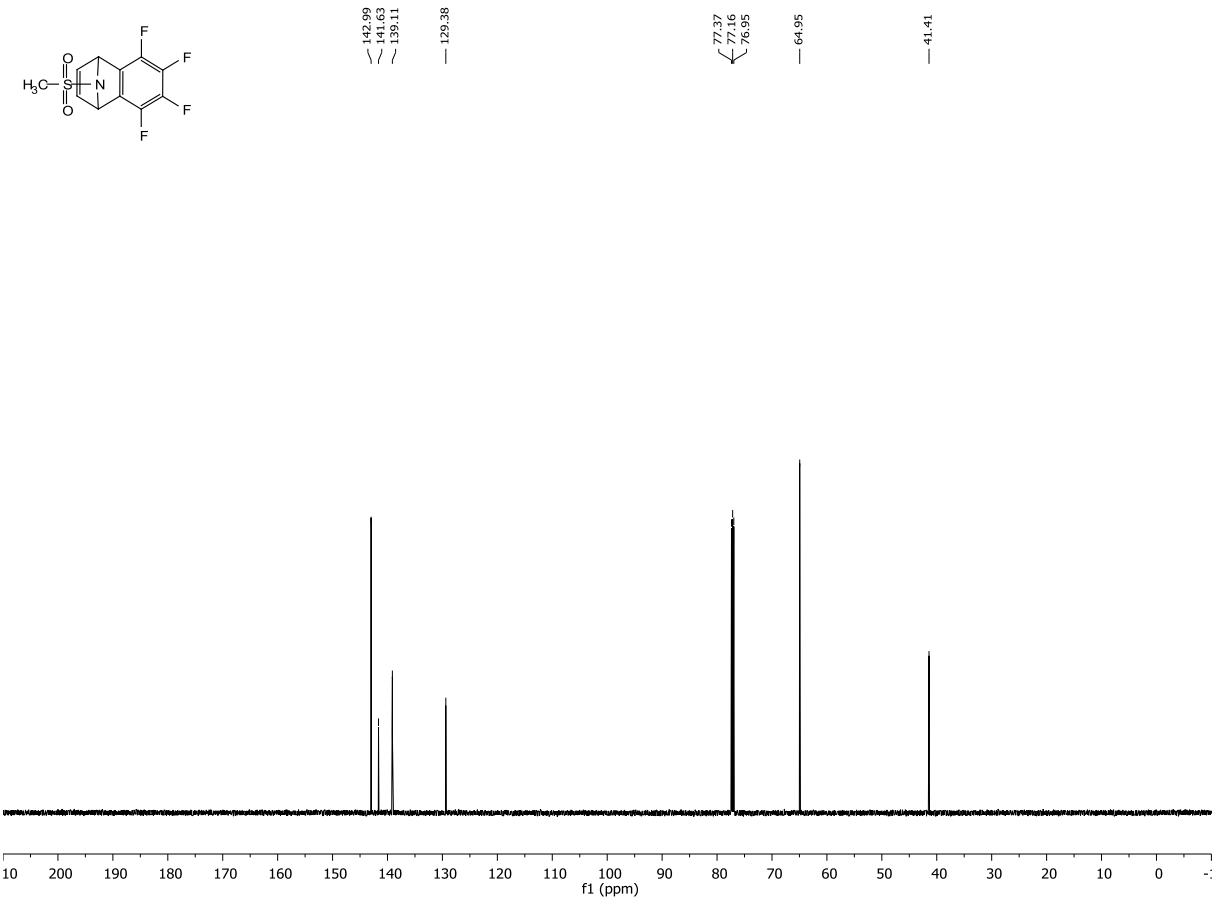

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

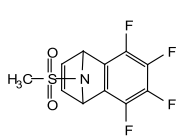

F
F
F
F
O


-143.81
-143.86
-143.88
-143.89
-143.90
-143.95
-158.49
-158.54
-158.55
-158.56
-158.57
-158.62


-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

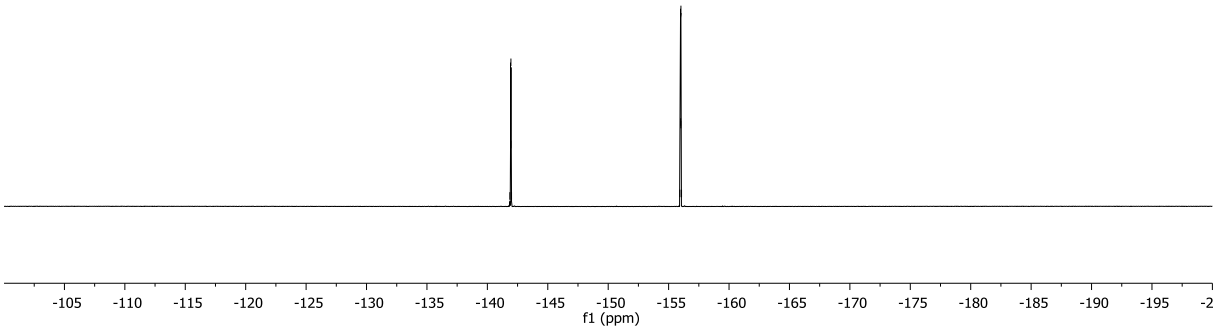

7.26
7.12
7.12
7.11
5.79
2.78
2.01
2.00
3.00
f1 (ppm)


