Supporting information.

Water Mediated Rearrangement of Alkynyl Cyclohexadienones: Access to *meta*-Alkenylated Phenols

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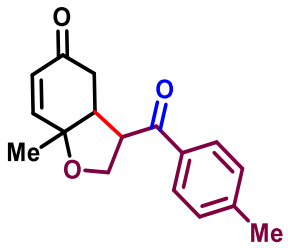
1). General Experimental Details

1H and 13C spectra were recorded on Bruker Avance 400 and 500 spectrophotometers. The chemical shifts (δ ppm) and coupling constants (Hz) were reported in the standard fashion with reference to internal chloroform. In the High resolution mass measurements were carried out using Micromass Q-ToF ESI instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) were performed on pre-coated 0.2 mm thick Merck 60 F245 silica plates and various combinations of ethyl acetate and Petroleum ether were used as eluent. Visualization of spots was accomplished by exposure to UV and basic KMnO4 solution. All compounds were purified using silica gel (100-200 mesh) column chromatography and gave spectroscopic data consistent with being ≥95%. All the commercial reagents were used as such without further purification. Alknylcyclohexadienones were synthesized as per the prior literature.[1]

7a-methyl-3-(4-methylbenzoyl)-2,3,3a,7a-tetrahydrobenzofuran-5(4H)-one (2a)



Colourless oil, 8 mg (15%) from 50.4 mg of **1a.**

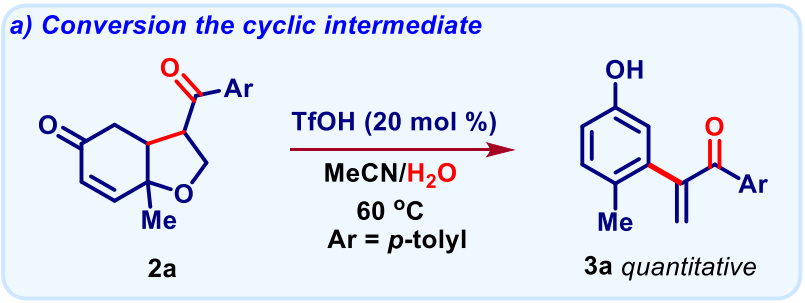
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 10.3 Hz, 1H), 6.03 (d, *J* = 10.3 Hz, 21H), 4.15 (t, *J* = 9.0 Hz, 1H), 3.85 (ddd, *J* = 16.2, 12.3, 6.9 Hz, 2H), 3.22 – 2.93 (m, 2H), 2.67 (dd, *J* = 17.4, 5.3 Hz, 1H), 2.56 (d, *J* = 17.3 Hz, 1H), 2.41 (s, 3H), 1.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 197.2, 153.0, 144.8, 133.8, 129.6, 128.9, 128.6, 80.6, 69.1, 51.6, 45.8, 37.5, 23.4, 21.7.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{19}O_3$ 271.1334; found 271.1339.

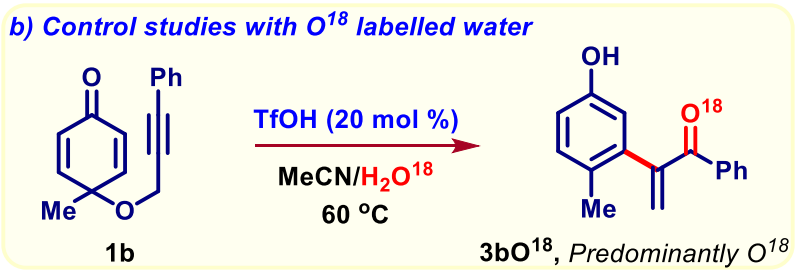
2). Mechanistic studies

Conversion of the cyclic intermediate.

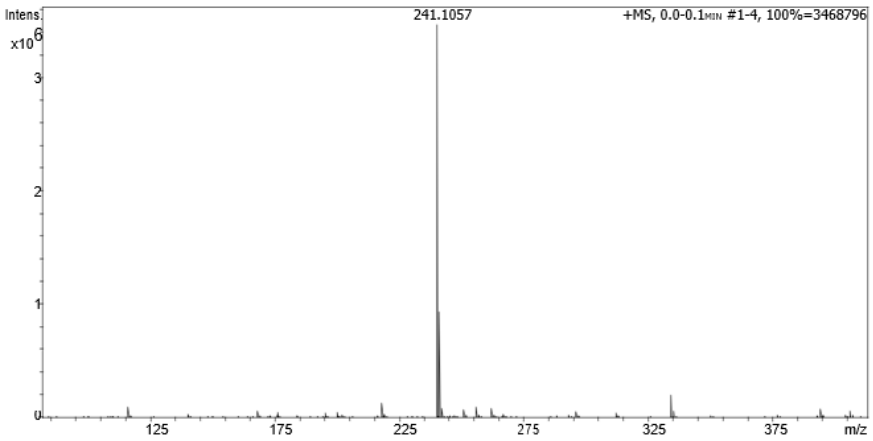


In an oven dried 3 mL dram vial equipped with a magnetic stirring bar was added **2a** (3 mg) triflic acid (0.3 mg) followed by 0.1 ml of MeCN:H_2O (1:1). Then the vial was closed and the reaction was stirred at 60 °C for 3 h in an oil bath. After the completion of the reaction the solvent was evaporated under vacuum. Proton and carbon NMR of the crude reaction mixture confirmed the quantitative formation of **3a**.

Oxygen labelled water experiment.

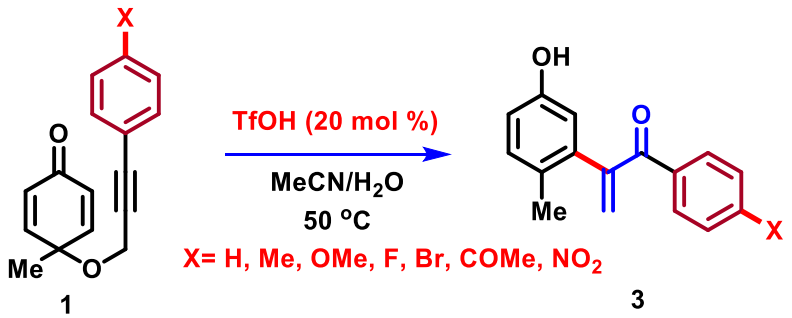


In an oven dried 3 mL dram vial equipped with a magnetic stirring bar was added **1b** (2.4 mg, 0.01 mmol.), triflic acid (0.3 mg, 0.002 mmol), followed by 0.1 ml of MeCN:H_2O^{18} (1:1). Then the vial was closed and the reaction was stirred at 60 °C for 6 h in an oil bath. After the completion of the reaction the solvent was evaporated under vacuum. The crude material was subjected to Silica gel column chromatography with 20 % EtOAc/Petroleum ether as eluent to afford the desired product **3bO^{18}** wherein the mass spectra showed predominant O^{18} incorporation M+H= 241.1057.



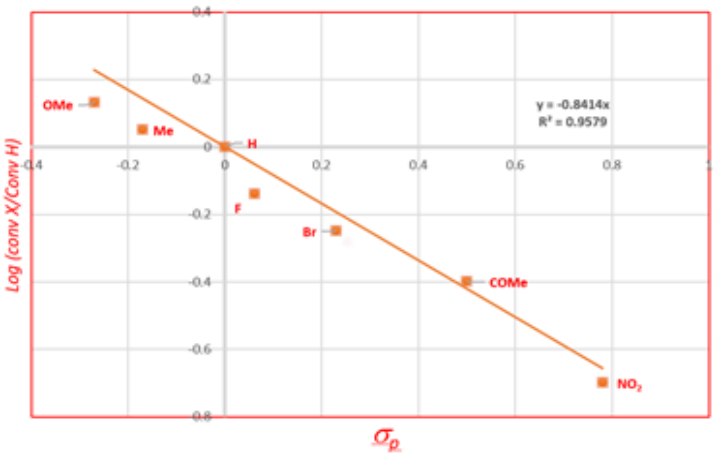
Hammet studies

c) Hammet studies and plot



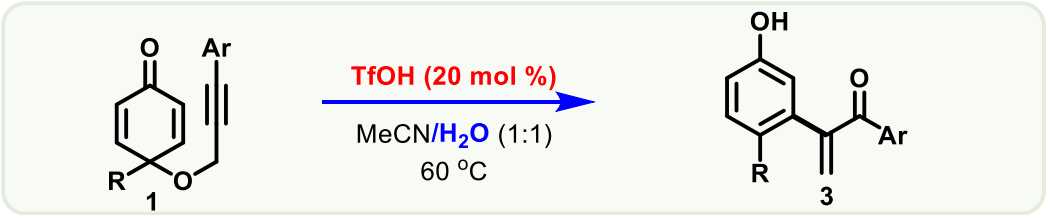
Sr. No	R=	SM (%)	conversion (%)	sp	log (conv.X/Conv.H)
1	OMe	66	34	-0.27	0.13
2	Me	72	28	-0.17	0.05
3	H	75	25	0.0	0
4	F	82	18	0.06	-0.14
5	Br	86	14	0.23	-0.25
6	COMe	90	10	0.5	-0.4
7	NO_2	95	5	0.78	-0.7

In an oven dried 10 mL dram vial equipped with a magnetic stirring bar was added **1** (0.1 mmol.), triflic acid (3 mg, 0.02 mmol), followed by 1 ml of MeCN:Water (1:1). Then the vial was closed and the reaction was stirred at 50 ºC for 3 h (TLC control) in an oil bath. After the completion of the reaction the solvent was evaporated under vacuum. The crude material was subjected to Silica gel column chromatography with EtOAc/Petroleum ether as eluent to isolate the remaining starting materials.



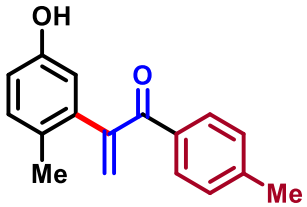
3) Experimental procedures and analytical data.

General procedure for the formation of *meta*-functionalised phenols.



General procedure: In an oven dried 10 mL dram vial equipped with a magnetic stirring bar was added **1a** (25.2 mg, 0.1 mmol.), triflic acid (3 mg, 0.02 mmol), followed by 1 ml of MeCN:Water (1:1). Then the vial was closed and the reaction was stirred at 60 °C for 6 h (TLC control) in an oil bath. After the completion of the reaction the solvent was evaporated under vacuum. The crude material was subjected to Silica gel column chromatography using 20% EtOAc in Petroleum ether as eluent to afford the desired product **3a** weighing 24.0 mg (95 %) as a colourless oil.

2-(5-hydroxy-2-methylphenyl)-1-phenylprop-2-en-1-one (3a)



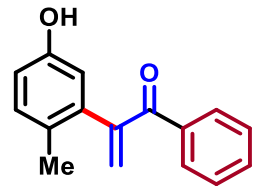
Colourless oil, 24 mg (95%) from 25.2 mg of **1a**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 2.6 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.98 (s, 1H), 5.96 (s, 1H), 2.44 (s, 3H), 2.13 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.3, 153.8, 149.0, 143.6, 139.4, 134.4, 131.3, 130.0, 129.1, 127.6, 127.3, 116.7, 115.3, 21.7, 19.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{17}O_2$ 253.1229; found 253.1220.

2-(5-hydroxy-2-methylphenyl)-1-phenylprop-2-en-1-one (3b).



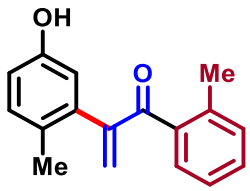
Colourless oil, 22.1 mg (93 %) from 23.8 mg of **1b**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 2.7 Hz, 1H), 6.73 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.02 (d, *J* = 0.8 Hz, 1H), 5.98 (d, *J* = 0.8 Hz, 1H), 2.13 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 154.1, 148.9, 139.0, 137.1, 132.8, 131.31, 129.9, 128.6 128.4, 127.3, 116.9, 115.5, 19.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{15}O_2$ 239.1072; found 239.1065.

2-(5-hydroxy-2-methylphenyl)-1-(o-tolyl)prop-2-en-1-one (3c)



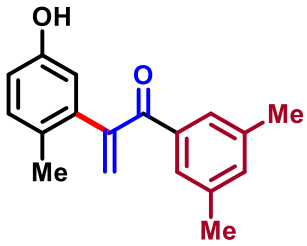
Colourless oil, 23.0 mg (91 %) from 25.2 mg of **1c.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.71 (s, 1H), 6.12 (s, 1H), 6.00 (s, 1H), 5.33 (br, 1H), 2.45 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 153.6, 150.2, 138.4, 138.2, 137.2, 132.0, 131.2, 131.2, 130.4, 128.7, 125.1, 116.8, 115.2, 20.0, 19.3.

HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{17}H_{17}O_2$ 253.1229; found 253.1219.

1-(3,5-dimethylphenyl)-2-(5-hydroxy-2-methylphenyl)prop-2-en-1-one (3d).



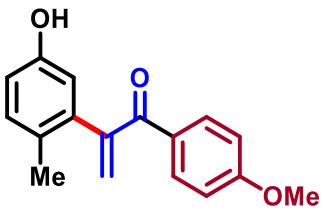
Yellow sticky solid, 24.5 mg (92%) from 26.6 mg of **1d.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.20 (s, 1H), 7.01 (d, J = 8.1 Hz, 1H), 6.74-6.69 (m, 2H), 6.00 (s, 1H), 5.94 (d, J = 0.7 Hz, 1H), 5.26 (s, 1H), 2.36 (s, 6H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 153.8, 149.0, 139.2, 138.0, 137.3, 134.4, 131.3, 128.0, 127.6, 127.6, 116.8, 115.3, 21.3, 19.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{19}O_2$ 267.1385; found 267.1381.

2-(5-hydroxy-2-methylphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (3e).



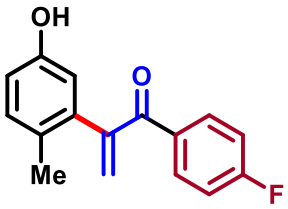
Colourless oil, 26.0 mg (97 %) from 26.8 mg of **1e**

^{1}H NMR (500 MHz, DMSO) δ 9.30 (s, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 8.7 Hz, 1H), 6.97 (d, J = 7.9 Hz, 2H), 6.75 – 6.59 (m, 1H), 5.92 (s, 1H), 5.81 (s, 1H), 3.84 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (126 MHz, DMSO) δ 195.0, 163.6, 155.8, 149.1, 139.7, 132.3, 131.5, 129.6, 126.3, 125.4, 116.7, 115.1, 114.4, 56.0, 19.6.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{17}O_3$ 269.1178; found 269.1170.

1-(4-fluorophenyl)-2-(5-hydroxy-2-methylphenyl)prop-2-en-1-one (3f)



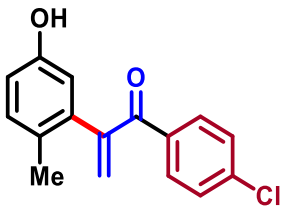
Colourless oil, 23.0 mg (90 %) from 25.6 mg of **1f**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.77 (s, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.00 (s, 1H), 5.98 (s, 1H), 5.59 (br, 1H), 2.12 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.3, 166.6 (C-F, *1J*C-F= 255.7 Hz), 164.6 (C-F, *1J*C-F= 255.7 Hz),154.0, 148.8, 138.9, 133.3, 132.5 (C-F, *3J*C-F 9.2 Hz), 132.4 (C-F, *3J*C-F 9.2 Hz) 131.4, 127.9, 127.4, 116.7, 115.7 (C-F, *2J*C-F = 21.3 Hz), 115.6 (C-F, *2J*C-F = 21.3 Hz), 115.6, 19.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{14}FO_2$ 257.0978; found 257.0968.

1-(4-chlorophenyl)-2-(5-hydroxy-2-methylphenyl)prop-2-en-1-one (3g)



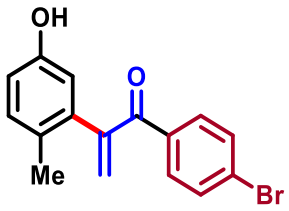
Colourless sticky solid, 24.2 mg (89%) from 27.2 mg of **1g**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.01 (s, 1H), 5.99 (s, 1H) 5.36 (br, 1H), 2.11 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.3, 153.9, 148.7, 139.2, 138.9, 135.3, 131.5, 131.2, 128.7, 128.1, 127.4, 116.7, 115.5, 19.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{14}ClO_2$ 273.0682; found 273.0765.

1-(4-bromophenyl)-2-(5-hydroxy-2-methylphenyl)prop-2-en-1-one (3h)



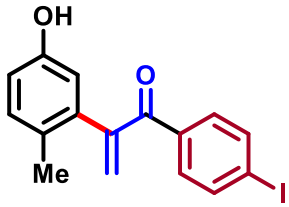
Yellow oil, 26.0 mg (86%) from 31.6 mg of **1h**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.61 – 7.53 (m, 2H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.77 – 6.68 (m, 2H), 5.98 (d, *J* = 0.8 Hz, 1H), 5.96 (d, *J* = 0.8 Hz, 1H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 154.0, 148.6, 138.8, 135.8, 132.3, 131.7, 131.3, 129.9, 128.3, 128.0, 116.7, 115.6, 19.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{14}BrO_2$ 317.0177; found 317.0166.

1-(4-iodophenyl)-2-(5-hydroxy-2-methylphenyl)prop-2-en-1-one (3i)



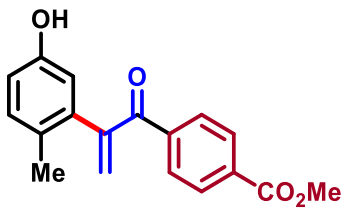
Colourless oil, 32.7 mg (90%) from 36.3 mg of **1i**

^{1}H NMR (400 MHz, DMSO) δ 9.33 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.65-6.63 (m, 2H), 6.01 (s, 1H), 5.87 (s, 1H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 195.9, 155.8, 148.4, 139.1, 138.0, 136.5, 131.5,128.7, 125.6, 116.8, 116.7, 115.6, 101.9, 19.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{14}IO_2$ 365.0038; found 365.0025.

methyl4-(2-(5-hydroxy-2-methylphenyl)acryloyl)benzoate (3j)



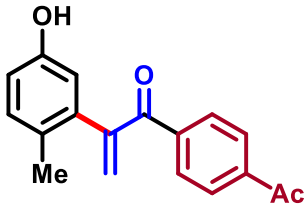
Colourless oil, 20.4 mg (69%) from 29.6 mg of **1j**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.84 – 6.69 (m, 2H), 6.06 (s, 1H), 6.03 (s, 1H), 3.97 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 166.3, 153.9, 148.7, 140.8, 138.7, 133.4, 131.4, 129.5, 129.1, 127.5, 116.6, 115.5, 52.5, 19.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{17}O_4$ 297.1127; found 297.1119.

1-(4-acetylphenyl)-2-(5-hydroxy-2-methylphenyl)prop-2-en-1-one (3k)



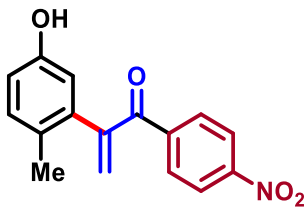
Colourless oil, 17.1 mg (61%) from 28.0 mg of **1k**

^{1}H NMR (400 MHz, DMSO) δ 9.37 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 1H), 6.66-6.65 (m, 2H), 6.07 (s, 1H), 5.91 (s, 1H), 2.60 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 198.3, 196.1, 155.8, 148.6, 140.8, 140.0, 138.9, 131.5, 130.0, 129.0, 128.8, 125.5, 116.9, 115.7, 27.4, 19.4.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{17}O_3$ 281.1178; found 281.1169.

2-(5-hydroxy-2-methylphenyl)-1-(4-nitrophenyl)prop-2-en-1-one (3l)



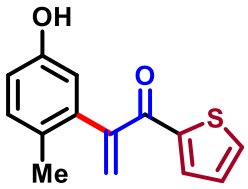
Colourless oil, 12.1 mg (43%) from 28.3 mg of **1l**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.7 Hz, 2H), 8.00 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.82 – 6.75 (m, 2H), 6.11 (s, 1H), 6.08 (s, 1H), 2.11 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.4, 153.9, 148.4, 142.3, 138.3, 132.4, 131.6, 130.5, 129.7, 127.5, 123.58, 116.6, 115.7, 19.4.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{14}NO_4$ 284.0923; found 284.0917.

2-(5-hydroxy-2-methylphenyl)-1-(thiophen-2-yl)prop-2-en-1-one (3m)



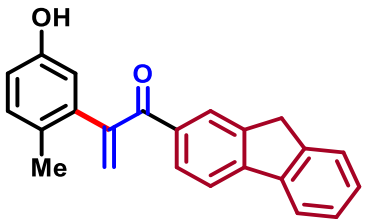
Colourless oil, 20.0 mg (82%) from 24.4 mg of **1m**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.61 – 7.48 (m, 1H), 7.12 – 7.05 (m, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 2.6 Hz, 1H), 6.77 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.19 (d, *J* = 0.8 Hz, 1H), 5.85 (s, 1H), 5.57 (br, 1H), 2.13 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 187.8, 153.9, 148.7, 143.3, 138.9, 134.6, 134.4, 131.4, 128.1, 127.8, 126.5, 116.9, 115.7, 19.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{14}H_{13}O_2S$ 245.0636; found 245.0633

1-(9H-fluoren-2-1-(9H-fluoren-2-yl)-2-(5-hydroxy-2-methylphenyl)prop-2-en-1-one (3n).



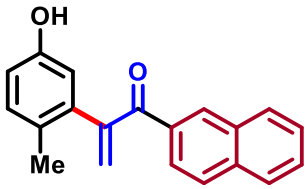
Colourless sticky solid, 27.0 mg (83%) from 32.6 mg of **1n**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.87-7.82 (m, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.46-7.39 (m, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 2.5 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.03 (s, 1H), 6.03 (s, 1H), 5.29 (s, 1H), 3.97 (s, 2H), 2.18 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 153.9, 149.2, 146.3, 144.5, 143.2, 140.5, 139.4, 135.4, 131.4, 129.4, 128.1, 127.6, 127.4, 127.1, 126.5, 125.3, 120.9, 119.4, 116.8, 115.4, 36.9, 19.6.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{19}O_2$ 327.1385; found 327.1385

2-(5-hydroxy-2-methylphenyl)-1-(naphthalen-2-yl)prop-2-en-1-one (3o)



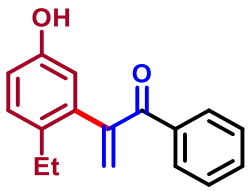
Colourless oil, 25.0 mg (87%) from 28.8 mg of **1o**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.26 (m, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.90 (dd, *J* = 6.8, 2.6 Hz, 1H), 7.75 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.53 – 7.44 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.75 (dd, *J* = 8.1, 2.7 Hz, 1H), 6.12 (d, *J* = 1.0 Hz, 1H), 6.05 (d, *J* = 0.9 Hz, 1H), 5.04 (br, 1H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 153.6, 150.7, 138.6, 135.7, 133.9, 131.8, 131.6, 131.3, 131.0, 128.4, 128.1, 127.5, 126.5, 125.5, 124.1, 116.9, 115.3, 19.4.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{17}O_2$ 289.1228; found 289.1226.

2-(2-ethyl-5-hydroxyphenyl)-1-phenylprop-2-en-1-one (3p)



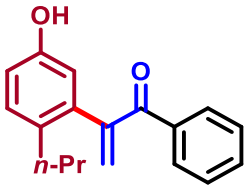
Colourless oil, 24.2 mg (96%) from 25.2 mg of **1p**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.85 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.79 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.03 (d, *J* = 0.8 Hz, 1H), 5.99 (s, 1H), 5.18 (br, 1H), 2.46 (q, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 153.6, 148.8, 138.8, 137.2, 133.8, 132.7, 129.8, 129.5, 128.5, 128.4, 117.0, 115.6, 25.8, 15.3.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{17}O_2$ 253.1229.; found 253.1226.

2-(5-hydroxy-2-propylphenyl)-1-phenylprop-2-en-1-one (3q)



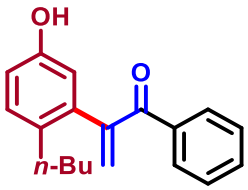
Colourless oil, 25.3 mg (95%) from 26.6 mg of **1q**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.82 – 6.67 (m, 2H), 6.03 (s, 1H), 5.98 (d, *J* = 0.5 Hz, 1H), 5.69 (s, 1H), 2.53 – 2.25 (m, 2H), 1.54–1.50 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 153.8, 148.8, 138.8, 137.1, 132.8, 132.2, 130.3, 129.9, 128.6, 128.4, 117.2, 115.6, 35.1, 24.5, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{19}O_2$ 267.1385; found 267.1394.

