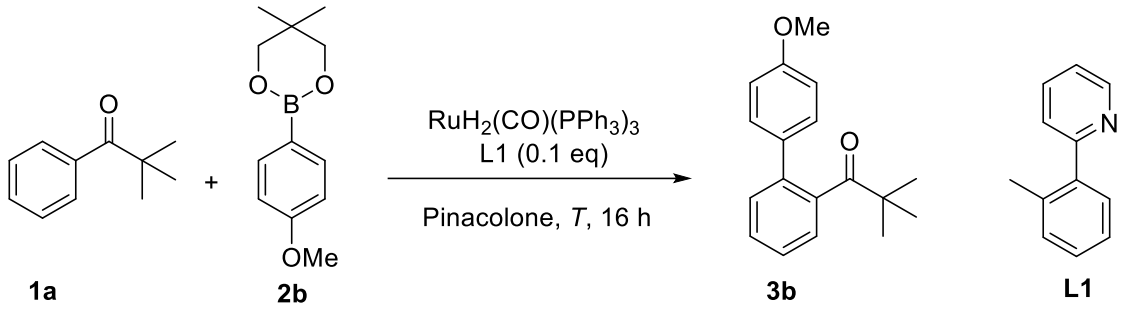
Contents

Table of further optimization

Table S1: Reaction optimization.

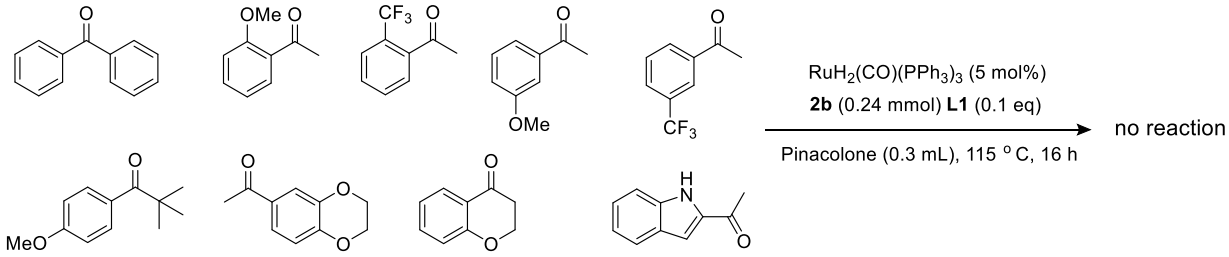


1a **2b** **3b** **L1**

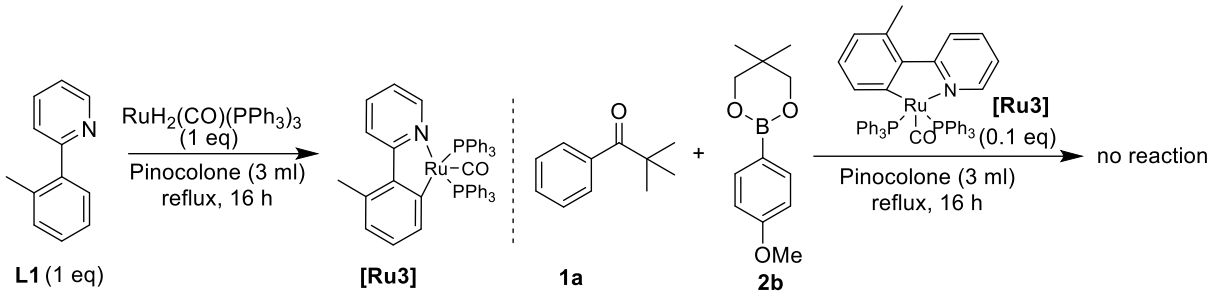
Entry	$RuH_2(CO)(PPh_3)_3$ [mol %]	*T* [° C]	**3b** Yield [%]
1[b]	5	115	44
2[c]	5	115	65
3	5	80	traces
4	2	115	traces
5	10	115	39

[a] Reaction conditions: **1a** (0.2 mmol), **2b** (0.24 mmol), ligand **L1** (0.1 equiv), $RuH_2(CO)(PPh_3)_3$, Pinacolone (0.3 mL), 16 h. Yield indicated yield of Isolated product. [b] 6 h. [c] acetone (3 mL, sealed tube) as solvent.

Scheme S1: Additional substrates tested.



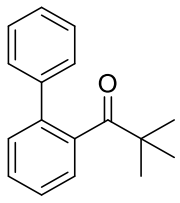
Scheme S2: Reaction with Isolated catalyst.



When 1 equiv. of **L1** was subjected to the reaction conditions in presence of 1 equiv. of $RuH_2(CO)(PPh_3)_3$ **[Ru3]** could be isolated. When subjecting this complex to the optimized reaction conditions in presence of substrates **1a** and **2b**, no product formation was observed. **[Ru3]** is eventually a relatively stable complex not involved in the catalytic cycle at all, or formed in a catalyst deactivation pathway.

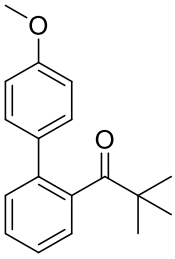
[Ru3] analytical data: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 – 8.77 (m, 1H), 7.67 (ddd, *J* = 12.0, 8.3, 1.3 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.30 – 7.26 (m, 5H), 7.26 – 7.23 (m, 6H), 7.16 (t, *J* = 7.3 Hz, 6H), 7.10 – 7.04 (m, 12H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 7.2 Hz, 1H), 6.25 (ddd, *J* = 7.1, 5.8, 1.1 Hz, 1H), 6.10 (dt, *J* = 72.3, 7.5 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.22, 180.64, 163.89, 151.96, 141.05, 140.27, 134.98, 134.05, 134.00, 133.95, 133.91, 132.76, 132.55, 132.34, 132.17, 132.07, 131.96, 128.80, 128.58, 128.46, 128.17, 127.41, 127.36, 127.31, 125.03, 120.95, 119.91, 77.35, 77.03, 76.72, 29.72, 25.14, 1.04. 31P NMR (162 MHz, CDCl3): δ = 33.85.

Analytical data of products

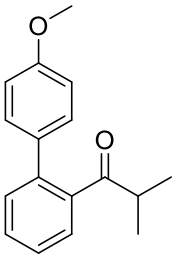


*1-([1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-one **(3a)***. Following the general procedure to yield 14.5 mg (30%) of the named compound as a pale-yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$):

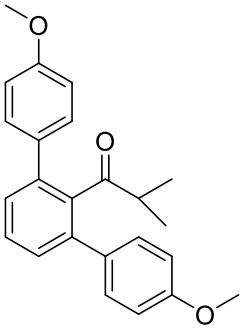
δ = 7.48 – 7.33 (m, 8H), 7.14 (d, *J* = 8.3 Hz, 1H), 0.87 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 216.63, 141.11, 140.98, 138.06, 129.76, 129.61, 128.72, 128.46, 127.60, 126.77, 125.71, 44.96, 27.23. Analytical data obtained are in agreement with reported value.[16]



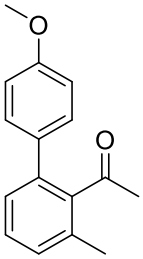
1-(4'-methoxy-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-one ***(3b)***. Following the general procedure to yield 36.5 mg (68 %) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 – 7.28 (m, 5H), 7.15 – 7.08 (m, 1H), 6.94 – 6.89 (m, 2H), 3.83 (s, 3H), 0.88 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 216.93, 159.23, 141.00, 137.69, 133.47, 130.72, 129.66, 128.67, 126.35, 125.68, 113.89, 55.30, 44.98, 27.24. Analytical data obtained are in agreement with reported value.[16]



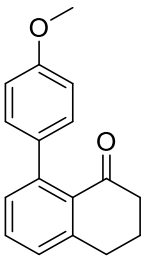
1-(4'-methoxy-[1,1'-biphenyl]-2-yl)-2-methylpropan-1-one ***(6)***. Following the general procedure to yield 8 mg (16 %) or 1.5 mg (3%, with 2.4 eq of 2a) of the named compound as pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.45 (m, 1H), 7.40 – 7.35 (m, 2H), 7.29 – 7.24 (m, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 2.46 (p, *J* = 6.9 Hz, 1H), 0.88 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 213.09, 159.40, 140.59, 132.97, 130.09, 129.96, 129.89, 127.97, 126.92, 114.16, 55.34, 40.17, 18.69. $[M + H]^+$ Calcd for $C_{17}H_{18}O_2$ 255.1380; Found 255.1388.



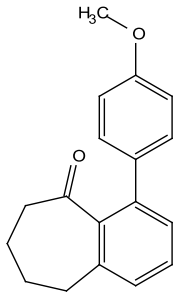
1-(4,4''-dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)-2-methylpropan-1-one ***(6a)***. Following the general procedure to yield 22 mg (31%) or 37.3 mg (52%, with 2.4 eq of 2a) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.28 (m, 6H), 6.91 (d, *J* = 8.7 Hz, 4H), 3.83 (s, 6H), 2.09 (p, *J* = 7.0 Hz, 1H), 0.51 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.42, 159.06, 140.67, 138.79, 132.84, 131.15, 128.82, 128.34, 113.47, 55.27, 42.13, 17.64. $[M + Na]^+$ Calcd for $C_{24}H_{24}O_3$ 383.1618; Found 383.1618.



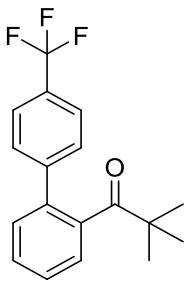
1-(4'-methoxy-3-methyl-[1,1'-biphenyl]-2-yl)ethan-1-one ***(7)***. Following the general procedure to yield 26 mg (54%) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.25 (m, 3H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.97 – 6.90 (m, 2H), 3.84 (s, 3H), 2.31 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.99, 159.35, 141.37, 138.24, 133.67, 132.81, 130.14, 129.20, 128.83, 127.30, 114.06, 55.31, 32.06, 19.57. Analytical data obtained are in agreement with reported value.[17]



8-(4-methoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one ***(8)***. Following the general procedure to yield 39 mg (77%) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (t, *J* = 7.6 Hz, 1H), 7.22 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.12 (d, *J* = 1.2 Hz, 1H), 6.93 – 6.89 (m, 2H), 3.84 (s, 3H), 3.00 (t, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.18 – 2.11 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.72, 158.53, 145.64, 143.63, 135.11, 131.78, 131.31, 130.46, 129.36, 127.83, 113.34, 55.24, 40.58, 30.79, 23.08. Analytical data obtained are in agreement with reported value.[18]

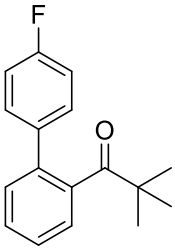


4-(4-methoxyphenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulun-5-one ***(9)***. Following the general procedure to yield 35 mg (66%) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.33 (t, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.12 – 7.08 (m, 1H), 6.92 – 6.87 (m, 2H), 3.82 (s, 3H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.70 – 2.63 (m, 2H), 1.98 – 1.83 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.58, 158.84, 140.43, 139.72, 137.49, 133.21, 129.73, 128.83, 127.40, 113.81, 55.24, 42.98, 32.56, 25.66, 22.98.Analytical data obtained are in agreement with reported value.[16]

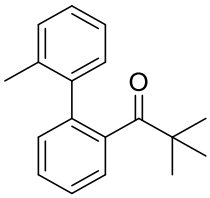


2,2-dimethyl-1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)propan-1-one ***(10)***. Following the general procedure to yield 50.6 mg (50%) of the named compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (m, 2H), 7.52 – 7.35 (m, 5H), 7.23 – 7.16 (m, 1H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.32, 146.85, 145.88, 142.54, 132,08, 130.92, 130.02,

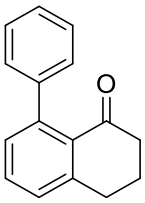
128.90, 128.84, 128.52, 128.44, 125.79, 124.77 (q, *J* = 3.7 Hz), 123.08, 40.35, 30.68, 23.00. Analytical data obtained are in agreement with reported value.[16]



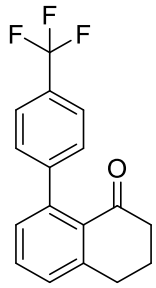
1-(4'-fluoro-[1,1'-biphenyl]-2-yl)-2,2-dimethylpropan-1-one ***(11)***. Following the general procedure to yield 23.5 mg (46%) of the named compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.30 (m, 5H), 7.16 – 7.04 (m, 3H), 0.89 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$); δ = 216.34, 163.70, 161.24, 141.02, 136.99, 131.24, 129.78, 128.75, 126.87, 125.67, 115.49, 115.28, 44.98, 27.19.^{19}F NMR (376 MHz, $CDCl_3$): δ = -114.70. Analytical data obtained are in agreement with reported value.[16]



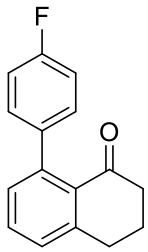
2,2-dimethyl-1-(2'-methyl-[1,1'-biphenyl]-2-yl)propan-1-one ***(12)***. Following the general procedure to yield 20 mg (39%) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 – 7.33 (m, 2H), 7.28 – 7.11 (m, 6H), 2.22 (s, 3H), 0.92 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 215.30, 141.75, 139.81, 137.50, 136.31, 130.75, 130.57, 130.27, 128.04, 127.80, 126.54, 125.35, 125.20, 44.51, 27.37, 20.39. Analytical data obtained are in agreement with reported value.[16]



8-phenyl-3,4-dihydronaphthalen-1(2H)-one ***(13)***. Following the general procedure to yield 26.5 mg (60%) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.28 – 7.19 (m, 3H), 7.16 – 7.12 (m, 1H), 3.02 (t, *J* = 6.1 Hz, 2H), 2.62 (t, *J* = 6.6 Hz, 2H), 2.15 (p, *J* = 6.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.46, 145.59, 143.99, 142.91, 131.80, 131.23, 130.28, 128.15, 127.79, 126.61, 40.48, 30.75, 23.08. Analytical data obtained are in agreement with reported value.[18]

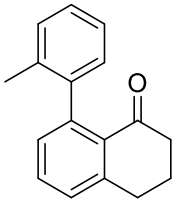


8-(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalen-1(2H)-one ***(14)***. Following the general procedure to yield 42 mg (72%) of the named compound as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 3H), 7.12 – 7.05 (m, 1H), 3.04 (t, *J* = 6.1 Hz, 2H), 2.62 (t, *J* = 6.6 Hz 2H), 2.16 (p, *J* = 6.5 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ = 198.32, 146.85, 145.88, 142.54, 132.08, 130.92, 130.02, 128.90, 128.84, 128.52, 128.44, 125.79, 124.80, 124.76, 124.72, 124.69, 123.08, 40.35, 30.68, 23.00; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.29. Analytical data obtained are in agreement with reported value.[18]

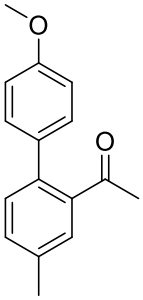


8-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one ***(15)***. Following the general procedure to yield 33.5 mg (70%) of the named compound as a colour less oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 7.6 Hz, 0H), 7.28 – 7.25 (m, 1H), 7.19 – 7.02 (m, 2H), 3.02 (t, *J* = 6.1 Hz, 1H), 2.62 (t, 1H), 2.19 – 2.11 (m, 1H); 13C NMR (101 MHz, $CDCl_3$): δ = 198.53, 163.14, 160.70, 145.75, 142.92, 138.76 (d, J = 3.4 Hz), 138.74, 131.90, 131.15, 130.36, 129.71 (d, J = 8.0 Hz),

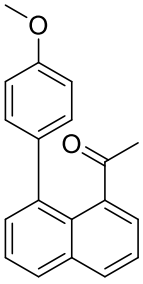
129.67, 128.37, 114.70 (d, J = 21.5 Hz), 114.59, 40.52, 30.75, 23.04. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -116.53. Analytical data obtained are in agreement with reported value.[18]



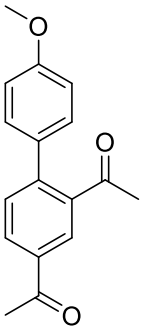
8-(o-toluyl)-3,4-dihydronaphthalen-1(2H)-one ***(16)***. Following the general procedure to yield 31.5 mg (67%) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.17 (m, 4H), 7.06 – 6.98 (m, 2H), 3.04 (t, *J* = 6.1 Hz, 2H), 2.58 (td, *J* = 6.3, 2.2 Hz, 2H), 2.19 – 2.09 (m, 2H), 1.99 (s, 3H); 13C NMR (101 MHz, CDCl3): δ = 198.08, 145.24, 143.29, 142.93, 134.80, 132.10, 131.12, 129.80, 129.32, 128.14, 127.54, 126.70, 125.33, 40.23, 30.80, 23.09, 20.03. Analytical data obtained are in agreement with reported value.[18]



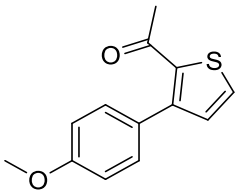
1-(4'-methoxy-4-methyl-[1,1'-biphenyl]-2-yl)ethan-1-one ***(17).*** Following the general procedure to yield 27 mg (56%) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 6.98 – 6.93 (m, 2H), 3.85 (s, 3H), 2.41 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 205.61, 159.41, 140.81, 137.37, 136.95, 133.02, 131.43, 130.12, 129.98, 128.29, 114.13, 55.33, 30.49, 20.95. Analytical data obtained are in agreement with reported value.[17]



1-(8-phenylnaphthalen-1-yl)ethan-1-one ***(18)***. Following the general procedure to yield 35 mg (63%) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.84 (m, 3H), 7.58 – 7.49 (m, 3H), 7.43 – 7.37 (m, 2H), 7.02 – 6.97 (m, 2H), 3.87 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.76, 159.59, 138.05, 135.77, 132.65, 132.39, 130.56, 129.40, 128.92, 128.25, 127.58, 127.40, 126.14, 124.70, 114.24, 55.36, 32.64. $[M + H]^+$ Calcd for $C_{19}H_{16}O_2$ 277.1223; Found 277.1232.



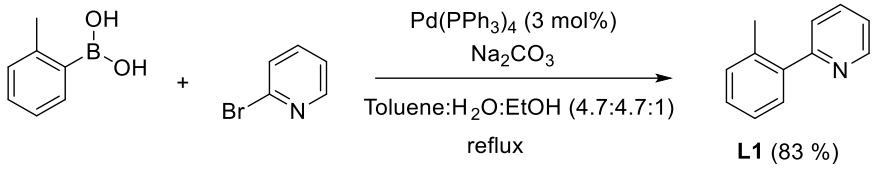
1,1'-(4'-methoxy-[1,1'-biphenyl]-2,4-diyl)bis(ethan-1-one) ***(19)***. Following the general procedure to yield 16.5 mg (31%) of the named compound as a pale-yellow oil.^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 – 8.06 (m, 2H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.03 – 6.96 (m, 2H), 3.87 (s, 3H), 2.65 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 204.50, 197.08, 160.19, 144.53, 141.01, 135.66, 131.80, 130.58, 130.03, 128.20, 114.43, 55.40, 30.37, 26.71. $[M + Na]^+$ Calcd for $C_{17}H_{16}O_3$ 291.0991; Found 291.0993.



1-(3-(4-methoxyphenyl)thiophen-2-yl)ethan-1-one ***(20)***. Following the general procedure to yield 24.5 mg (53%) of the named compound as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 5.0 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.04 (d, *J* = 5.0 Hz, 1H), 6.99 – 6.95 (m, 2H), 3.86 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.31, 159.73, 146.68, 139.49, 132.12, 130.90, 130.38, 128.61, 113.84, 55.35, 29.26. Analytical data obtained are in agreement with reported value.[19]

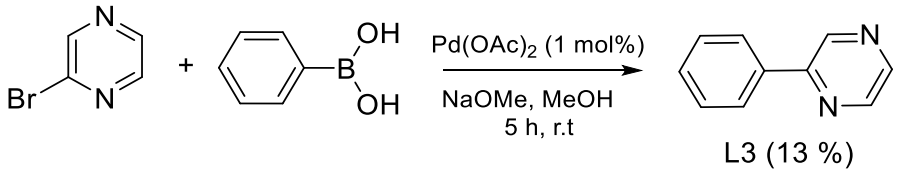
General Procedure for the preparation of starting materials

1. Preparation of ligands.

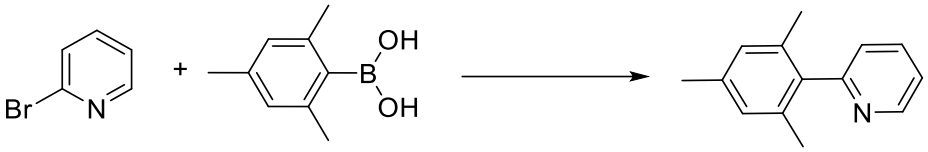


The procedure is same as that of literature.[20] A 100 mL round bottom flask was charges with a solution of 2-Methylphenylboronic acid (3.89 mmol), Na_2CO_3 (22.5 mmol), and 2-bromopyridine (3 mmol) in toluene (3.5 mL)/H_2O (3.5 mL)/EtOH (0.75 mL). $Pd(PPh_3)_4$ (3 mol%) was added and refluxed the reaction mixture for 18 h under argon atmosphere. After this time, the reaction was cooled to room temperature and neutralised the reaction mixture by adding aqueous NH_4Cl (15 mL), extracted with EtOAc (3 × 15 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was evaporated under vacuum to afford the crude product. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc to yield 83% of the product as yellow oil.

2-(o-toluyl)pyridine ***(L1)***. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.76 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.34 – 7.27 (m, 3H), 7.26 – 7.23 (m, 1H), 2.37 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.85, 148.97, 140.11, 136.41, 135.78, 130.78, 129.66, 128.40, 125.92, 124.24, 121.72, 20.29.

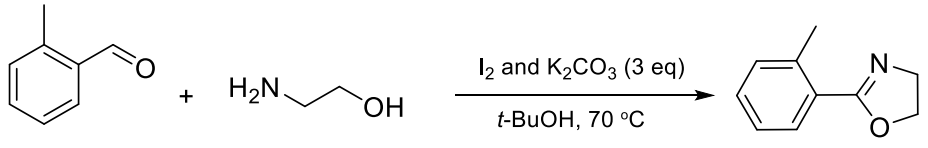


The procedure is same as that reported in the literature.[21] To a solution of Bromopyrazine (2 mmol), Phenylboronic acid (2.4 mmol), NaOMe (4 mol), and MeOH (4 mol) was added $Pd(OAc)_2$ (1 mol%). The reaction mixture was stirred for 5 h in room temperature. The progress of the reaction was monitored using TLC. On complete consumption of starting material, the reaction mixture was filtered and evaporated. The resulting residue was purified by flash column chromatography on silica gel with PE/EtOAc to yield 13% of the product as yellow oil.
*2-phenylpyrazine **(L3)***. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.06 – 9.03 (m, 1H), 8.67 – 8.63 (m, 1H), 8.52 (d, *J* = 2.4 Hz, 1H), 8.05 – 8.00 (m, 2H), 7.57 – 7.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.95, 144.24, 142.78, 142.12, 136.31, 130.00, 129.10, 126.98.



L4 (25 %)

The procedure is same as that reported in the literature.[22] A 100 mL Schleck tube was charged with K_3PO_4 (0.85 mmol), $Pd(OAc)_2$ (0.01 mmol), $PtBu_3.HBF_4$ (0.012 mmol), 2-bromopyridine (0.50 mmol), 2-mesitylboronic acid (0.75 mmol) and 4:1 dioxane/H_2O in glove box. The reaction mixture was pre-stirred for 15 min. A solution of NaOH (0.85 mmol) in 0.68 mL of degassed H_2O was added to initiate the Suzuki reaction and stirred the reaction mixture for 24 h at 25 °C. Organic phase separated and further the aqueous phase was extracted with Et_2O (3mL × 3) and combined organic layer was concentrated under vacuum. The resulting residue was purified by flash column chromatography on silica gel with PE/EtOAc to yield 25% of the product as colourless oil.
*2-mesitylpyridine **(L4)***. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.76 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.28 – 7.21 (m, 2H), 6.96 – 6.91 (m, 2H), 2.32 (s, 3H), 2.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.79, 148.29, 136.50, 135.48, 134.63, 127.28, 123.83, 120.59, 20.07, 19.09.