142.99
141.63
139.11
129.38
77.37
77.16
76.95
64.95
41.41
f1 (ppm)



-141.86
-141.91
-141.92
-141.94
-141.95
-142.00

-155.93
-155.98
-155.99
-156.01
-156.02
-156.07



9.12

7.30
7.29
7.28
7.23
7.21
7.11
7.10
7.09
7.08
7.06
7.04
7.01
6.85
6.83
6.80
6.72
6.69
6.68

4.25
4.22
4.19

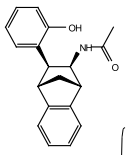
3.49

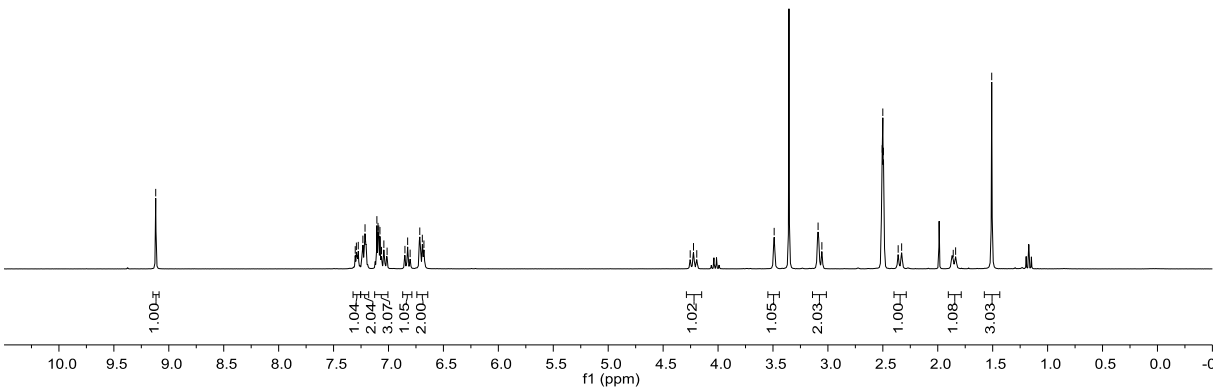
3.09
3.05

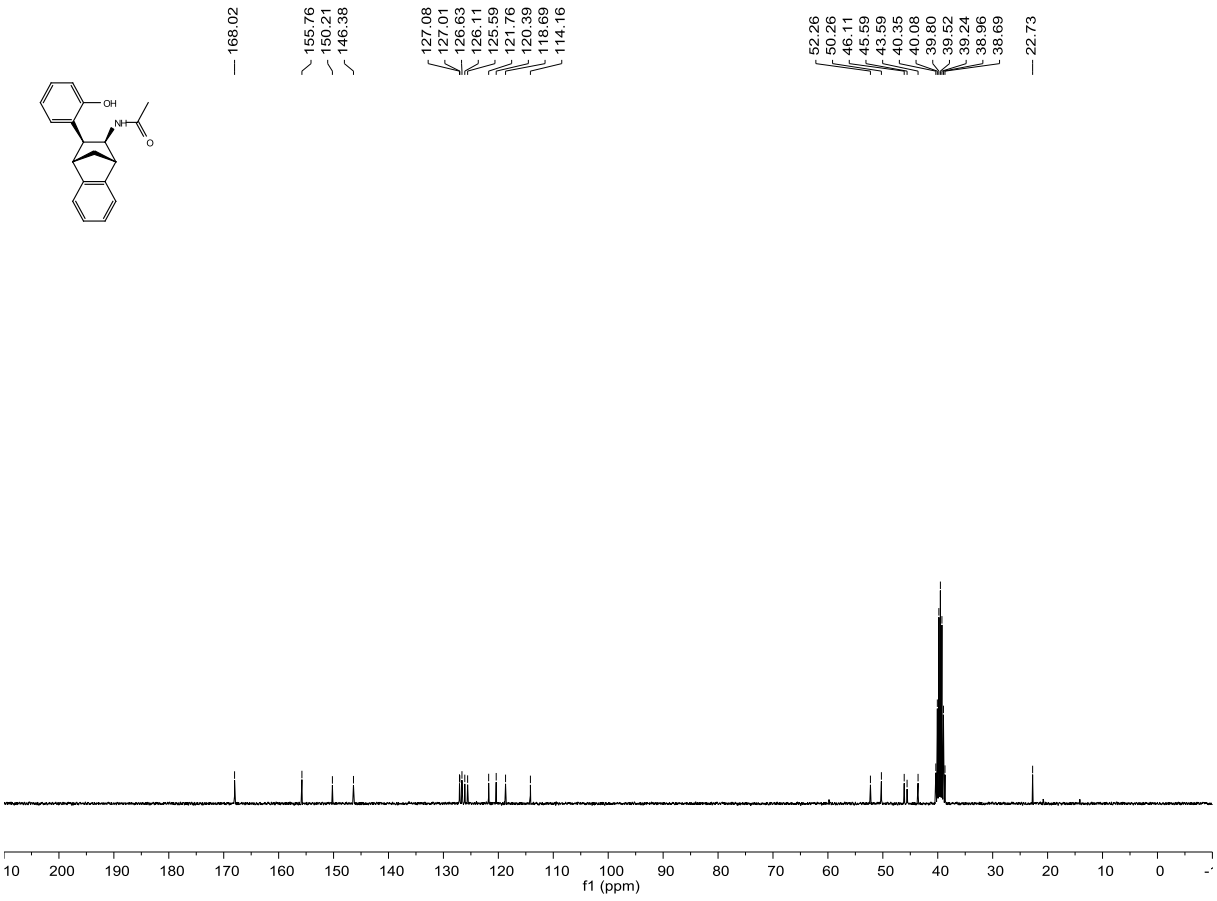
2.51
2.50