2-(2-butyl-5-hydroxyphenyl)-1-phenylprop-2-en-1-one (3r)



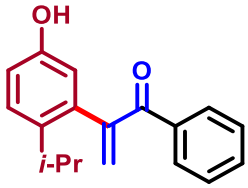
Yellow oil, 25.8 mg (92%) from 28.0 mg of **3r**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.83 – 6.70 (m, 2H), 6.03 (s, 1H), 5.98 (s, 1H), 2.49 – 2.28 (m, 2H), 1.50-1.44 (m, 2H), 1.36 – 1.19 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 153.8, 148.8, 138.8, 137.1, 132.8, 132.3, 130.2, 129.9, 128.6, 128.4, 117.2, 115.6, 33.4, 32.7, 22.6, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{21}O_2$ 281.1541; found 281.1540.

2-(5-hydroxy-2-isopropylphenyl)-1-phenylprop-2-en-1-one (3s)



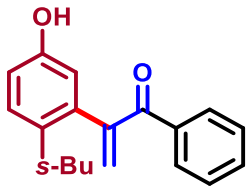
Colourless oil, 24.7 mg (93%) from 26.6 mg of **1s**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 14.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.80 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.71 (d, *J* = 2.7 Hz, 1H), 6.01 (s, 1H), 5.99 (s, 1H), 2.83-2.77 (m, 1H), 1.11 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 153.4, 148.8, 138.6, 138.2, 137.1, 132.7, 129.9, 128.9, 128.4, 126.6, 116.9, 116.0, 30.2, 24.0.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{19}O_2$ 267.1385; found 267.1384.

2-(2-(sec-butyl)-5-hydroxyphenyl)-1-phenylprop-2-en-1-one (3t)



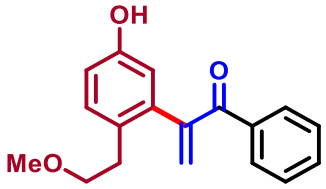
Colourless oil, 26.3 mg (94%) from 28.0 mg of **1t**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.82 – 6.76 (m, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 5.99 (s, 1H), 5.97 (s, 1H), 4.85 (s, 1H), 2.50 (dd, *J* = 13.9, 6.9 Hz, 1H), 1.62 – 1.39 (m, 2H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.70 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 153.4, 148.9, 138.8, 137.4, 137.1, 132.7, 129.9, 128.9, 128.4, 126.8, 117.0, 116.0, 37.3, 31.2, 21.7, 12.2.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{21}O_2$ 281.1541; found 281.1545.

2-(5-hydroxy-2-(2-methoxyethyl)phenyl)-1-phenylprop-2-en-1-one (3u).



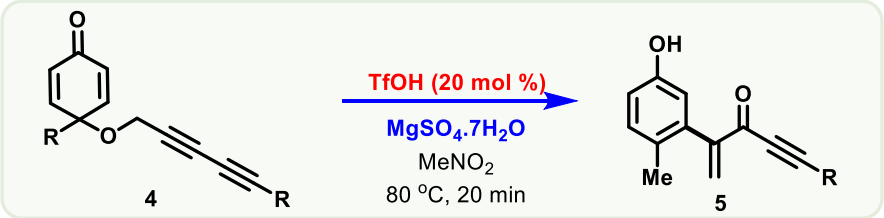
Colourless oil, 23.1 mg (82%) from 28.2 mg of **1u**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.11 – 6.97 (m, 1H), 6.82 – 6.60 (m, 2H), 6.02 (s, 1H), 5.98 (s, 1H), 3.48 (t, *J* = 7.2 Hz, 2H), 3.26 (s, 3H), 2.72 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 154.4, 148.4, 139.2, 137.1, 132.8, 130.8, 129.9, 129.1, 128.4, 128.0, 117.2, 115.6, 73.1, 58.5, 32.9.

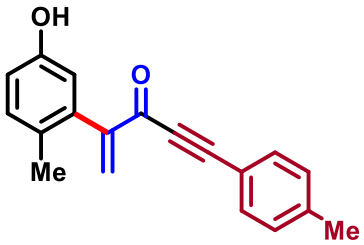
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{19}O_3$ 283.1334; found 283.1328.

General procedure for the formation of *meta*- enynone tethered phenols.



General procedure: In an oven dried 10 mL dram vial equipped with a magnetic stirring bar was added **4a** (27.6 mg, 0.1 mmol.), 1 mL of $MeNO_2$ and 150 mg $MgSO_4.7H_2O$ followed by triflic acid (3 mg, 0.02 mmol), Then the vial was closed and the reaction was stirred at 80 °C for 20 mins (TLC control) in an oil bath. After the completion of the reaction the solvent was evaporated under vacuum. The crude material was subjected to Silica gel column chromatography using 20% EtOAc in Petroleum ether as eluent to afford the desired product **5a** weighing 25.4 mg (92 %) as a colourless oil.

2-(5-hydroxy-2-methylphenyl)-5-(p-tolyl)pent-1-en-4-yn-3-one (5a).



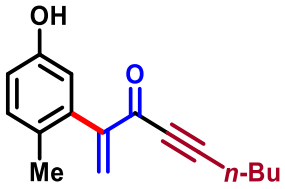
Colourless oil, 25.4 mg (92%) from 27.6 mg of **5a**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.84 (s, 1H), 6.80 – 6.72 (m, 1H), 6.61 (s, 1H), 6.11 (s, 1H), 5.56 (s, 1H), 2.39 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.63, 153.61, 149.76, 141.63, 136.97, 133.16, 132.16, 130.99, 129.48, 128.18, 116.79, 115.51, 93.86, 86.53, 21.77, 19.08.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{17}O_2$ 277.1229; found 277.1224.

2-(5-hydroxy-2-methylphenyl)non-1-en-4-yn-3-one (5b)



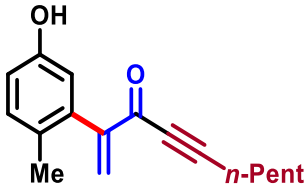
Colourless oil, 20.8 mg (86%) from 24.2 mg of **5b**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.2 Hz, 1H), 6.81 – 6.68 (m, 2H), 6.56 (d, *J* = 2.6 Hz, 1H), 6.06 (s, 1H), 2.42 (t, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.64 – 1.49 (m, 2H), 1.49 – 1.38 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 153.6, 149.8, 137.0, 132.3, 130.9, 128.0, 116.6, 115.3, 96.3, 79.2, 29.7, 22.0, 19.0, 18.8, 13.5.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{19}O_2$ 243.1385; found 243.1385.

2-(5-hydroxy-2-methylphenyl)dec-1-en-4-yn-3-one (5c)



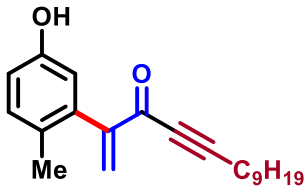
Colourless oil, 21.0 mg (82%) from 25.6 mg of **5c**

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 1.1 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.53 (d, *J* = 2.7 Hz, 1H), 6.06 (d, *J* = 1.1 Hz, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.04 (s, 3H), 1.65 – 1.53 (m, 2H), 1.44 – 1.25 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2, 153.7, 149.8, 136.7, 132.9, 130.9, 127.7, 116.7, 115.5, 97.1, 79.2, 31.0, 27.4, 22.1, 19.1, 19.0, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{21}O_2$ 257.1542; found 257.1540.

2-(5-hydroxy-2-methylphenyl)tetradec-1-en-4-yn-3-one (5d)



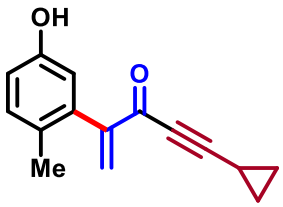
Colourless oil, 26.2 mg (84%) from 31.2 mg of **5d.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 0.8 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.58 (d, *J* = 2.6 Hz, 1H), 6.09 (d, *J* = 0.8 Hz, 1H), 5.17 (br, 1H) 2.44 (t, *J* = 7.1 Hz, 2H), 2.08 (s, 3H), 1.67 – 1.56 (m, 2H), 1.45 – 1.39 (m, 2H), 1.28 (br, 10H), 0.91 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 153.4, 149.8, 136.7, 132.4, 130.9, 128.2, 116.6, 115.3, 96.4, 79.2, 31.9, 29.4, 29.3, 29.0, 28.9, 27.7, 22.7, 19.1, 19.0, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{29}O_2$ 313.2168; found 313.2164

5-cyclopropyl-2-(5-hydroxy-2-methylphenyl)pent-1-en-4-yn-3-one (5e)



Colourless oil, 18.5 mg (82%) from 22.6 mg of **5e.**

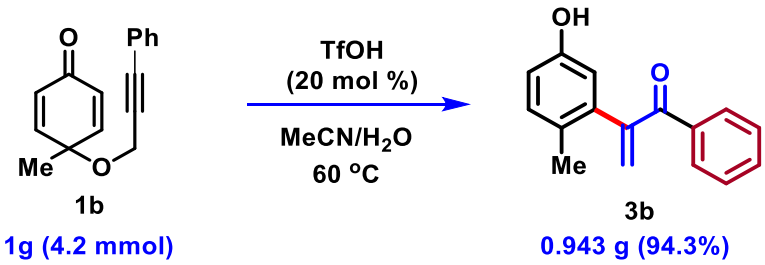
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.2 Hz, 1H), 6.71 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.68 (s, 1H), 6.54 (d, *J* = 2.6 Hz, 1H), 6.02 (s, 1H), 5.27 (s, 1H), 2.05 (s, 3H), 1.47-1.40 (m, 1H), 1.11 – 0.79 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 153.4, 149.7, 137.1, 131.8, 130.9, 128.2, 116.7, 115.3, 100.9, 75.1, 19.0, 9.8.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{15}H_{15}O_2$ 227.1072; found 227.1067.

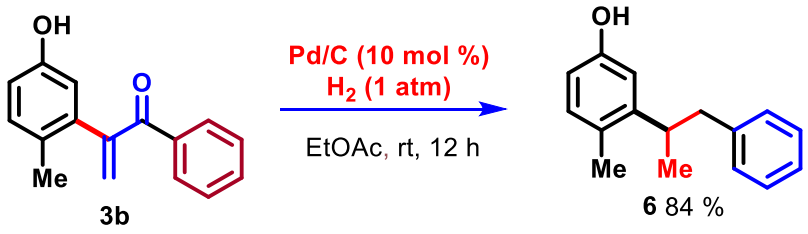
Synthetic utility

Gram scale synthesis



General procedure: In an oven dried 50 mL dram vial equipped with a magnetic stirring bar was added **1b** (1 g, 4.2 mmol.), triflic acid (126 mg, 0.84 mmol), followed by 20 mL of MeCN:Water (1:1). Then the vial was closed and the reaction was stirred at 60 °C for 6 h (TLC control) in an oil bath. After the completion of the reaction the solvent was evaporated under vacuum. The crude material was subjected to Silica gel column chromatography using 20% EtOAc in Petroleum ether as eluent to afford the desired product **3b** weighing 0.943 g (94.3%) as a colourless sticky solid.

4-methyl-3-(1-phenylpropan-2-yl)phenol (6)



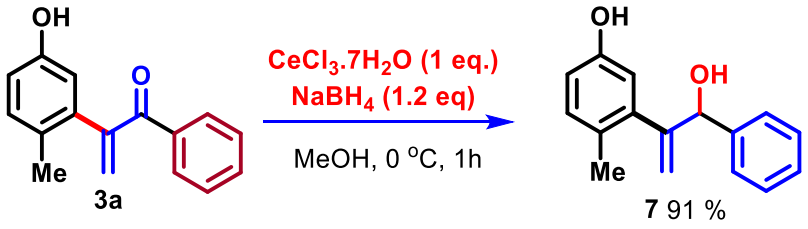
3b (50 mg, 0.21 mmol) was dissolved in 1 mL EtOAc in a round bottom flask, 10% Pd/C (22 mg) was added under nitrogen atmosphere. The reaction mixture was stirred under hydrogen atmosphere overnight at room temperature after which the mixture was filtered through a celite pad and concentrated under vacuum and purified by flash chromatography using 20% EtOAc in Petroleum ether to furnish 40 mg (84%) of **6** as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 2.6 Hz, 1H), 6.62 (dd, *J* = 8.1, 2.6 Hz, 1H), 4,84 (br, 1H) 3.32 – 3.14 (m, 1H), 2.96-2.92 (m, 1H), 2.74-2.69 (m, 1H), 2.19 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 146.8, 140.9, 131.1, 129.1, 128.2, 127.5, 125.9, 112.6, 112.6, 44.3, 36.8, 20.4, 18.6.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{19}O$ 227.1436; found 227.1434.

3-(3-hydroxy-3-phenylprop-1-en-2-yl)-4-methylphenol (7)



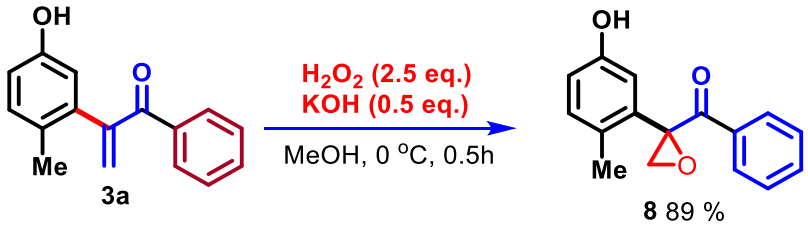
3b (50 mg, 0.21 mmol) was dissolved in 1 ml MeOH in a round bottom flask, $CeCl_3.7H_2O$ (78.2 mg was added and the reaction was cooled to 0 °C. 10 mg of $NaBH_4$ was then added slowly under stirring and the reaction was continued for 60 mins. The mixture was then partitioned between water and EtOAc, the organic layer was collected, dried over Na_2SO_4 evaporated under vacuum and purified by flash chromatography using 40% EtOAc in Petroleum ether to furnish 45.8 mg (91%) of **7** as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.15 (m, 5H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.65 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.43 (d, *J* = 2.6 Hz, 1H), 5.57 (s, 1H), 5.41 (s, 1H), 5.07 (s, 1H), 2.03 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 150.6, 141.3, 140.6, 131.1, 128.3, 127.9, 127.8, 126.8, 116.1, 114.3, 114.3, 77.3, 18.6.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{17}O_2$ 241.1228; found 241.1223.

(2-(5-hydroxy-2-methylphenyl)oxiran-2-yl)(phenyl)methanone (8)



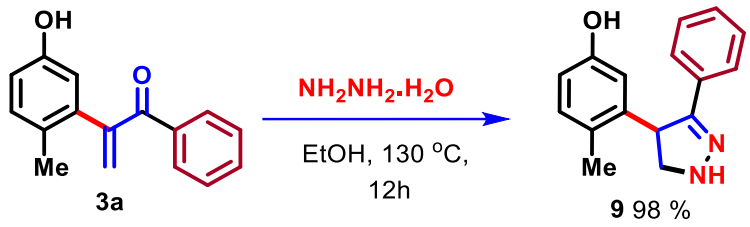
3b (50 mg, 0.21 mmol) and 6 mg of KOH were dissolved in 1 ml MeOH in a round bottom flask, the rection was cooled to 0 °C. 24 mg of 30% H_2O_2 solution was then added slowly under stirring and the reaction was continued for 30 mins. The mixture was then evaporated under vacuum and purified by flash chromatography using 20% EtOAc in Petroleum ether to furnish 47.5 mg (89%) of **8** as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.95 (m ,2H), 7.50 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 2.6 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.72 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.95 (s, 1H), 3.41 (d, *J* = 5.7 Hz, 1H), 3.15 (d, *J* = 5.7 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1 154.0, 135.4, 134.9, 133.3, 131.7, 129.4, 129.4, 128.4, 115.8, 114.6, 63.7, 53.0, 18.8.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{15}O_3$ 255.1021; found 255.1024.

4-methyl-3-(3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)phenol (9)



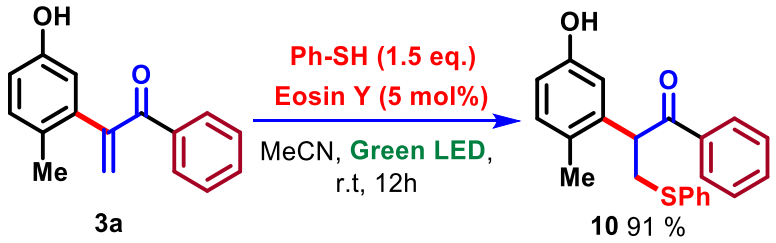
3b (50 mg, 0.21 mmol) was dissolved in 1 ml EtOH in a reaction tube, 0.5 ml of hydrazine hydrate was added and the rection was stirred at 130 °C overnight in an oil bath. The mixture was then evaporated under vacuum and purified by flash chromatography using 50% EtOAc in Petroleum ether to furnish 51.9 mg (98%) of **9** as a colourless sticky solid.

^{1}H NMR (400 MHz, DMSO) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.12 (m, 3H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.49 (d, *J* = 6.1 Hz, 1H), 6.28 (s, 1H), 4.59 (dd, *J* = 10.9, 4.1 Hz, 1H), 3.88 – 3.71 (m, 1H), 3.24 – 3.05 (m, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 155.9, 152.4, 140.5, 133.1, 131.7, 128.9, 128.3, 126.1, 125.3, 114.3, 114.0, 56.3, 46.8, 19.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{17}N_2O$ 253.1341; found 253.1345.

2-(5-hydroxy-2-methylphenyl)-1-phenyl-3-(phenylthio)propan-1-one (10)



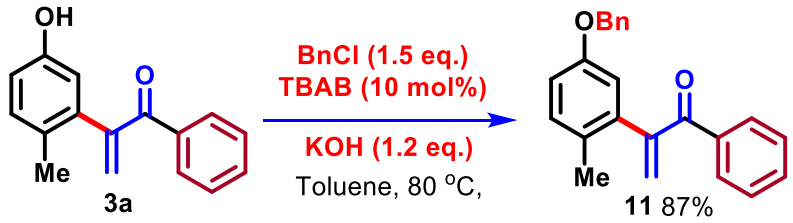
3b (50 mg, 0.21 mmol), 35 mg of thiophenol and 6.8 mg of Eosin Y were dissolved in 1 ml MeCN in a 5 ml dram vial. The reaction mixture was then stirred overnight under green LED irradiation. The mixture was then evaporated under vacuum and purified by flash chromatography using 30% EtOAc in Petroleum ether to furnish 63.6 mg (87%) of **10** as a colourless sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.54 – 7.44 (m, 1H), 7.42 – 7.19 (m, 7H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 2.5 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.33 (br, 1H) 4.92 (dd, *J* = 9.4, 4.5 Hz, 1H), 3.71 (dd, *J* = 13.4, 9.4 Hz, 1H), 3.13 (dd, *J* = 13.4, 4.5 Hz, 1H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 154.8, 137.2, 136.7, 136.0, 133.4, 132.4, 130.8, 129.0, 128.7, 128.5, 126.8, 115.0, 113.9, 49.6, 37.4, 18.7.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{21}O_2S$ $[M+H]^+$ 349.1262; found 349.1254.

2-(5-(benzyloxy)-2-methylphenyl)-1-phenylprop-2-en-1-one (11)



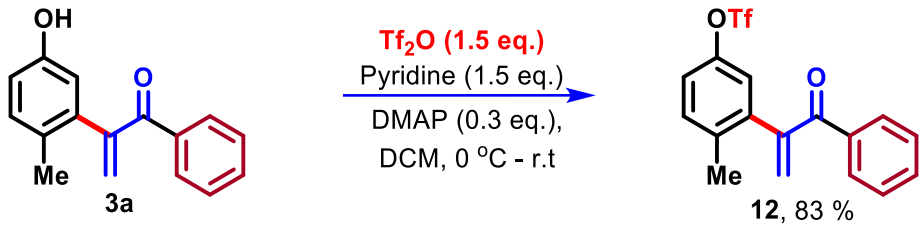
3b (50 mg, 0.21 mmol), 40 mg benzyl chloride, 6.8 mg TBAB and 14.1 mg of KOH were dissolved in 1 ml toluene in a rection tube, the rection was then heated to 80 °C and stirred overnight in an oil bath. The mixture was then evaporated under vacuum and purified by flash chromatography using 20% EtOAc in Petroleum ether to furnish 59.9 mg (87%) of **11** as a brown sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.51 – 7.30 (m, 7H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.90 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.01 (d, *J* = 5.1 Hz, 2H), 5.08 (s, 2H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 157.1, 149.2, 139.3, 137.3, 137.1, 132.6, 131.2, 129.8, 128.6, 128.5, 128.4, 128.3, 128.0, 127.6, 116.5, 114.6, 70.2, 19.6.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{21}O_2$ 329.1542; found 329.1548

4-methyl-3-(3-oxo-3-phenylprop-1-en-2-yl)phenyl trifluoromethanesulfonate (12)



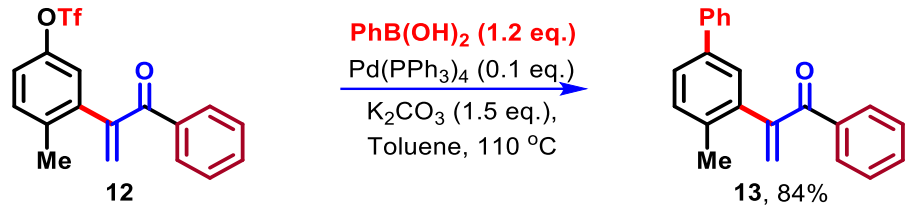
3b (50 mg, 0.21 mmol), 25.0 mg pyridine and 7.7 mg of DMAP were dissolved in 2 ml DCM in a round bottom flask, the rection was cooled to 0 °C. 89 mg of triflic anhydride was then added slowly under stirring and the reaction was continued overnight at room temperature. The mixture was then evaporated under vacuum and purified by flash chromatography using 20% EtOAc in Petroleum ether to furnish 64.5 mg (83%) of **12** as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.27-7.24 (m, 2H), 7.19 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.12 (s, 2H), 2.25 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 147.6, 147.4, 140.4, 136.9, 136.5, 132.9, 131.8, 129.7, 128.5, 122.6 (C-F, *1J*C-F= 320.8 Hz), 122.5, 120.8, 120.1 (C-F, *1J*C-F= 320.8 Hz), 117.5 (C-F, *1J*C-F= 320.8 Hz), 115.0 (C-F, *1J*C-F= 320.8 Hz), 19.9.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{14}F_3O_4S$ 371.0565; found 371.0557.

2-(4-methyl-[1,1'-biphenyl]-3-yl)-1-phenylprop-2-en-1-one (13)



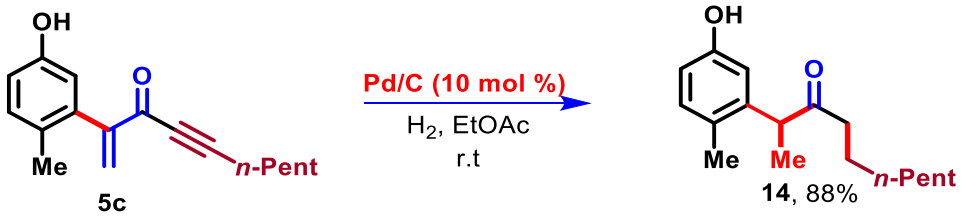
To **12** (37 mg, 0.1 mmol), 30.7 mg of phenylboronic acid, 24.2 mg of $Pd(PPh_3)_4$ and 43.5 mg of K_2CO_3 in a reaction tube with stirrer was added 1 ml toluene and the reaction was continued for 24 hrs at 130 °C under argon atmosphere in an oil bath. The mixture was then evaporated under vacuum and purified by flash chromatography using 20% EtOAc in Petroleum ether to furnish 25 mg (84%) of **13** as a white sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.52 – 7.41 (m, 6H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 6.11 (s, 1H), 6.04 (s, 1H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 149.2, 140.7, 139.1, 138.7, 137.3, 134.8, 132.6, 130.8, 129.8, 128.7, 128.5, 128.4, 127.2, 127.0, 20.2.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{19}O$ $[M+H]^+$ 299.1436; found 299.1432.