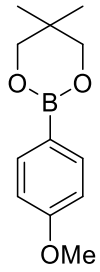
L8 (74 %)

The procedure is same as that of literature.[23] To a solution of o-toluyldehyde (5 mmol) in *t*-BuOH (25 mL) was added aminoethanol (5.5 mmol) and stirred for 30 min at room temperature under argon atmosphere. Then to the reaction mixture was added K_2CO_3 (15 mmol) and I_2 (10 mmol) and stirred at 70 °C for 18 h. After the time the reaction mixture was quenched with saturated $Na_2S_2O_3$ until the iodine colour almost disappeared, and was extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel with PE/EtOAc to yield 74% of the product as yellow oil.

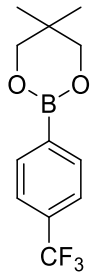
2-(o-toluyl)-4,5-dihydrooxazole ***(L8)***. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 7.8 Hz, 1H), 7.31 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.25 – 7.18 (m, 2H), 4.37 (t, *J* = 9.9 Hz, 2H), 4.08 (t, *J* = 9.7 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.07, 138.73, 131.20, 130.49, 129.82, 127.20, 125.56, 66.79, 55.40, 21.78. Analytical data obtained are in agreement with reported value.[23]

2. Synthesis of (Hetero)arylboronate Ester.

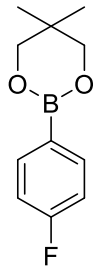
A 100 mL round bottom flask was charged with appropriate (hetero)arylboronic acid (5-10 mmol) and 2,2-dimethylpropane-1,3-diol (1.1 eq) and toluene (10-20 mL). The reaction mixture was stirred at room temperature. After 12 h the reaction was concentrated in reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (30 mL) and washed with water (3 × 10 mL) and the organic layer was dried and filtered. The anticipated (hetero)arylboronate Ester was obtained in full conversion upon concentrating the filtrate.



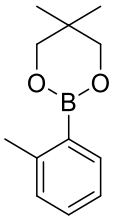
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 – 7.72 (m, 2H), 6.91 – 6.86 (m, 2H), 3.82 (s, 3H), 3.75 (s, 4H), 1.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.76, 135.53, 113.16, 72.28, 55.07, 31.91, 21.94.



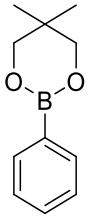
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 3.79 (s, 4H), 1.03 (s, 6H); 13C NMR (101 MHz, CDCl3): δ = 158.79, 148.29, 136.50, 135.48, 134.63, 127.28, 123.83, 120.59, 20.07, 19.09.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 8.6, 6.3 Hz, 2H), 7.06 – 7.00 (m, 2H), 3.76 (s, 4H), 1.02 (s, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -109.85; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.09, 163.61, 136.03, 135.99 (d, *J* = 8.1 Hz), 114.60 (d, *J* = 20.0 Hz), 114.50, 72.32, 31.90, 21.90.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.15 (dd, *J* = 7.4 Hz, 2H), 3.78 (s, 4H), 2.52 (s, 3H), 1.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.95, 134.83, 130.04 (d, *J* = 8.2 Hz), 129.96, 124.68, 72.29, 31.66, 22.40, 21.91.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.46 – 7.40 (m, 1H), 7.38 – 7.33 (m, 2H), 3.78 (s, 4H), 1.03 (s, 6H); 13C NMR (101 MHz, CDCl3): δ = 133.83, 130.68, 127.59, 72.33, 31.91, 21.93.