2.49
2.36
2.33

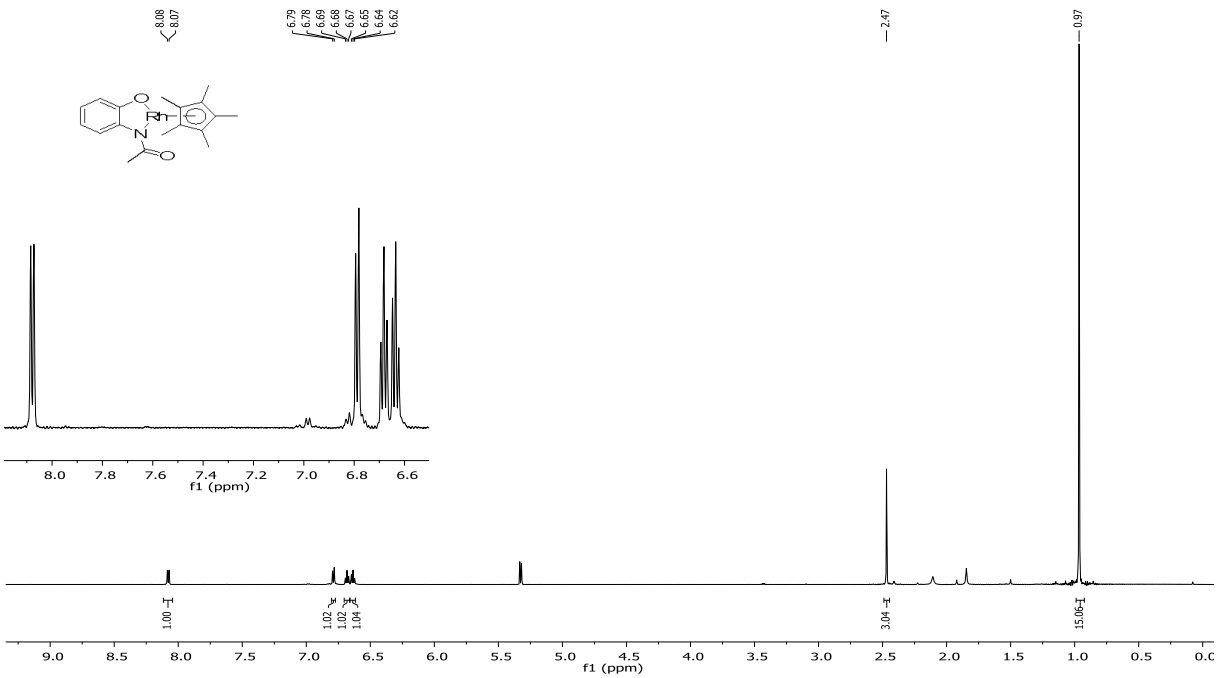
1.86
1.84

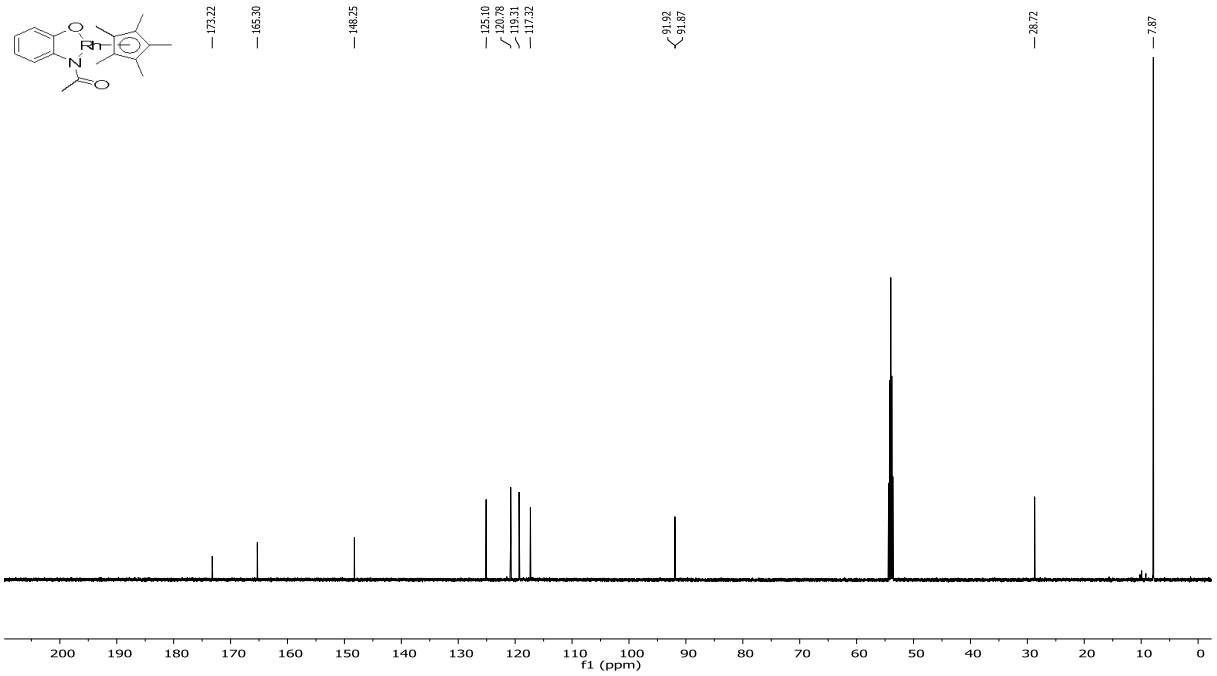
1.51

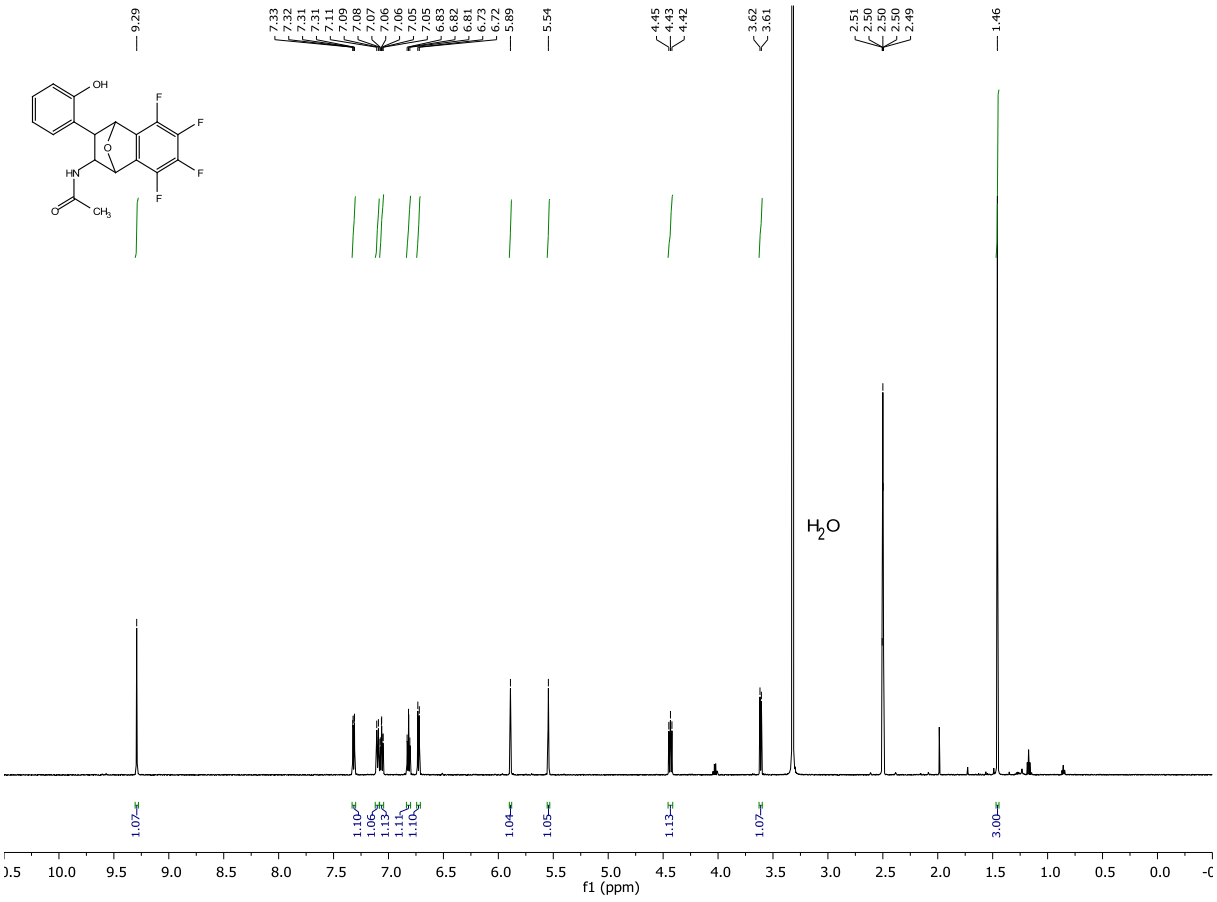


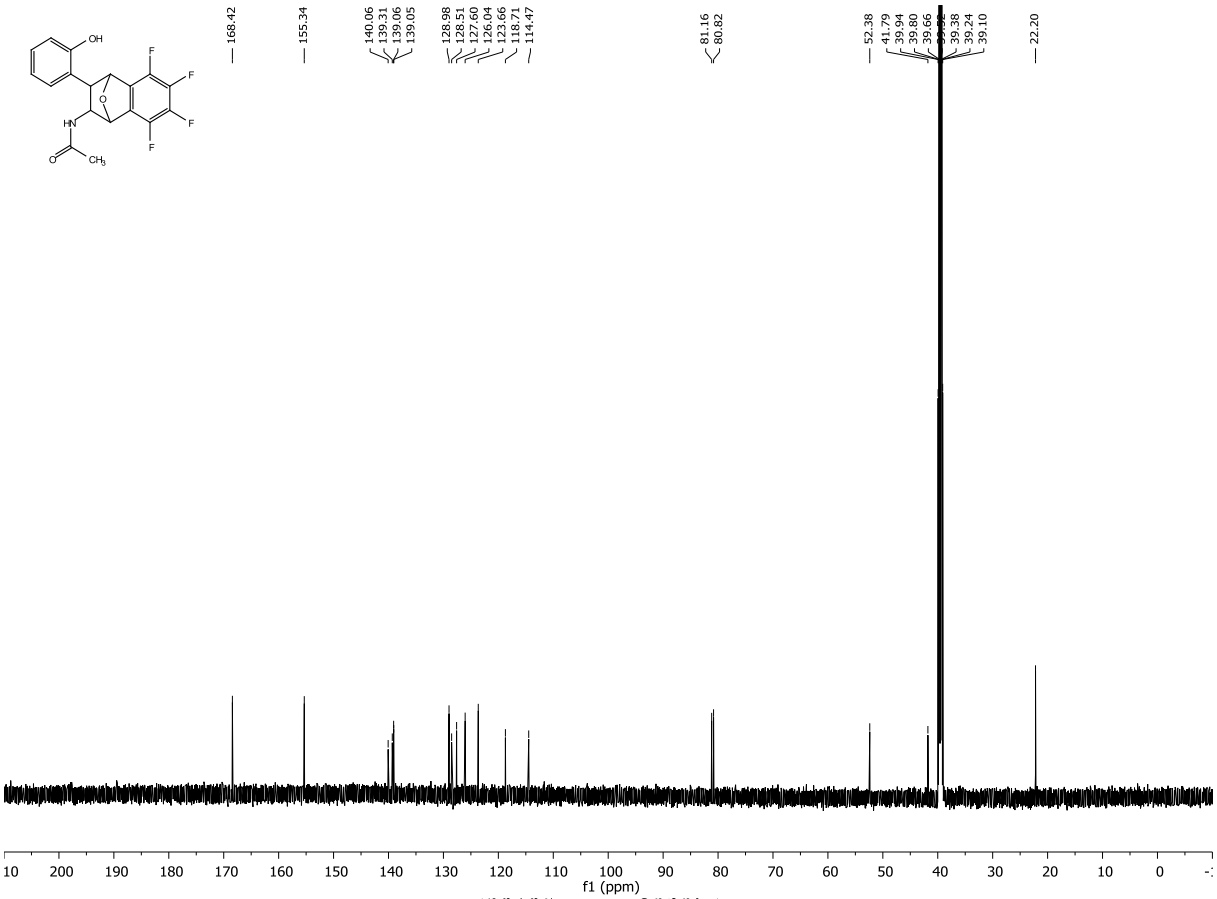