2-(5-hydroxy-2-methylphenyl)decan-3-one (14)



5c (20.5 mg, 0.08 mmol) was dissolved in 0.5 ml EtOAc in a round bottom flask, 10% Pd/C (8.4 mg) was added under nitrogen atmosphere. The reaction mixture was stirred under hydrogen atmosphere overnight at room temperature after which the mixture was filtered

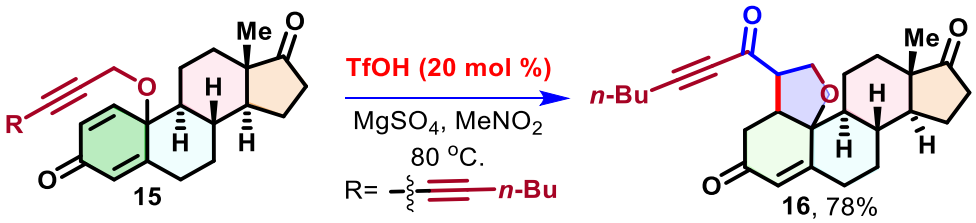
through a celite pad and concentrated under vacuum and purified by flash chromatography using 20% EtOAc in Petroleum ether as eluent to furnish 18.4 mg (88%) of **14** as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.3 Hz, 1H), 6.73 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 3.98 (q, *J* = 6.8 Hz, 1H), 2.48 – 2.28 (m, 5H), 1.63 – 1.43 (m, 2H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.30 – 1.15 (m, 8H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.7, 155.1, 139.9, 131.9, 126.8, 114.3, 113.5, 48.7, 41.4, 31.6, 29.0, 28.9, 24.0, 22.6, 18.9, 16.9, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_{27}O_2$ 263.2011; found 263.2007.

(3aS,5aS,8R,8aS,13aS,13bS)-8-(hept-2-ynoyl)-3a-methyl-1,2,3a,4,5,5a,7,8,8a,9,12,13,13a,13b-tetradecahydrocyclopenta[7,8]phenanthro[4a,4-b]furan-3,10-dione (16)



A 10 ml dram vial equipped with a magnetic stirring bar was charged **15** (10 mg, 0.026 mmol.), 0.3 ml of $MeNO_2$ and 150 mg $MgSO_4.7H_2O$ followed by triflic acid (0.8 mg). Then the vial was closed and the reaction was stirred at 80 °C for 20 mins (TLC control) in an oil bath. After the completion of the reaction the solvent was evaporated under vacuum. The crude material was subjected to silica gel column chromatography with 40% EtOAc in Petroleum ether as eluent to afford **16** weighing 8.6 mg (78 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (s, 1H), 4.11 (dd, *J* = 9.1, 5.3 Hz, 1H), 3.83 (t, *J* = 8.8 Hz, 1H), 3.21 – 2.96 (m, 2H), 2.77 – 2.62 (m, 2H), 2.55 – 2.43 (m, 2H), 2.39 (t, *J* = 7.1 Hz, 2H), 2.28 – 2.18 (m, 1H), 2.16 – 2.09 (m, 2H), 2.01 – 1.84 (m, 2H), 1.83 – 1.72 (m, 2H), 1.62 – 1.52 (m, 4H), 1.49 – 1.37 (m, 4H), 1.36 – 1.26 (m, 2H), 0.98 – 0.89 (m, 6H).

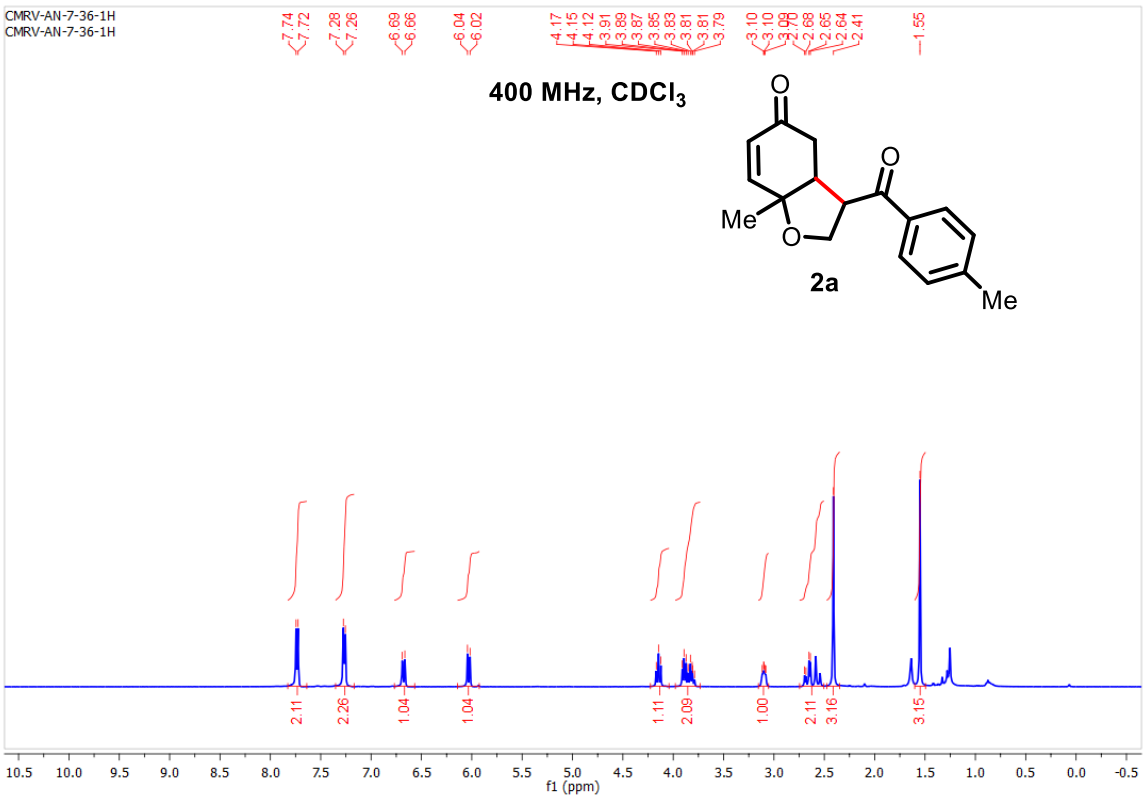
^{13}C NMR (101 MHz, $CDCl_3$) δ 220.2, 196.4, 186.0, 165.7, 124.8, 97.5, 84.2, 80.0, 66.6, 57.9, 50.7, 48.7, 47.9, 40.4, 37.5, 36.4, 35.8, 32.1, 31.7, 31.0, 29.6, 22.0, 21.8, 21.0, 18.7, 13.8, 13.5.

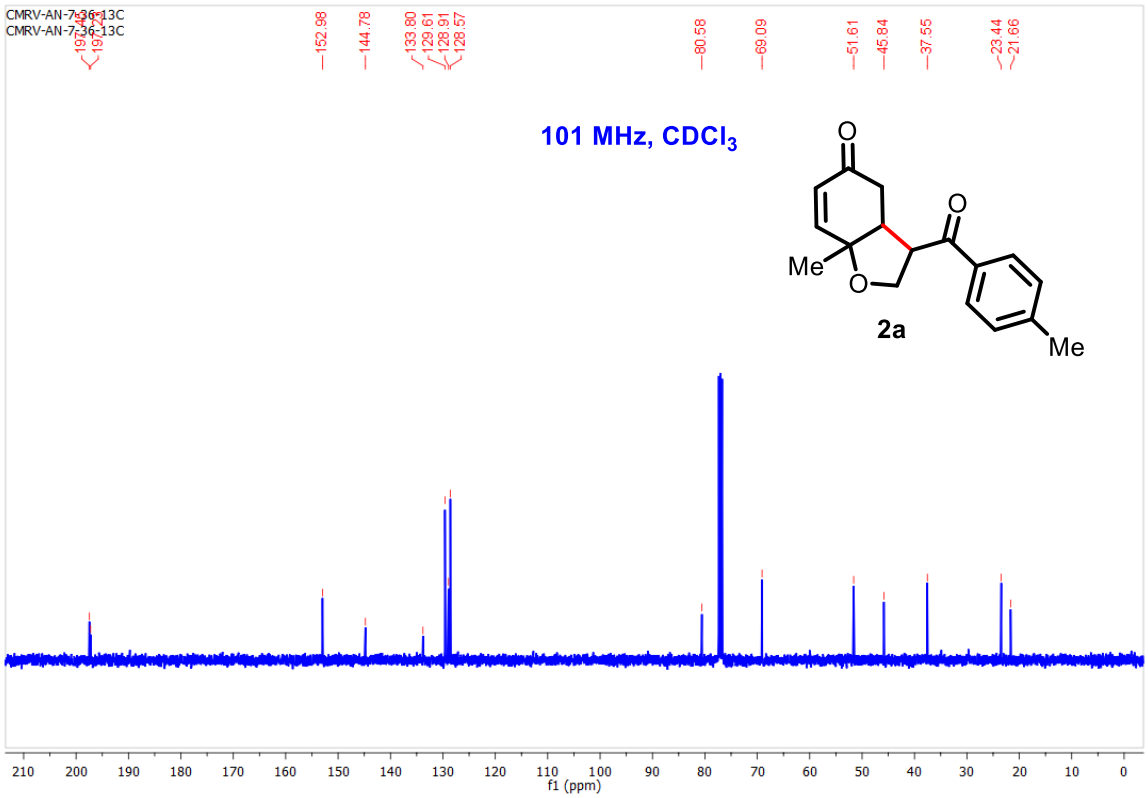
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{27}H_{35}O_4$ $[M+H]^+$ 423.2535; found 423.2532.

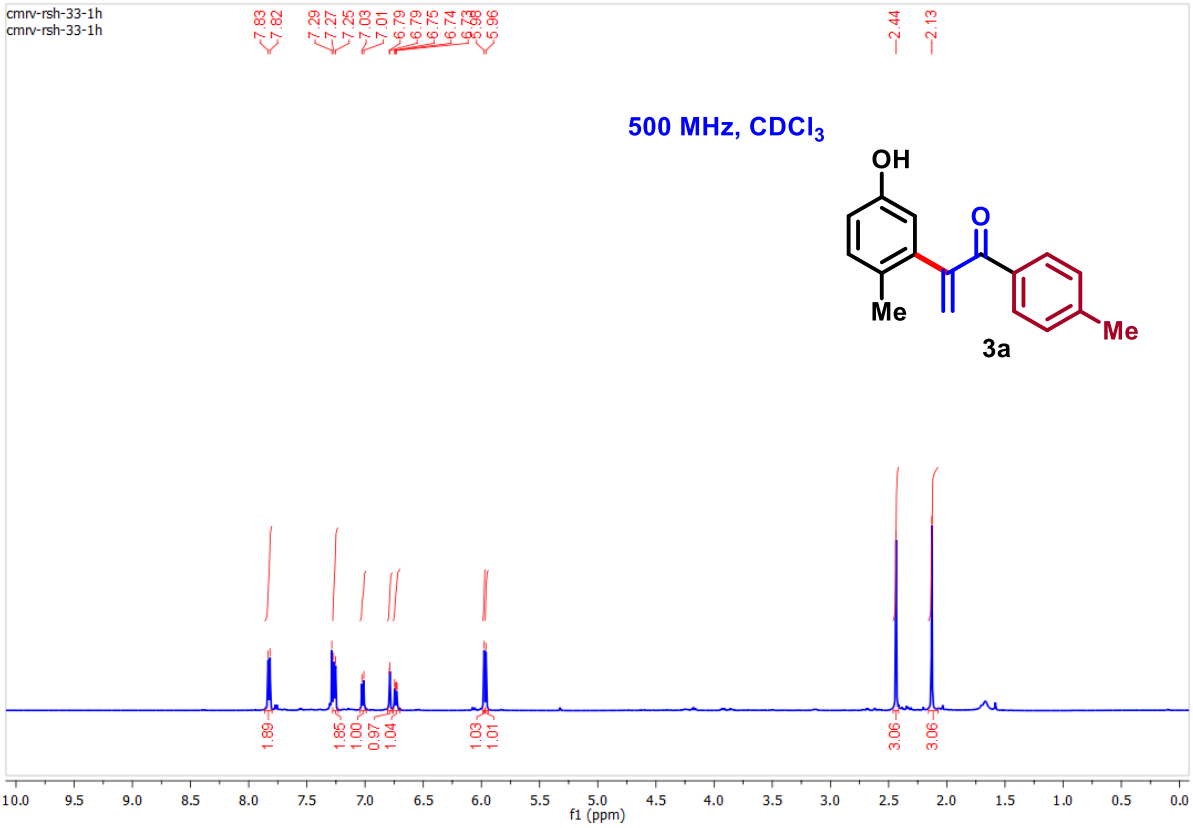
4). References:

1. (a) Kumar, R.; Hoshimoto, Y.; Tamai, E.; Ohashi, M.; Ogoshi, S. *Nat. Commun.* **2017**, *8*, 32. (b) Takenaka, K.; Mohanta, S. C.; Sasai, H. *Angew. Chem., Int. Ed*. **2014**, 53, 4675.

5). ^{1}H and ^{13}C NMR spectras:



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7.25
7.03
7.01
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6.73
5.98
5.96
2.44
2.13
500 MHz, CDCl3
OH
O
Me
Me
3a
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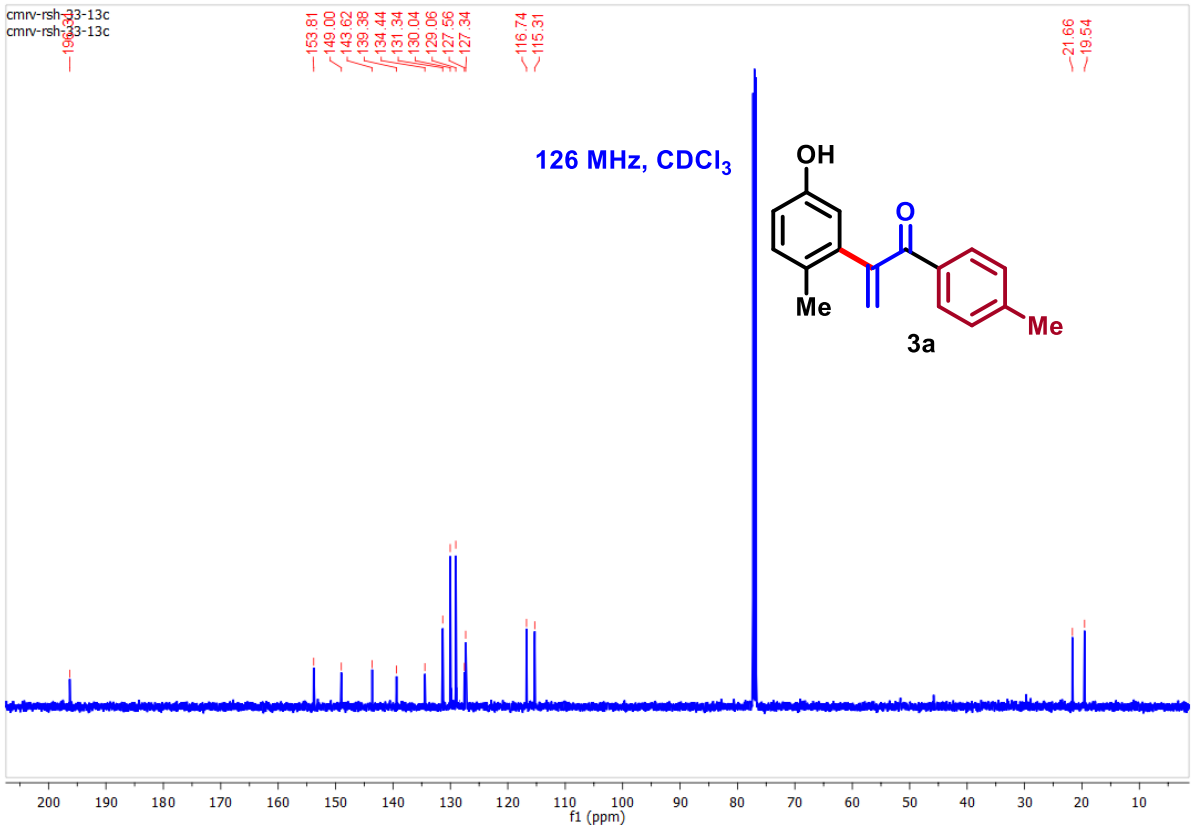
1.85
1.00
0.97
1.04
1.03
1.01
3.06
3.06
f1 (ppm)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cmrv-rsh-33-13c
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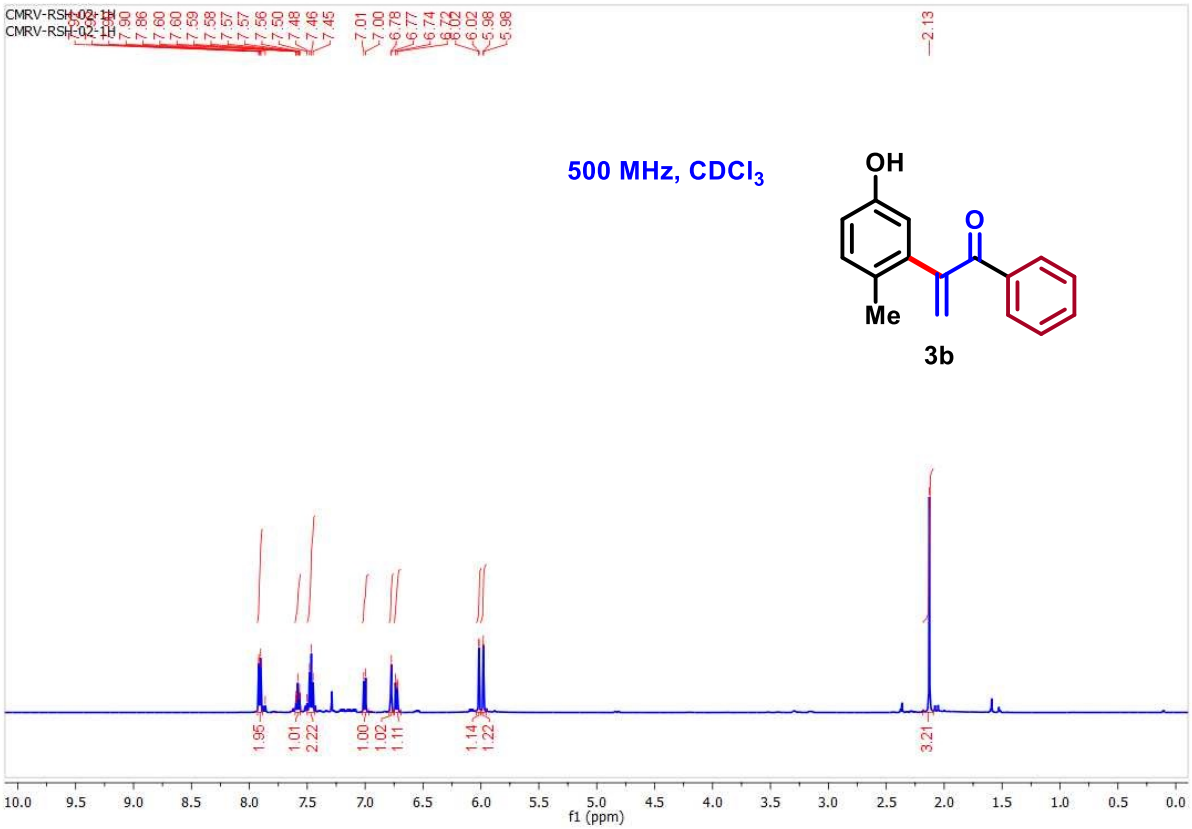
OH
O
Me
Me
3a
f1 (ppm)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7.01
7.00
6.78
6.77
6.74
6.72
6.02
5.98
5.98
2.13
500 MHz, CDCl3
OH
O
Me
3b
1.95
1.01
2.22
1.00
1.02
1.11
1.14
1.22
3.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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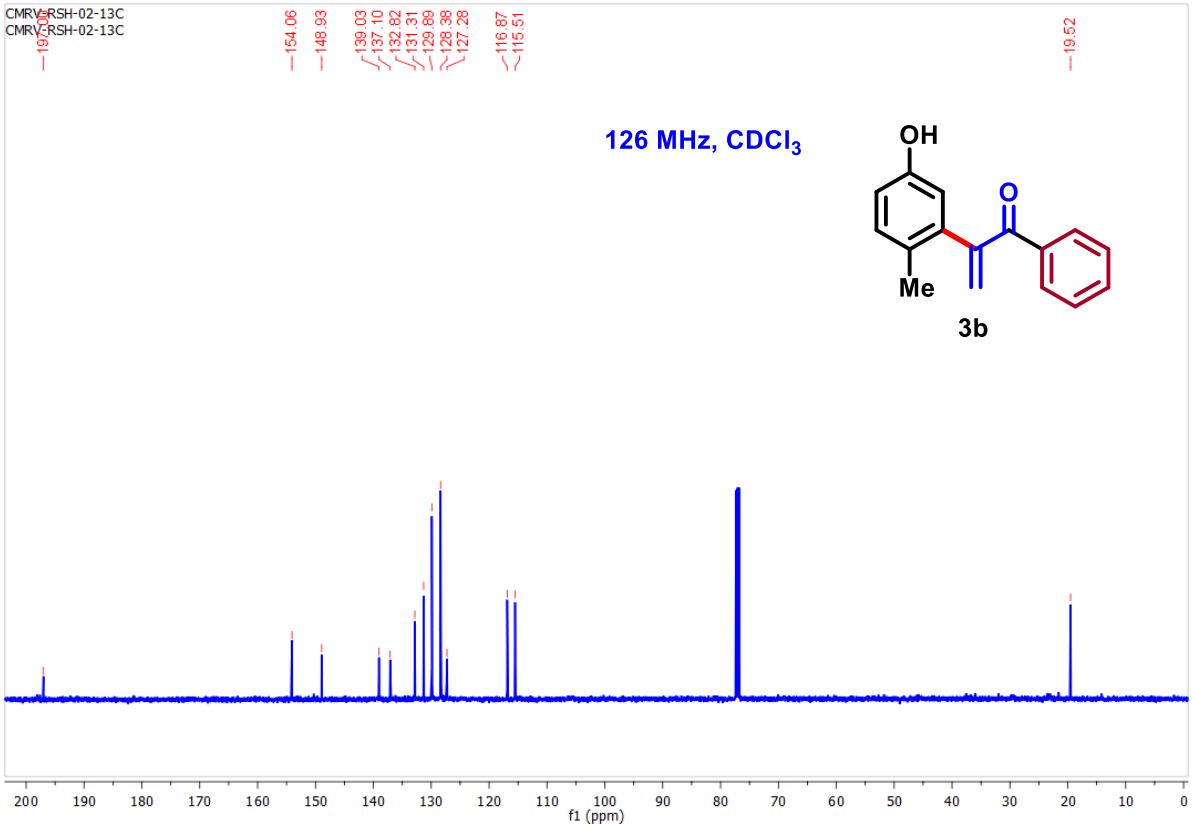
f1 (ppm)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CMRV-RSH-02-13C
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19.52
126 MHz, CDCl3
OH
O
Me
3b
200
190
180
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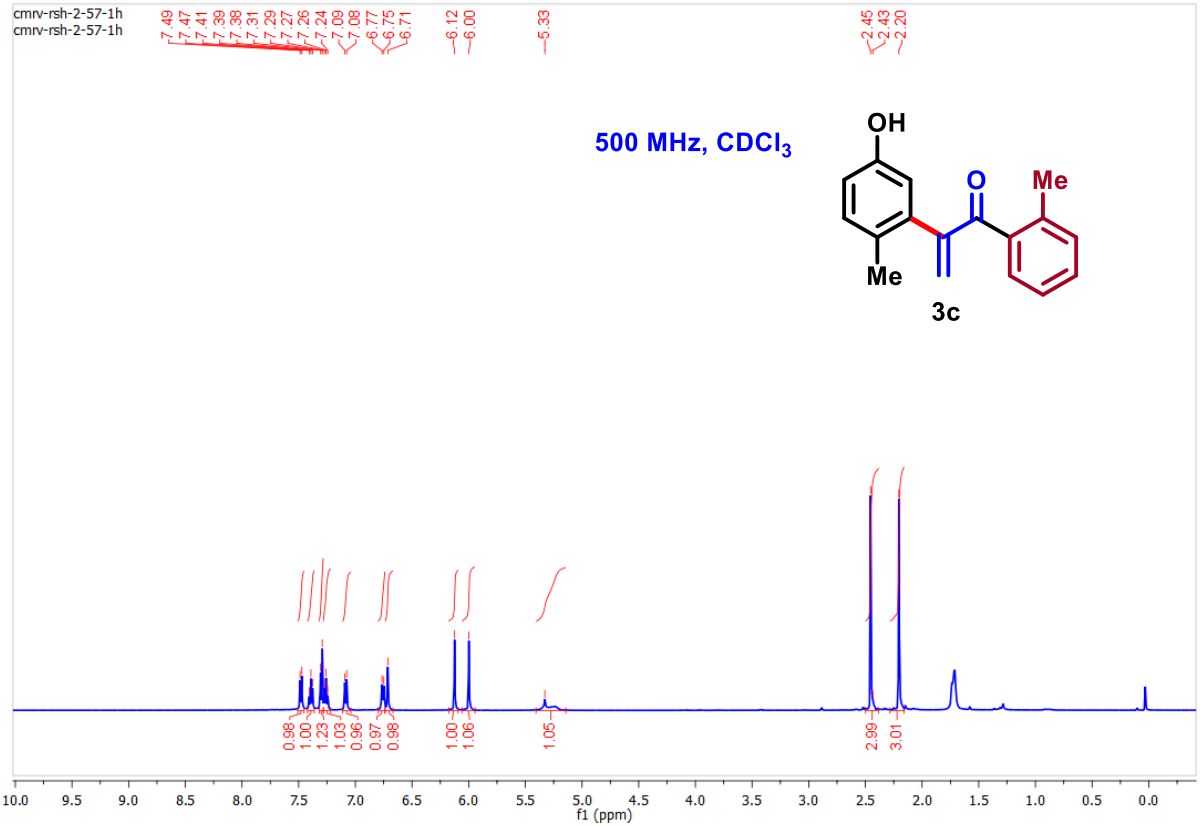
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OH
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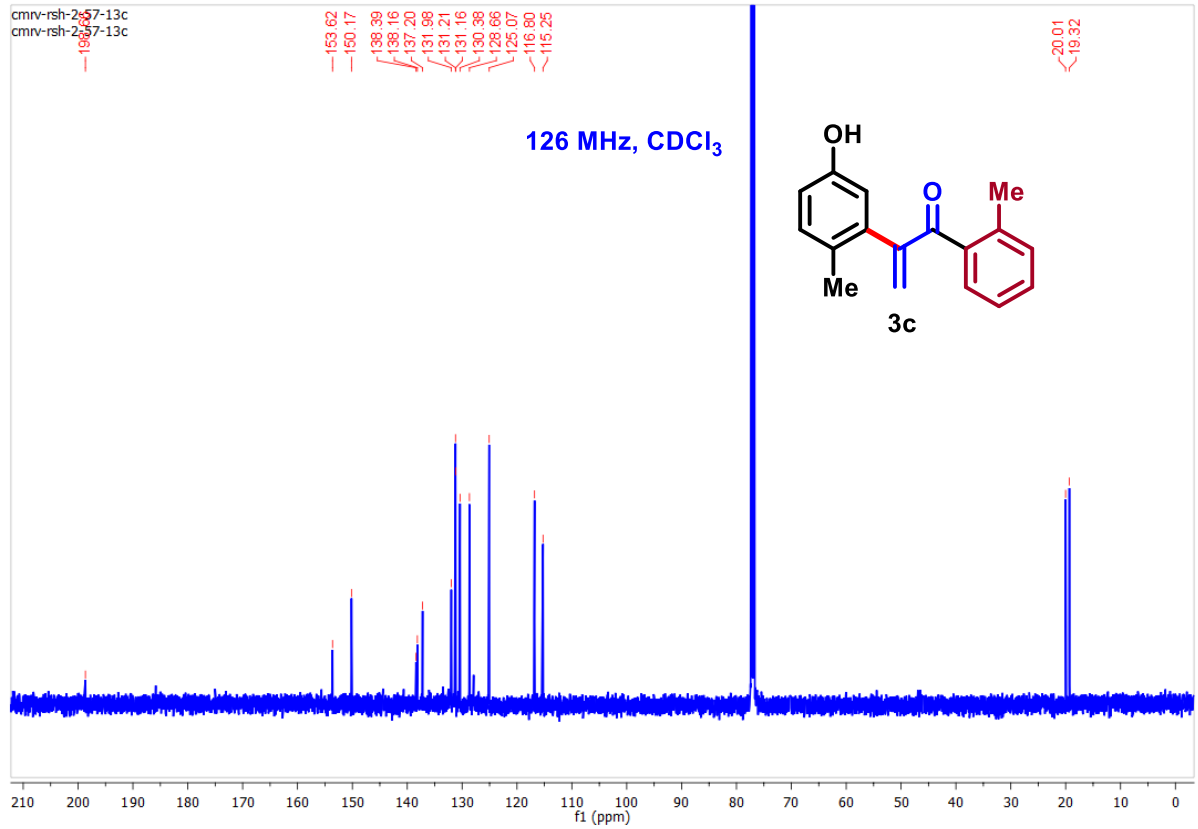
Me
Me
3c
f1 (ppm)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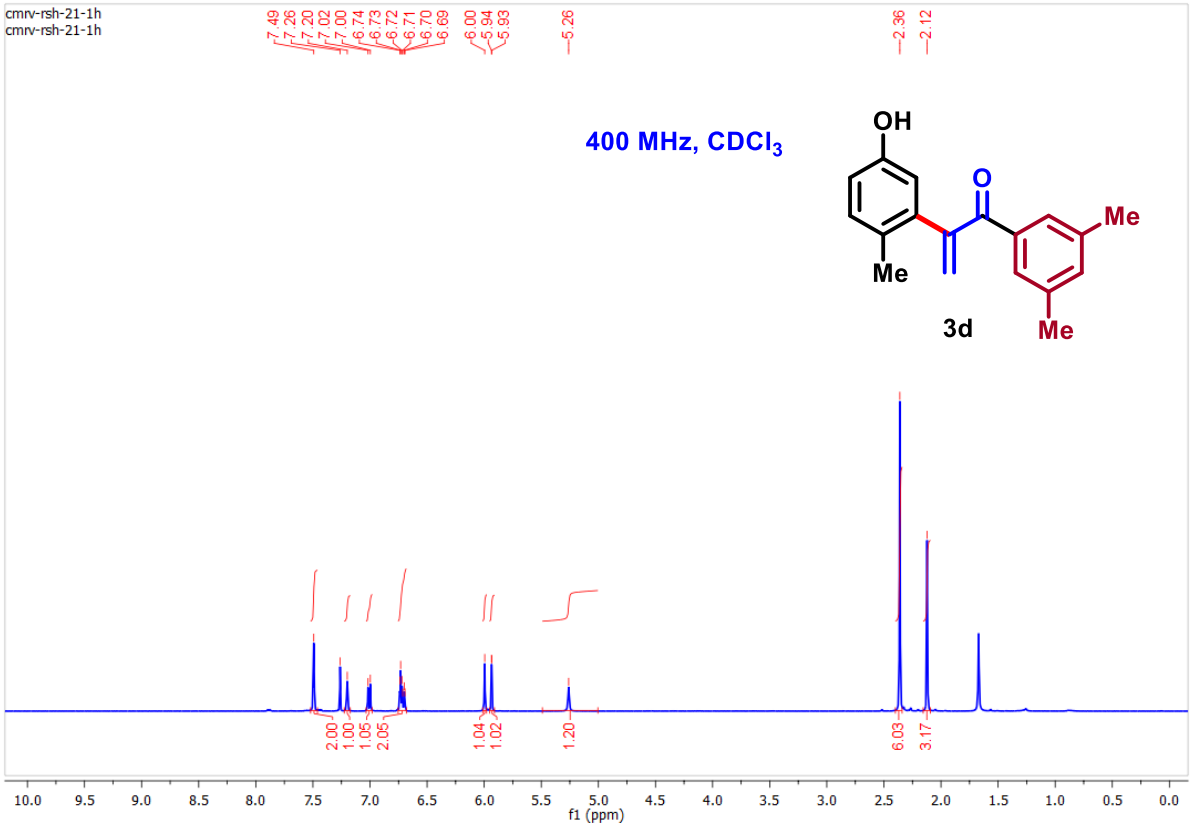
Me
Me
3c
f1 (ppm)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5.93
5.26
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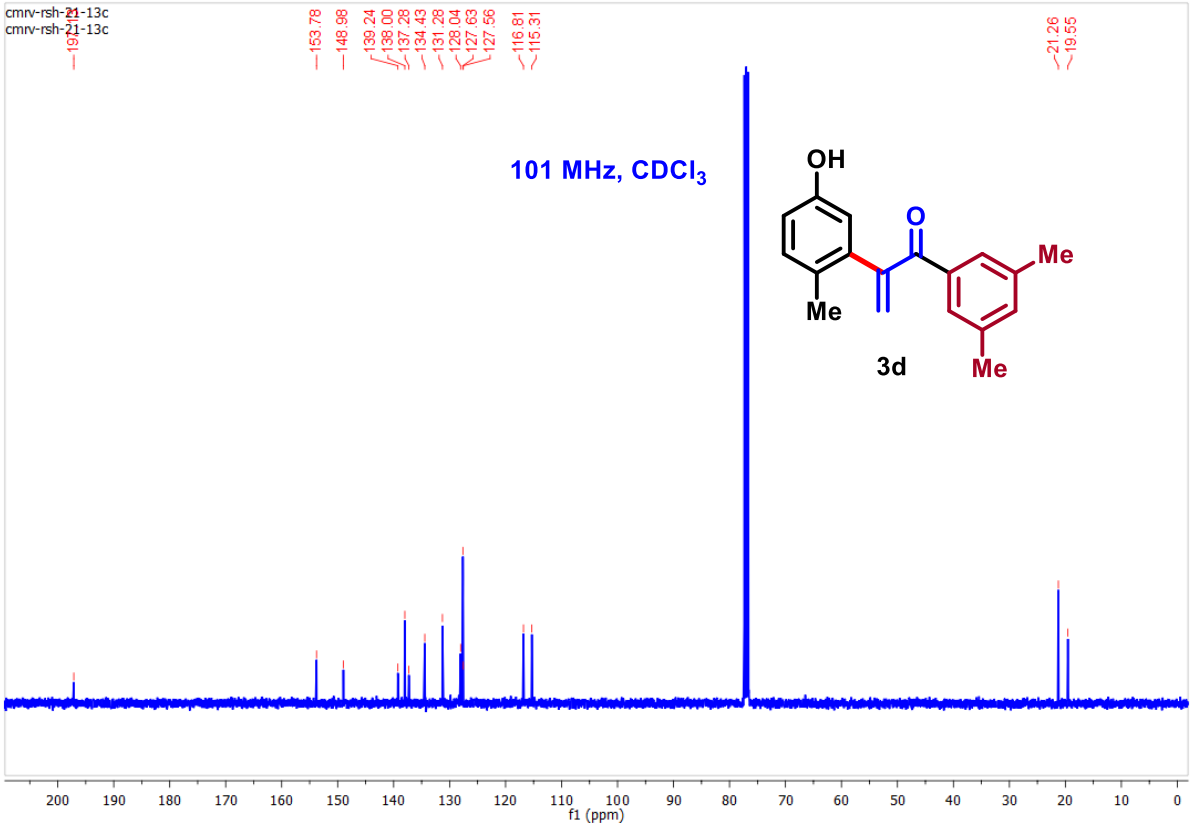
1.02
1.20
6.03
3.17
f1 (ppm)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O
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Me
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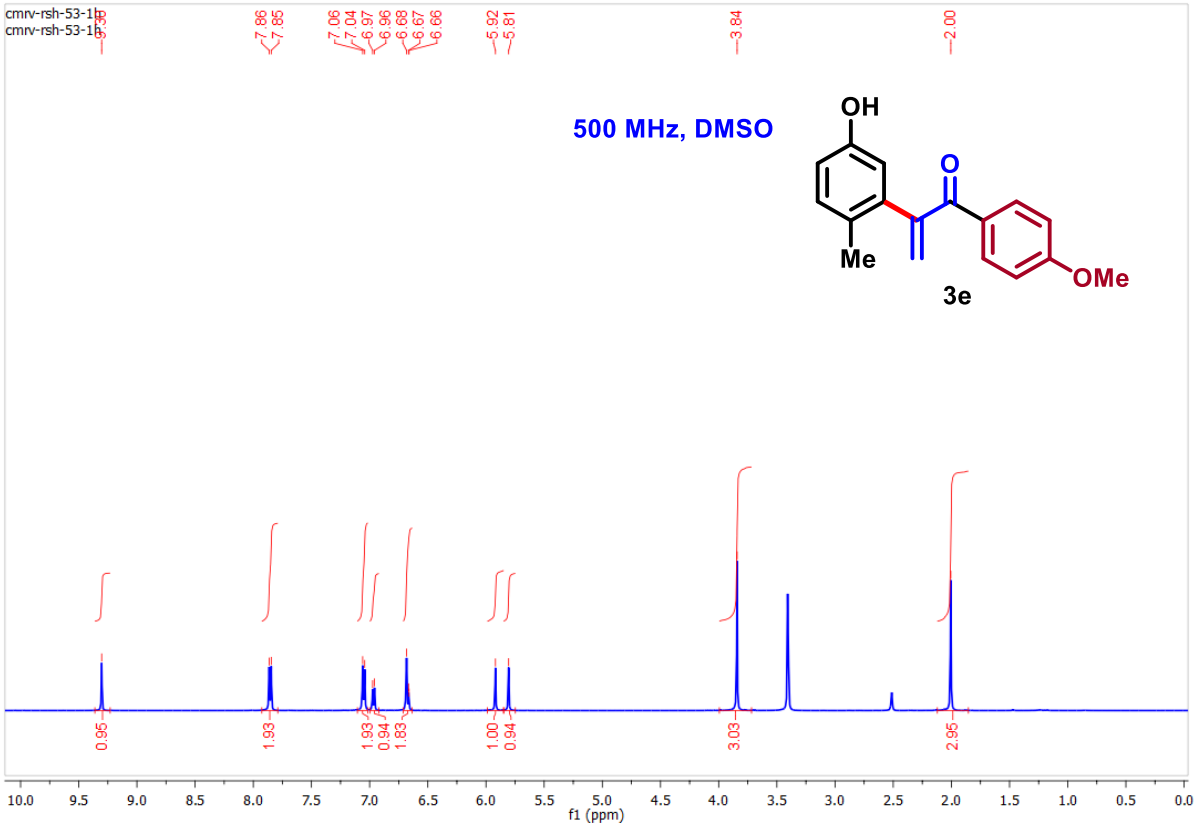
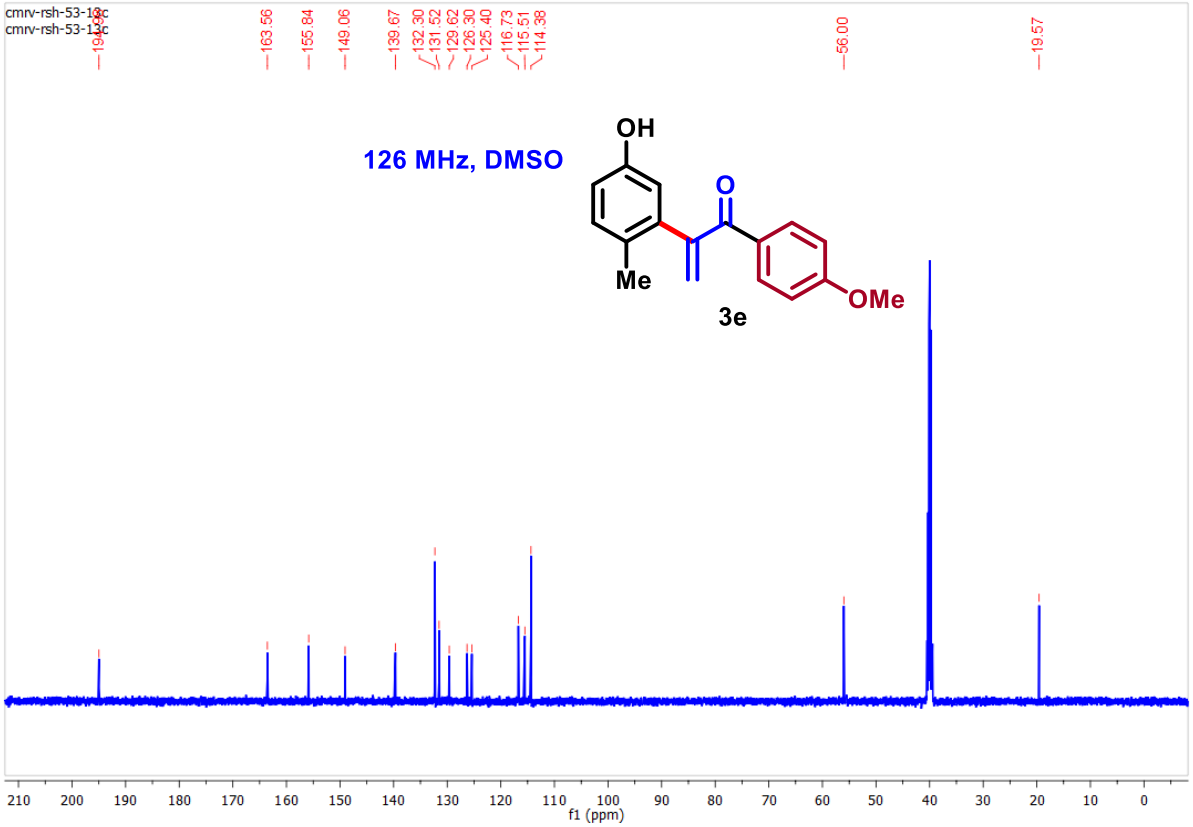
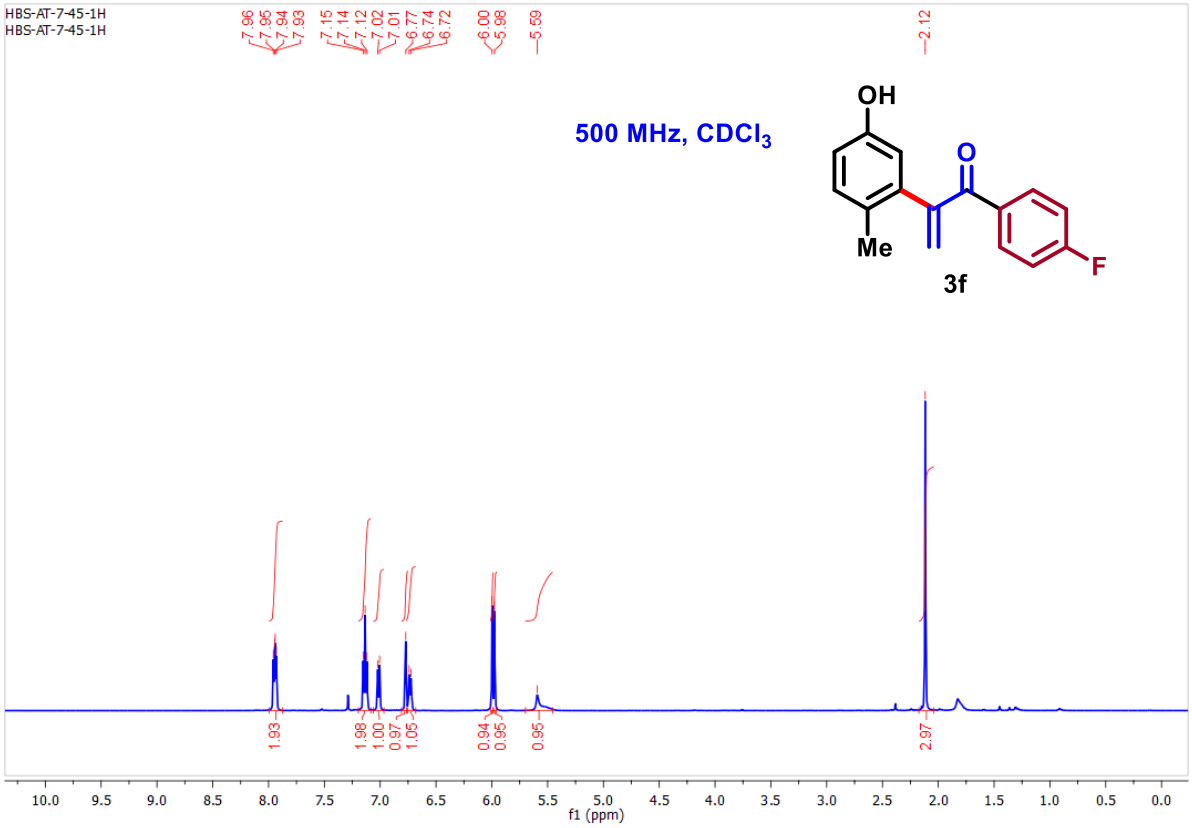
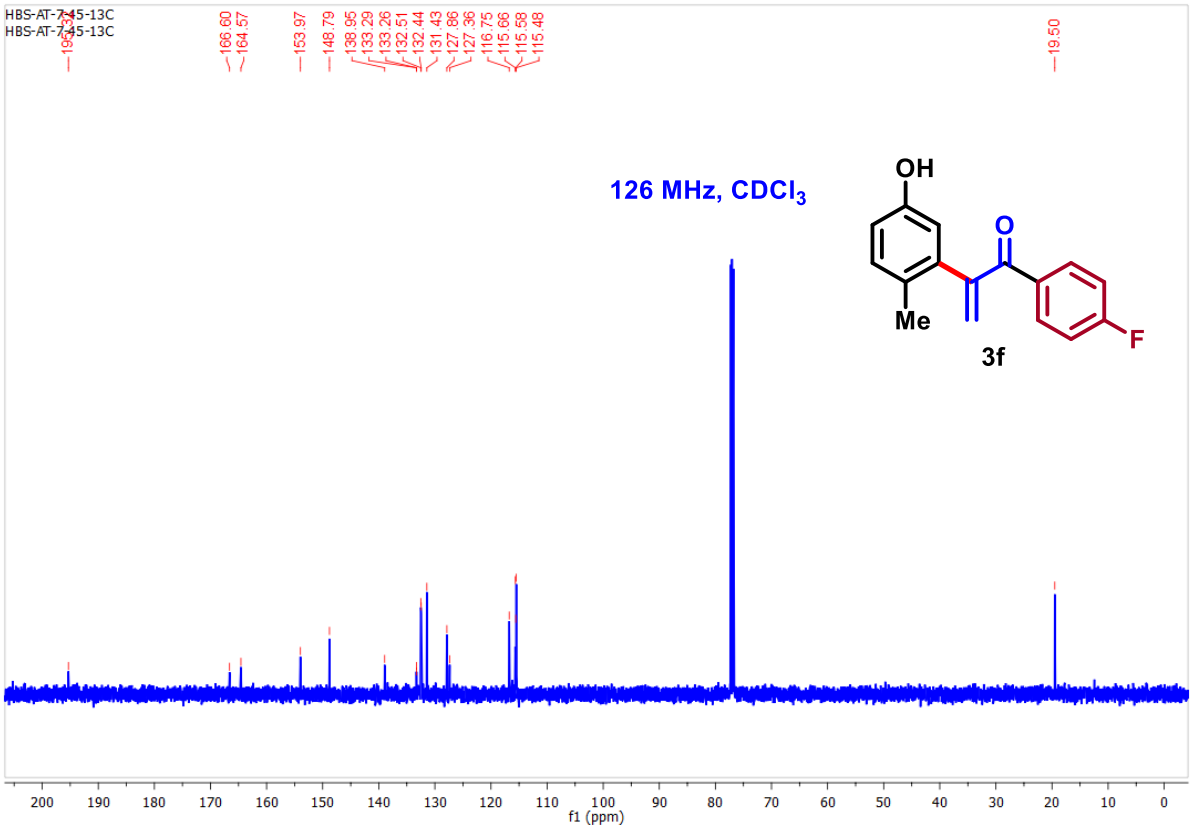
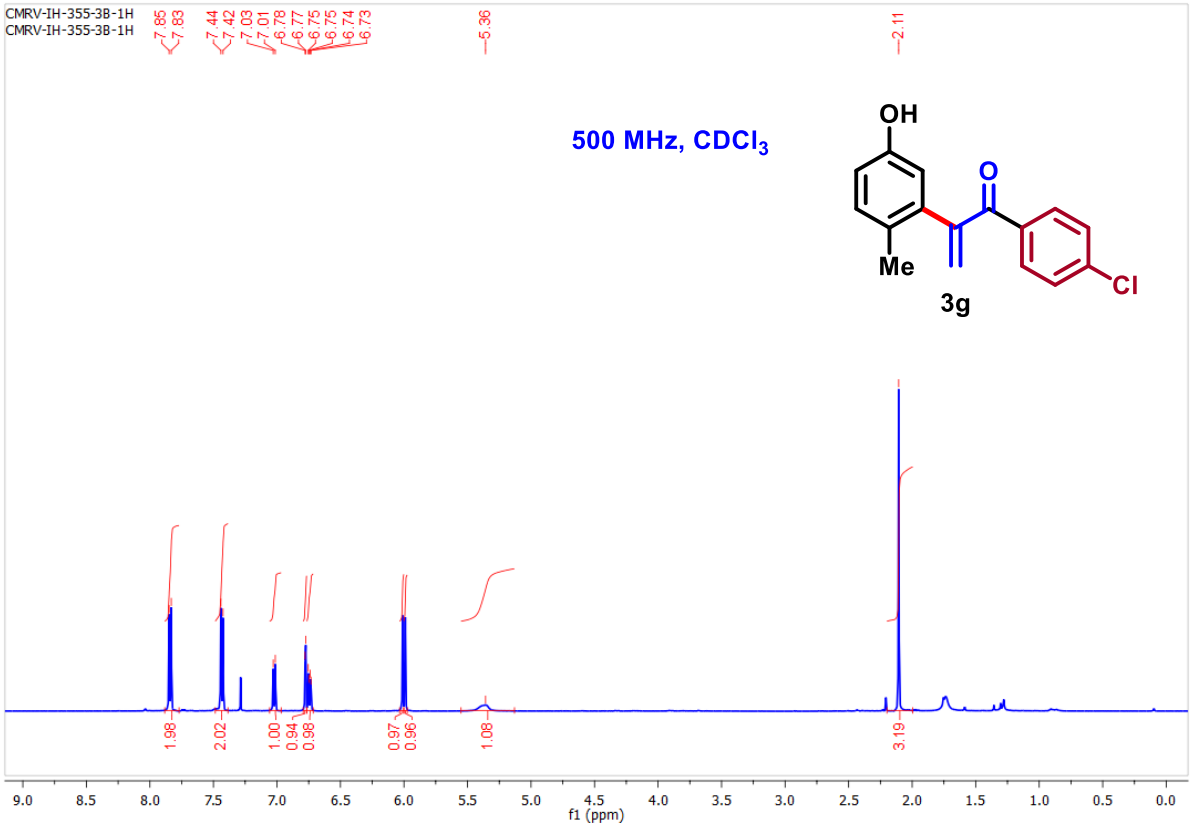
f1 (ppm)