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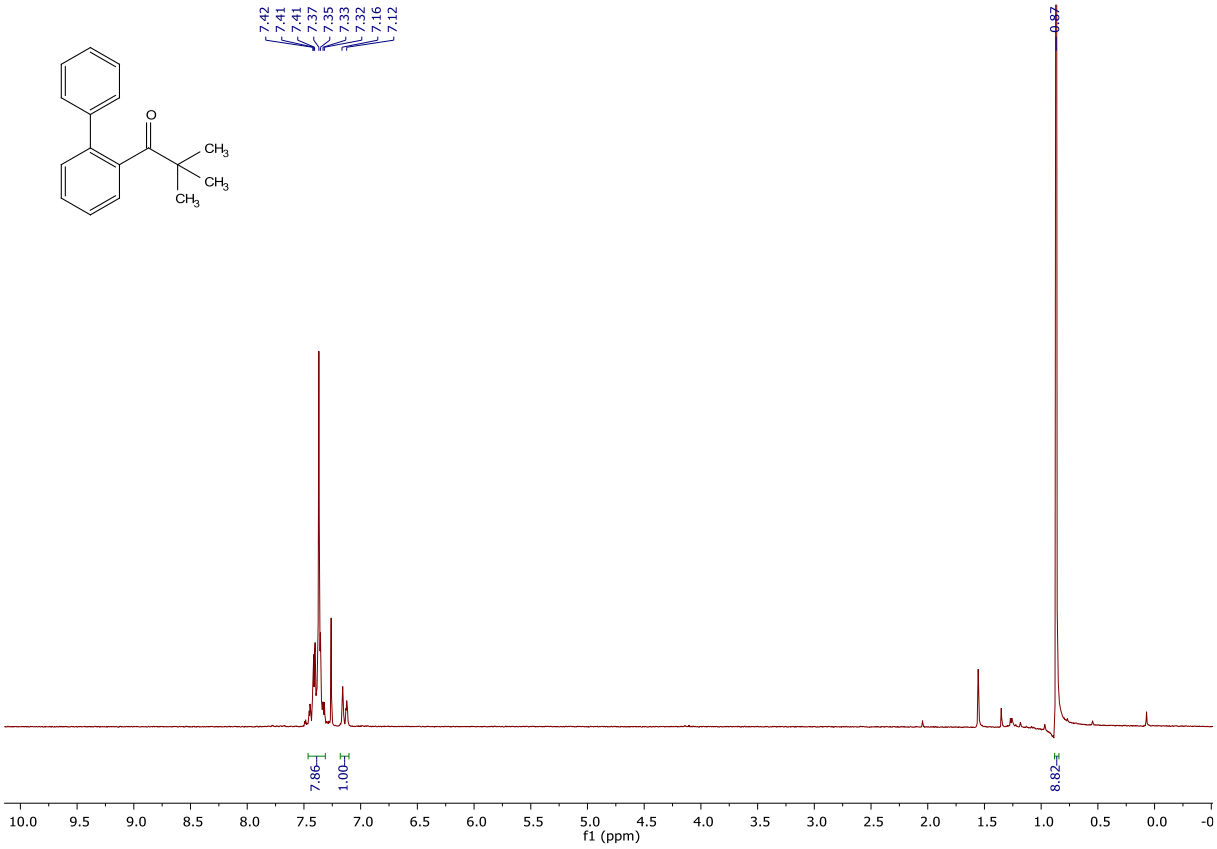
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CH3
CH3
7.86
1.00
8.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
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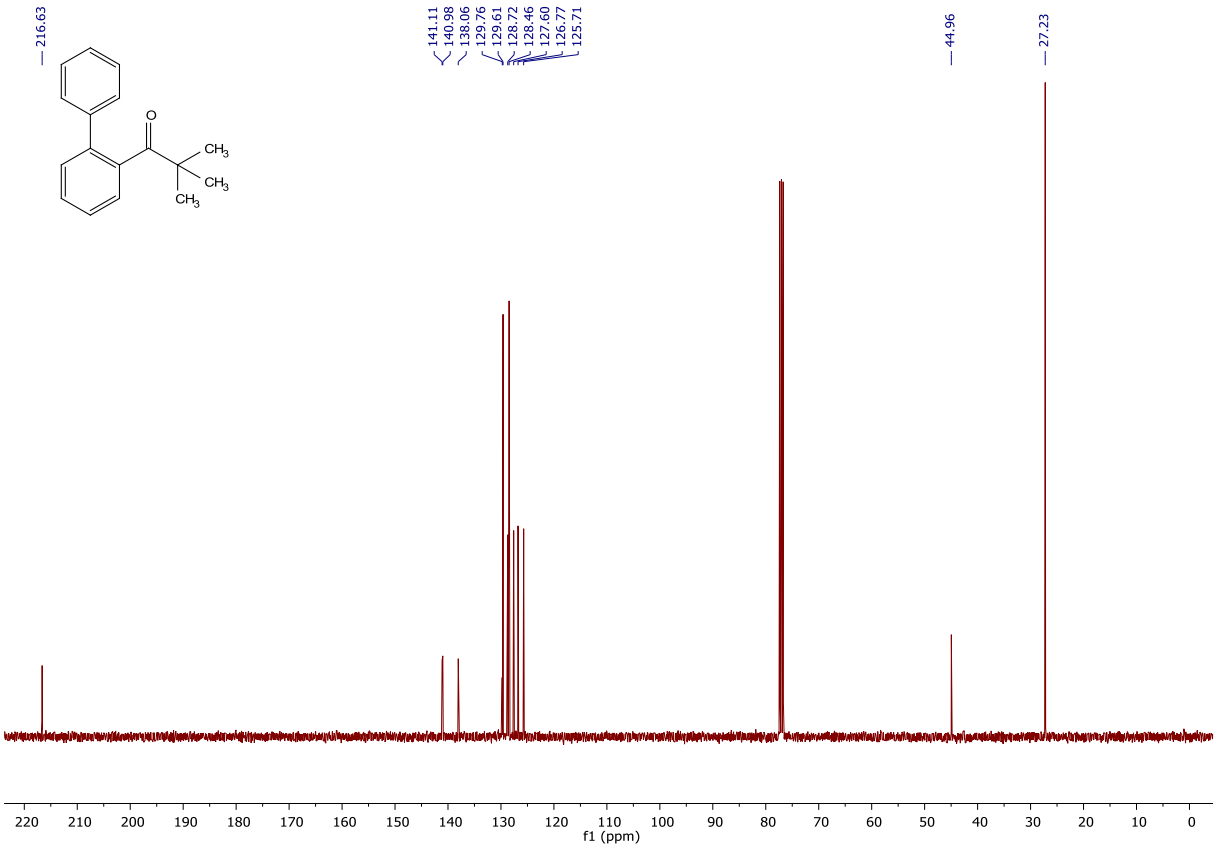
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CH3
CH3
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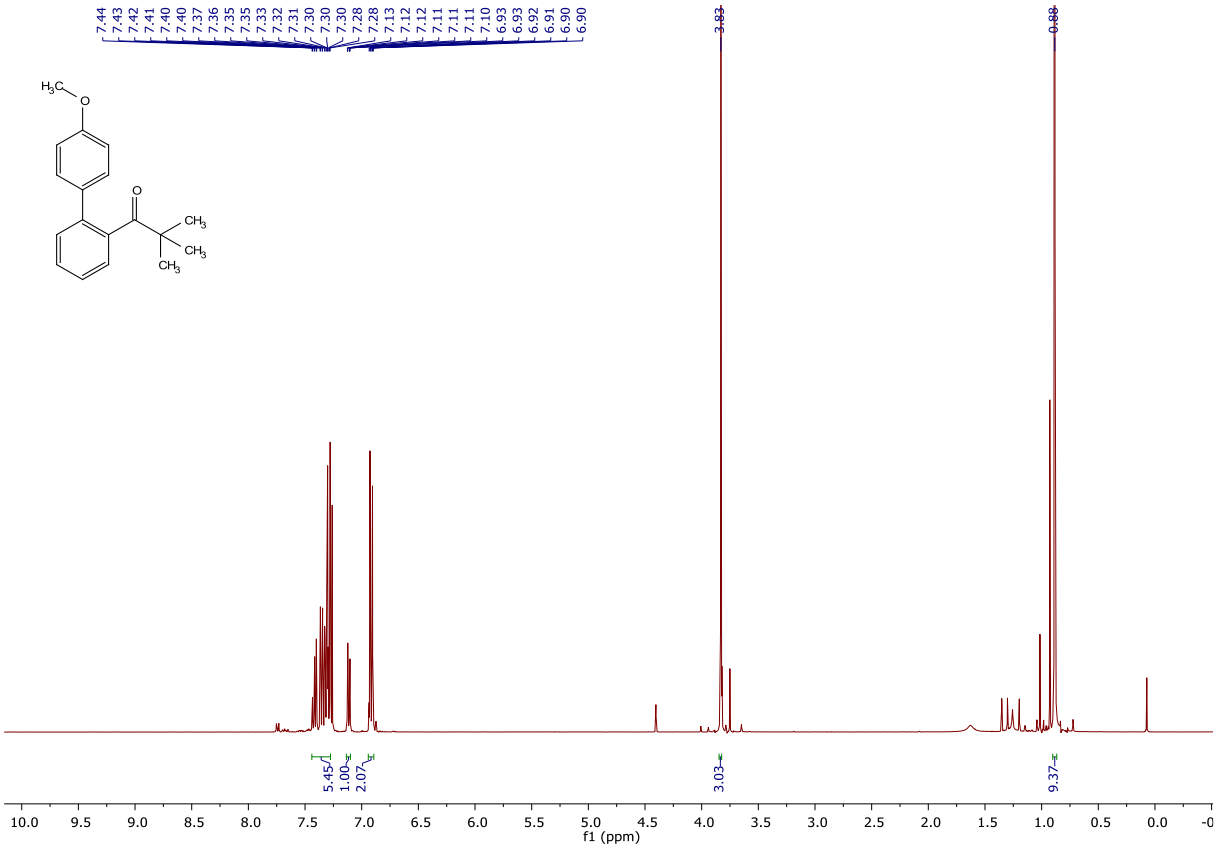
f1 (ppm)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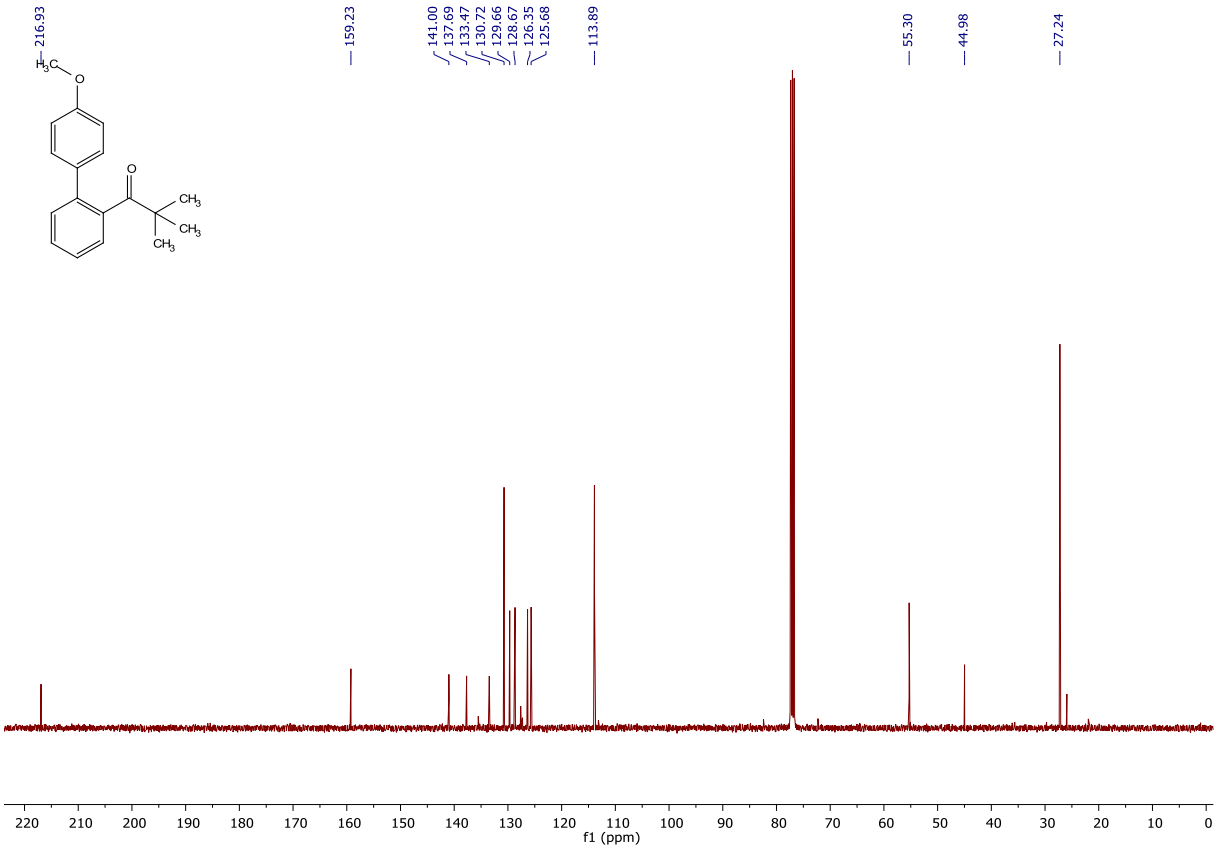
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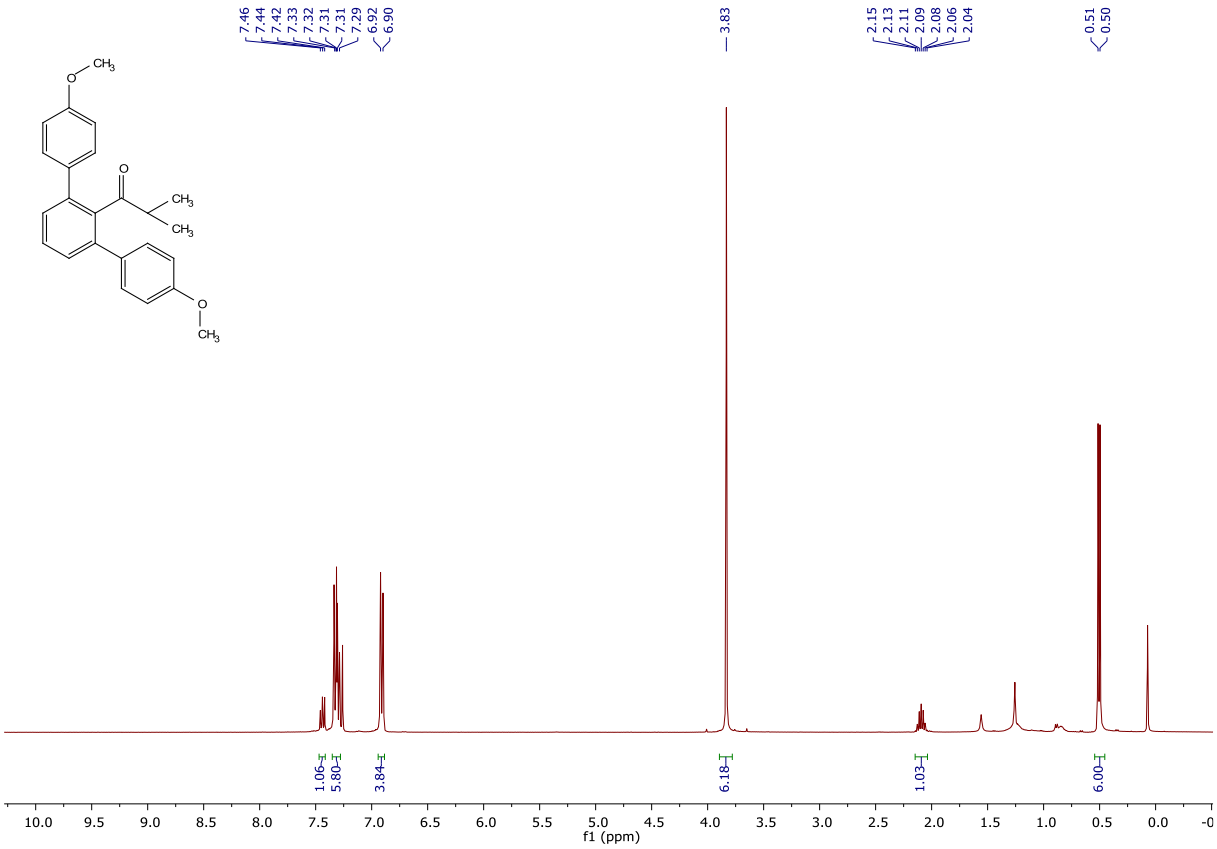
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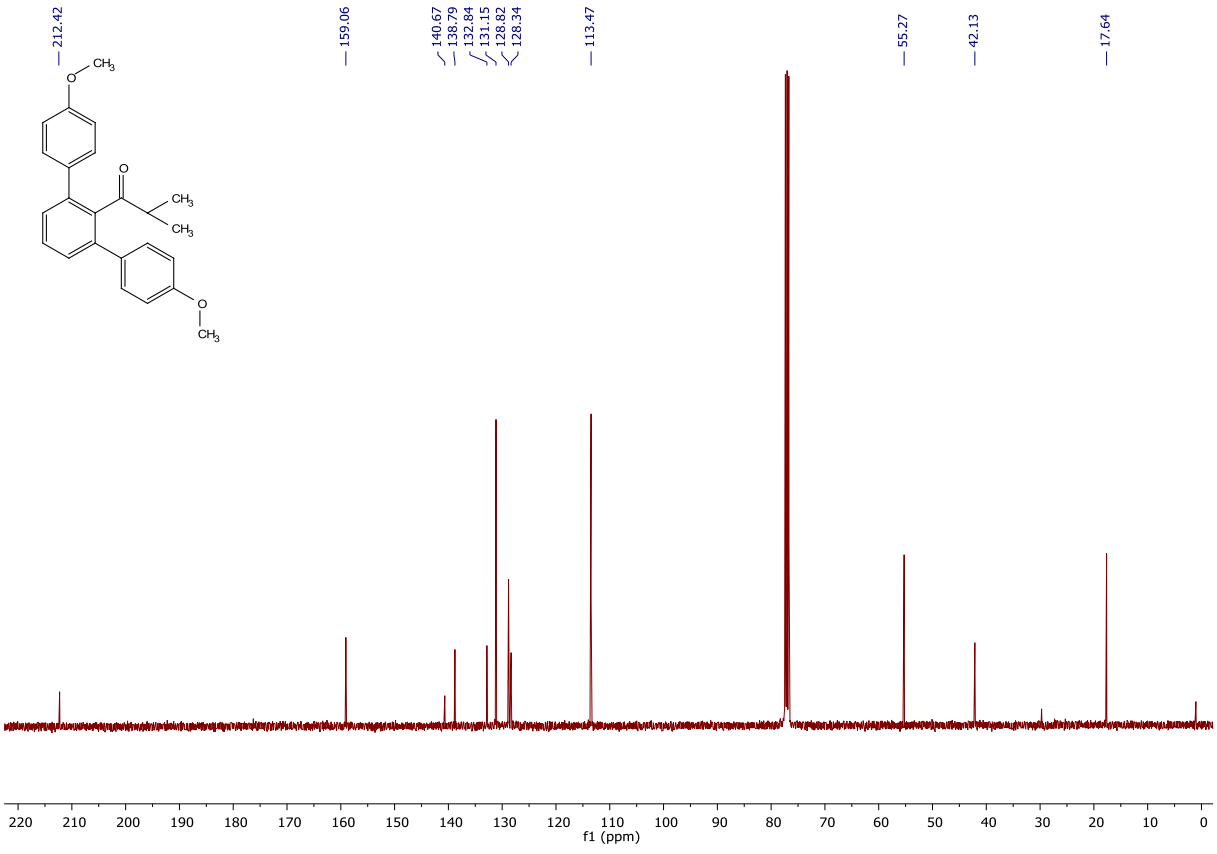
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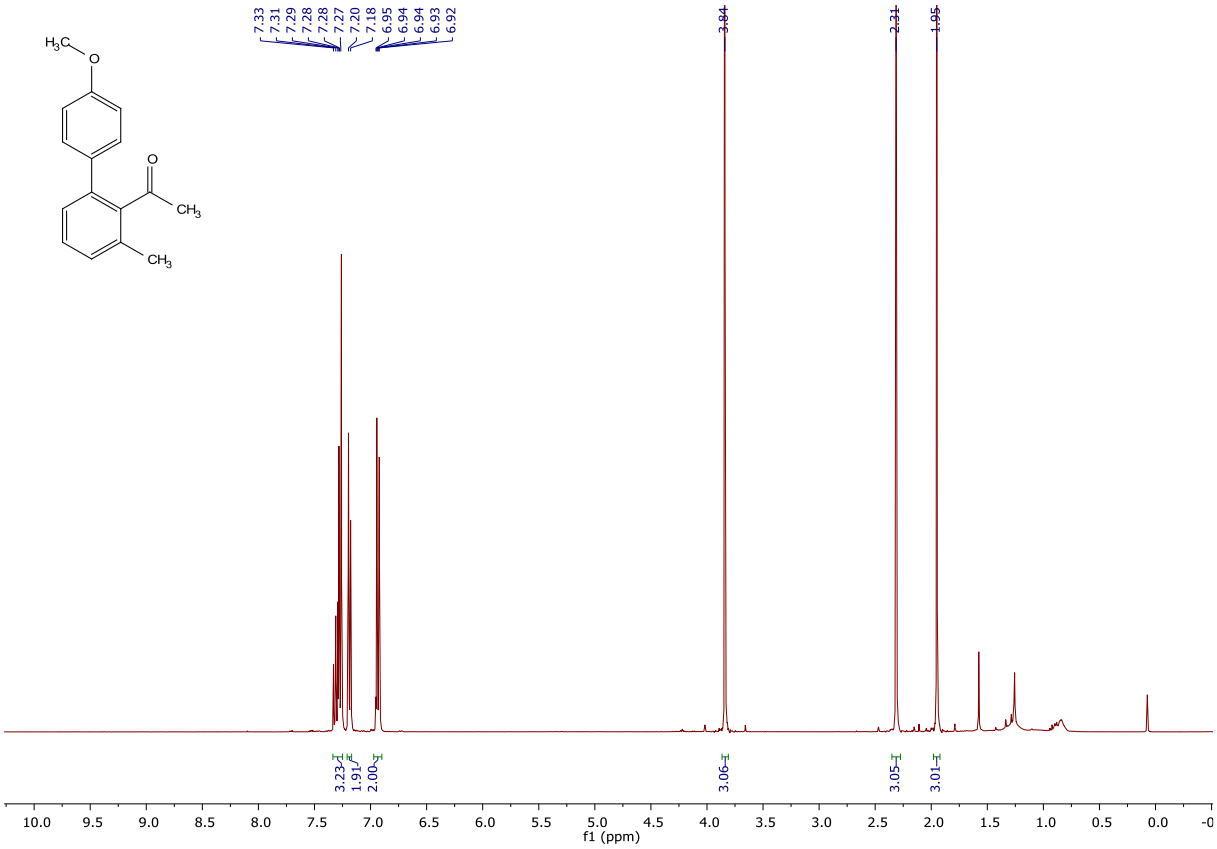
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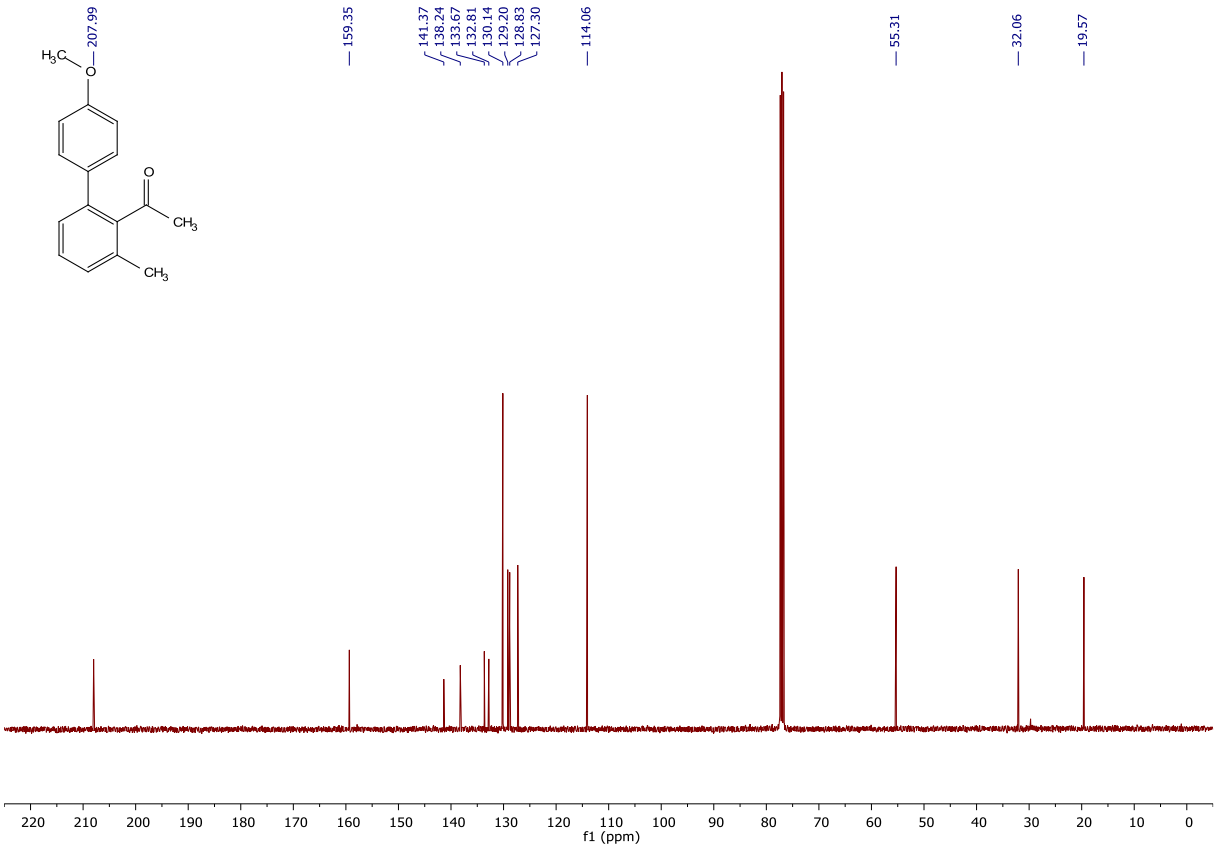
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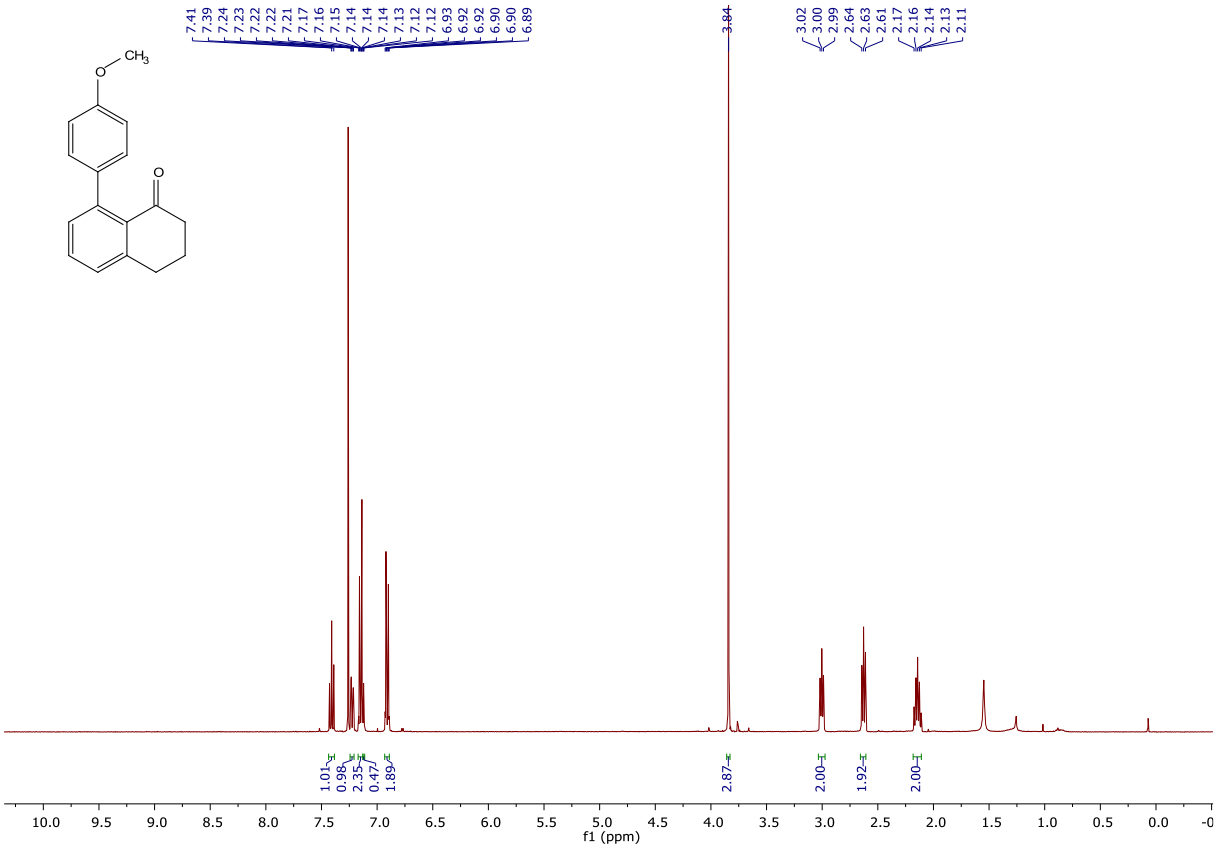
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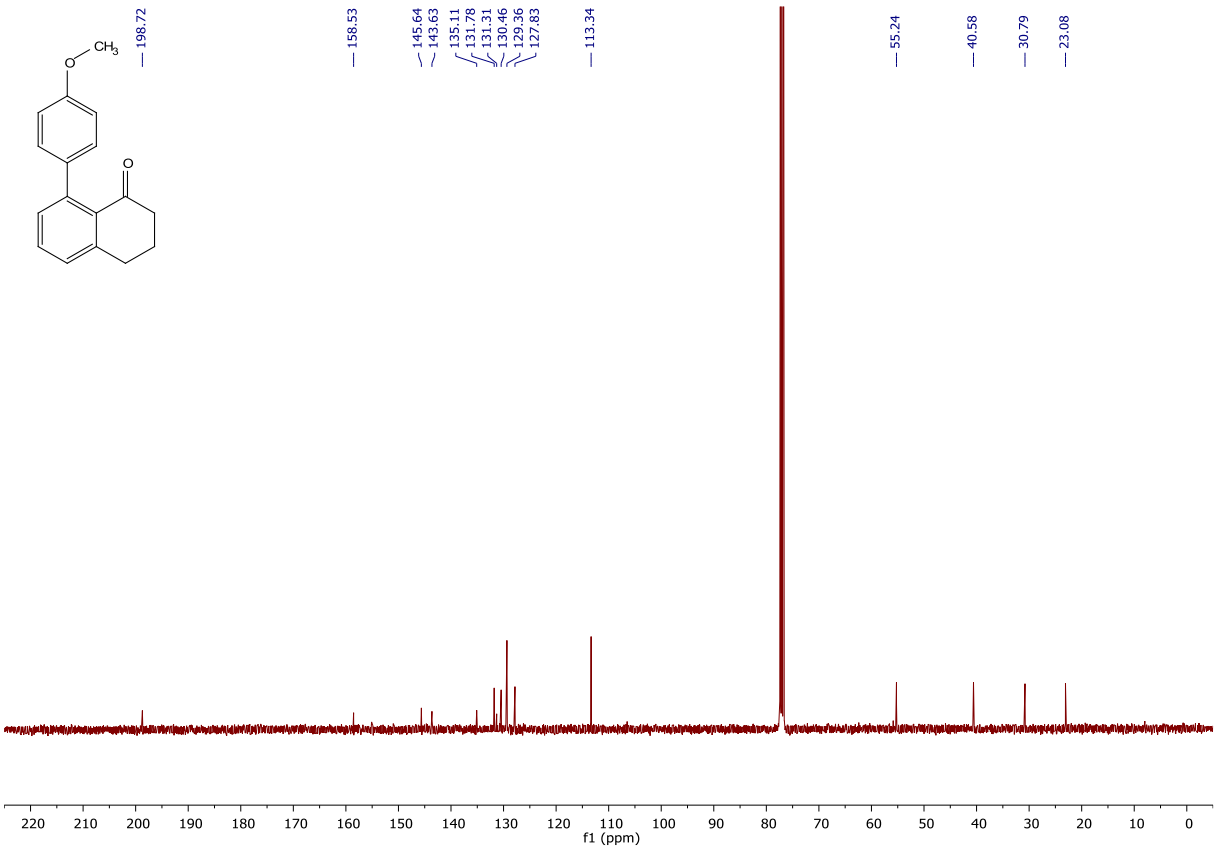
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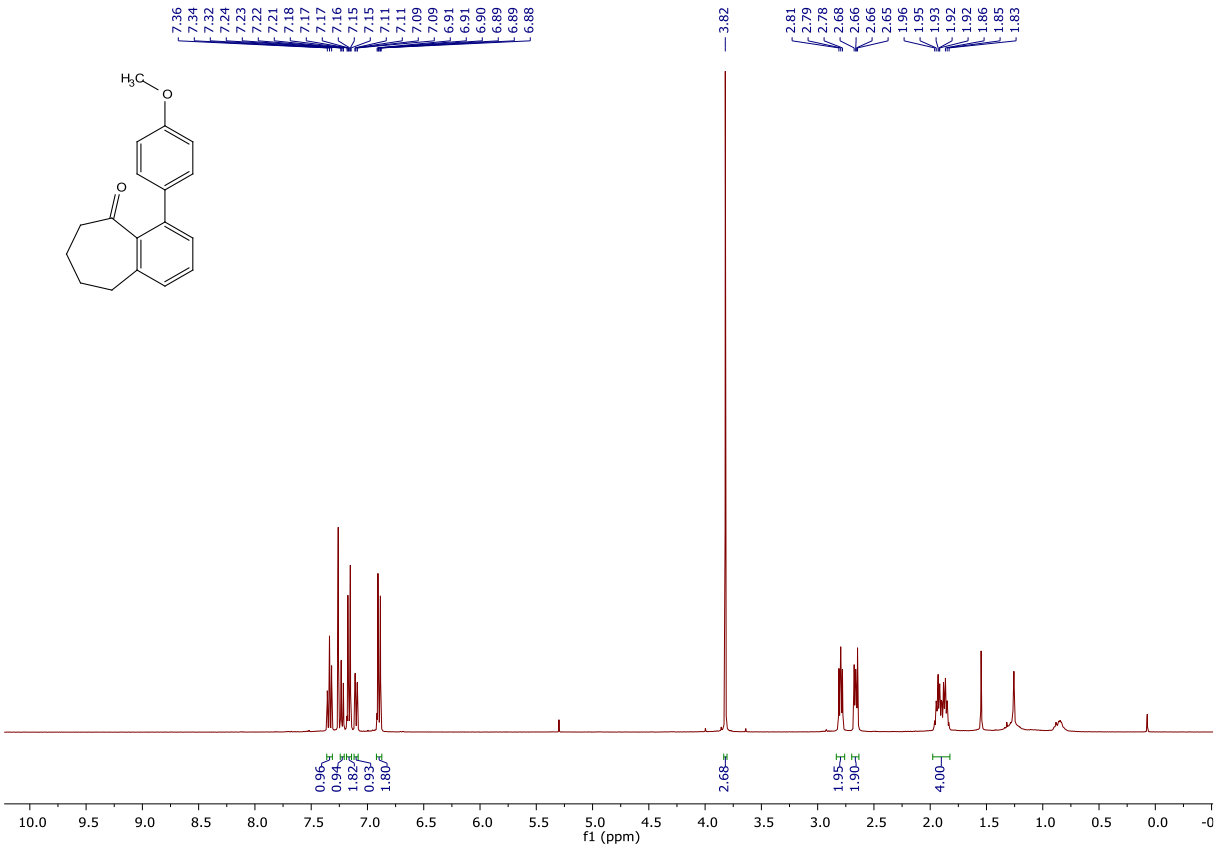
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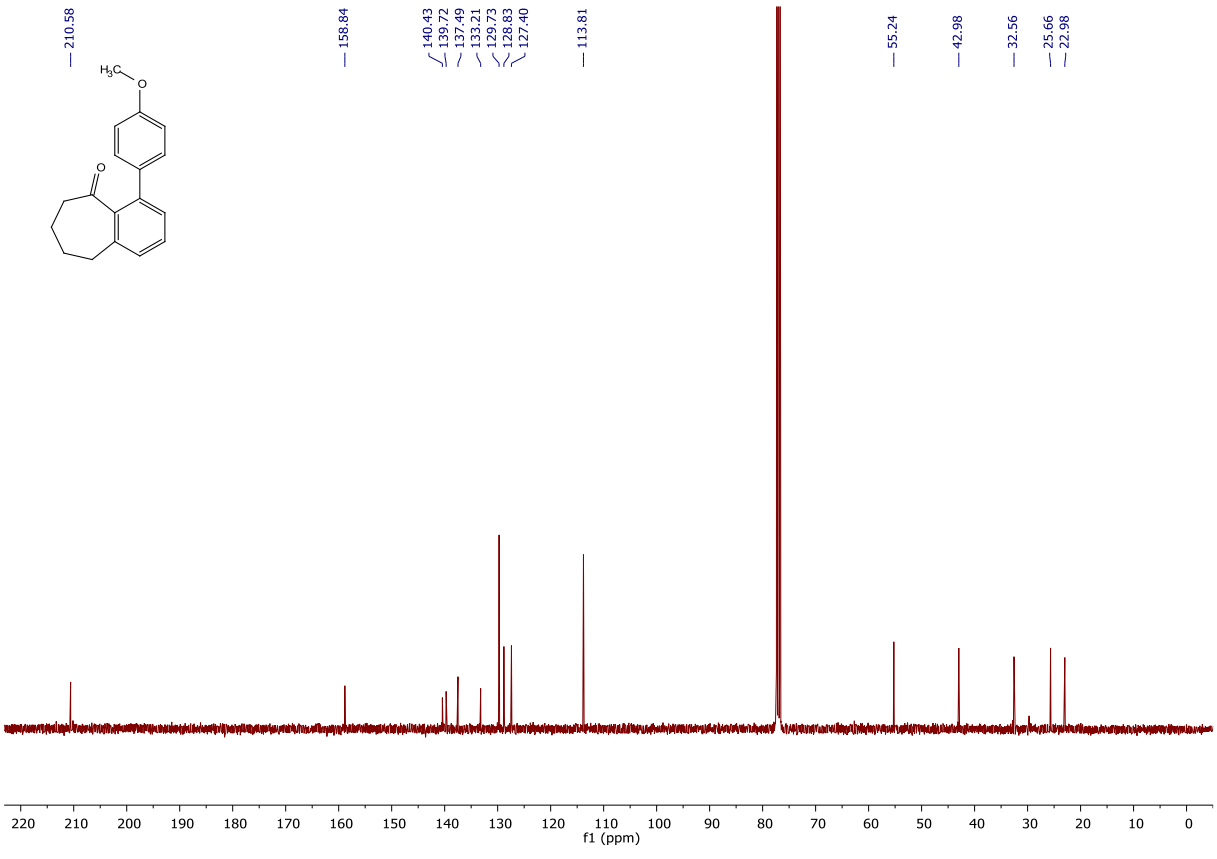