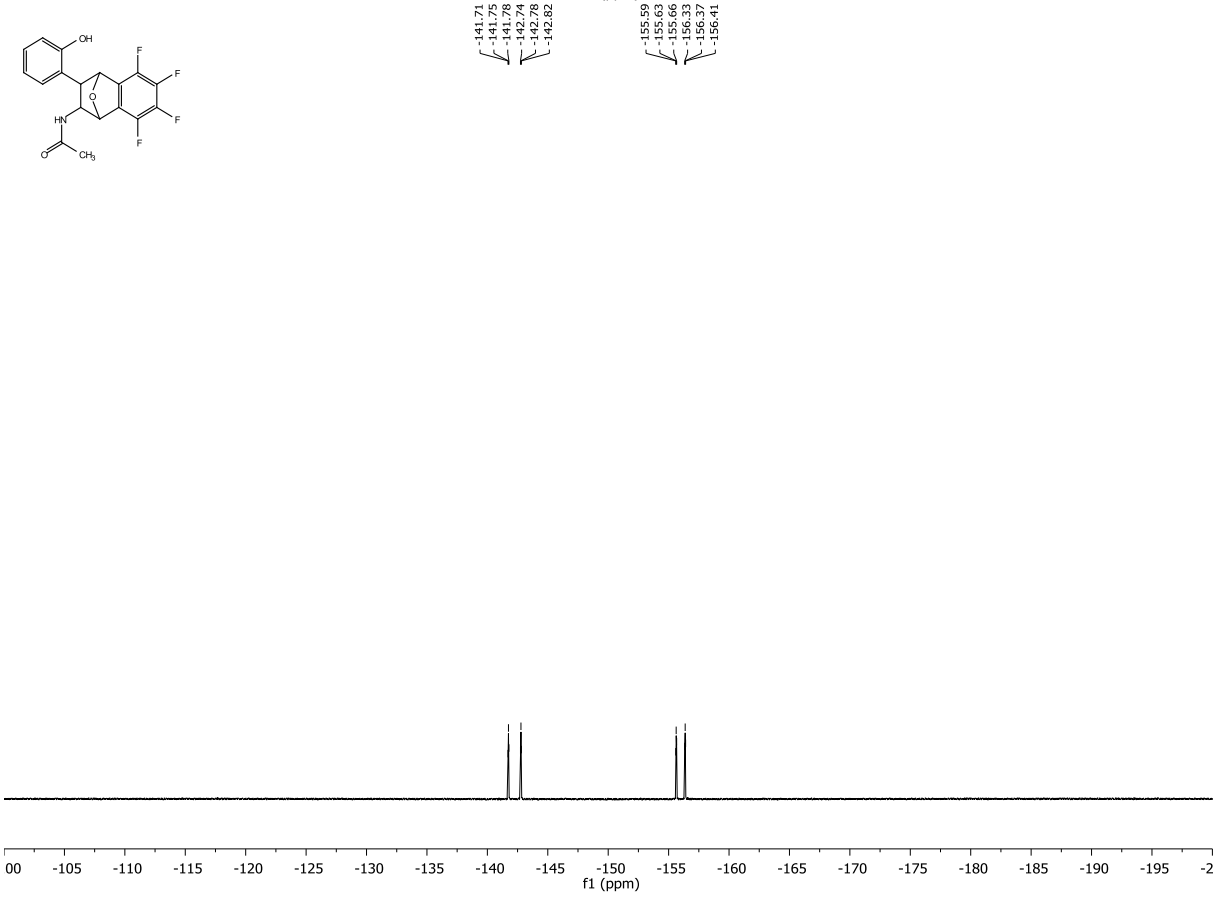

168.02
155.76
150.21
146.38
127.08
127.01
126.63
126.11
125.59
121.76
120.39
118.69
114.16
52.26
50.26
46.11
45.59
43.59
40.35
40.08
39.80
39.52
39.24
38.96
38.69
22.73
OH
NH
O
f1 (ppm)