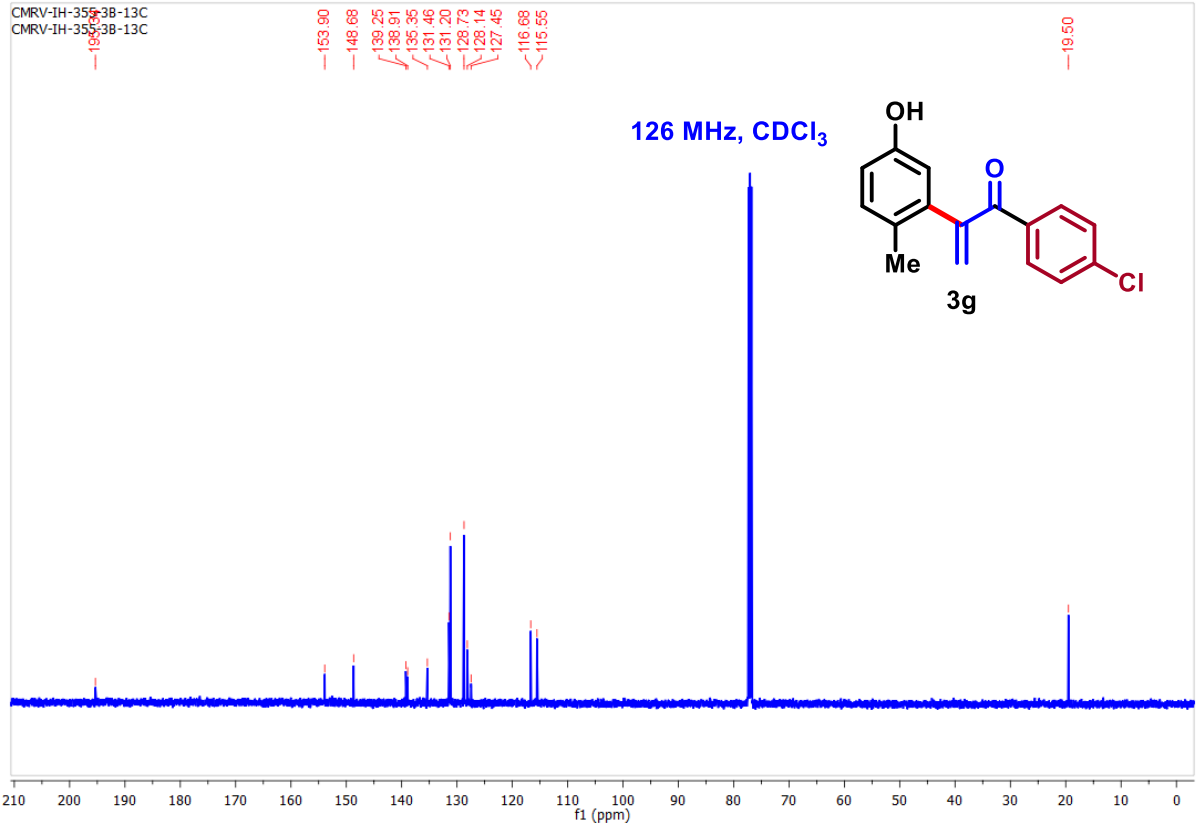

cmrv-rsh-53-1h
7.86
7.85
7.06
7.04
6.97
6.96
6.68
6.67
6.66
5.92
5.81
3.84
2.00
500 MHz, DMSO
OH
O
Me
OMe
3e
0.95
1.93
1.93
0.94
1.83
1.00
0.94
3.03
2.95
f1 (ppm)

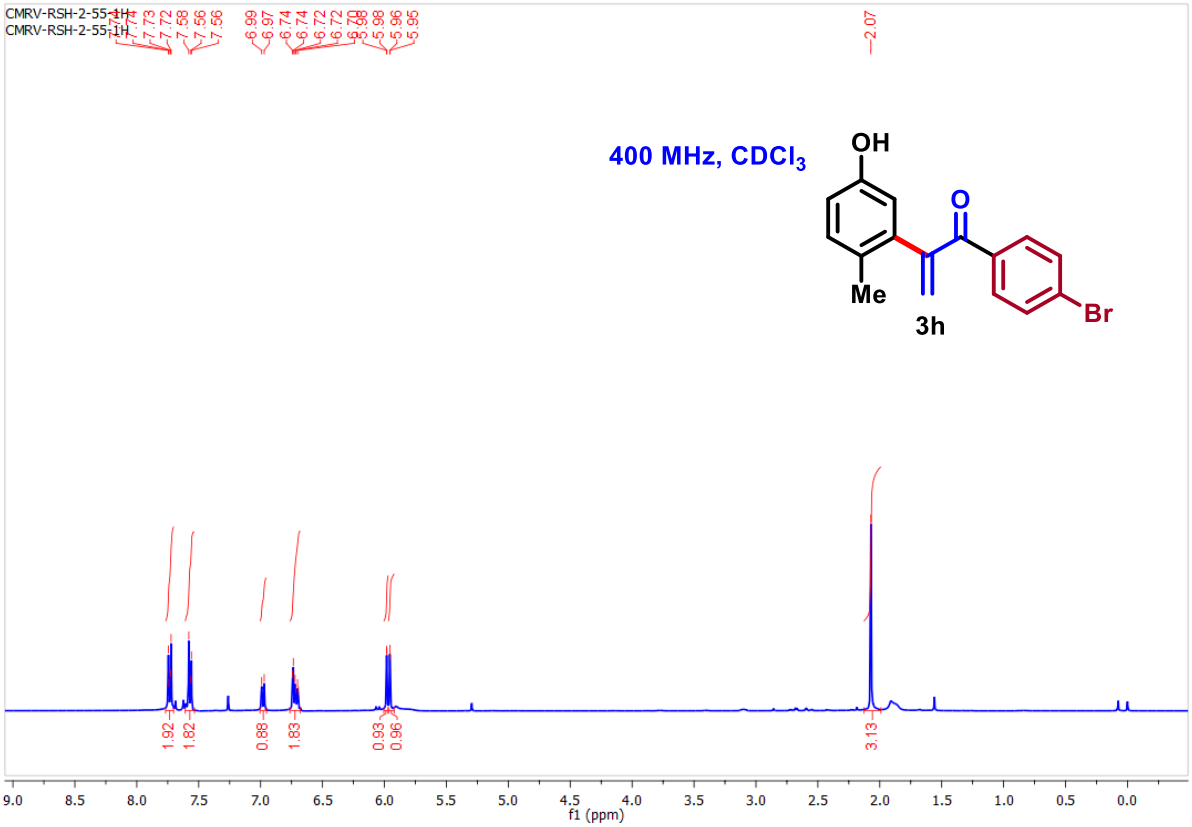

cmrv-rsh-53-13c
163.56
155.84
149.06
139.67
132.30
131.52
129.62
126.30
125.40
116.73
115.51
114.38
56.00
19.57
126 MHz, DMSO
OH
O
Me
OMe
3e
f1 (ppm)

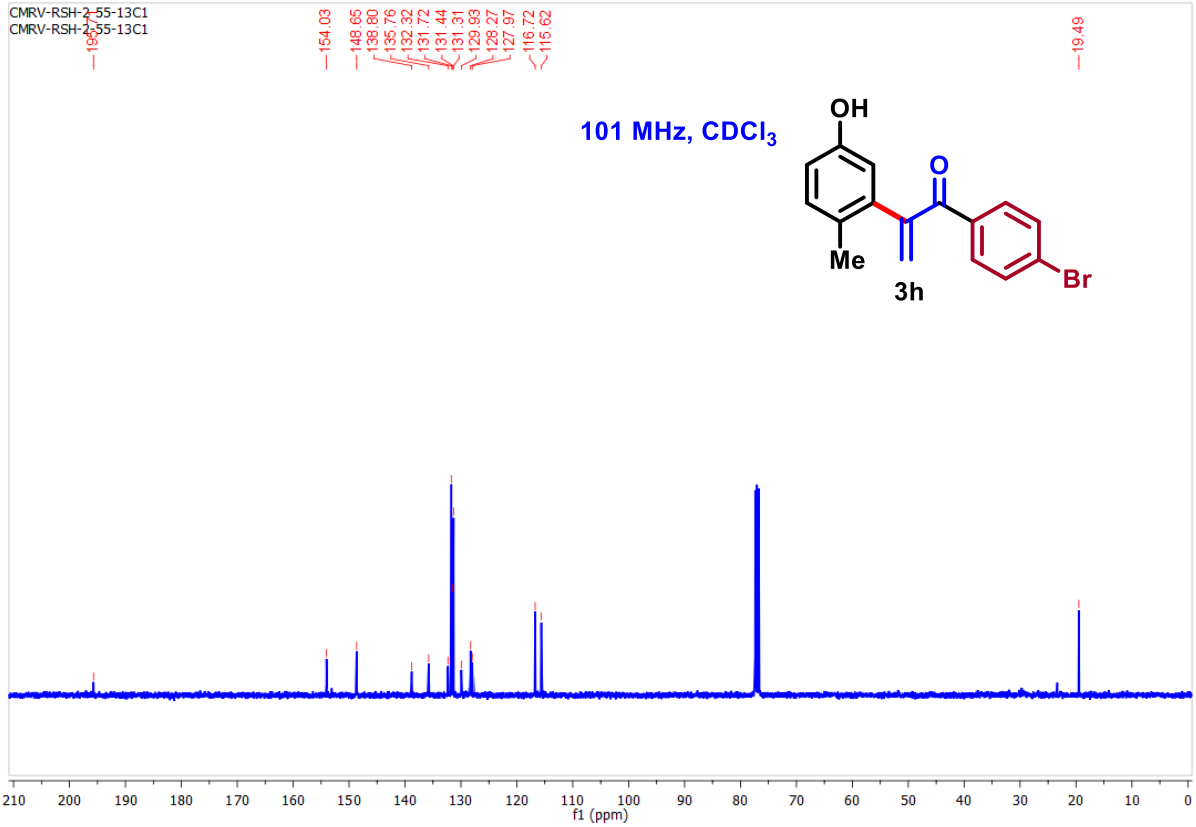

HBS-AT-7-45-1H
HBS-AT-7-45-1H
7.96
7.95
7.94
7.93
7.15
7.14
7.12
7.02
7.01
6.77
6.74
6.72
6.00
5.98
5.59
2.12
500 MHz, CDCl3
OH
O
Me
F
3f
1.93
1.98
1.00
0.97
1.05
0.94
0.95
0.95
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

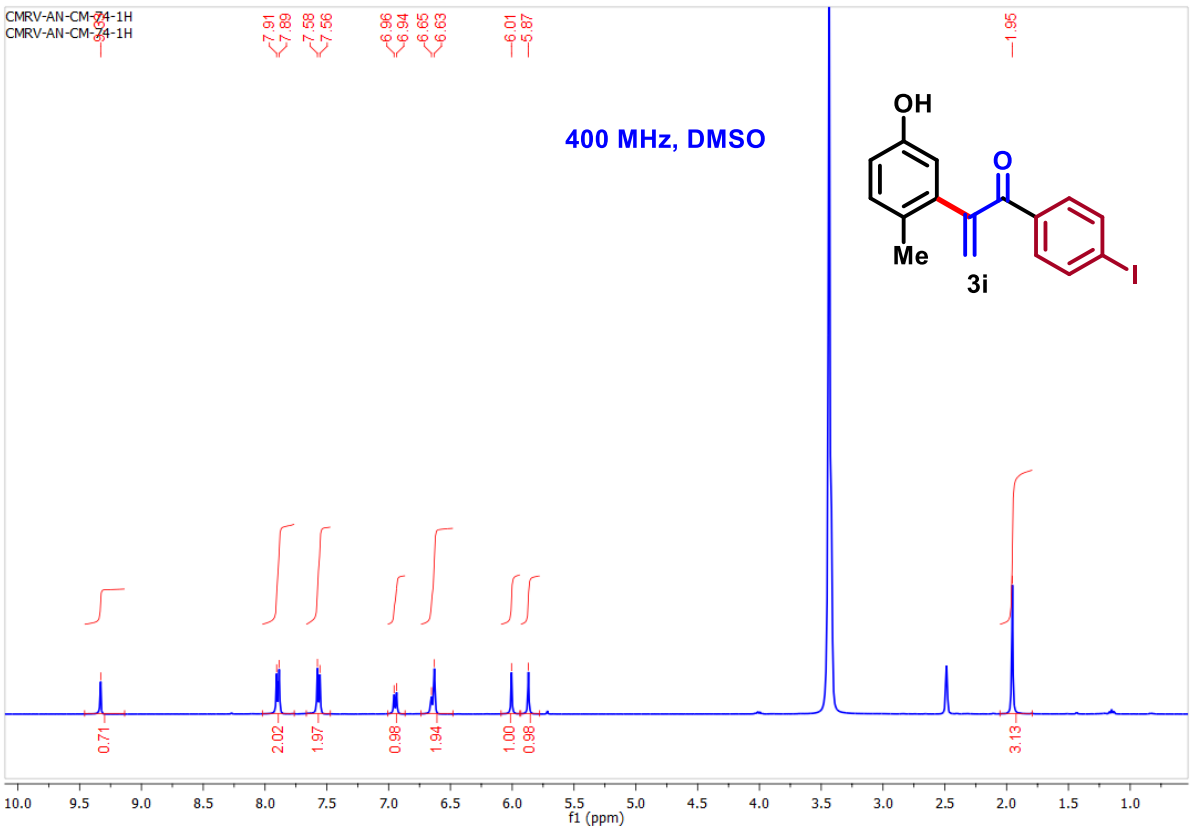

HBS-AT-7-45-13C
HBS-AT-7-45-13C
166.60
164.57
153.97
148.79
138.95
133.29
133.26
132.51
132.44
131.43
127.86
127.36
116.75
115.66
115.58
115.48
19.50
126 MHz, CDCl3
OH
O
Me
F
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

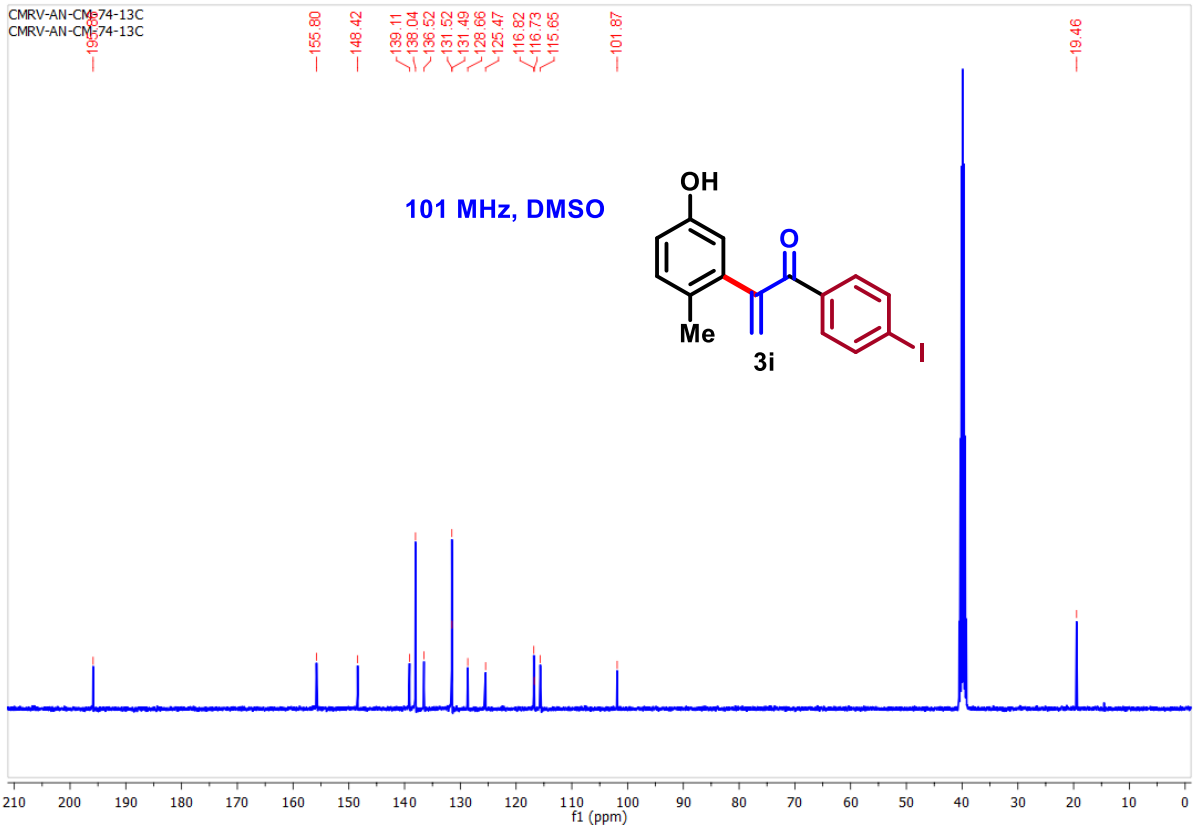

CMRV-IH-355-3B-1H
CMRV-IH-355-3B-1H
7.85
7.83
7.44
7.42
7.03
7.01
6.78
6.77
6.75
6.75
6.74
6.73
5.36
2.11
500 MHz, CDCl3
OH
O
Me
Cl
3g
1.98
2.02
1.00
0.94
0.98
0.97
0.96
1.08
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

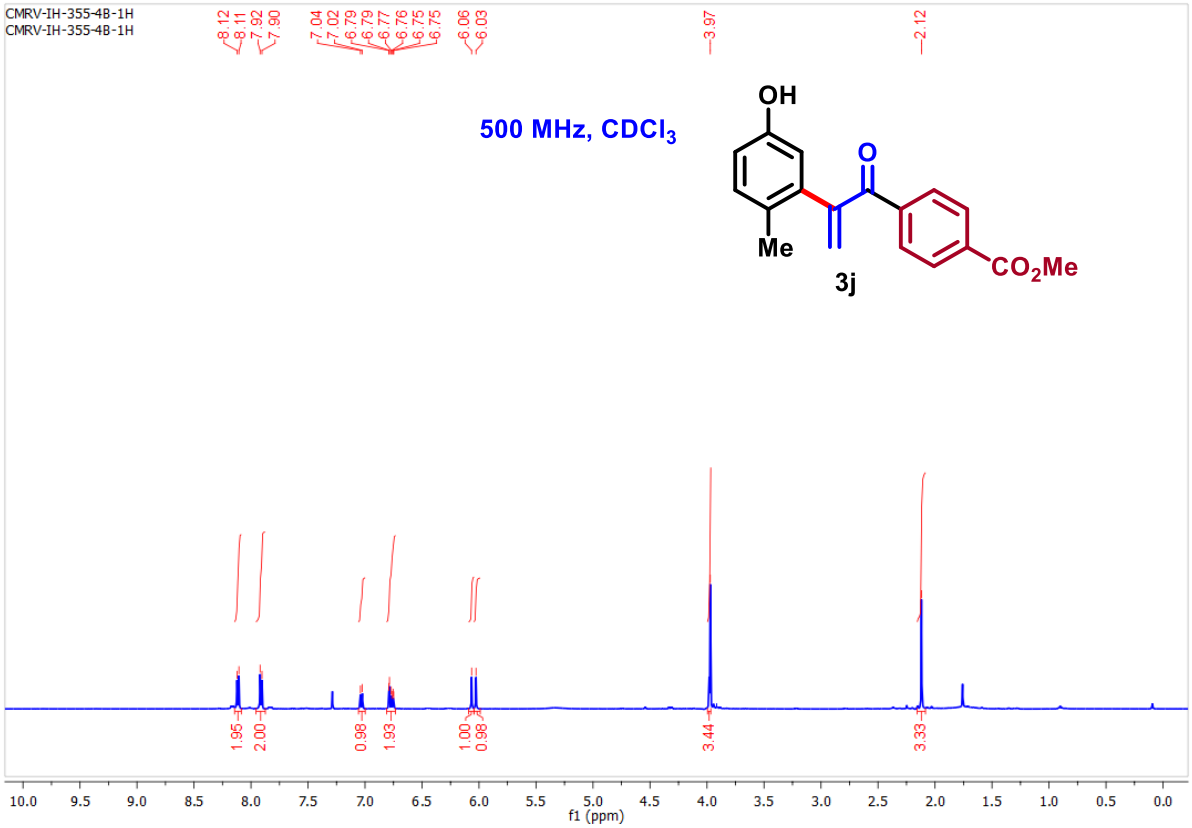

CMRV-IH-355-3B-13C
CMRV-IH-355-3B-13C
153.90
148.68
139.25
138.91
135.35
131.46
131.20
128.73
128.14
127.45
116.68
115.55
19.50
126 MHz, CDCl3
OH
O
Me
Cl
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

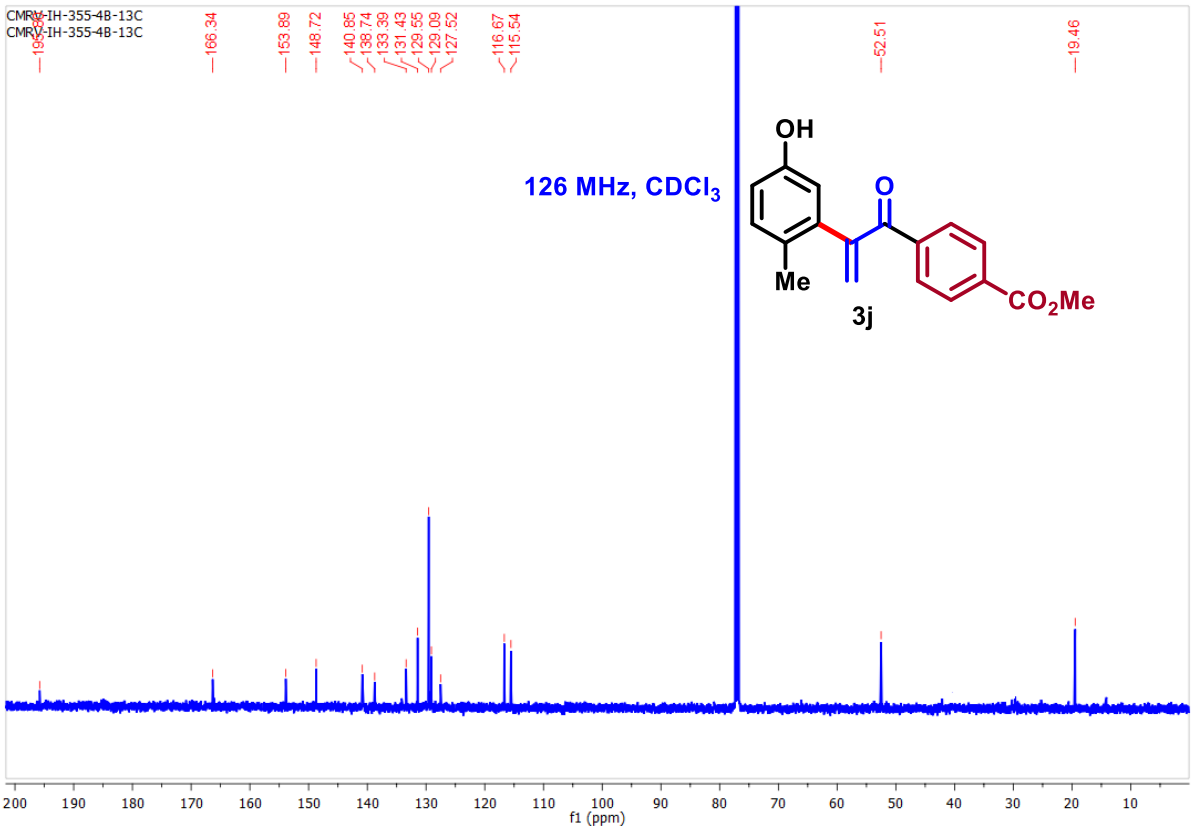

CMRV-RSH-2-55-1H
CMRV-RSH-2-55-1H
7.73
7.72
7.58
7.56
7.56
6.99
6.97
6.74
6.74
6.72
6.72
6.70
5.98
5.96
5.95
2.07
400 MHz, CDCl3
OH
O
Me
Br
3h
1.92
1.82
0.88
1.83
0.93
0.96
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