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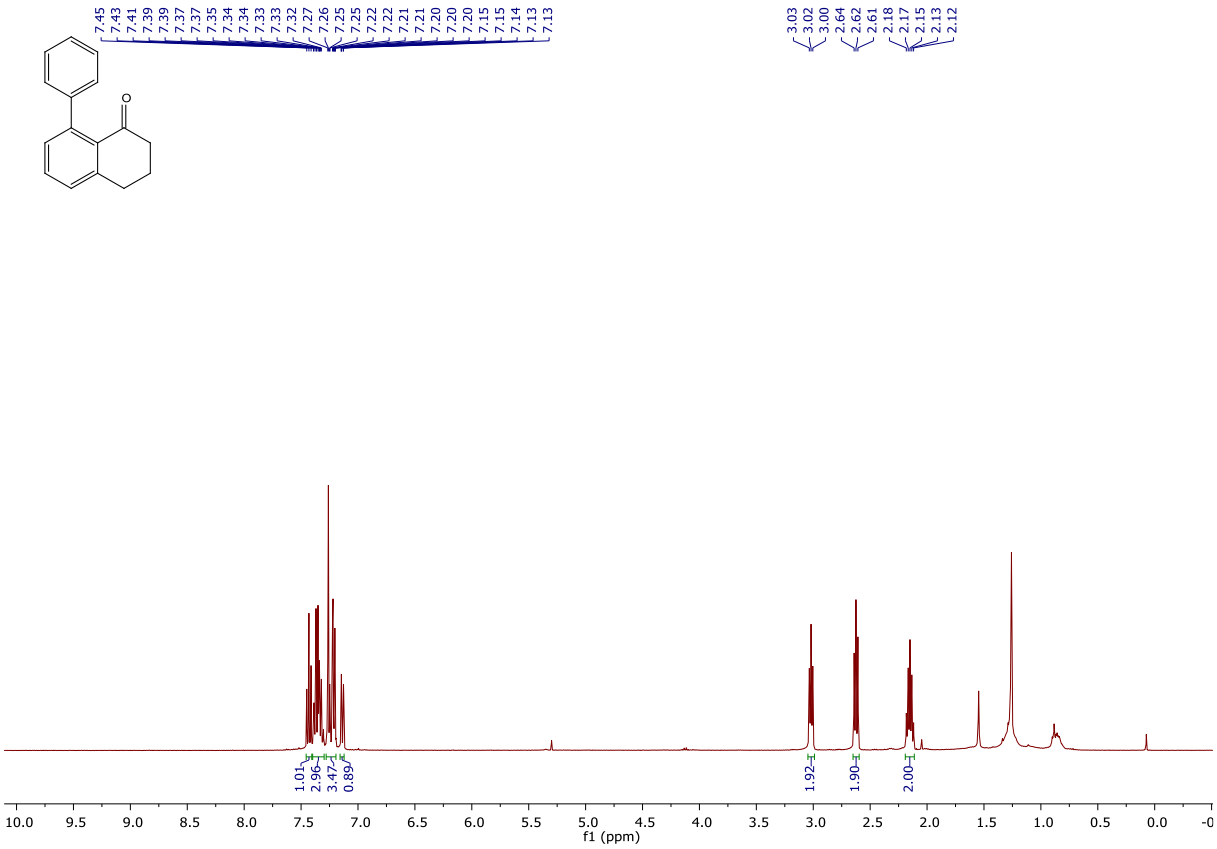
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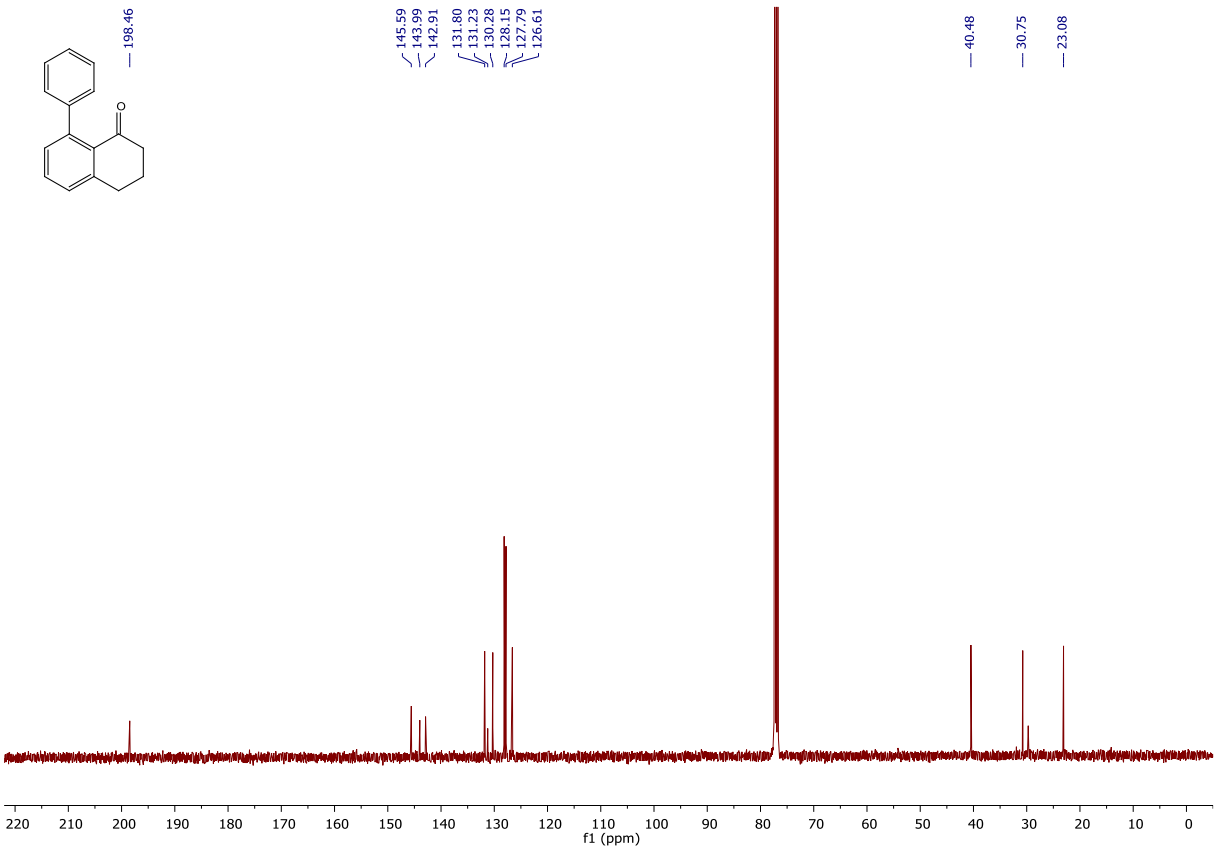
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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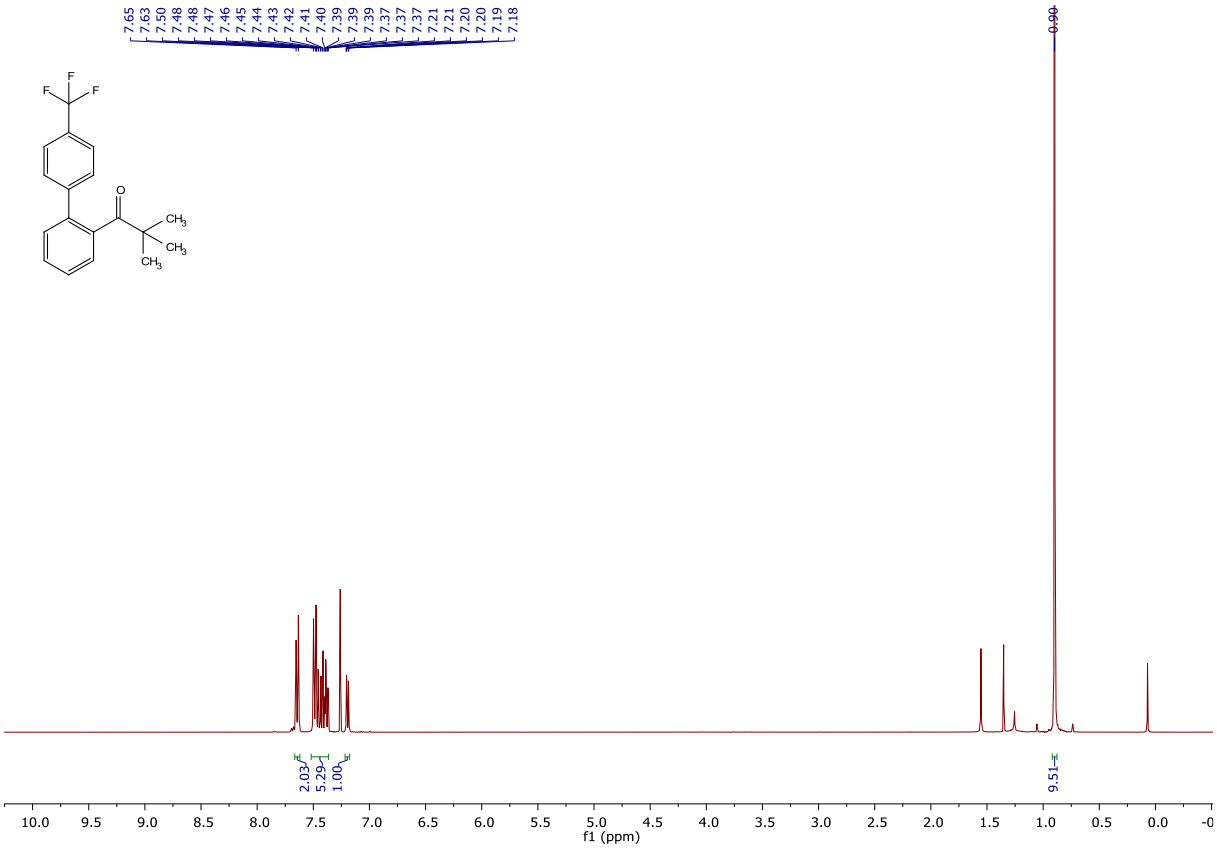
131.23
130.28
128.15
127.79
126.61
40.48
30.75
23.08
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.43
7.42
7.41
7.40
7.39
7.39
7.39
7.37
7.37
7.37
7.21
7.20
7.20
7.19
7.18
0.90
F
F
F
O
CH3
CH3
CH3
2.03
5.29
1.00
9.51
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
1.0
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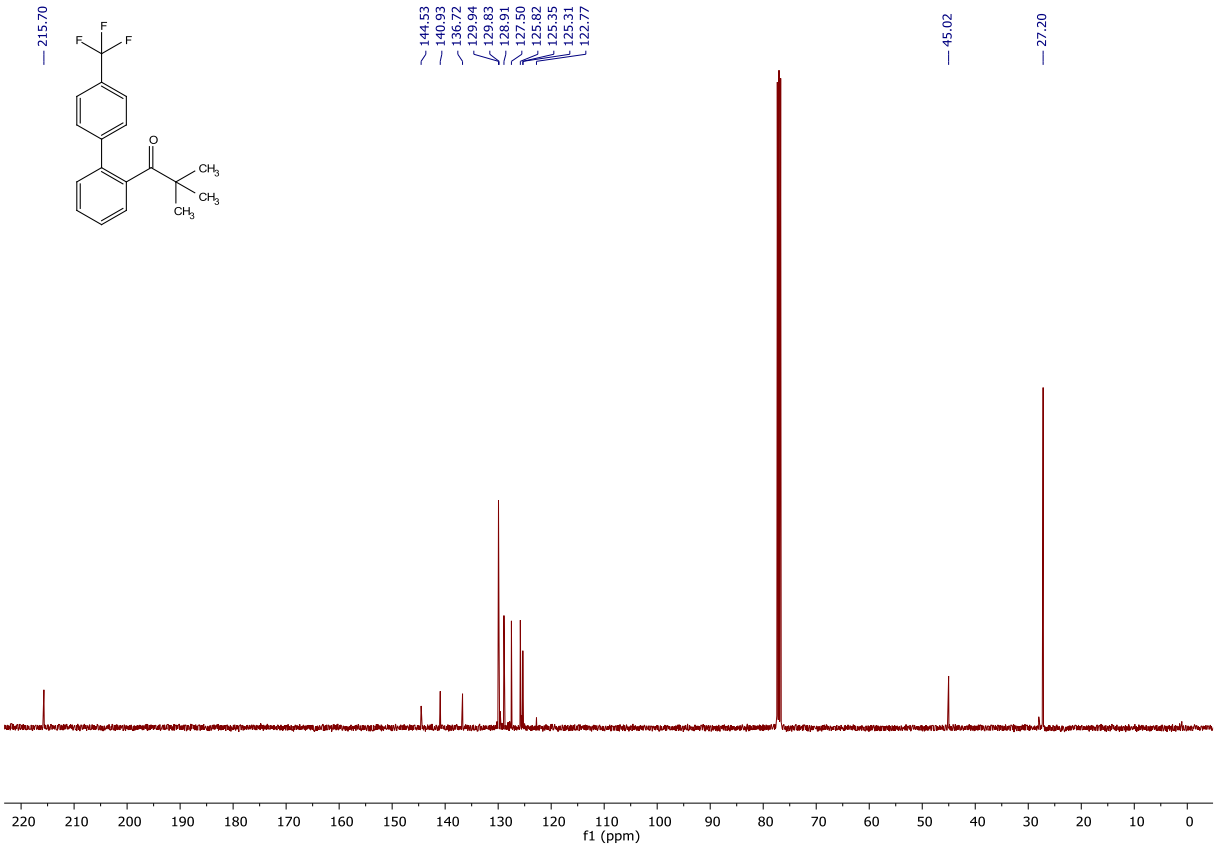
0.0
f1 (ppm)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144.53
140.93
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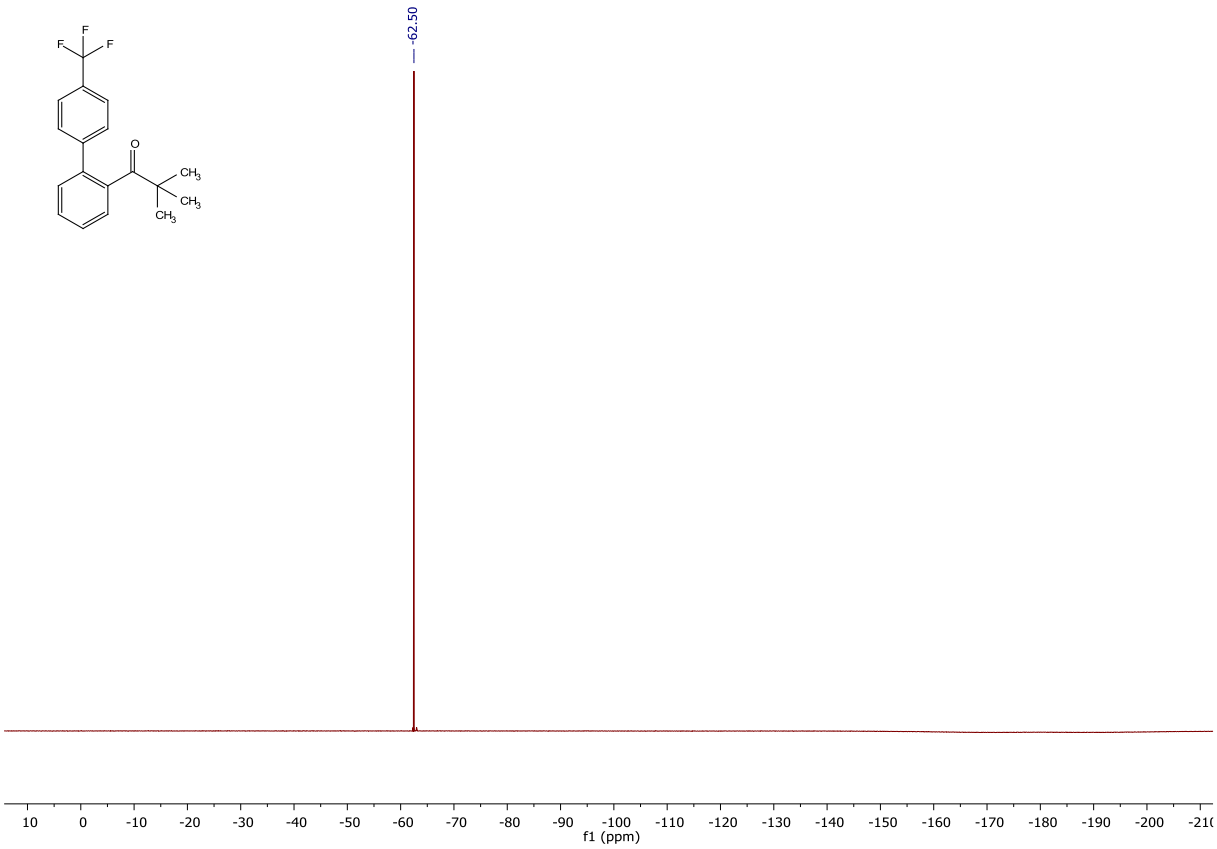
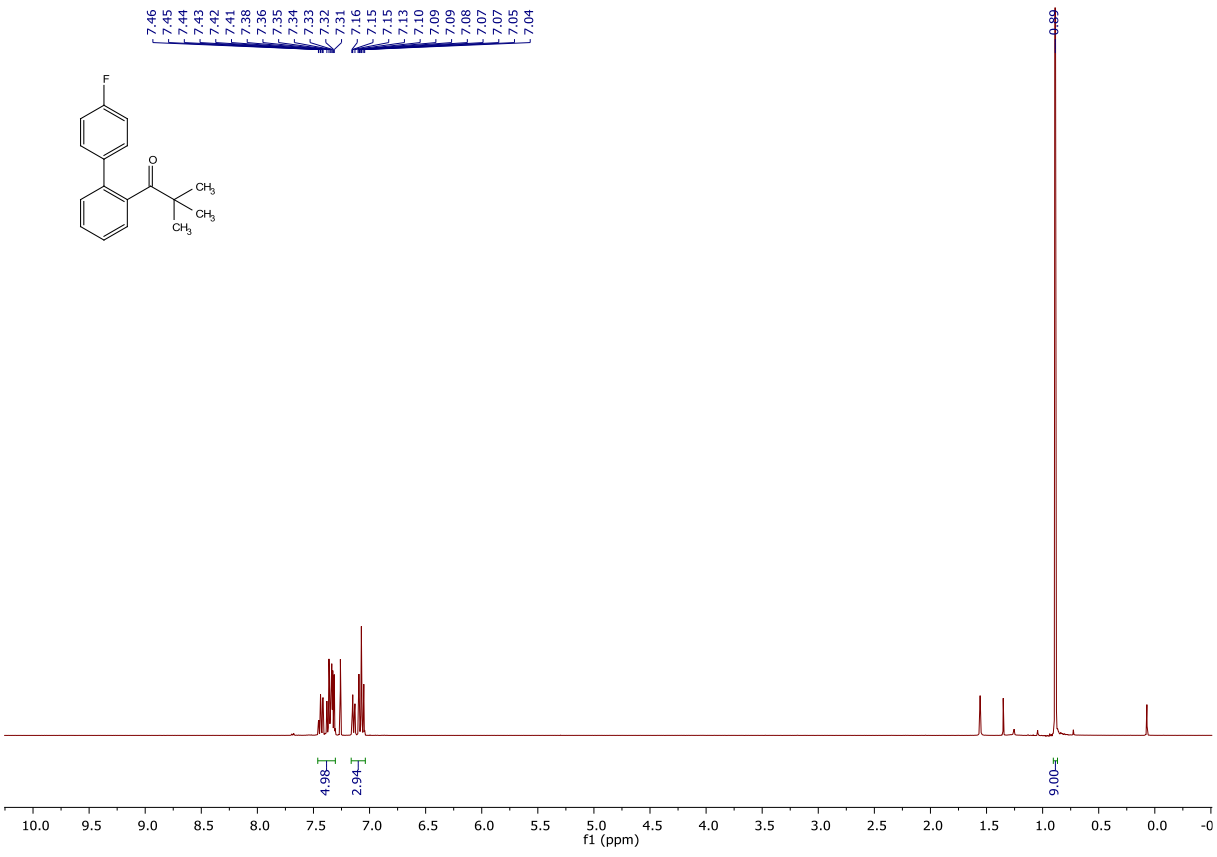
129.83
128.91
127.50
125.82
125.35
125.31
122.77
45.02
27.20
F
F
F
O
CH3
CH3
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
O
CH3
CH3
CH3
-62.50
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.33
7.32
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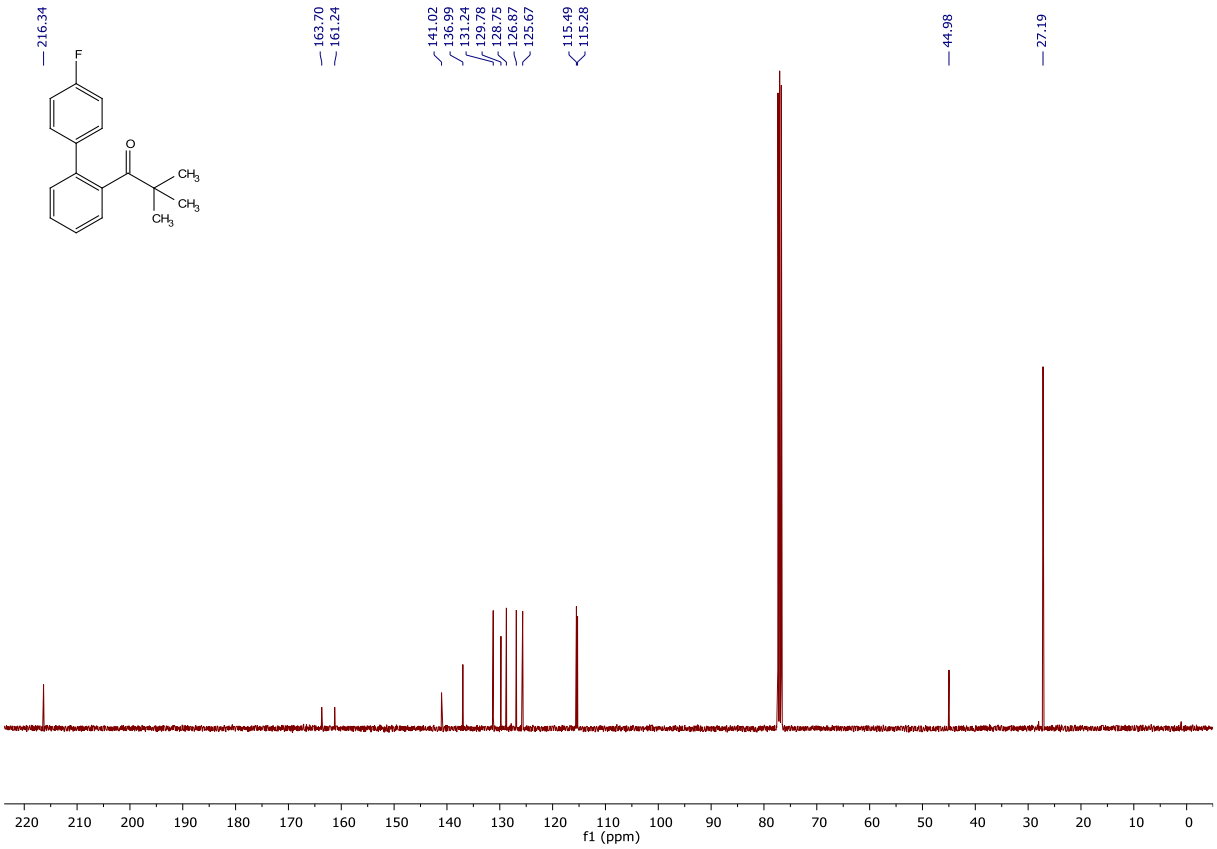
7.16
7.15
7.15
7.13
7.10
7.09
7.09
7.08
7.07
7.07
7.05
7.04
0.89
F
O
CH3
CH3
CH3
4.98
2.94
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