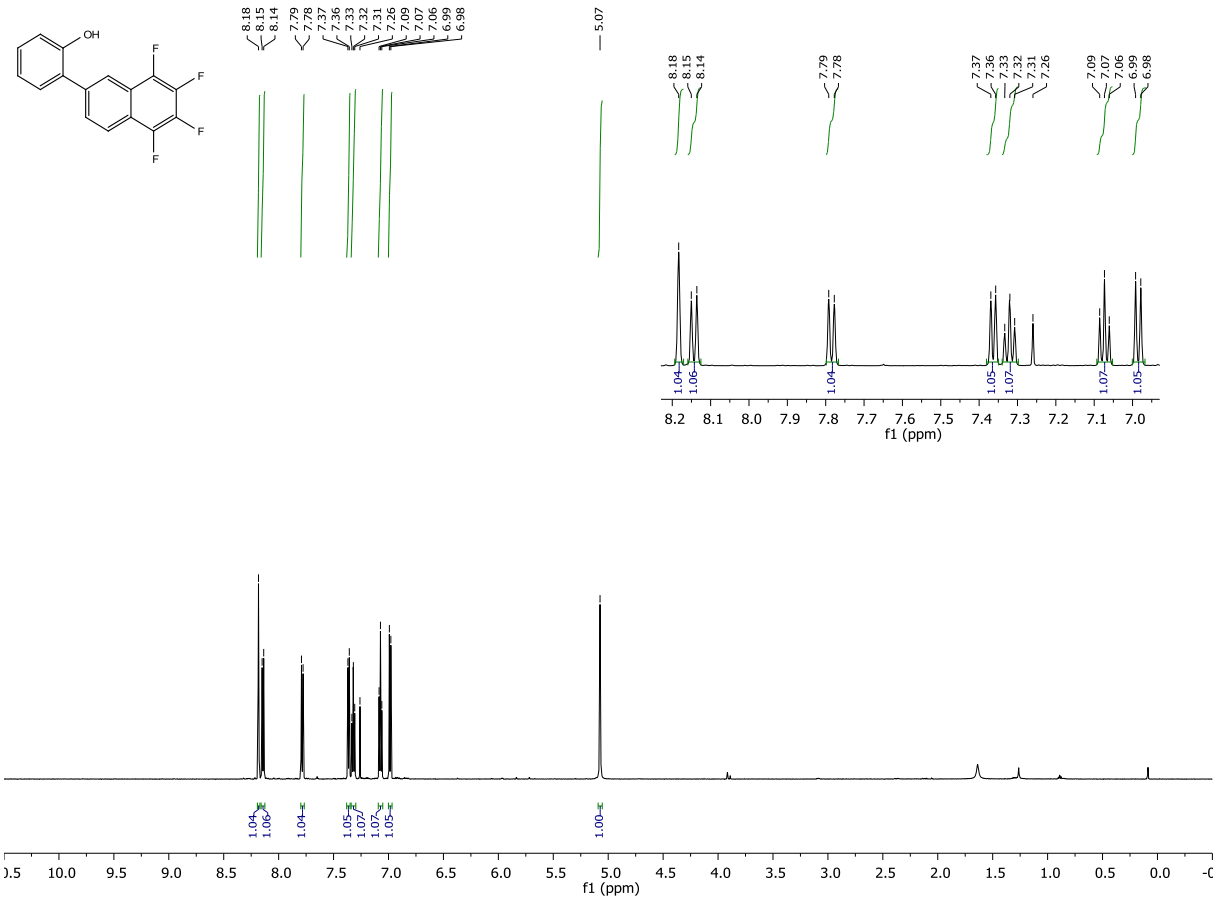

8.08
8.07
6.79
6.78
6.69
6.68
6.67
6.65
6.64
6.62
2.47
0.97
Fe
N
O
1.00
1.02
1.02
1.04
3.04