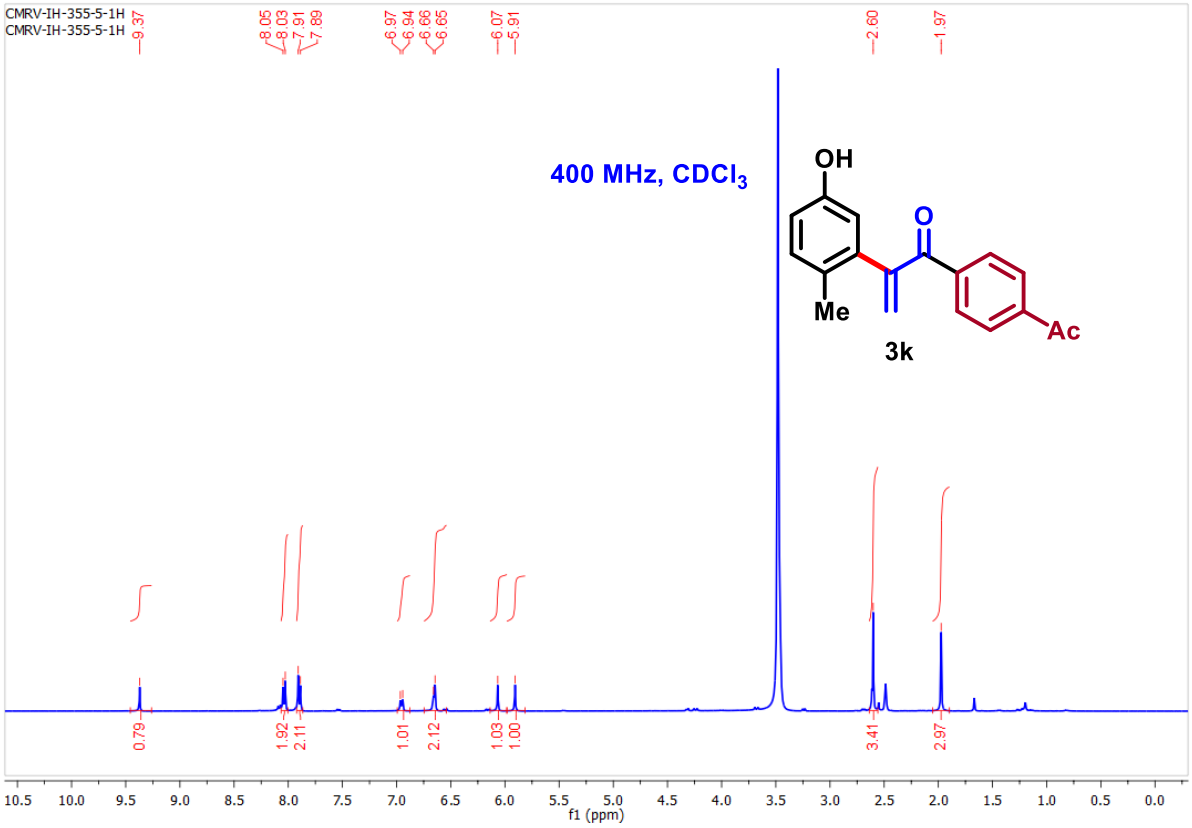

CMRV-RSH-2-55-13C1
CMRV-RSH-2-55-13C1
154.03
148.65
138.80
135.76
132.32
131.72
131.44
131.31
129.93
128.27
127.97
116.72
115.62
19.49
101 MHz, CDCl3
OH
O
Me
Br
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

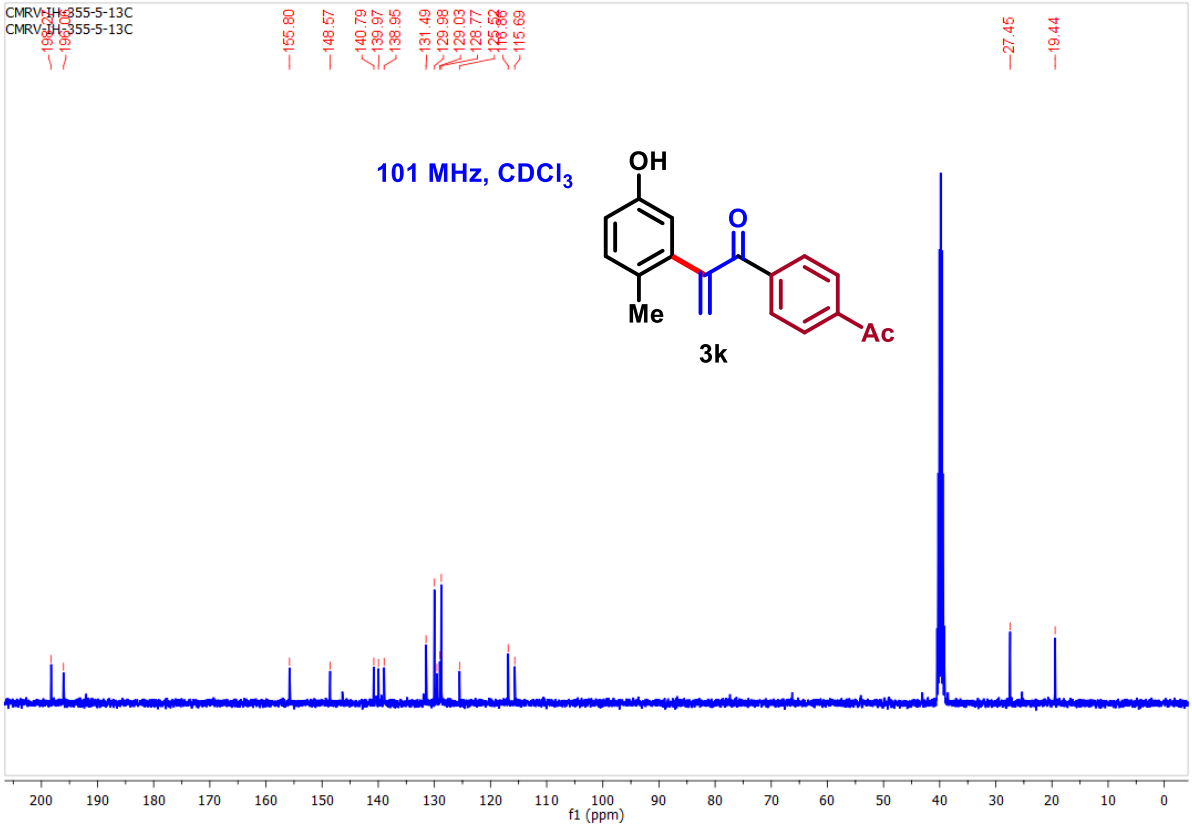

CMRV-AN-CM-74-1H
CMRV-AN-CM-74-1H
7.91
7.89
7.58
7.56
6.96
6.94
6.65
6.63
6.01
5.87
1.95
400 MHz, DMSO
OH
O
Me
3i
0.71
2.02
1.97
0.98
1.94
1.00
0.98
3.13
f1 (ppm)

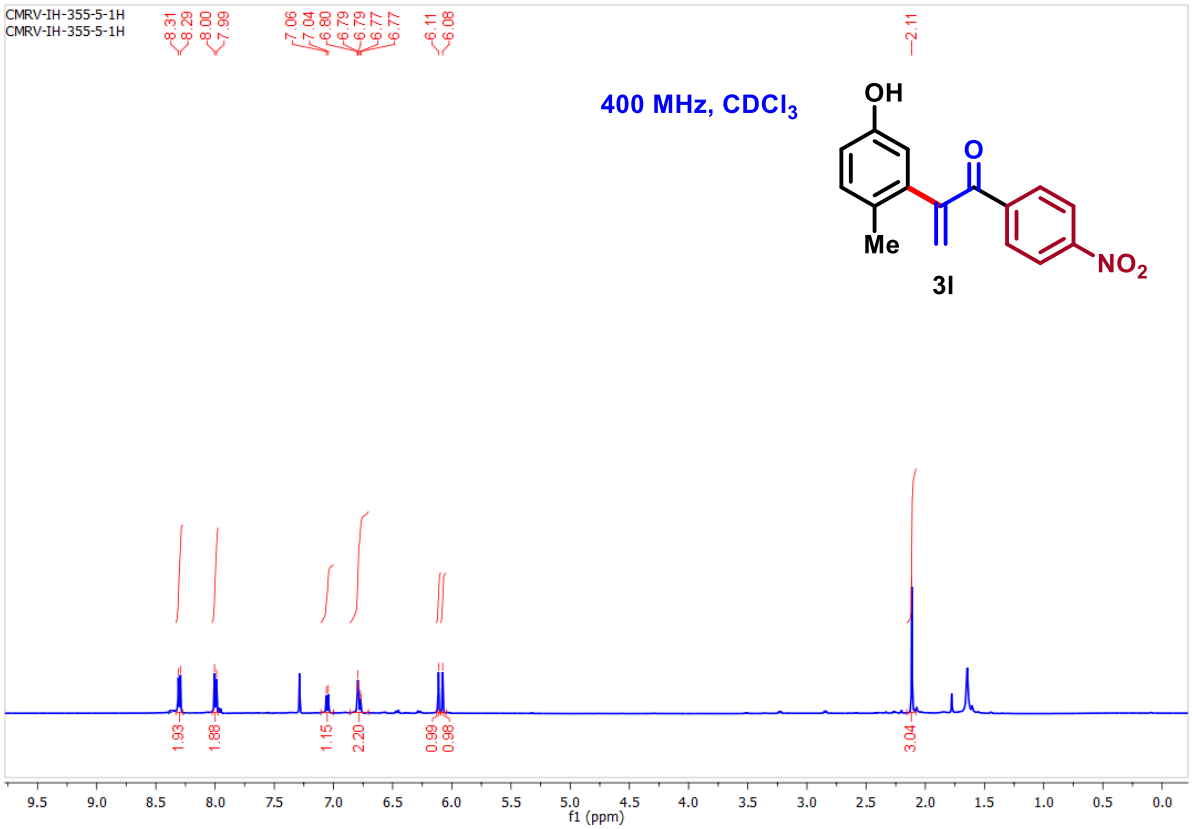

CMRV-AN-CM-74-13C
CMRV-AN-CM-74-13C
155.80
148.42
139.11
138.04
136.52
131.52
131.49
128.66
125.47
116.82
116.73
115.65
101.87
19.46
101 MHz, DMSO
OH
O
Me
3i
f1 (ppm)

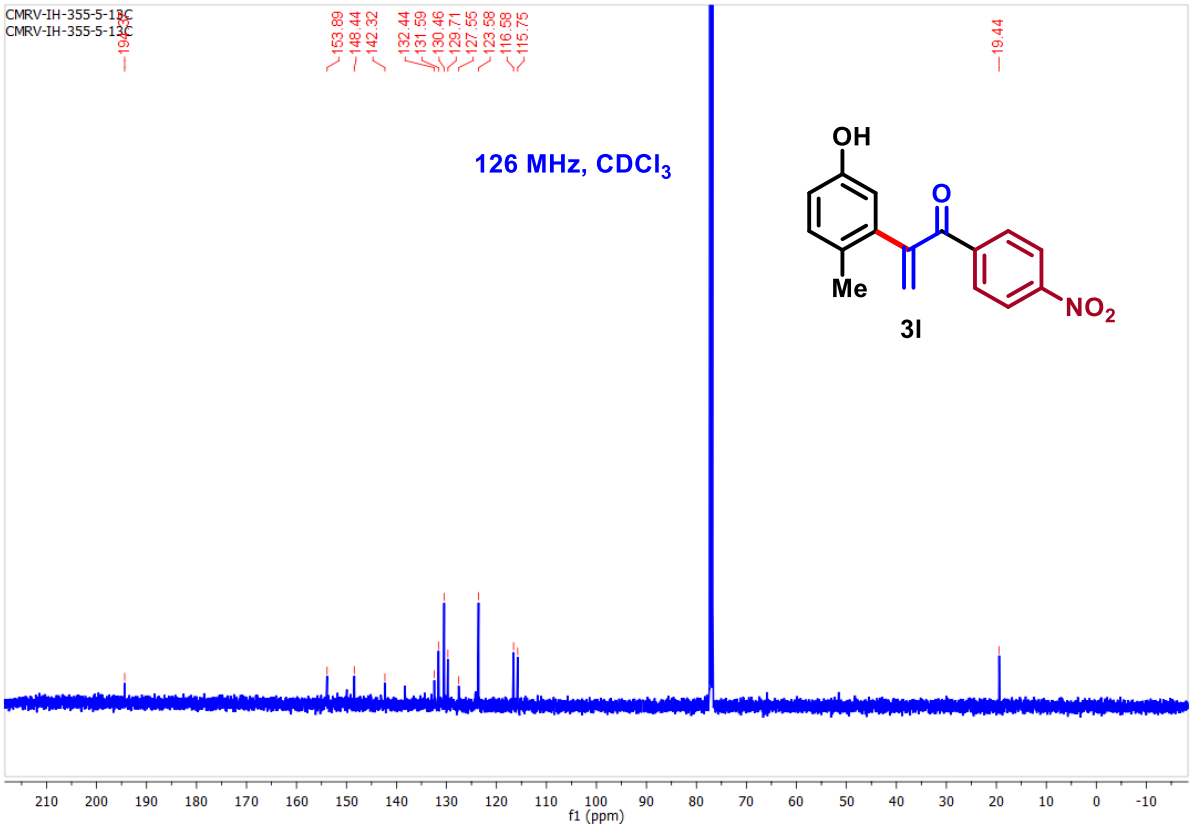

CMRV-IH-355-4B-1H
CMRV-IH-355-4B-1H
8.12
8.11
7.92
7.90
7.04
7.02
6.79
6.79
6.77
6.76
6.75
6.75
6.06
6.03
3.97
2.12
500 MHz, CDCl3
OH
O
Me
CO2Me
3j
1.95
2.00
0.98
1.93
1.00
0.98
3.44
3.33
f1 (ppm)

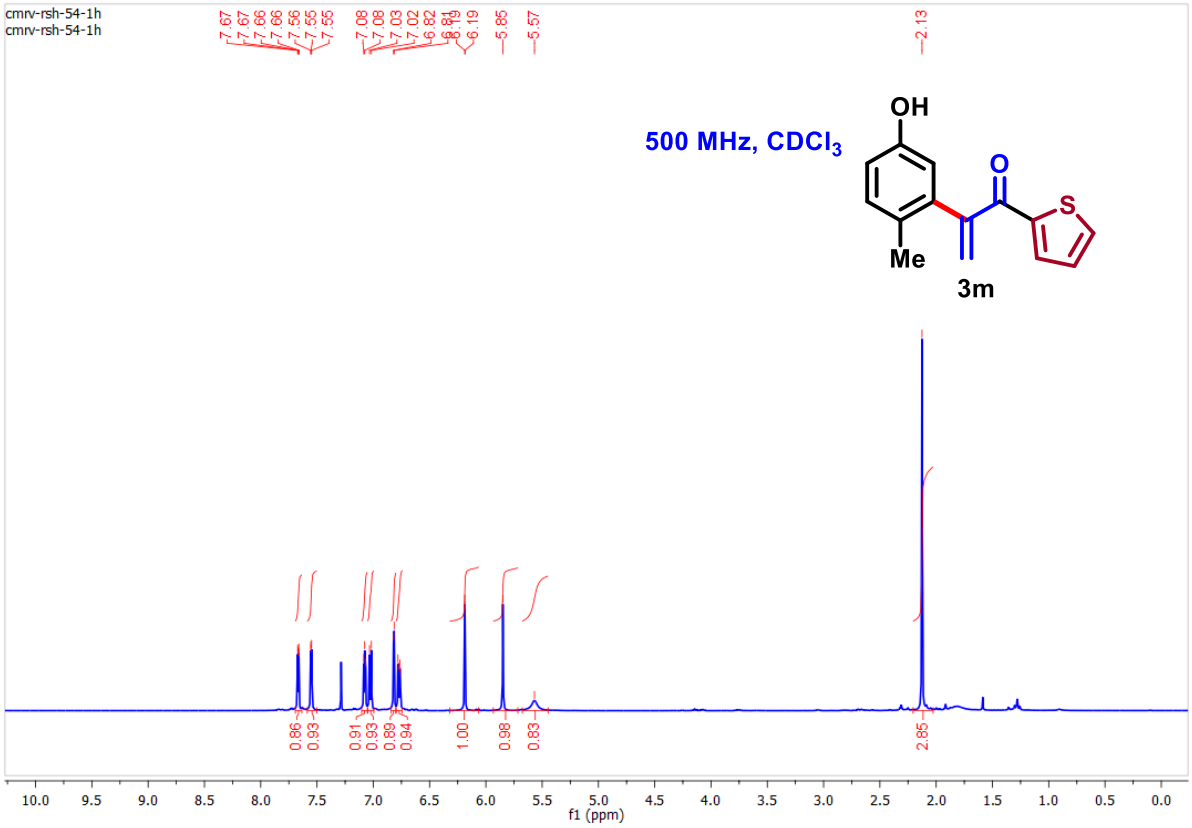

CMRV-IH-355-4B-13C
CMRV-IH-355-4B-13C
166.34
153.89
148.72
140.85
138.74
133.39
131.43
129.55
129.09
127.52
116.67
115.54
52.51
19.46
126 MHz, CDCl3
OH
O
Me
CO2Me
3j
f1 (ppm)

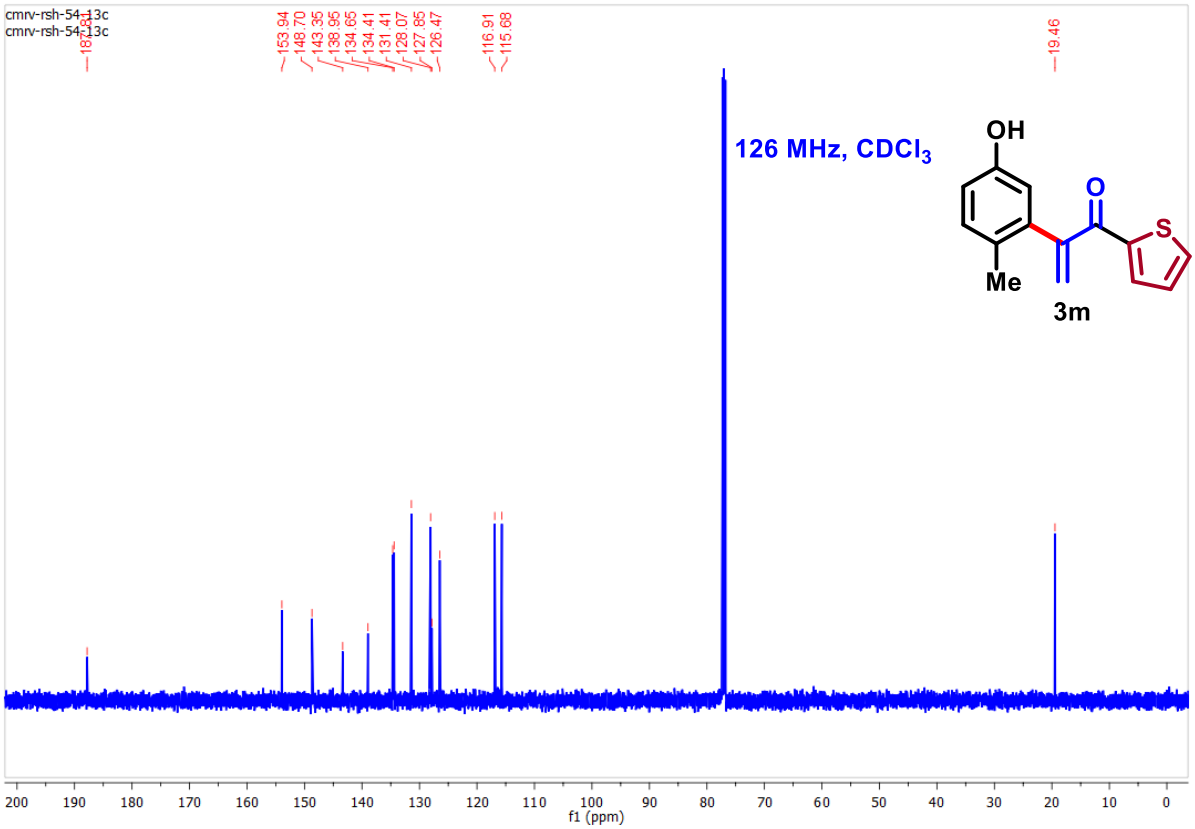

CMRV-IH-355-5-1H
CMRV-IH-355-5-1H
9.37
8.05
8.03
7.91
7.89
6.97
6.94
6.66
6.65
6.07
5.91
2.60
1.97
400 MHz, CDCl3
OH
O
Me
Ac
3k
0.79
1.92
2.11
1.01
2.12
1.03
1.00
3.41
2.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

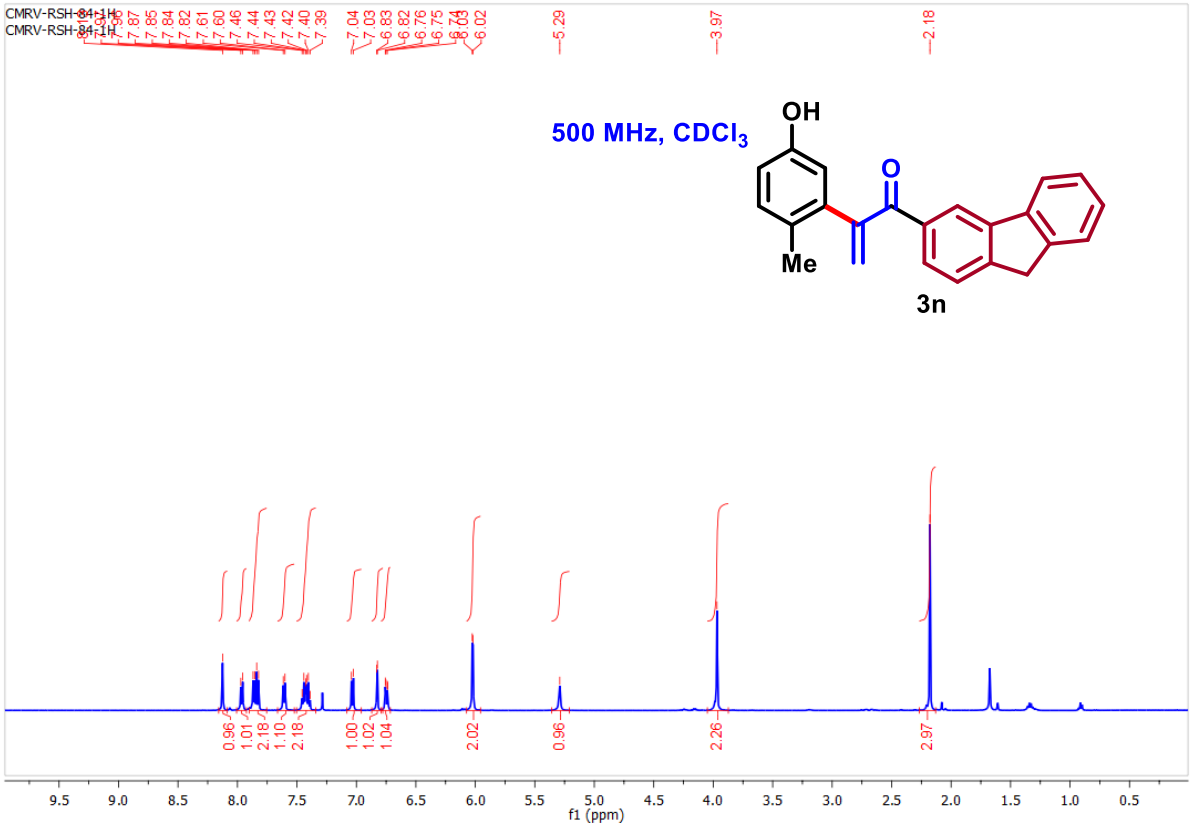

CMRV-IH-355-5-13C
CMRV-IH-355-5-13C
155.80
148.57
140.79
139.97
138.95
131.49
129.98
129.03
128.77
116.66
115.69
27.45
19.44
101 MHz, CDCl3
OH
O
Me
Ac
3k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