216.34
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131.24
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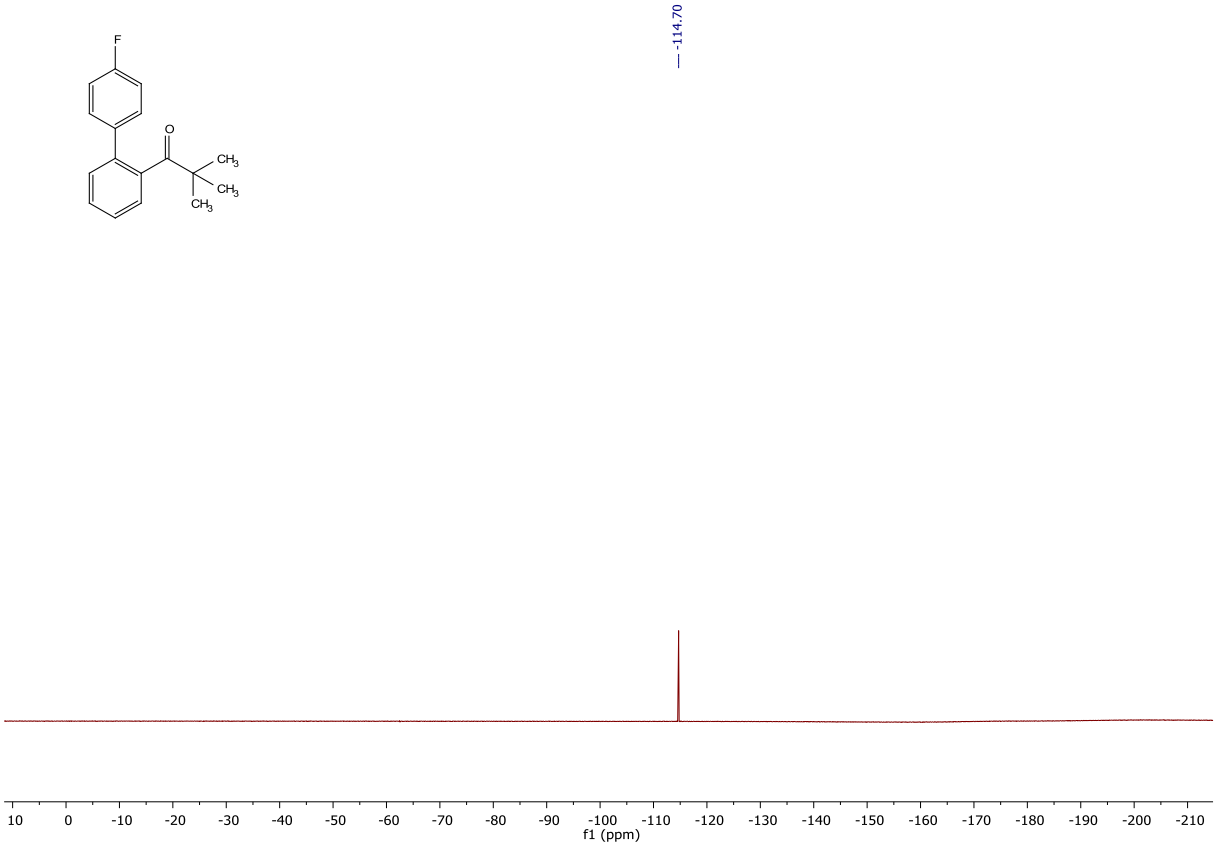
128.75
126.87
125.67
115.49
115.28
44.98
27.19
F
O
CH3
CH3
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-114.70
F
O
CH3
CH3
CH3
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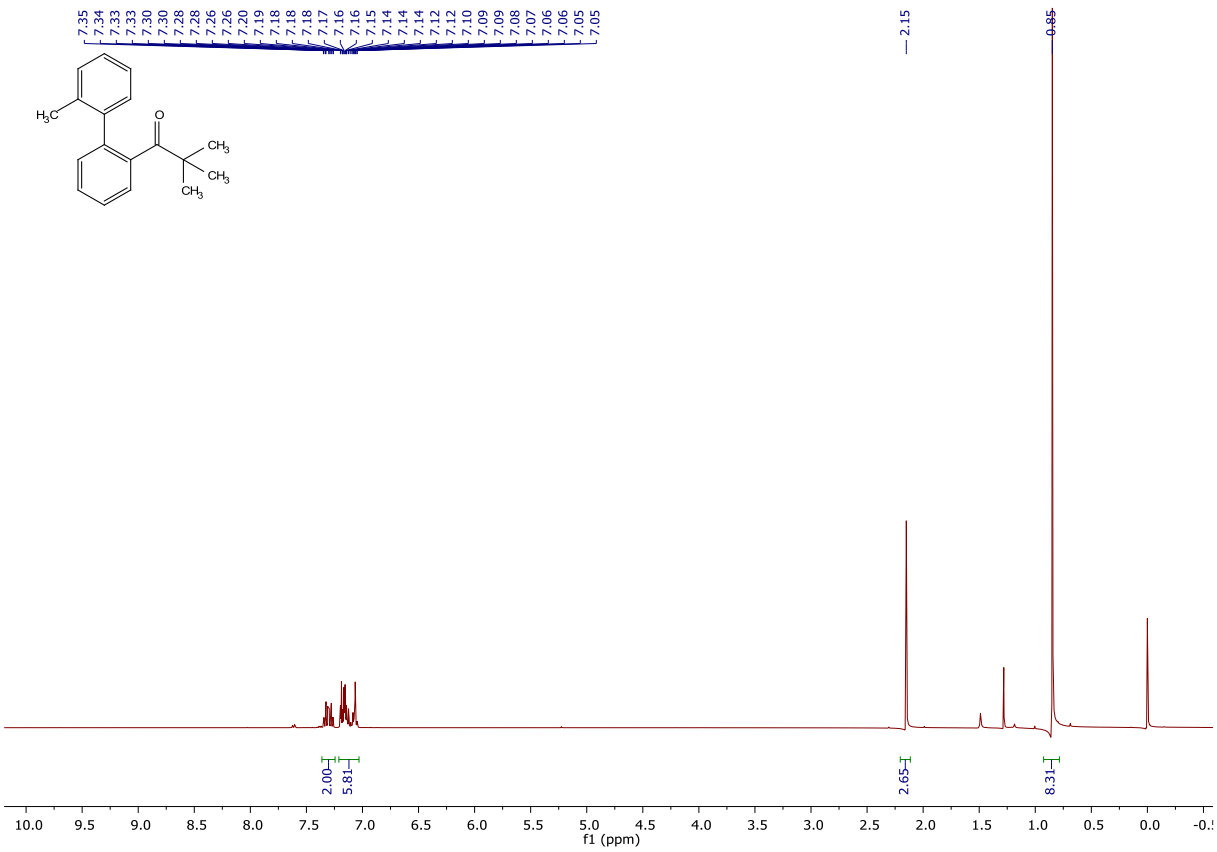
f1 (ppm)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7.34
7.33
7.33
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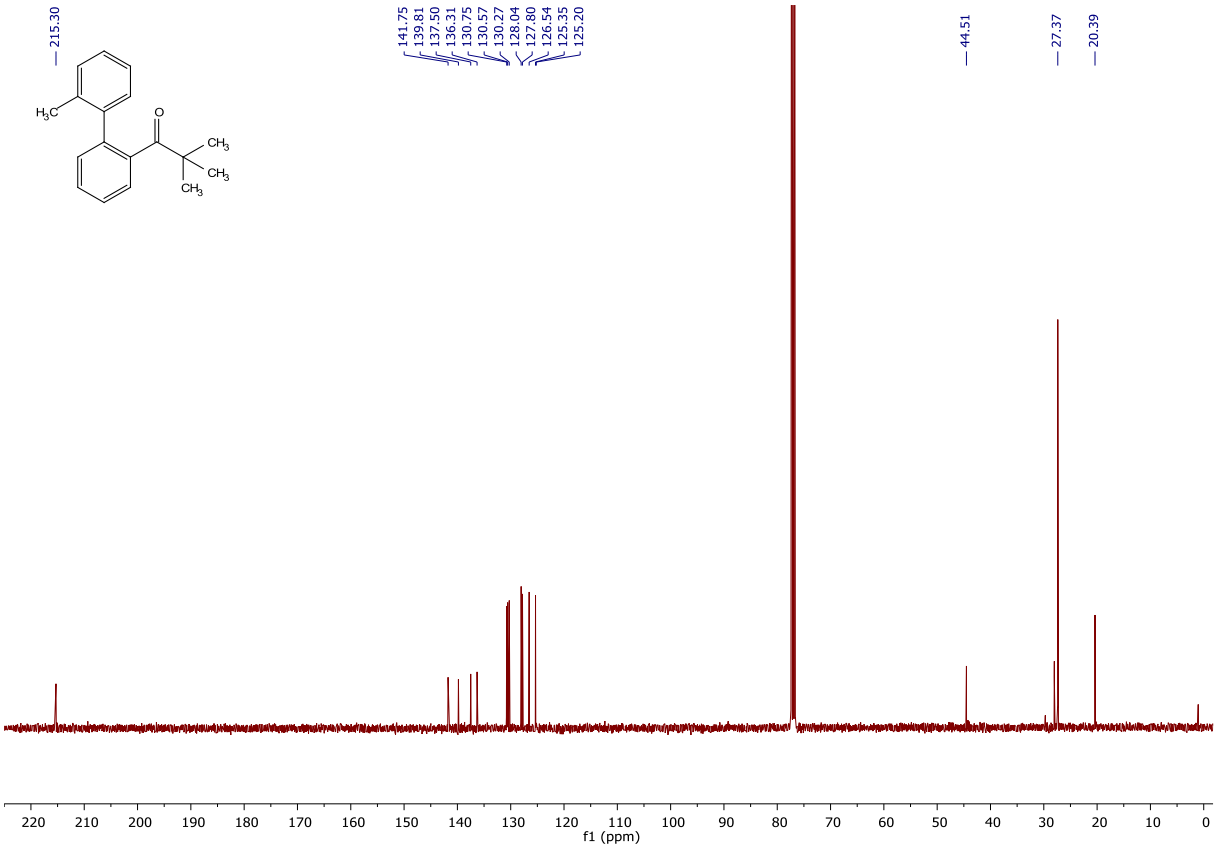
7.30
7.28
7.28
7.26
7.26
7.20
7.19
7.18
7.18
7.18
7.17
7.16
7.16
7.15
7.14
7.14
7.14
7.12
7.12
7.10
7.09
7.09
7.08
7.07
7.06
7.06
7.05
7.05
2.15
0.85
H3C
O
CH3
CH3
CH3
2.00
5.81
2.65
8.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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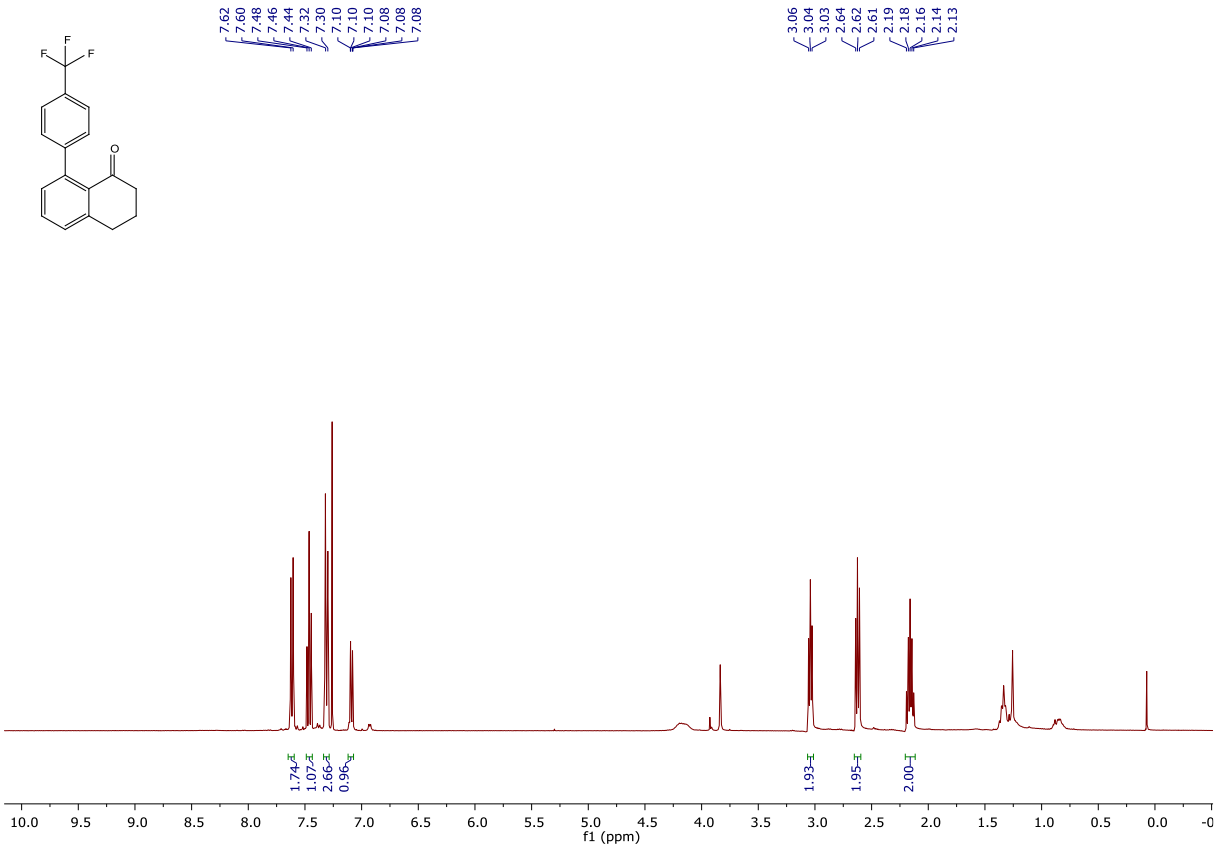
141.75
139.81
137.50
136.31
130.75
130.57
130.27
128.04
127.80
126.54
125.35
125.20
44.51
27.37
20.39
H3C
O
CH3
CH3
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.62
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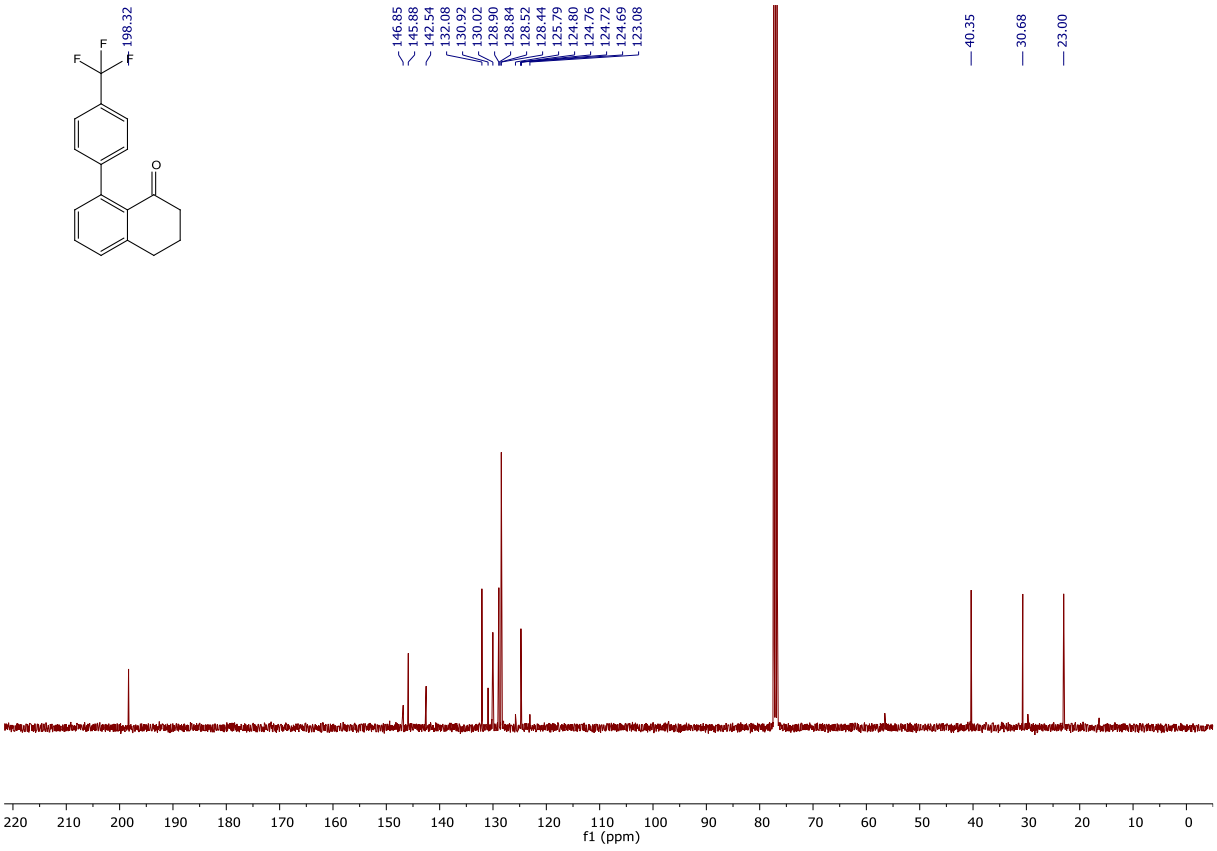
7.30
7.10
7.10
7.10
7.08
7.08
7.08
3.06
3.04
3.03
2.64
2.62
2.61
2.19
2.18
2.16
2.14
2.13
F
F
F
O
1.74
1.07
2.66
0.96
1.93
1.95
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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132.08
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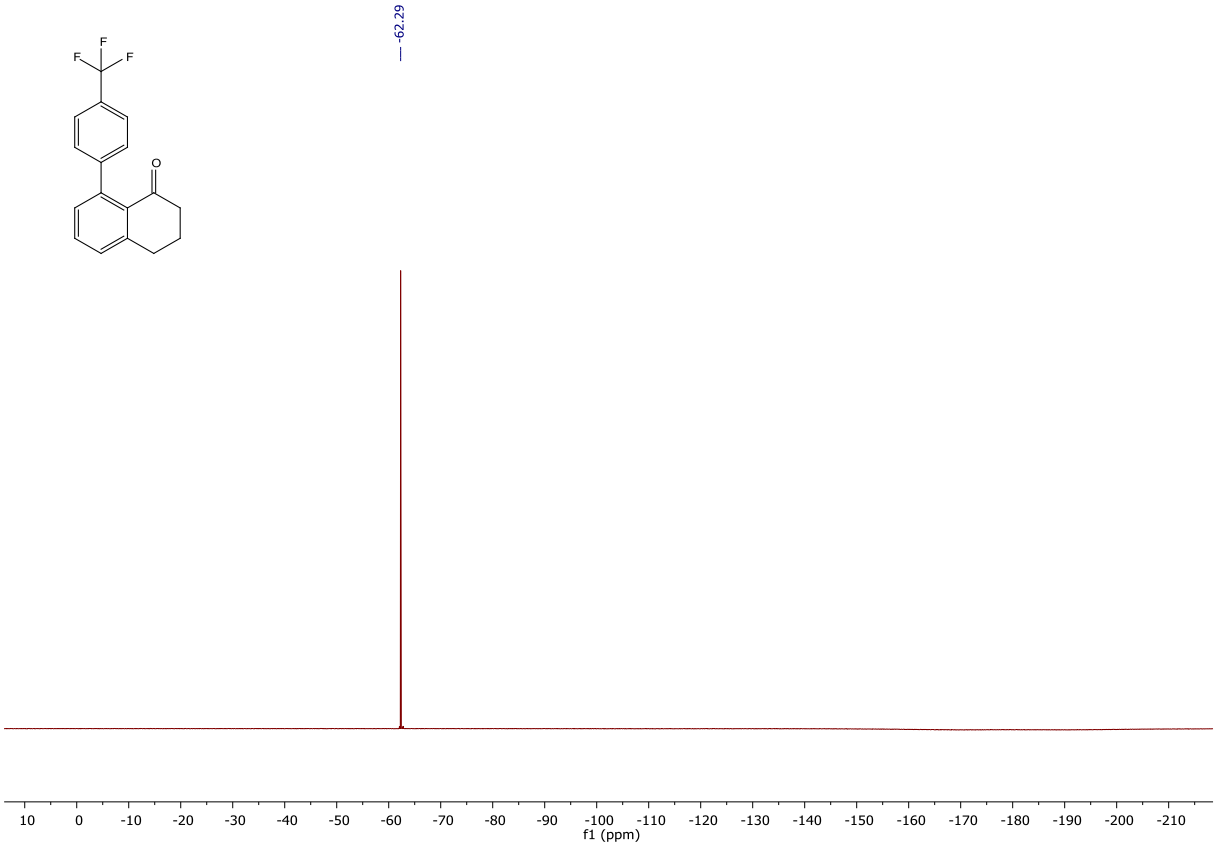
128.44
125.79
124.80
124.76
124.72
124.69
123.08
40.35
30.68
23.00
F
F
F
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
F
O
-62.29
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-120
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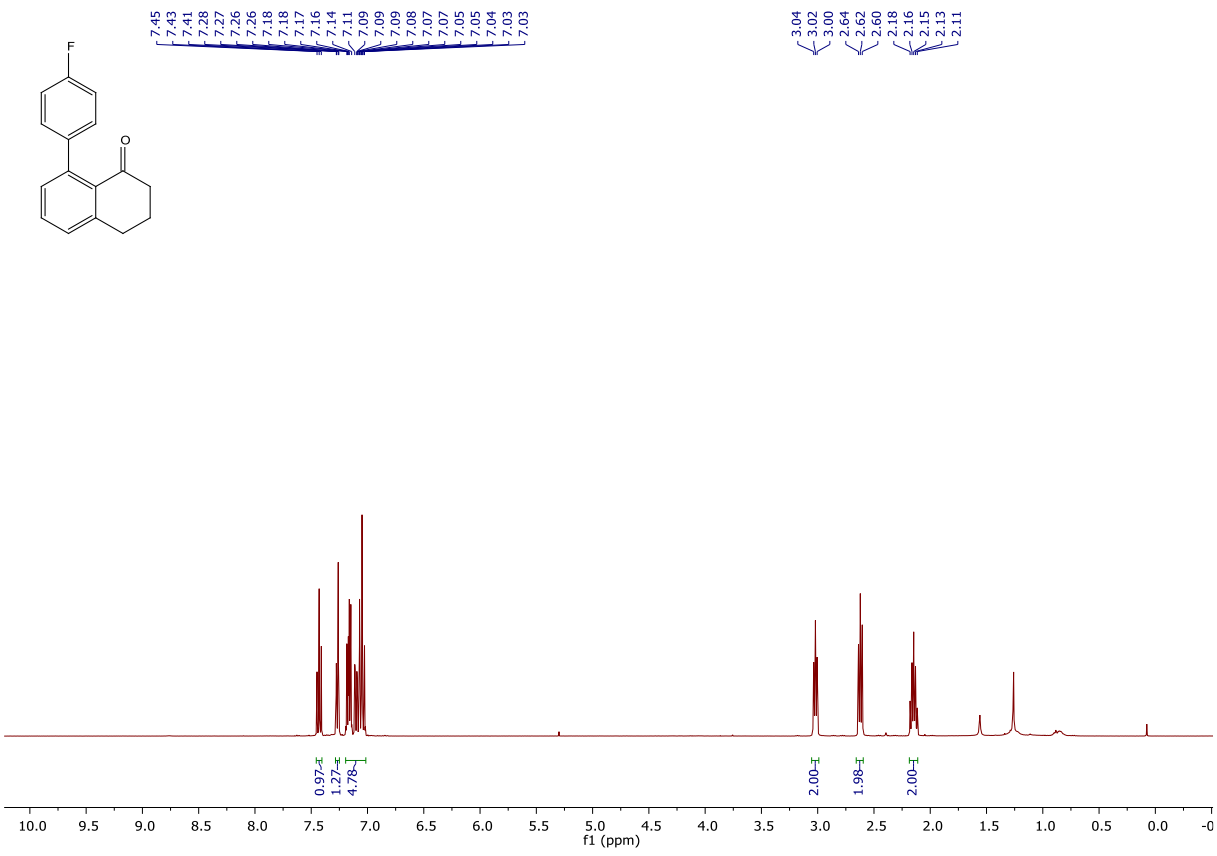
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