15.06
f1 (ppm)

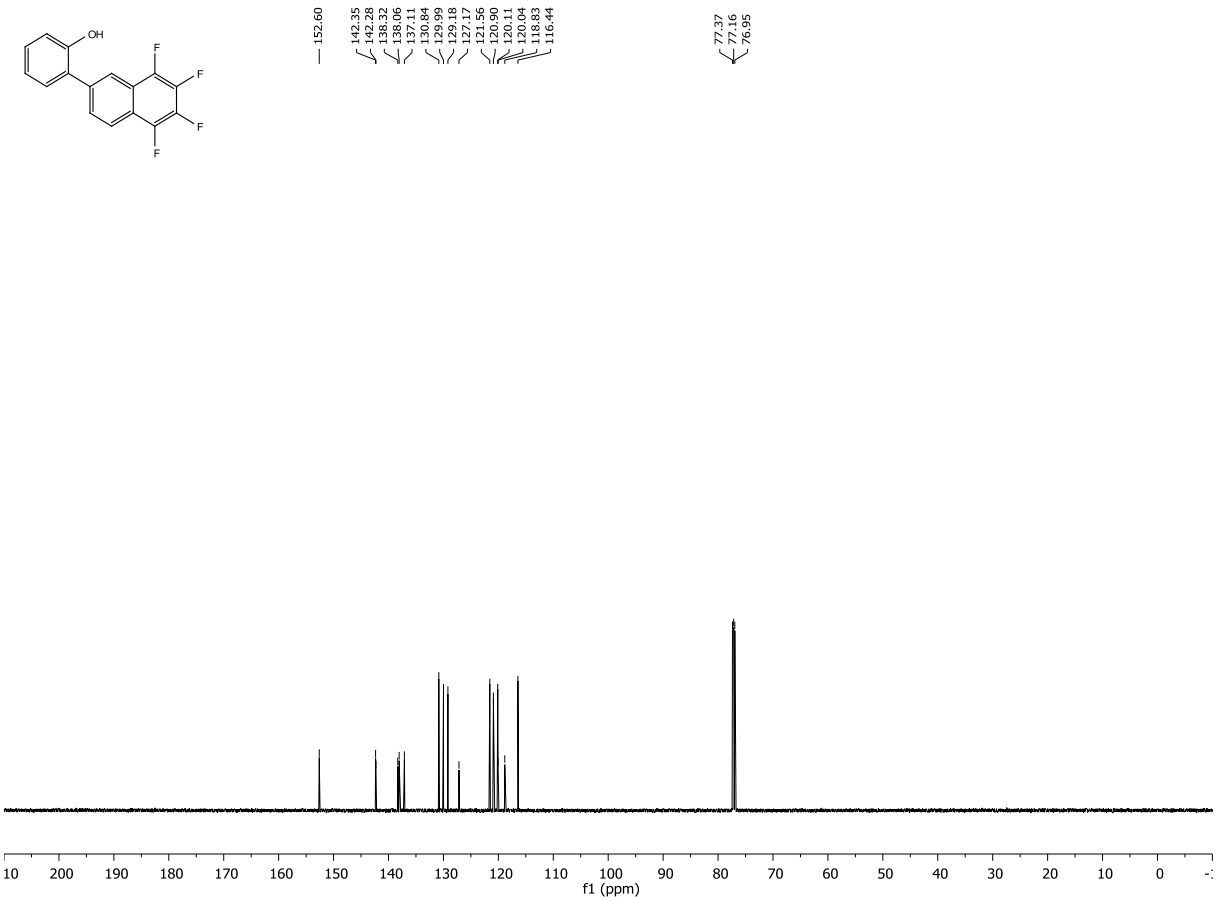

173.22
165.30
148.25
125.10
120.78
119.31
117.32
91.92
91.87
28.72
7.87
f1 (ppm)