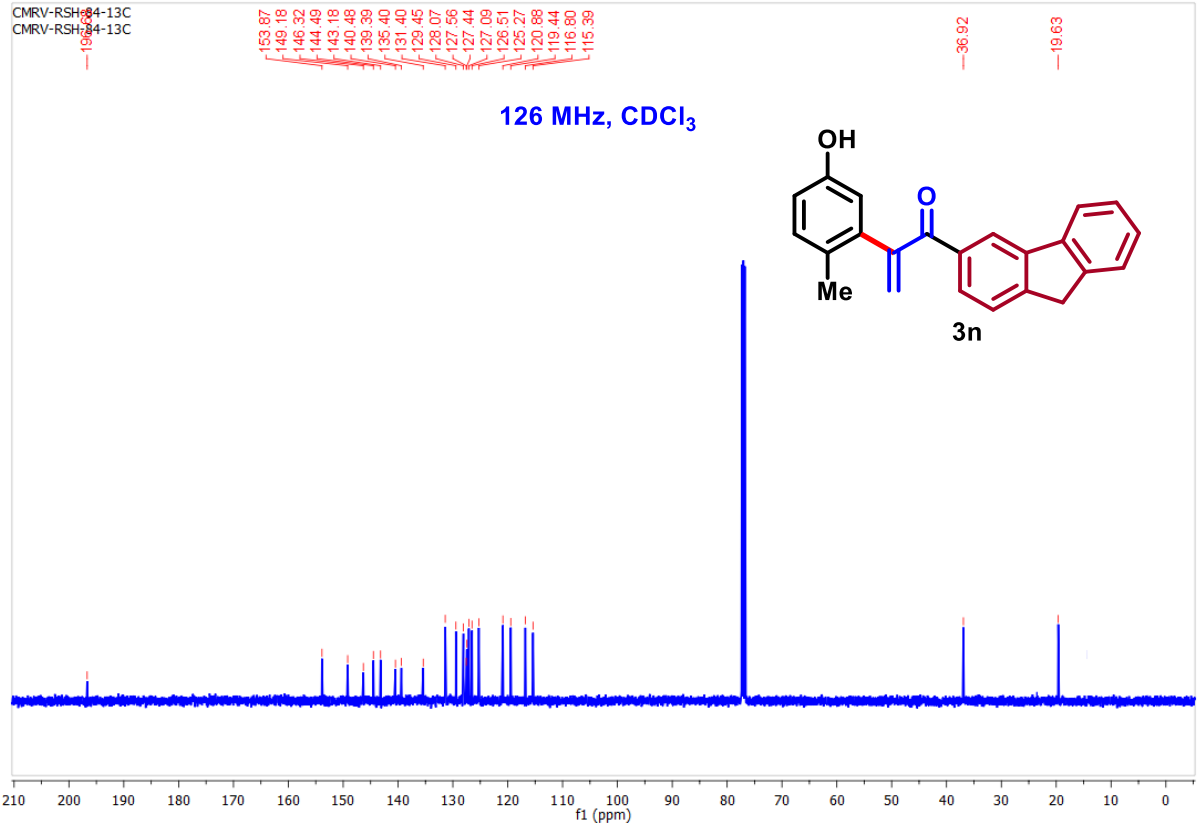

CMRV-IH-355-5-1H
CMRV-IH-355-5-1H
8.31
8.29
8.00
7.99
7.06
7.04
6.80
6.79
6.79
6.77
6.77
6.11
6.08
2.11
400 MHz, CDCl3
OH
O
Me
NO2
3l
1.93
1.88
1.15
2.20
0.99
0.98
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

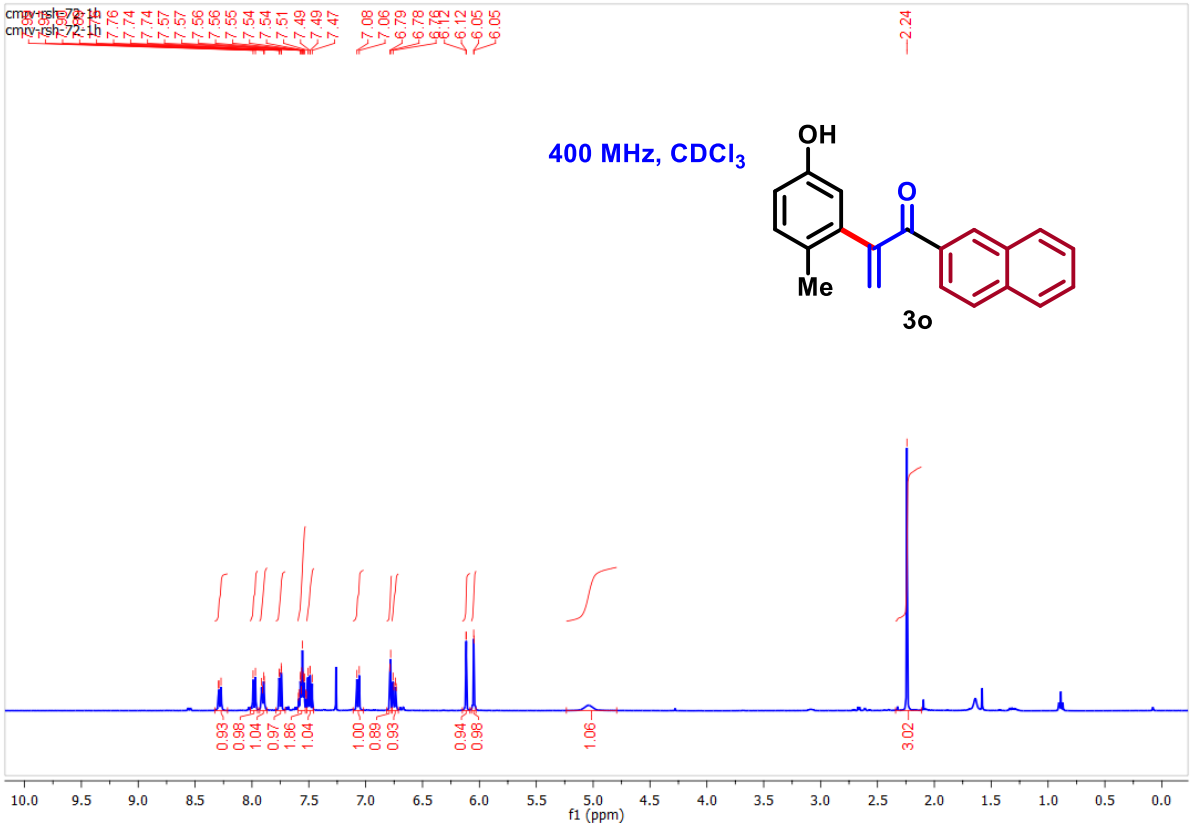

CMRV-IH-355-5-13C
CMRV-IH-355-5-13C
153.89
148.44
142.32
132.44
131.59
130.46
129.71
127.55
123.58
116.58
115.75
19.44
126 MHz, CDCl3
OH
O
Me
NO2
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

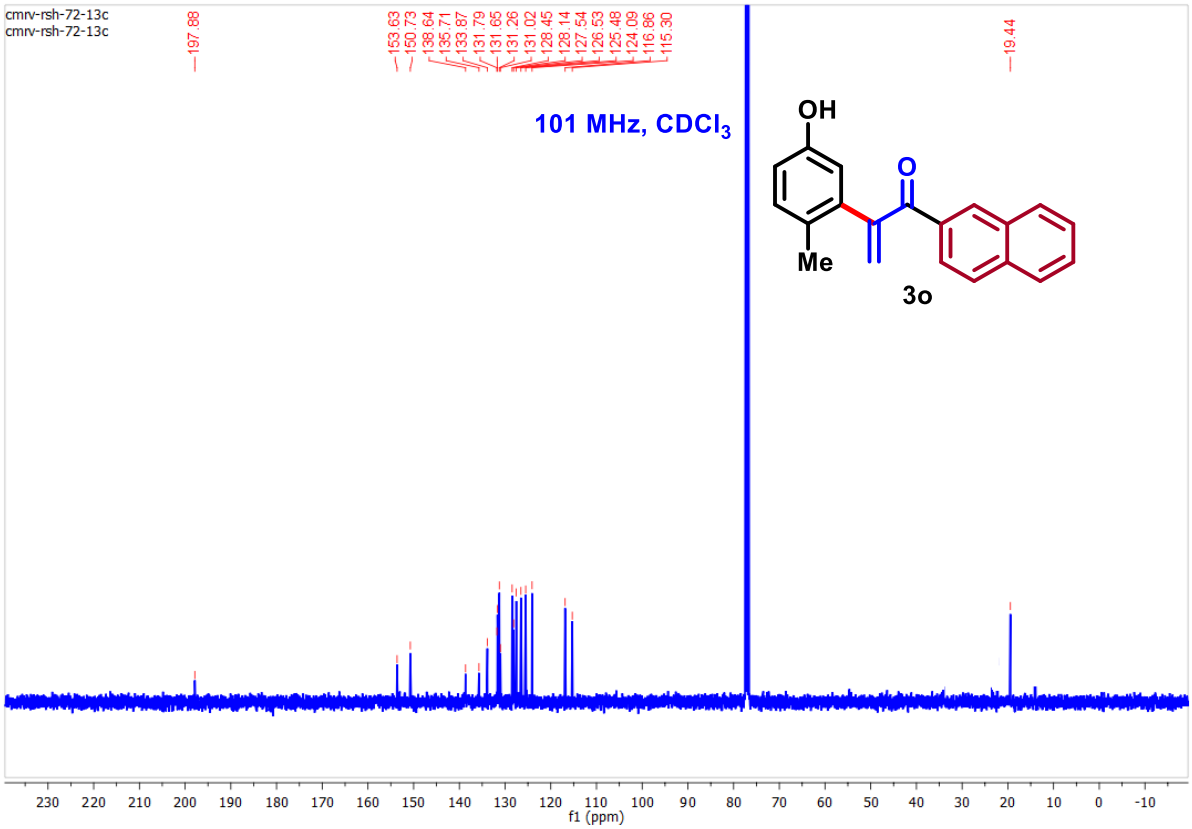

cmrv-rsh-54-1h
cmrv-rsh-54-1h
500 MHz, CDCl3
OH
O
S
Me
3m
f1 (ppm)

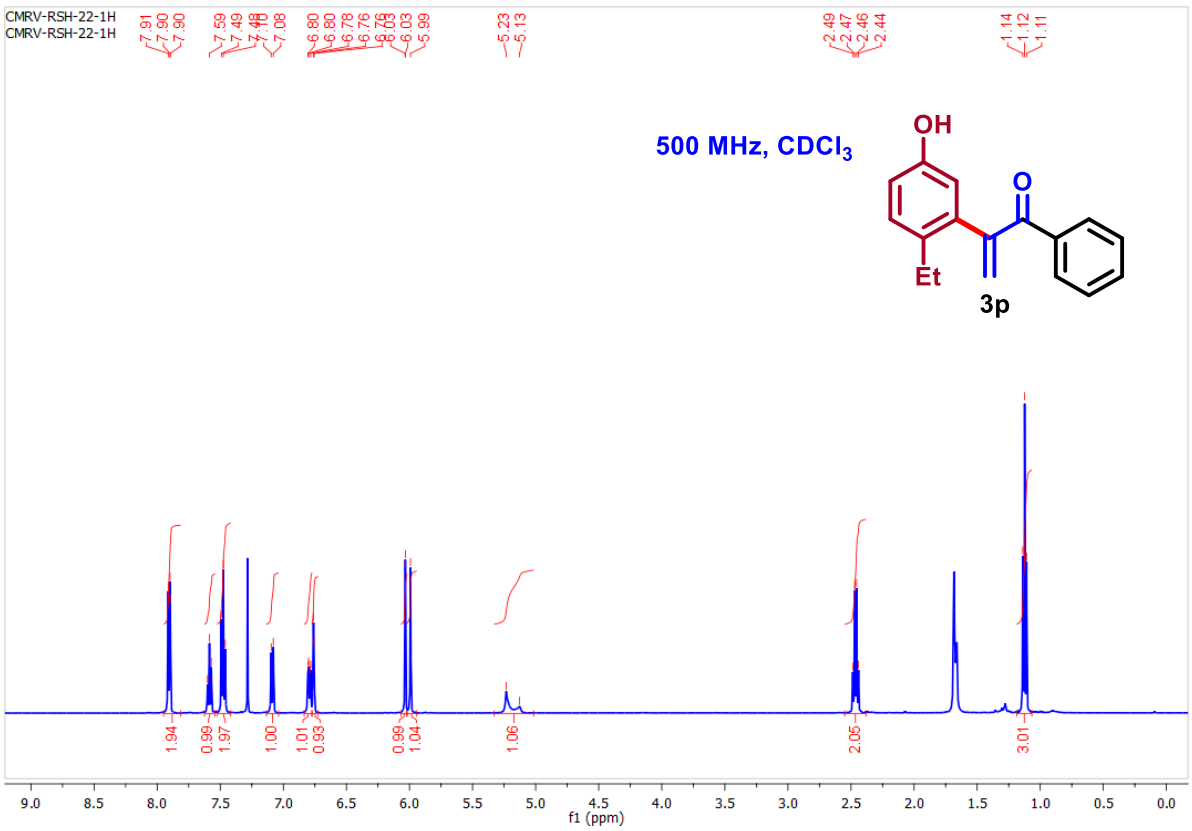

cmrv-rsh-54-13c
cmrv-rsh-54-13c
126 MHz, CDCl3
OH
O
S
Me
3m
f1 (ppm)

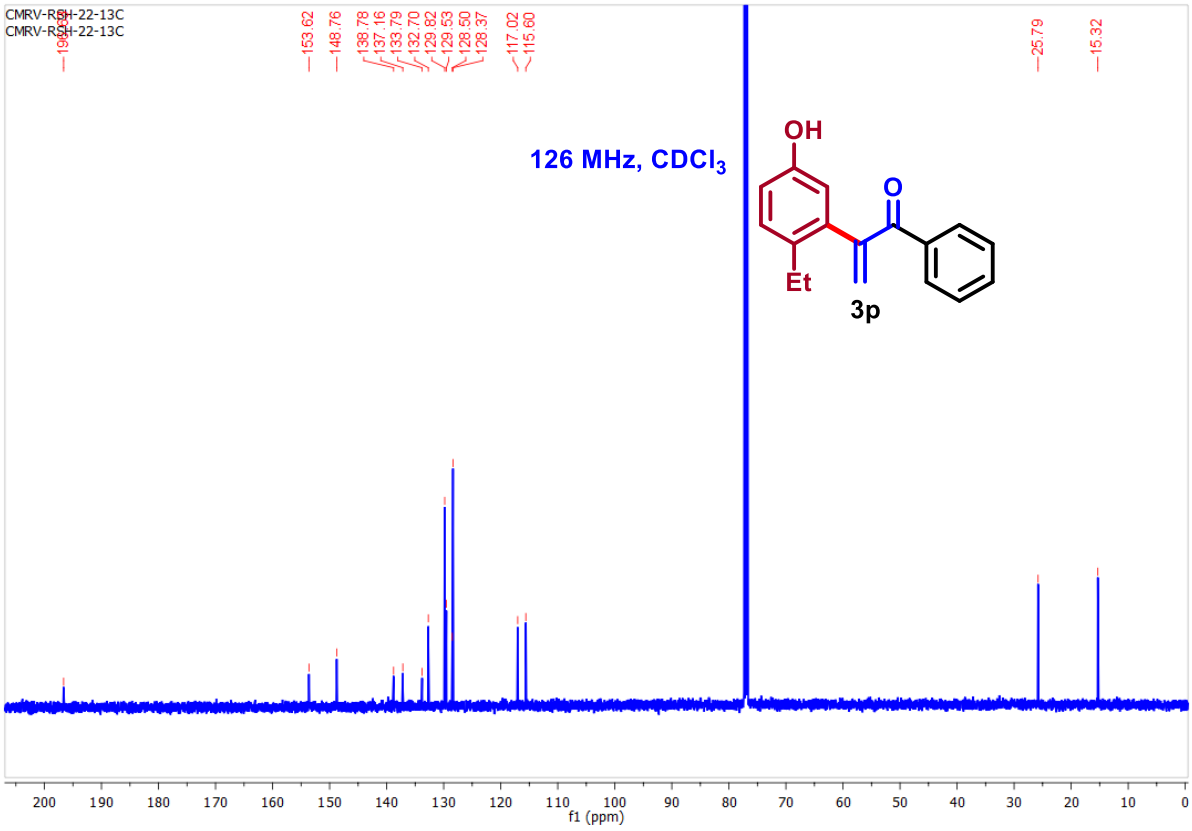

CMRV-RSH-84-1H
500 MHz, CDCl3
OH
O
Me
3n
f1 (ppm)

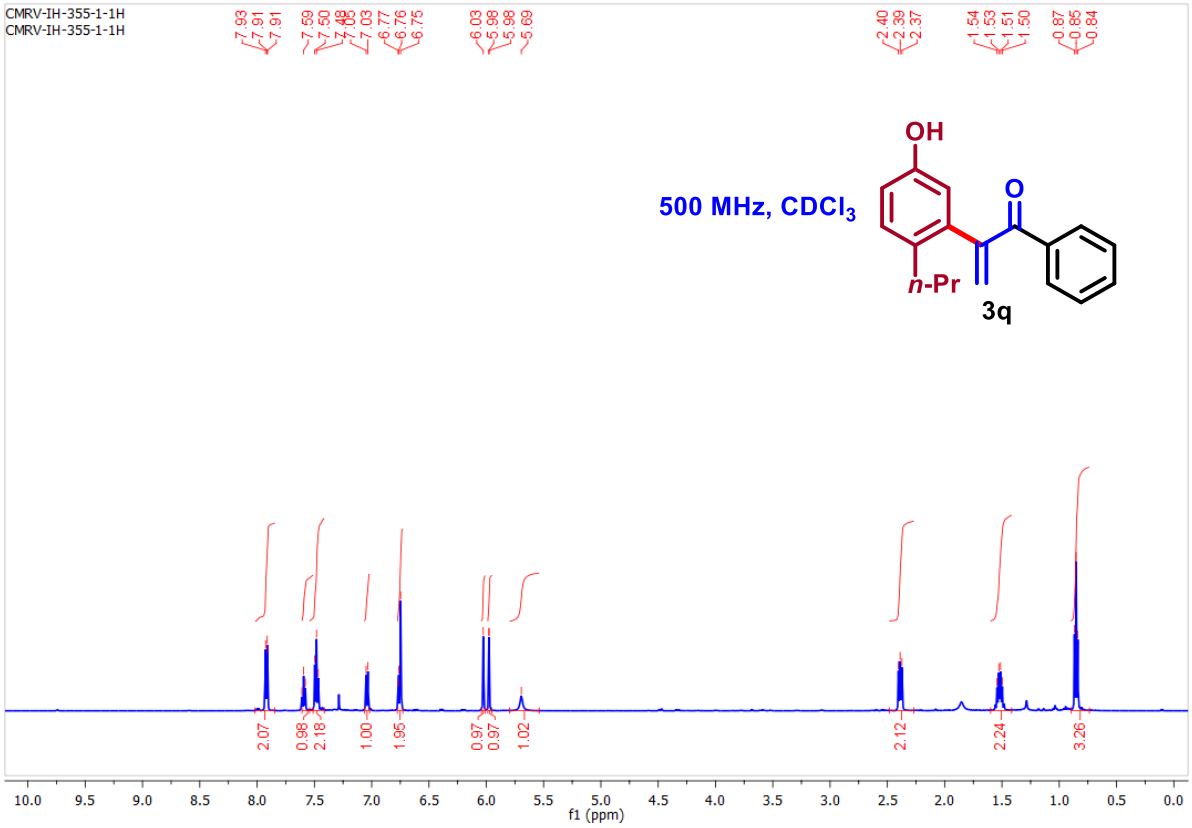

CMRV-RSH-84-13C
126 MHz, CDCl3
OH
O
Me
3n
f1 (ppm)