F
O
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7.27
7.26
7.26
7.18
7.18
7.17
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7.14
7.11
7.09
7.09
7.09
7.08
7.07
7.07
7.05
7.05
7.04
7.03
7.03
3.04
3.02
3.00
2.64
2.62
2.60
2.18
2.16
2.15
2.13
2.11
0.97
1.27
4.78
2.00
1.98
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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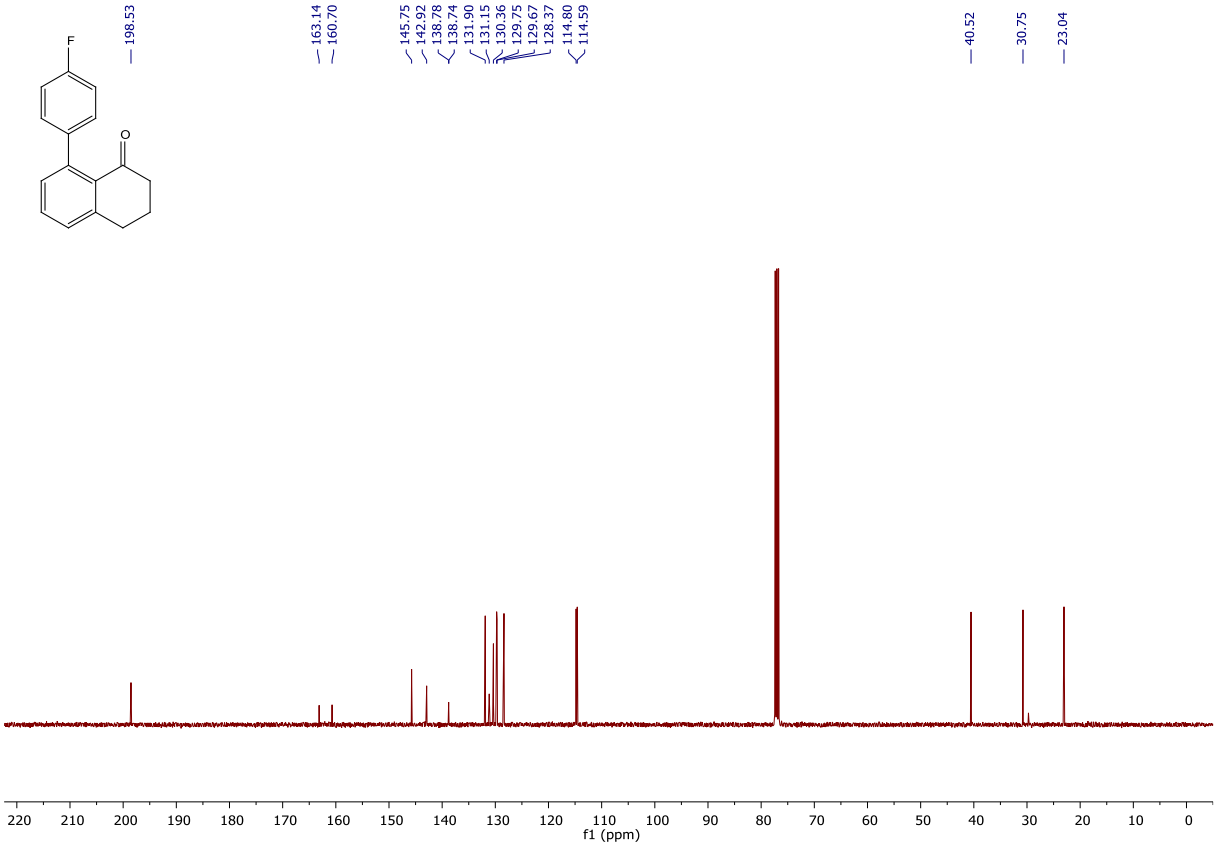
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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142.92
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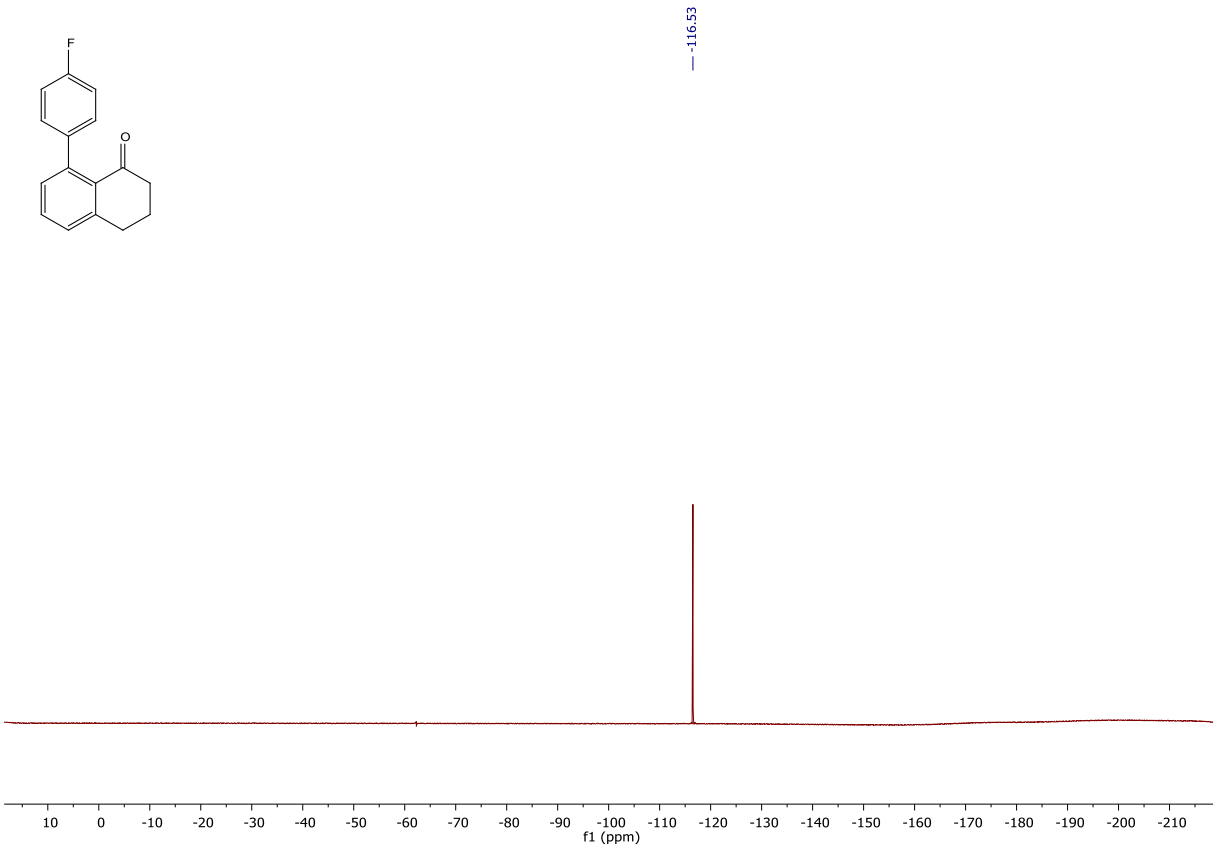
131.15
130.36
129.75
129.67
128.37
114.80
114.59
40.52
30.75
23.04
F
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-116.53
F
O
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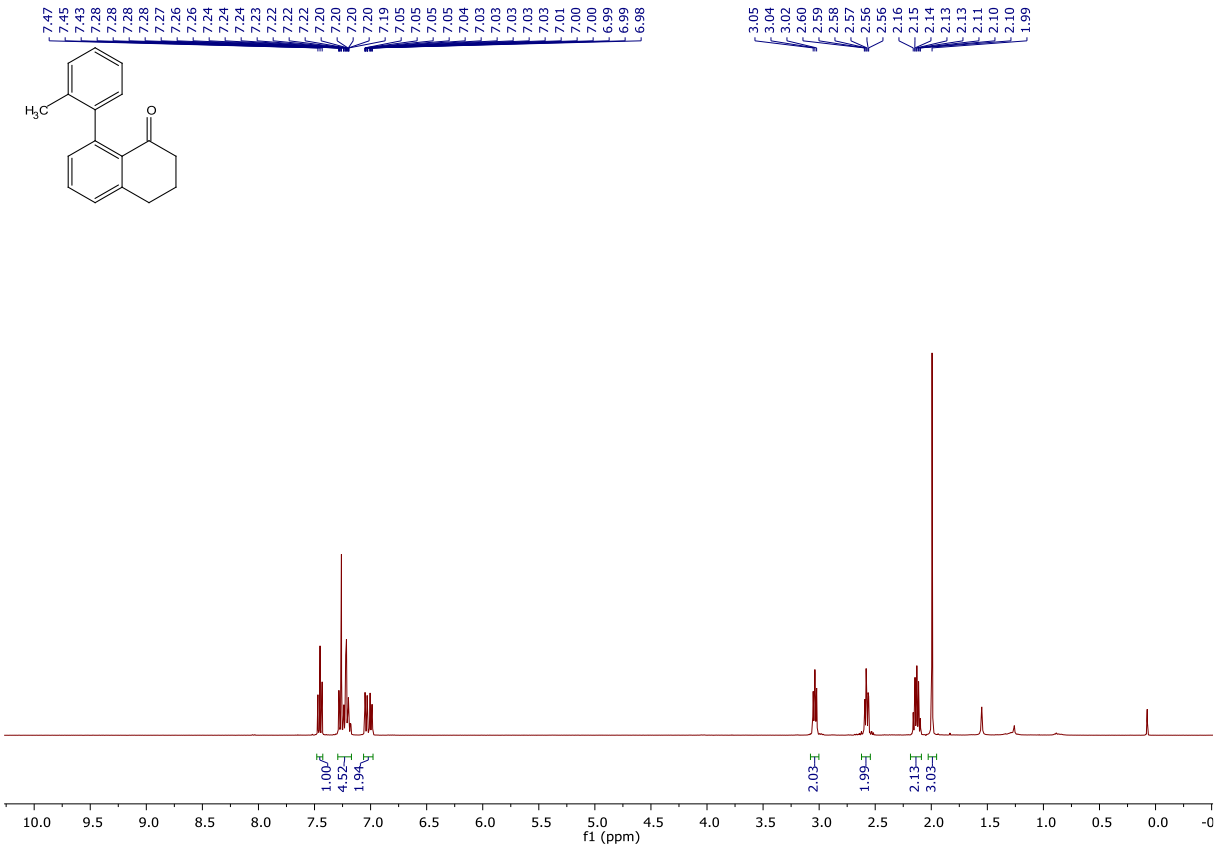
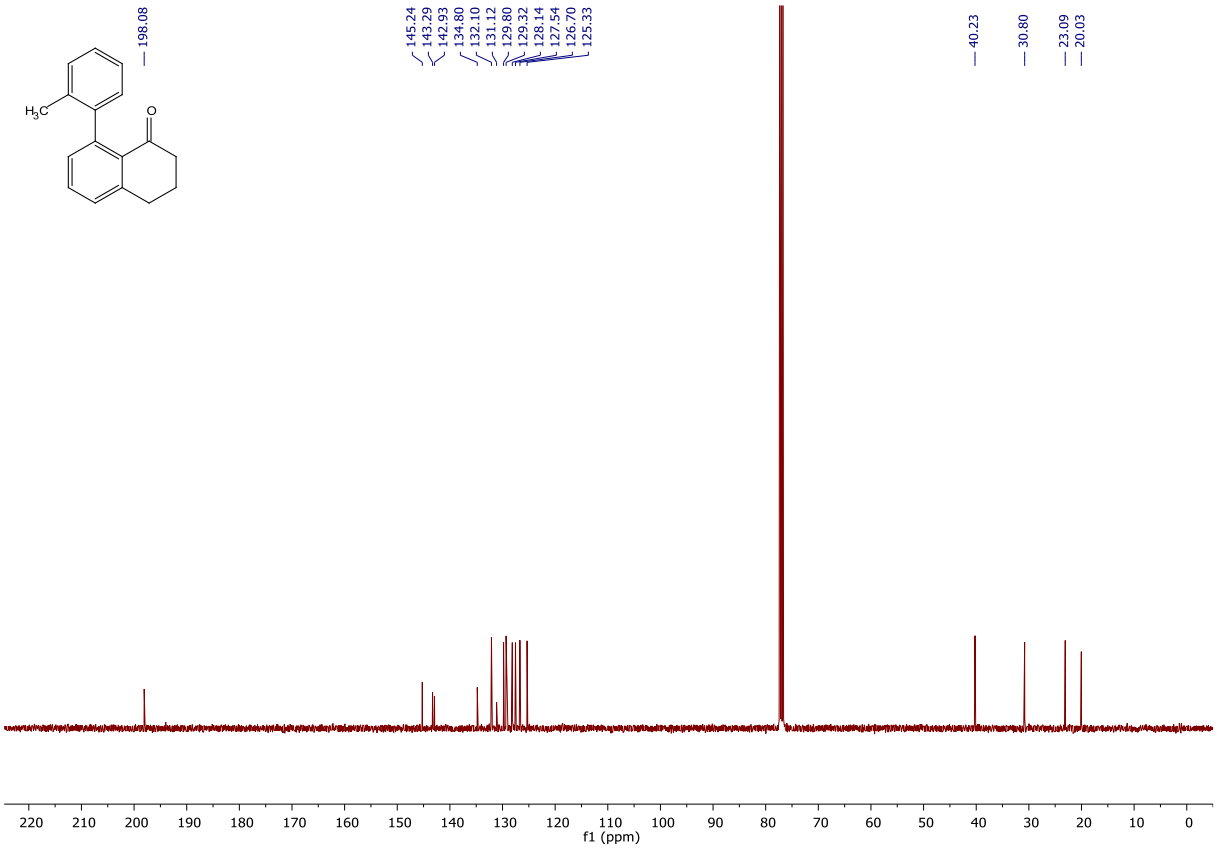
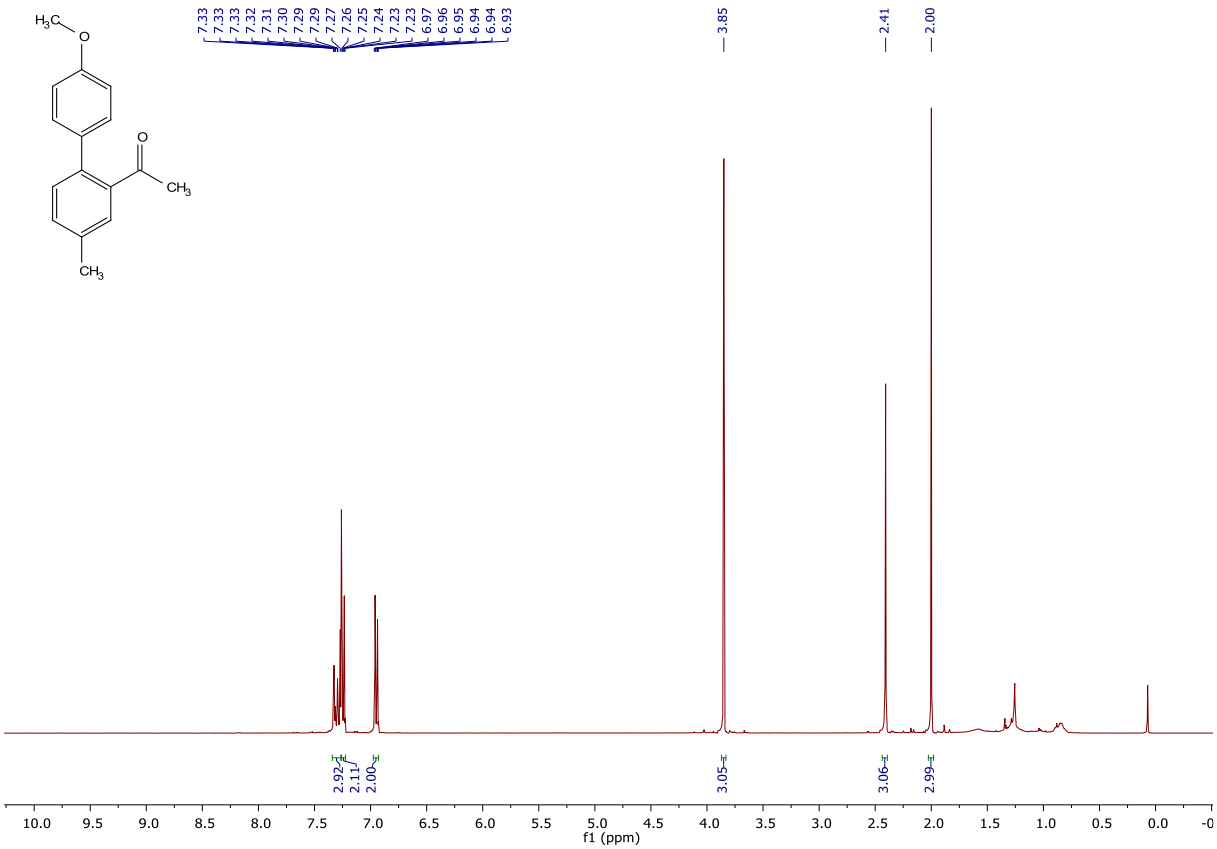
f1 (ppm)