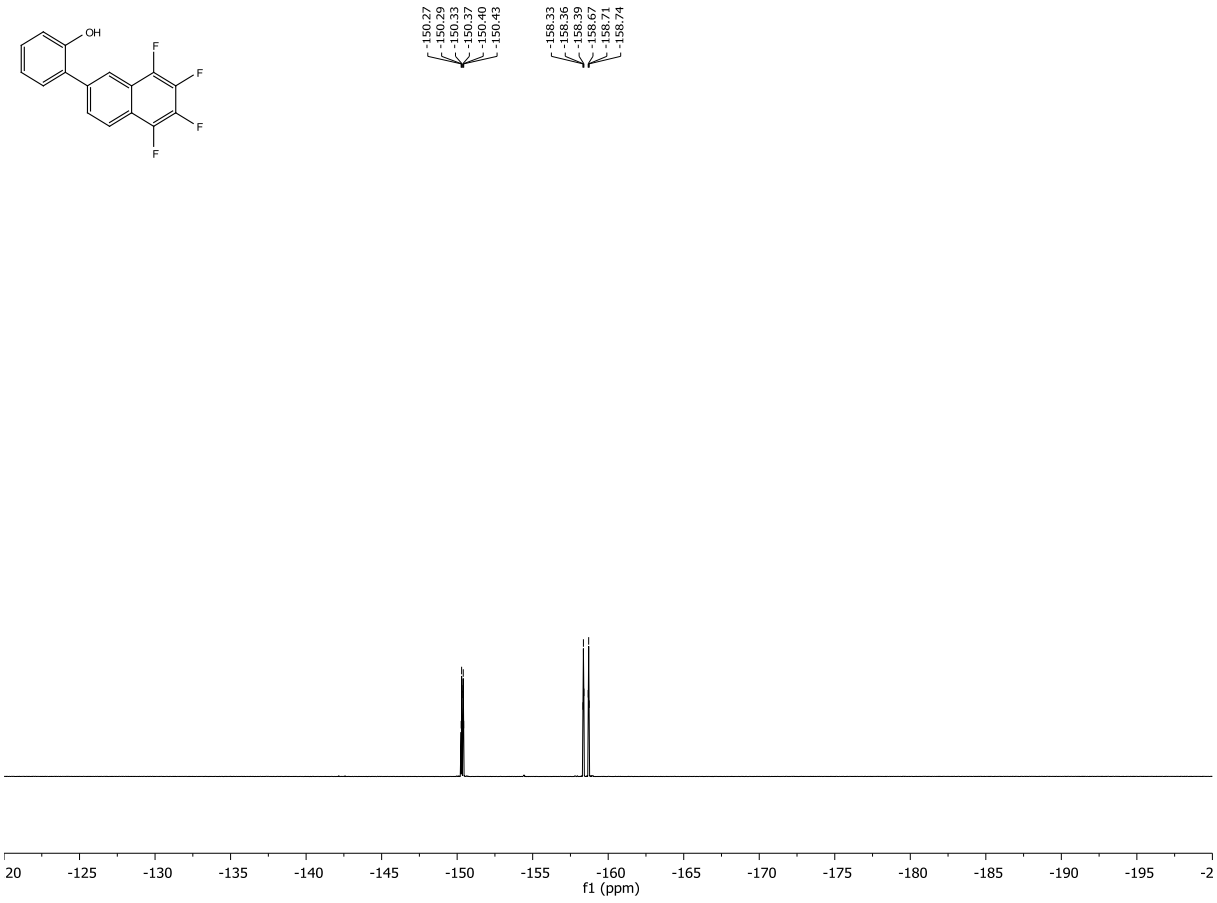

9.29
7.33
7.32
7.31
7.31
7.11
7.09
7.08
7.07
7.06
7.06
7.05
7.05
6.83
6.82
6.81
6.73
6.72
5.89
5.54
4.45
4.43
4.42
3.62
3.61
2.51
2.50
2.50
2.50
2.49
1.46
H2O
1.07
1.10
1.06
1.13
1.11
1.10
1.04
1.05
1.13
1.07
3.00
f1 (ppm)


OH
F
F
F
F
O
HN
O
CH3
168.42
155.34
140.06
139.31
139.06
139.05
128.98
128.51
127.60
126.04
123.66
118.71
114.47
81.16
80.82
52.38
41.79
39.94
39.80
39.66
39.52
39.38
39.24
39.10
22.20
f1 (ppm)


OH
F
F
F
F
O
HN
O
CH3
-141.71
-141.75
-141.78
-142.74
-142.78
-142.82
-155.59
-155.63
-155.66
-156.33
-156.37
-156.41
f1 (ppm)


OH
F
F
F
F
8.18
8.15
8.14
7.79
7.78
7.37
7.36
7.33
7.32
7.31
7.26
7.09
7.07
7.06
6.99
6.98
5.07
1.04
1.06
1.04
1.05
1.07
1.07
1.05
1.00
f1 (ppm)


OH
F
F
F
F
152.60
142.35
142.28
138.32
138.06
137.11
130.84
129.99
129.18
127.17
121.56
120.90
120.11
120.04
118.83
116.44
77.37
77.16
76.95
f1 (ppm)


OH
F
F
F
F
-150.27
-150.29
-150.33
-150.37
-150.40
-150.43
-158.33
-158.36
-158.39
-158.67
-158.71
-158.74
20
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-2
f1 (ppm)