7.47 7.45 7.43 7.28 7.28 7.28 7.28 7.27 7.26 7.26 7.24 7.24 7.24 7.23 7.22 7.22 7.22 7.20 7.20 7.20 7.20 7.19 7.05 7.05 7.05 7.04 7.03 7.03 7.03 7.03 7.01 7.00 7.00 6.99 6.99 6.98
3.05 3.04 3.02 2.60 2.59 2.58 2.57 2.56 2.56 2.16 2.15 2.14 2.13 2.13 2.11 2.10 2.10 1.99
H3C
O
1.00 4.52 1.94 2.03 1.99 2.13 3.03
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)


198.08
145.24 143.29 142.93 134.80 132.10 131.12 129.80 129.32 128.14 127.54 126.70 125.33
40.23 30.80 23.09 20.03
H3C
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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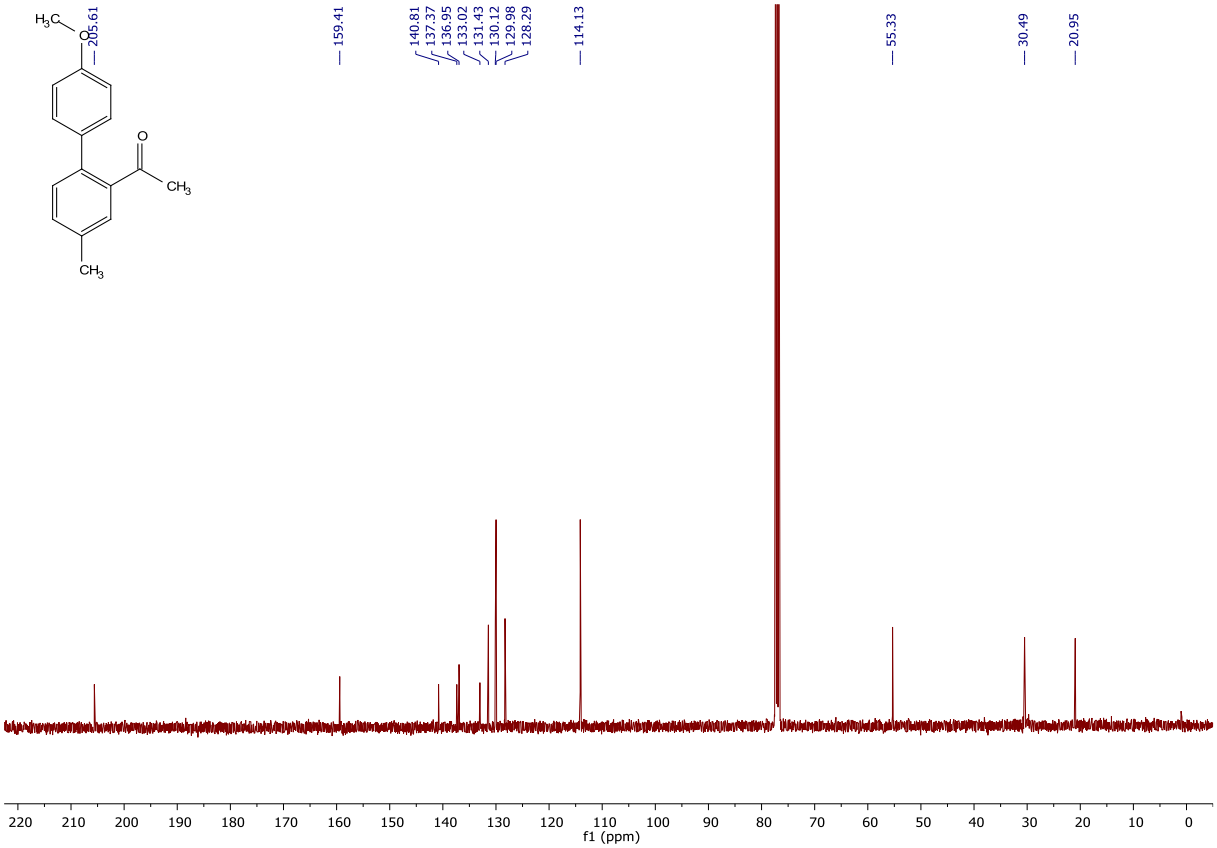
7.29
7.27
7.26
7.25
7.24
7.23
7.23
6.97
6.96
6.95
6.94
6.94
6.93
3.85
2.41
2.00
2.92
2.11
2.00
3.05
3.06
2.99
f1 (ppm)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137.37
136.95
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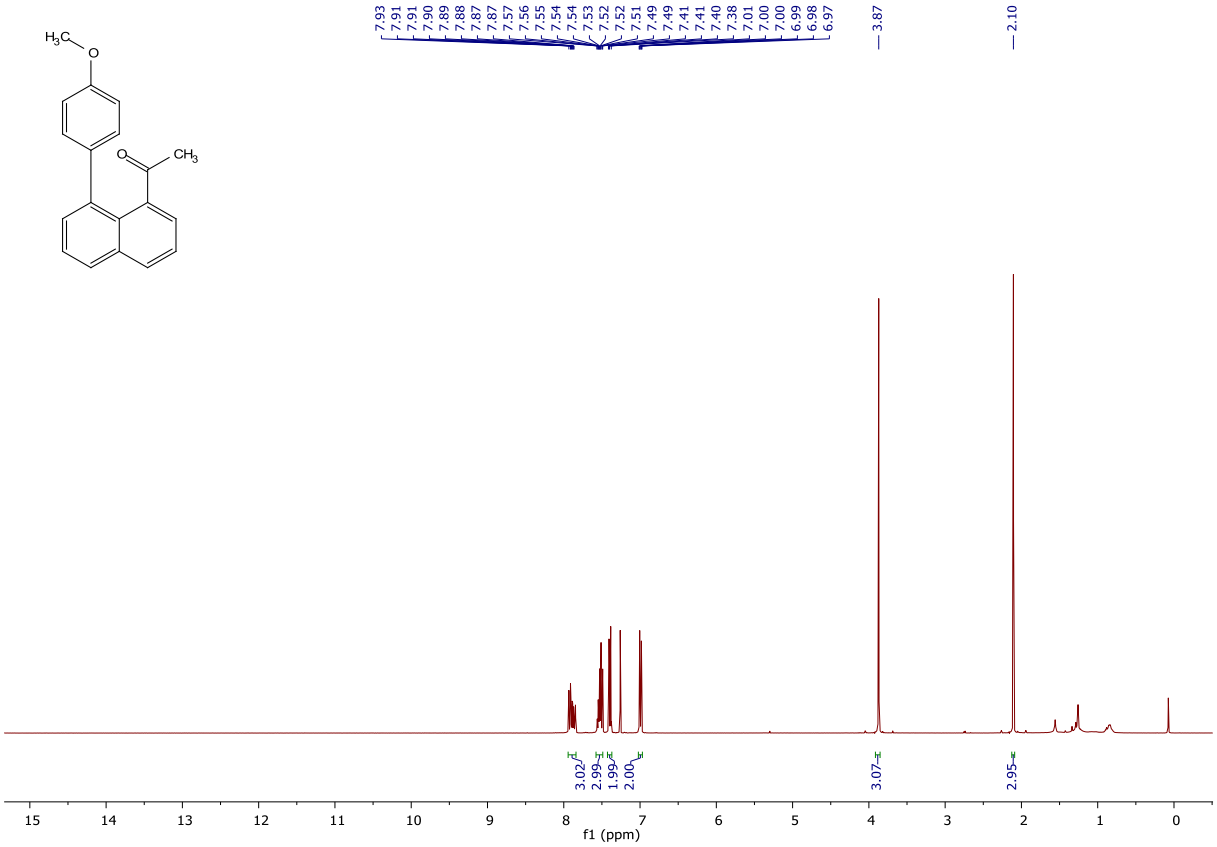
131.43
130.12
129.98
128.29
114.13
55.33
30.49
20.95
f1 (ppm)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7.56
7.55
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7.54
7.53
7.52
7.52
7.51
7.49
7.49
7.41
7.41
7.40
7.38
7.01
7.00
7.00
6.99
6.98
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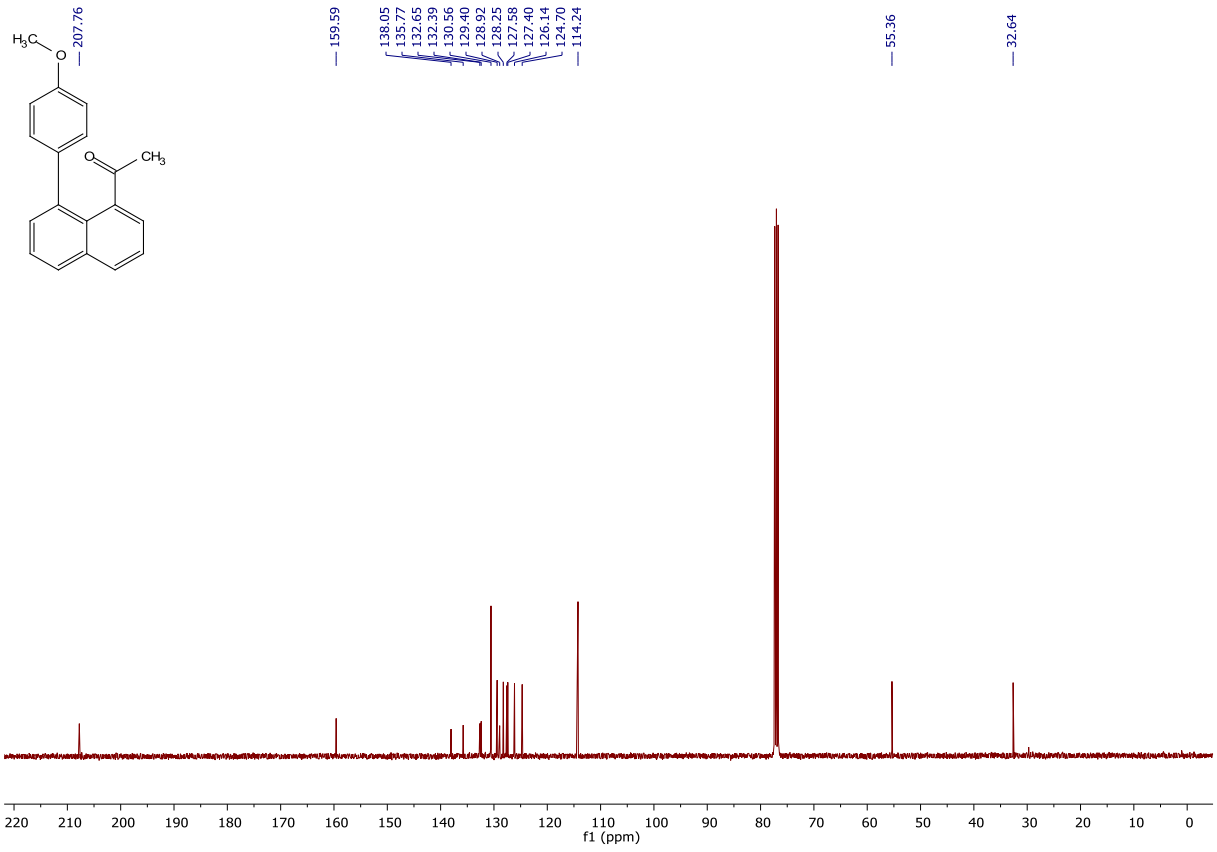
3.87
2.10
3.02
2.99
1.99
2.00
3.07
2.95
f1 (ppm)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128.25
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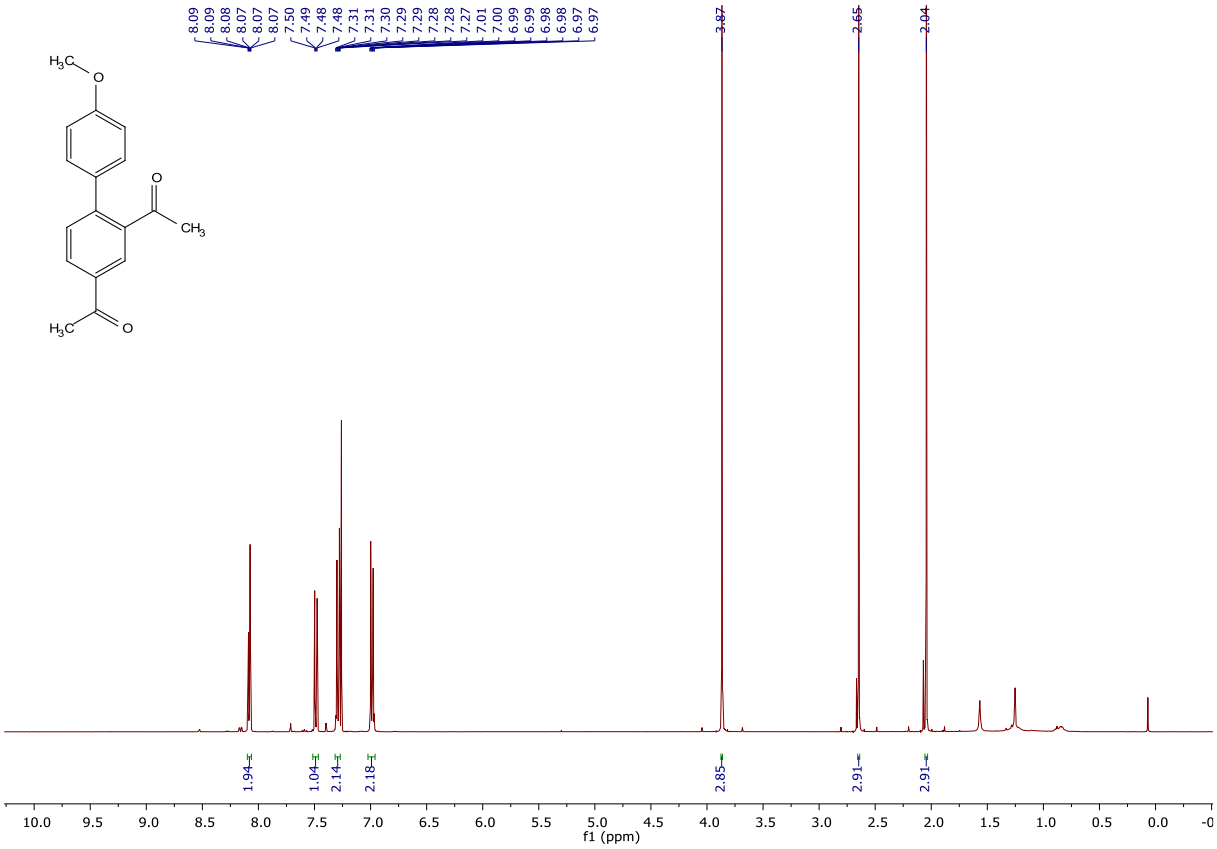
127.40
126.14
124.70
114.24
55.36
32.64
f1 (ppm)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8.07
8.07
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7.49
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7.48
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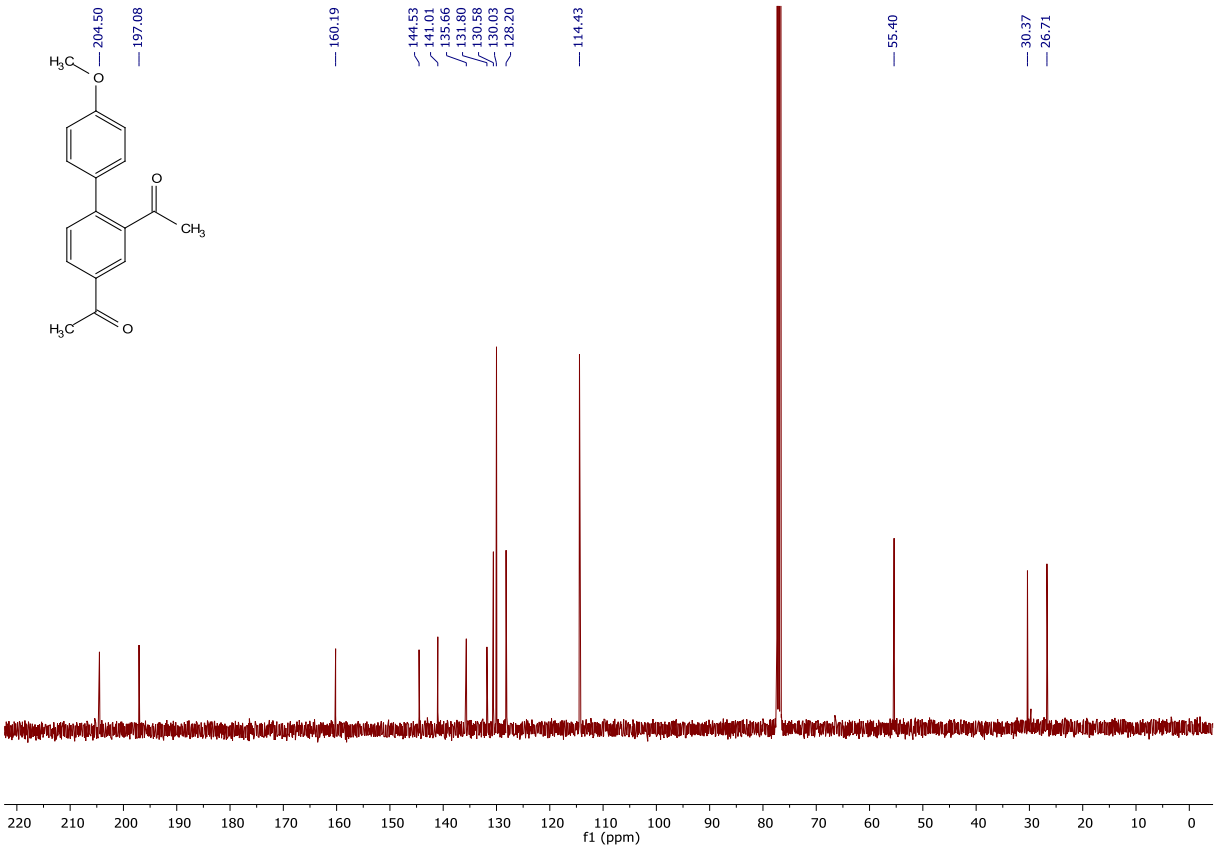
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.01
7.00
6.99
6.99
6.98
6.98
6.97
6.97
3.87
2.65
2.04
1.94
1.04
2.14
2.18
2.85
2.91
2.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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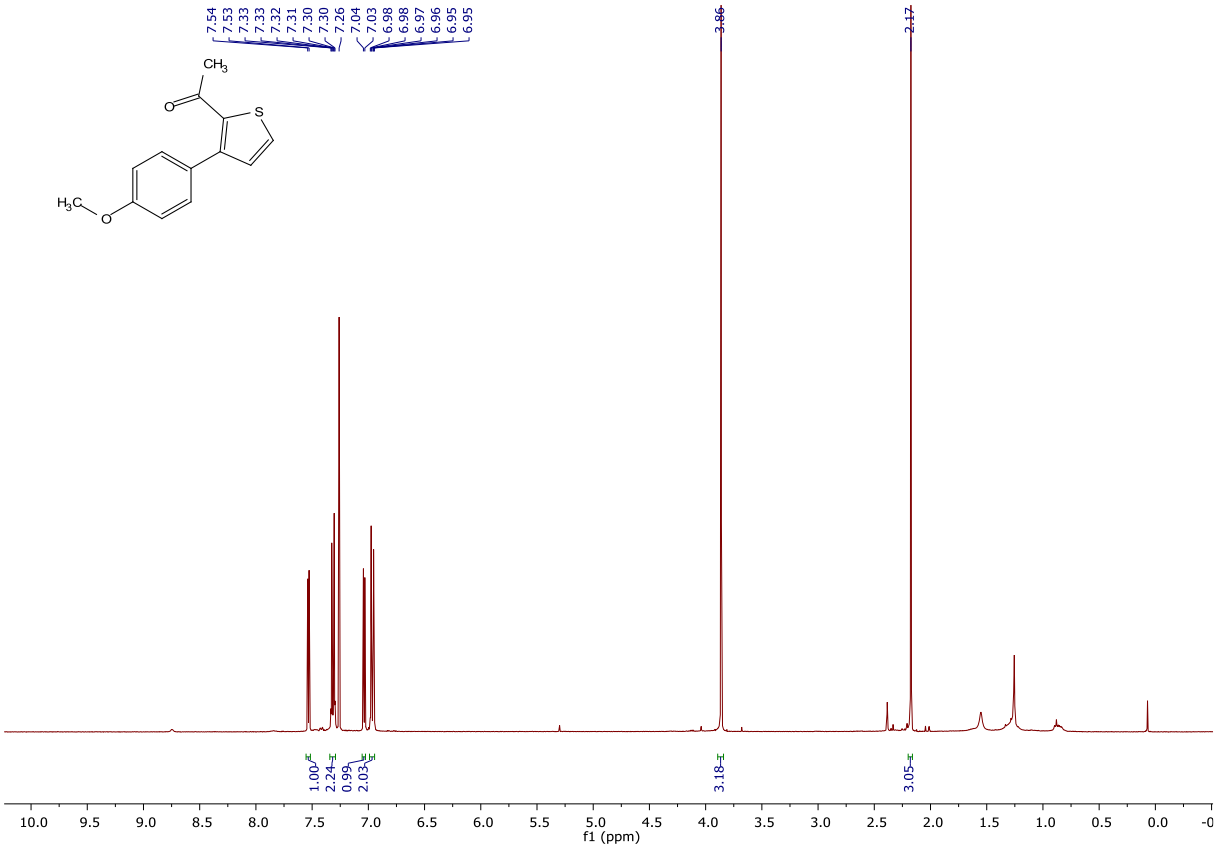
144.53
141.01
135.66
131.80
130.58
130.03
128.20
114.43
55.40
30.37
26.71
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.30
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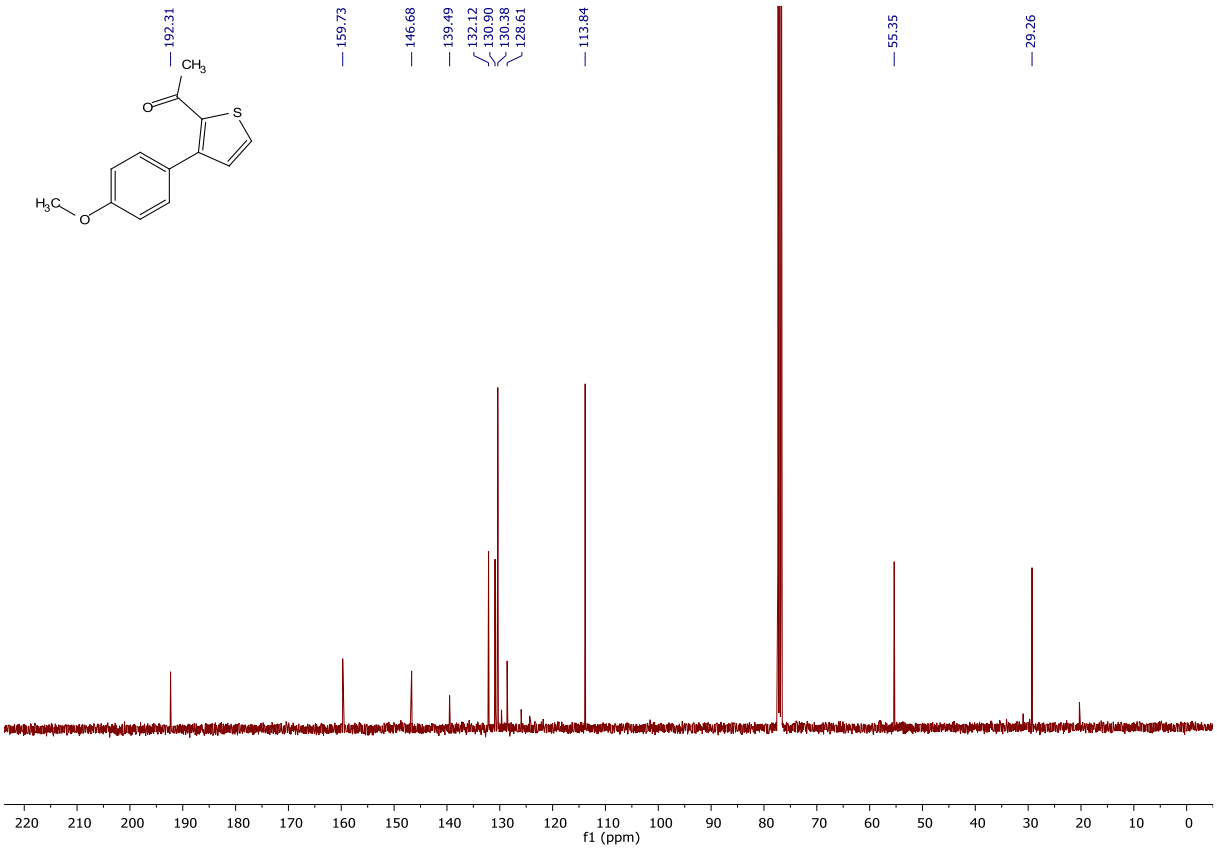
7.03
6.98
6.98
6.97
6.96
6.95
6.95
3.86
2.17
CH3
O
S
H3C
O
1.00
2.24
0.99
2.03
3.18
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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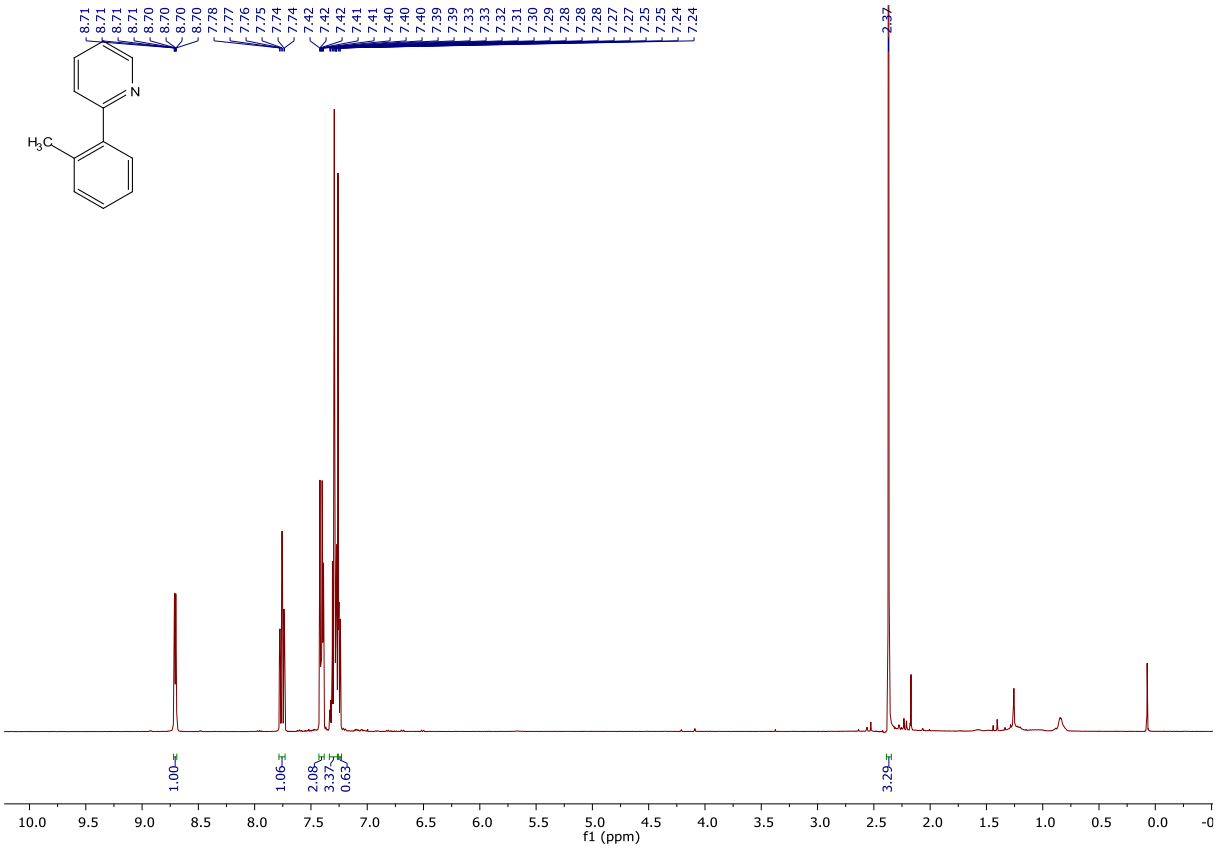
130.38
128.61
113.84
55.35
29.26
CH3
O
S
H3C
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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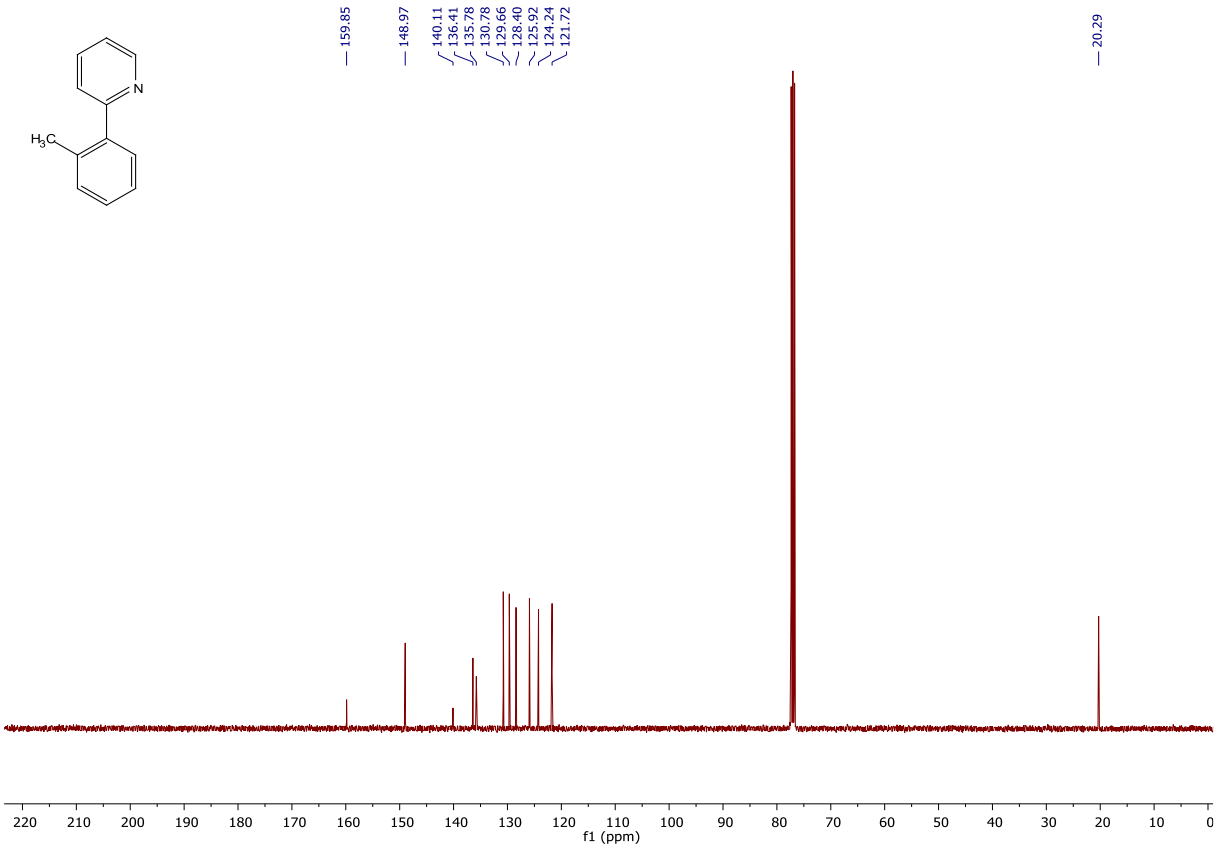
7.28
7.28
7.27
7.27
7.25
7.25
7.24
7.24
2.37
N
H3C
1.00
1.06
2.08
3.37
0.63
3.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.78
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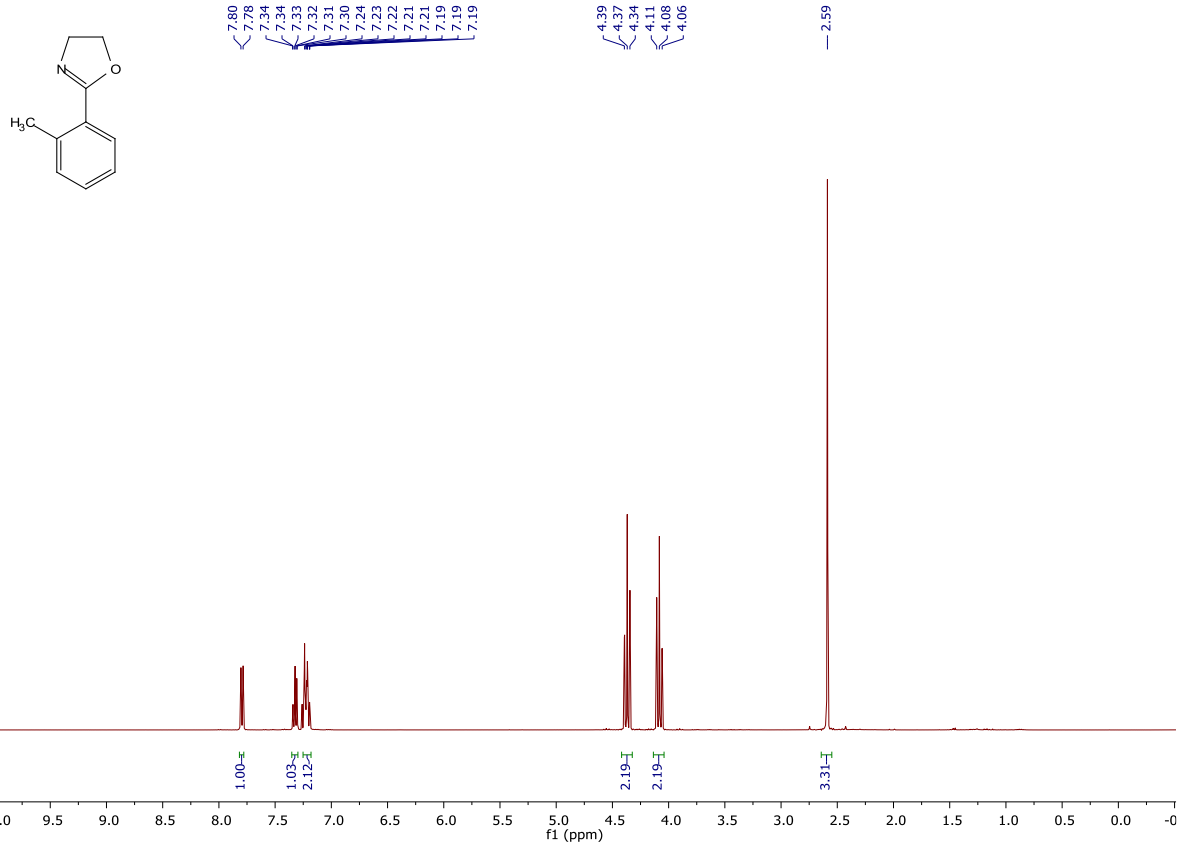
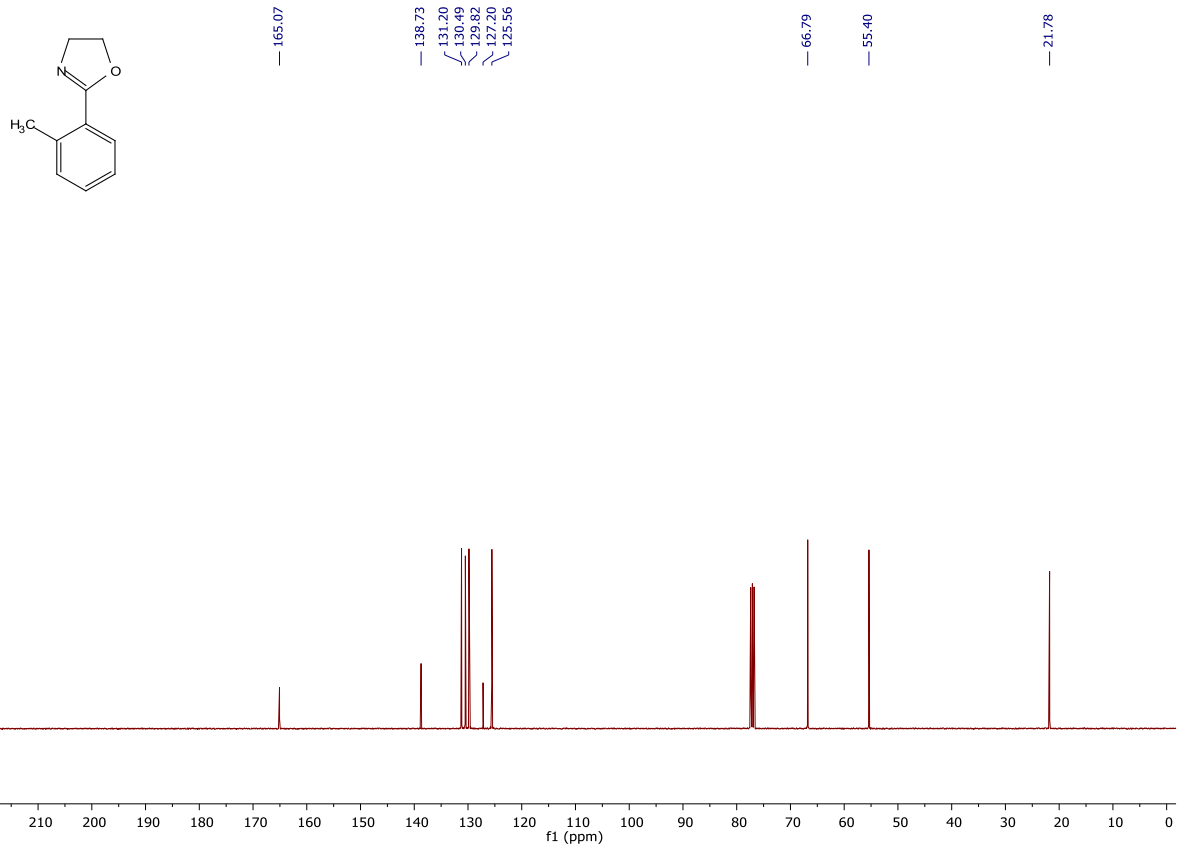
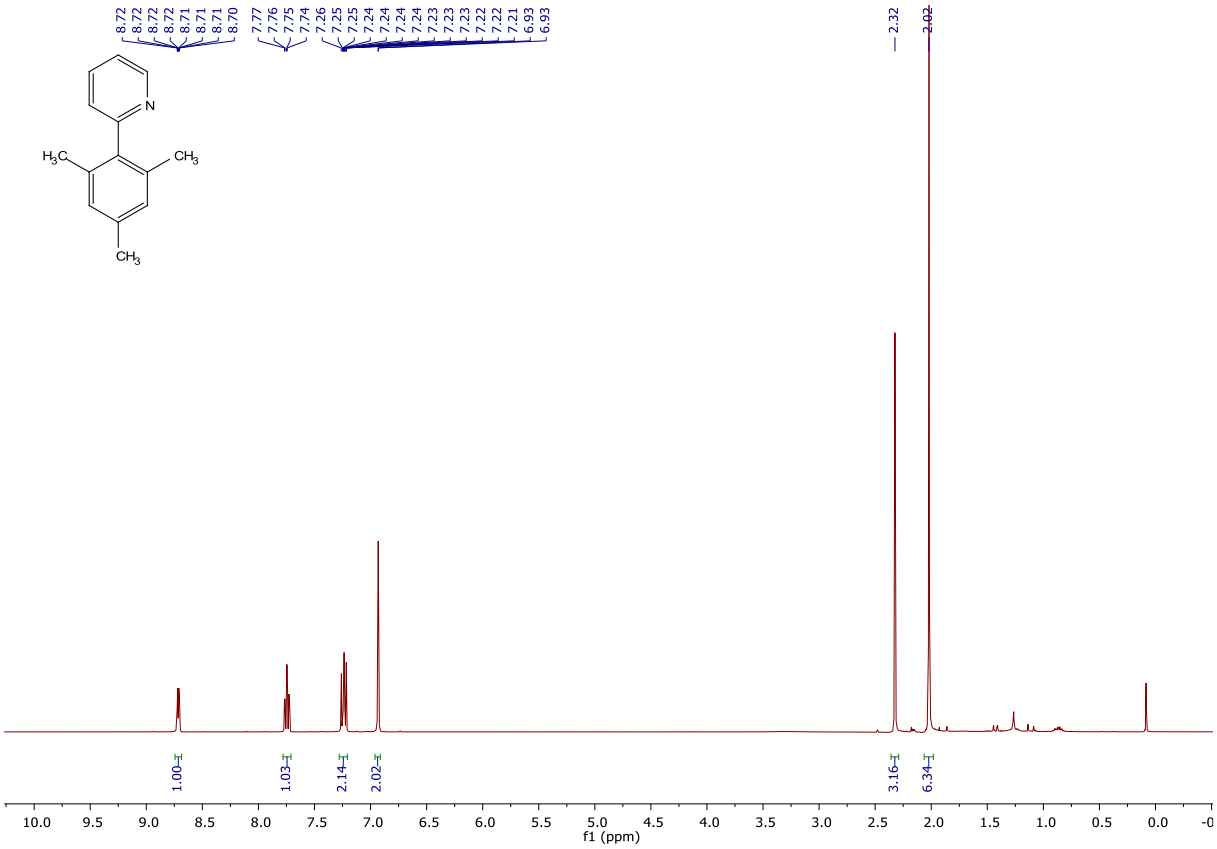
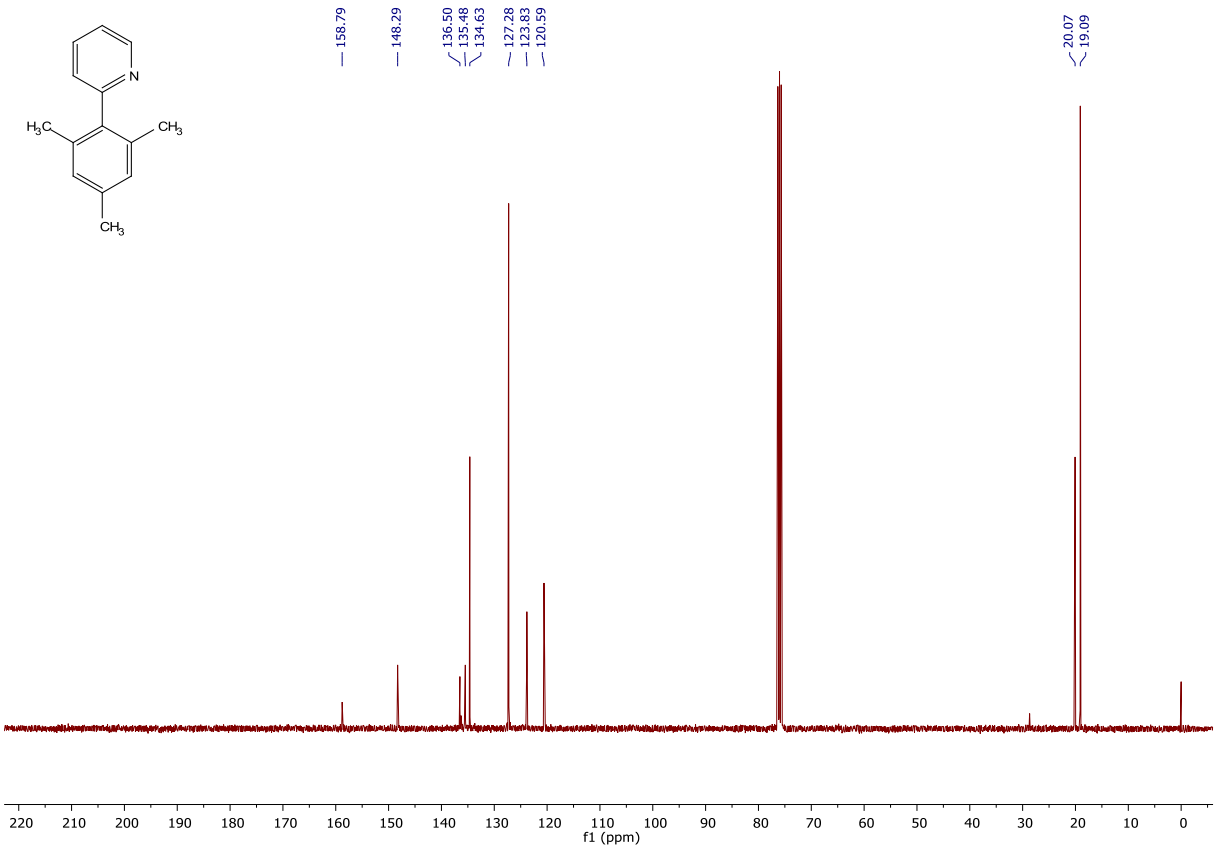
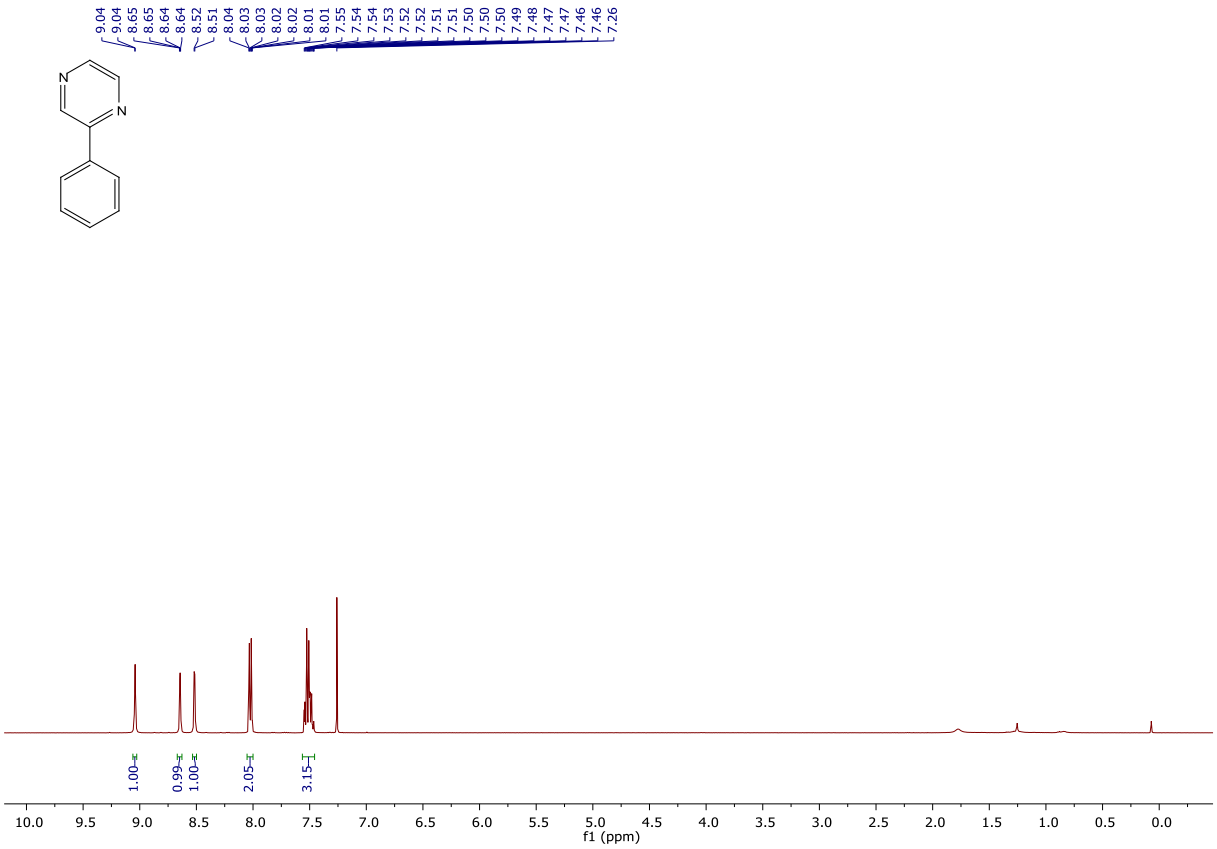
128.40
125.92
124.24
121.72
20.29
N
H3C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

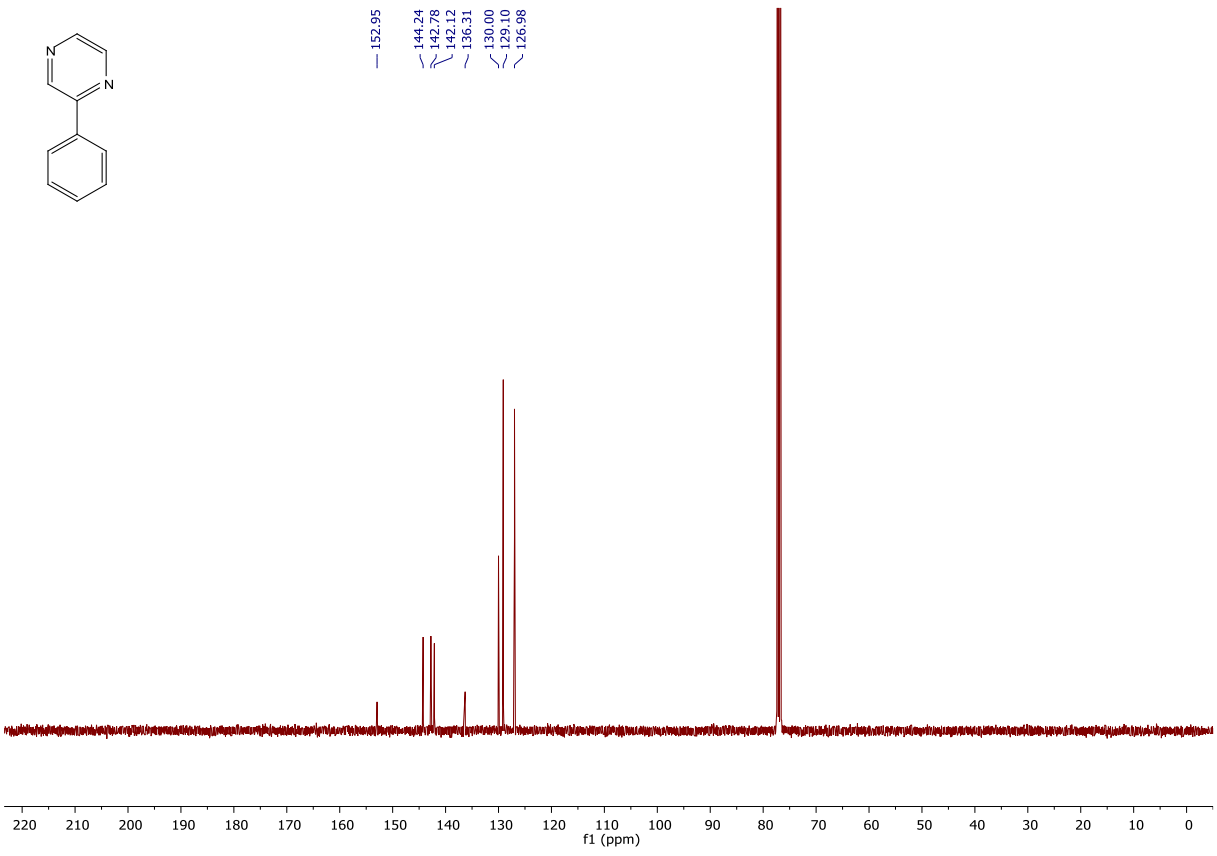

7.80
7.78
7.34
7.34
7.33
7.32
7.31
7.30
7.24
7.23
7.22
7.21
7.21
7.19
7.19
7.19
4.39
4.37
4.34
4.11
4.08
4.06
2.59
1.00
1.03
2.12
2.19
2.19
3.31
f1 (ppm)

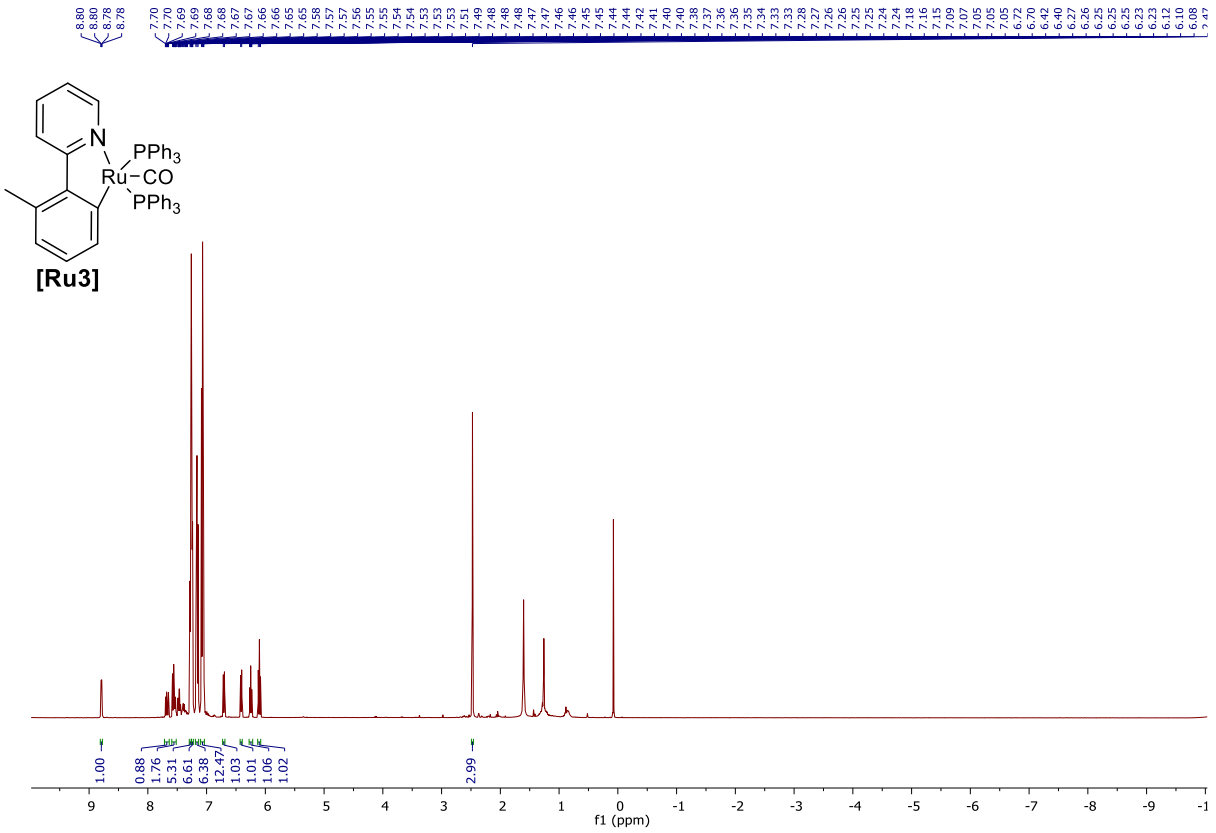

165.07
138.73
131.20
130.49
129.82
127.20
125.56
66.79
55.40
21.78
f1 (ppm)

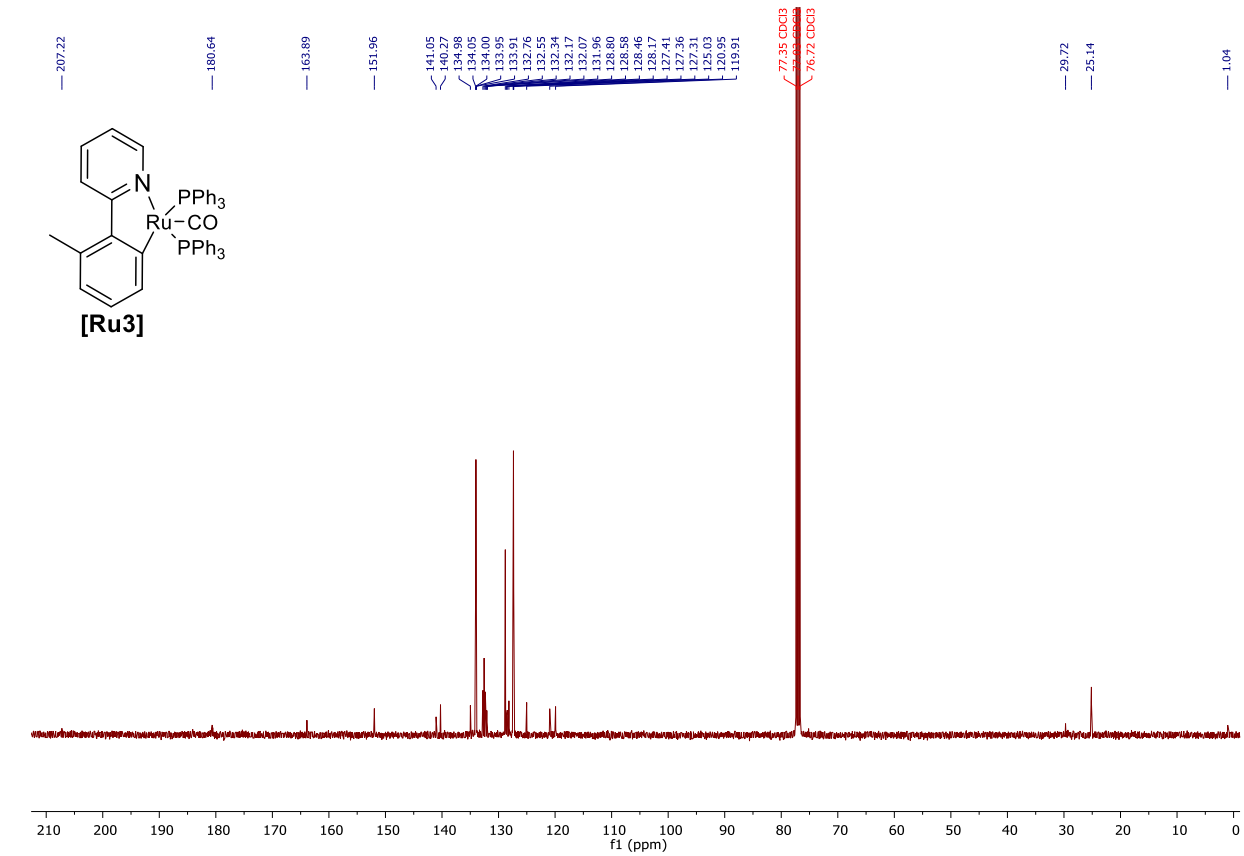

8.72
8.72
8.72
8.72
8.71
8.71
8.71
8.70
7.77
7.76
7.75
7.74
7.26
7.25
7.25
7.24
7.24
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.21
6.93
6.93
2.32
2.02
N
H3C
CH3
CH3
1.00
1.03
2.14
2.02
3.16
6.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

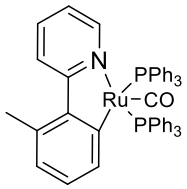

158.79
148.29
136.50
135.48
134.63
127.28
123.83
120.59
20.07
19.09
N
H3C
CH3
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.04
9.04
8.65
8.65
8.64
8.64
8.52
8.51
8.04
8.03
8.03
8.02
8.02
8.01
8.01
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.46
7.26
N
N
1.00
0.99
1.00
2.05
3.15
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)


N
N
152.95
144.24
142.78
142.12
136.31
130.00
129.10
126.98
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
PPh3
Ru–CO
PPh3
[Ru3]
f1 (ppm)


N
PPh3
Ru–CO
PPh3
[Ru3]
f1 (ppm)


N
PPh3
Ru−CO
PPh3

[Ru3]

33.85
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)