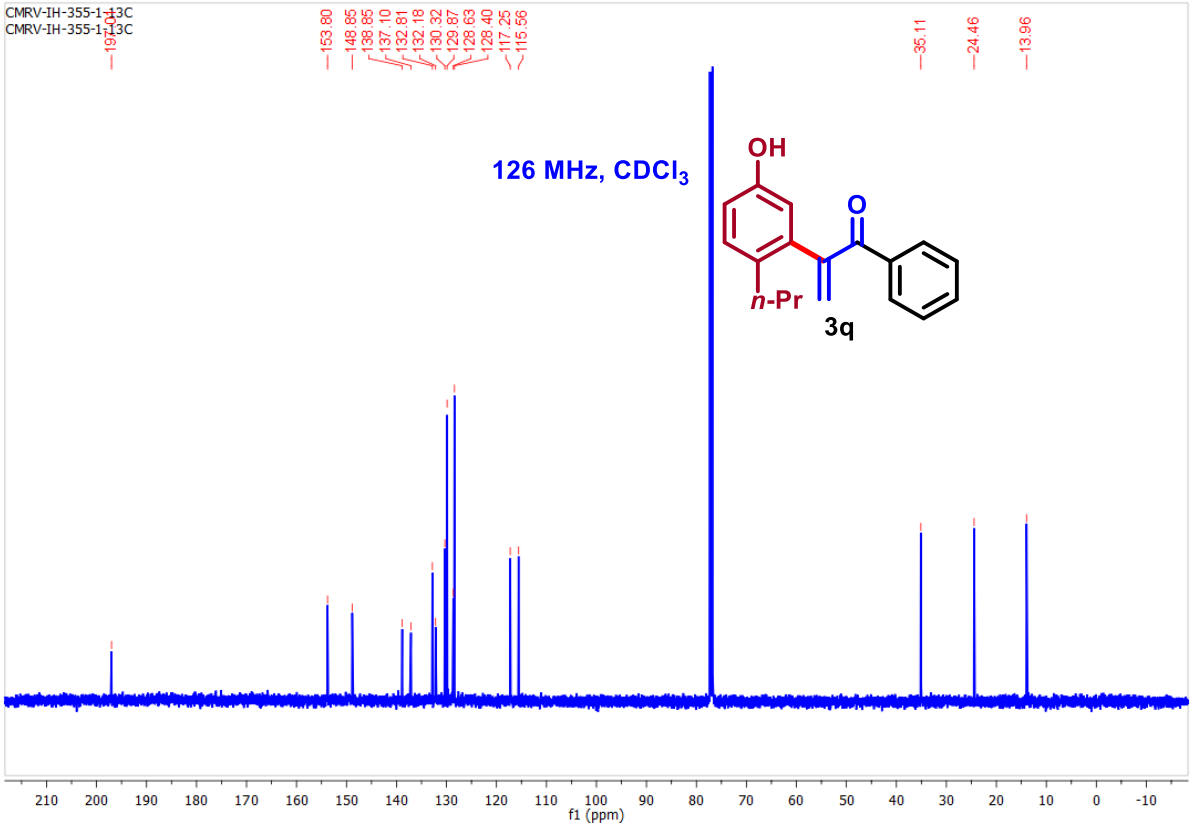

400 MHz, CDCl3
OH
O
Me
3o
f1 (ppm)

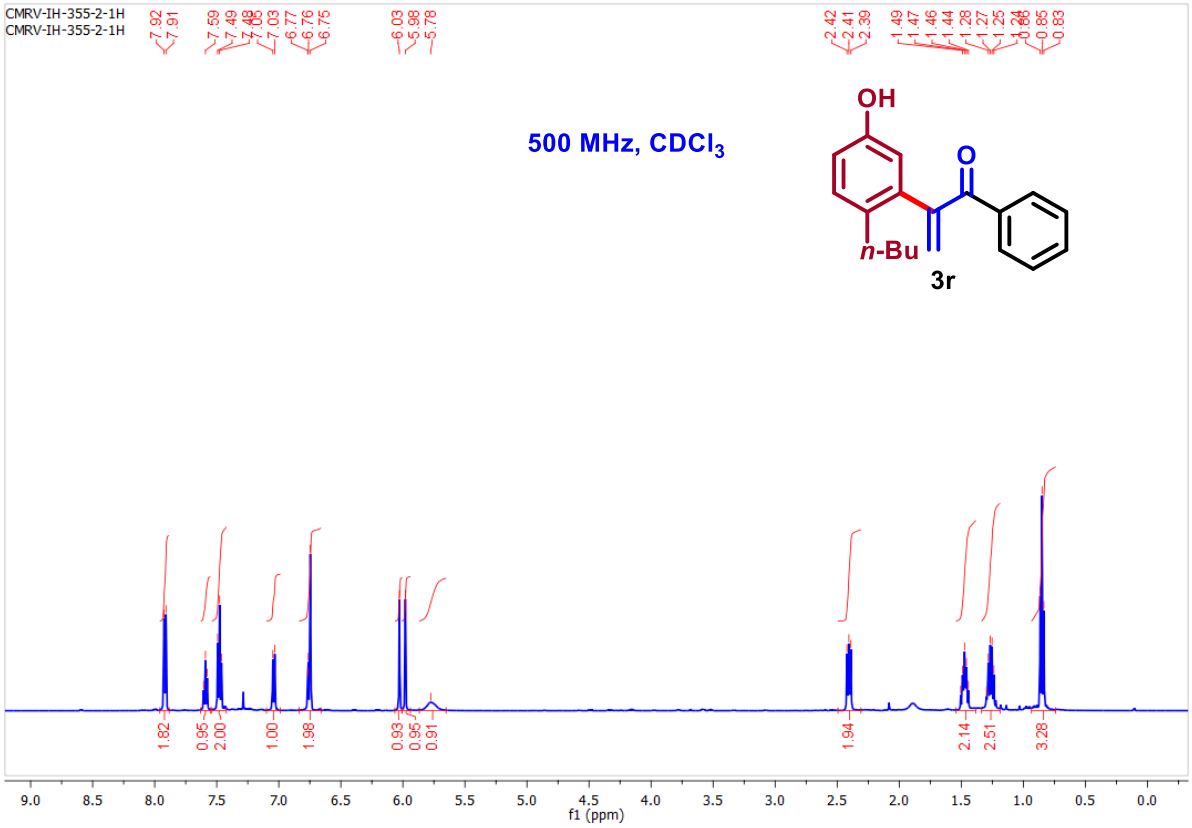

101 MHz, CDCl3
OH
O
Me
3o
f1 (ppm)

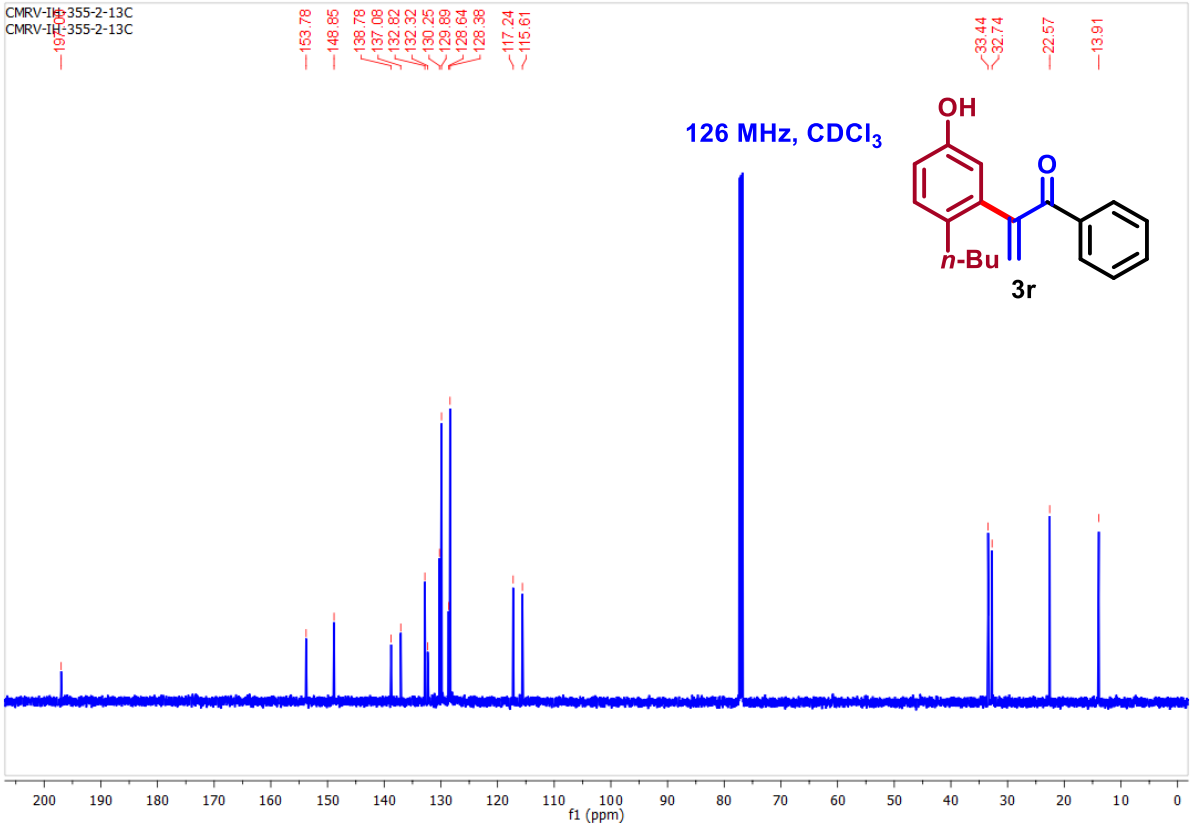

CMRV-RSH-22-1H
CMRV-RSH-22-1H
500 MHz, CDCl3
OH
O
Et
3p
f1 (ppm)

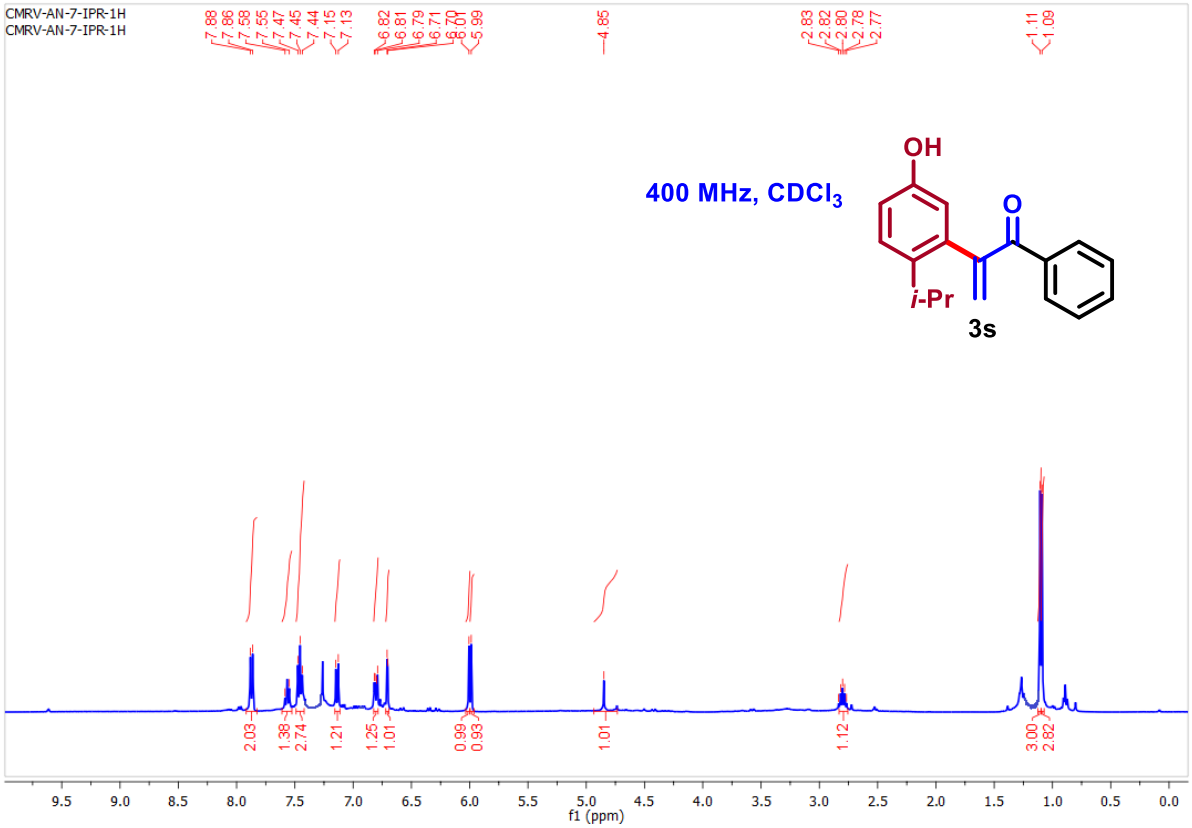

CMRV-RSH-22-13C
CMRV-RSH-22-13C
126 MHz, CDCl3
OH
O
Et
3p
f1 (ppm)

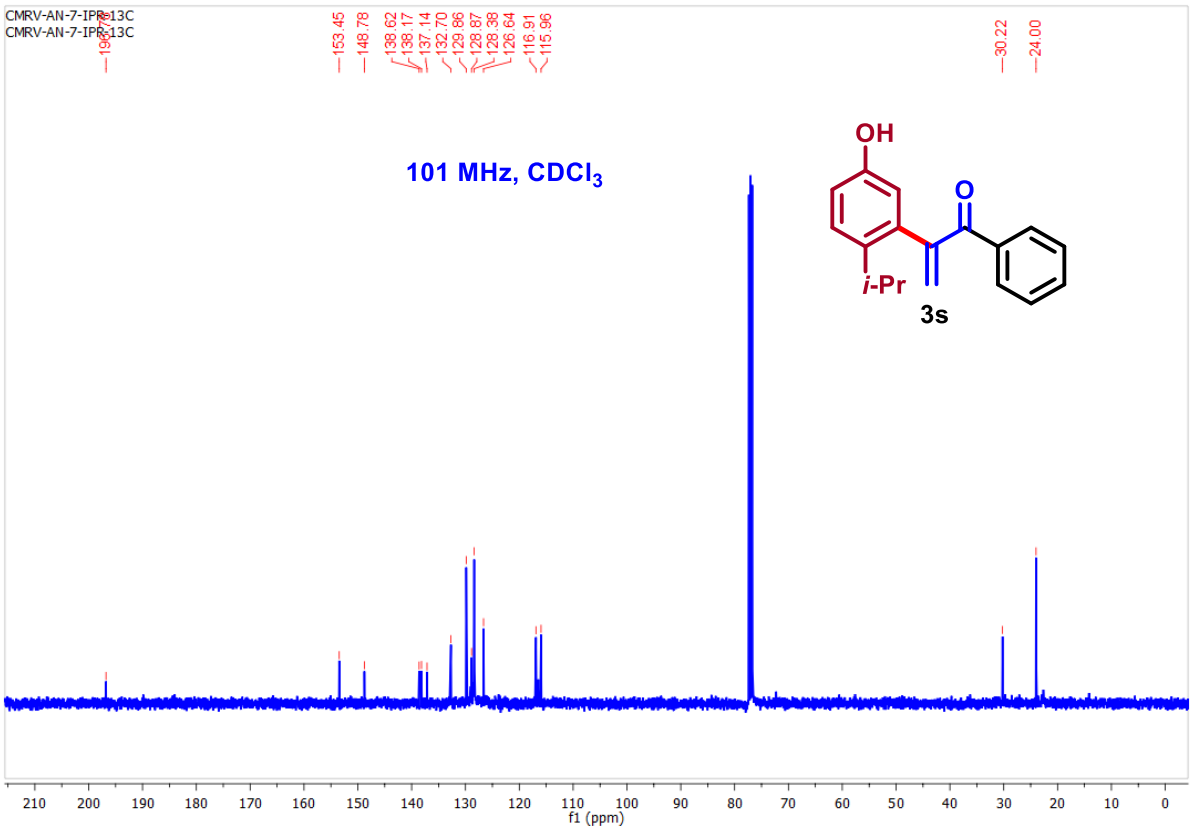

CMRV-IH-355-1-1H
CMRV-IH-355-1-1H
500 MHz, CDCl3
OH
O
n-Pr
3q
f1 (ppm)

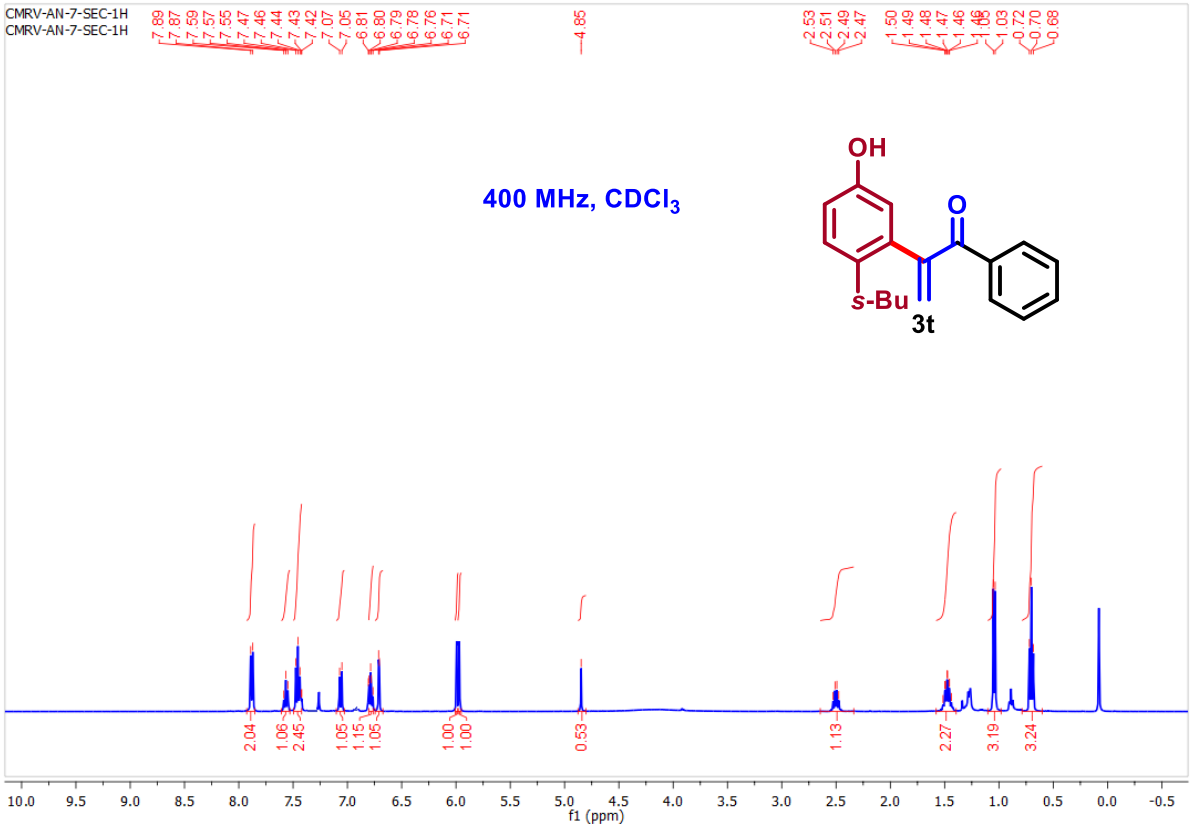

CMRV-IH-355-1-13C
CMRV-IH-355-1-13C
126 MHz, CDCl3
OH
O
n-Pr
3q
f1 (ppm)

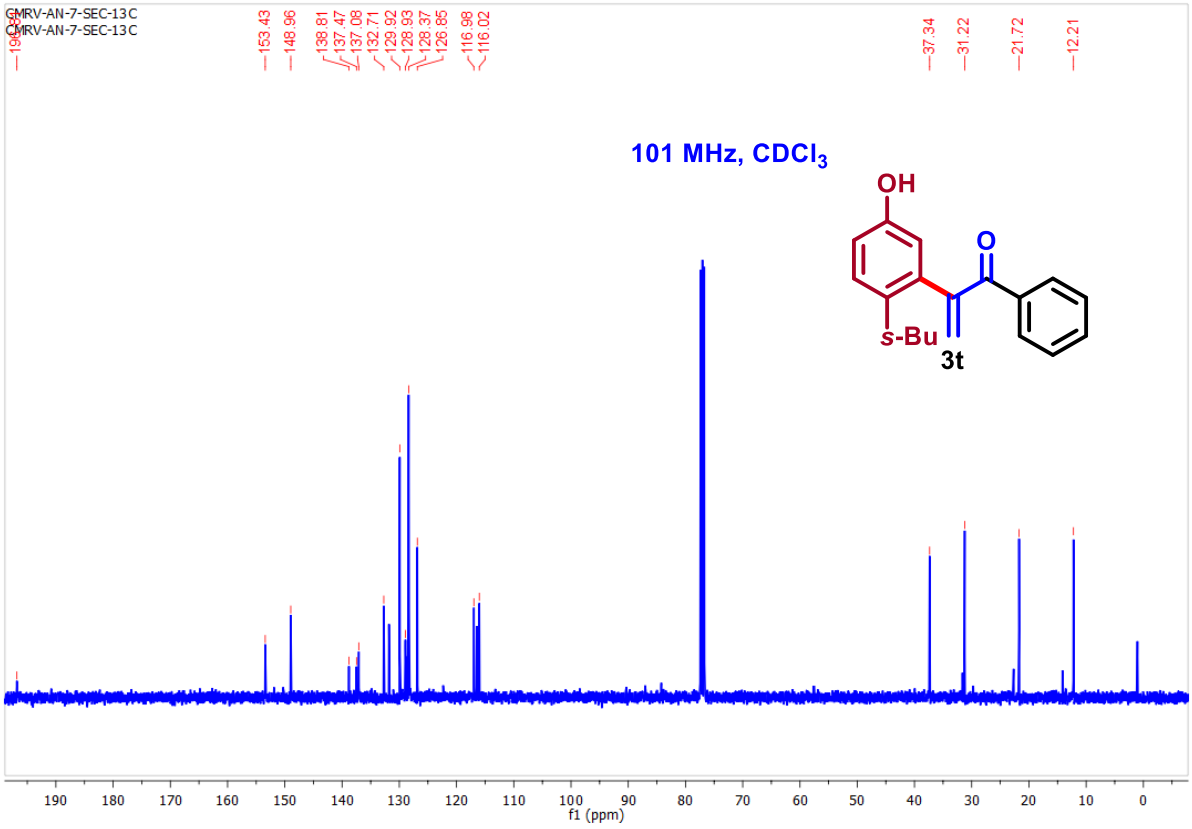

CMRV-IH-355-2-1H
CMRV-IH-355-2-1H
500 MHz, CDCl3
OH
O
n-Bu
3r
f1 (ppm)

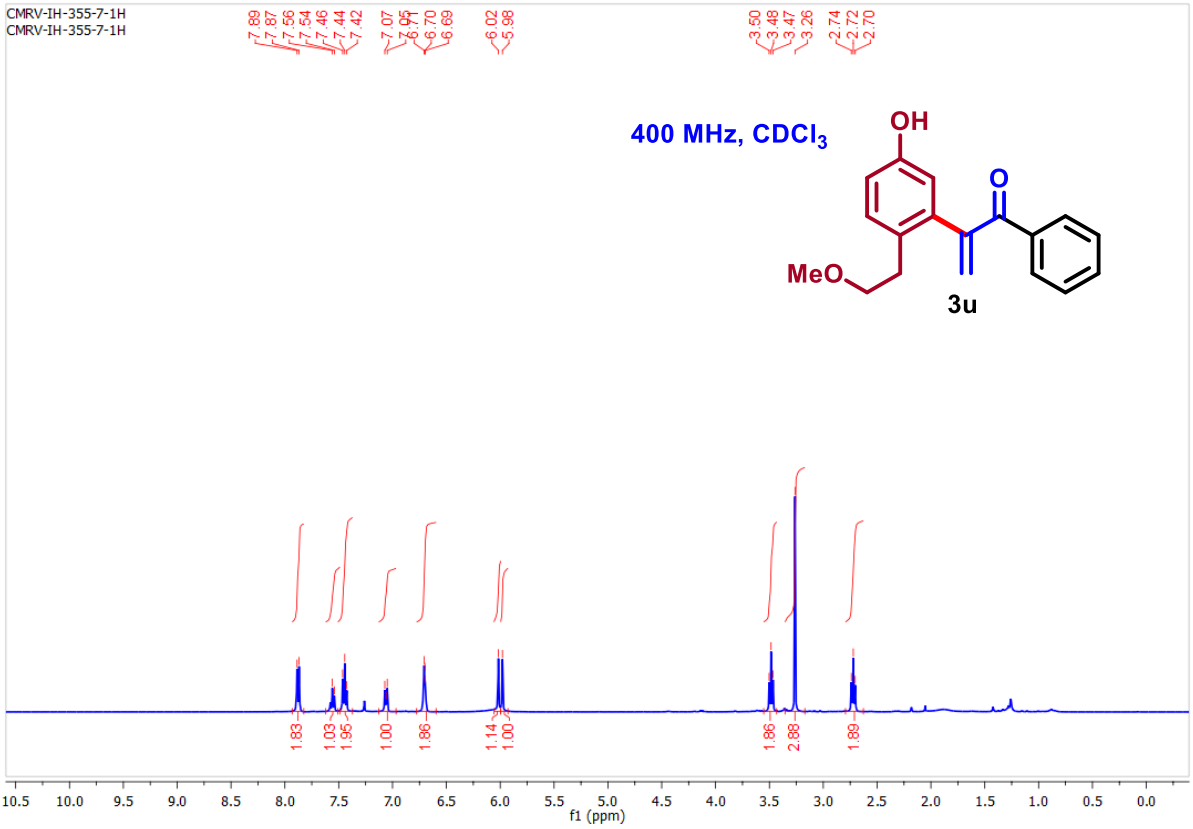

CMRV-IH-355-2-13C
CMRV-IH-355-2-13C
126 MHz, CDCl3
OH
O
n-Bu
3r
f1 (ppm)

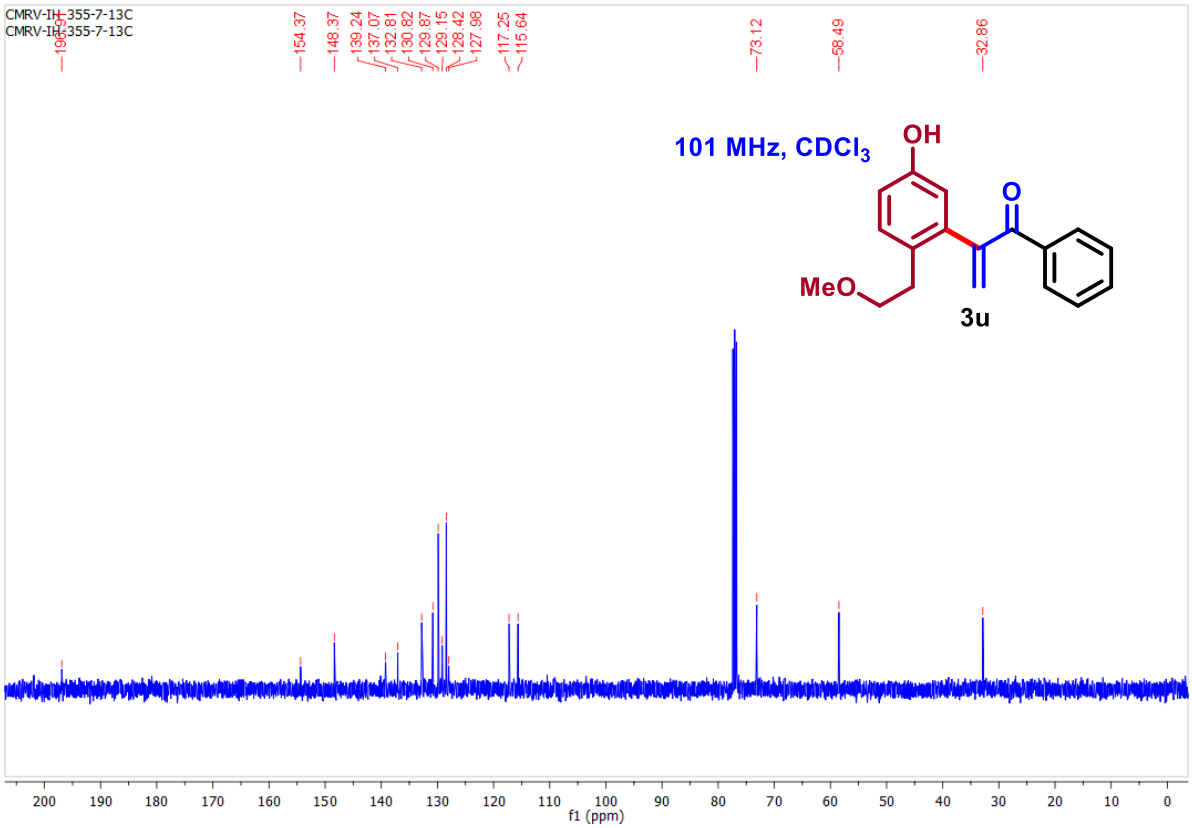

CMRV-AN-7-IPR-1H
CMRV-AN-7-IPR-1H
7.88
7.86
7.58
7.55
7.47
7.45
7.44
7.15
7.13
6.82
6.81
6.79
6.71
6.70
6.01
5.99
4.85
2.83
2.82
2.80
2.78
2.77
1.11
1.09
400 MHz, CDCl3
OH
O
i-Pr
3s
2.03
1.38
2.74
1.21
1.25
1.01
0.99
0.93
1.01
1.12
3.00
2.82
f1 (ppm)

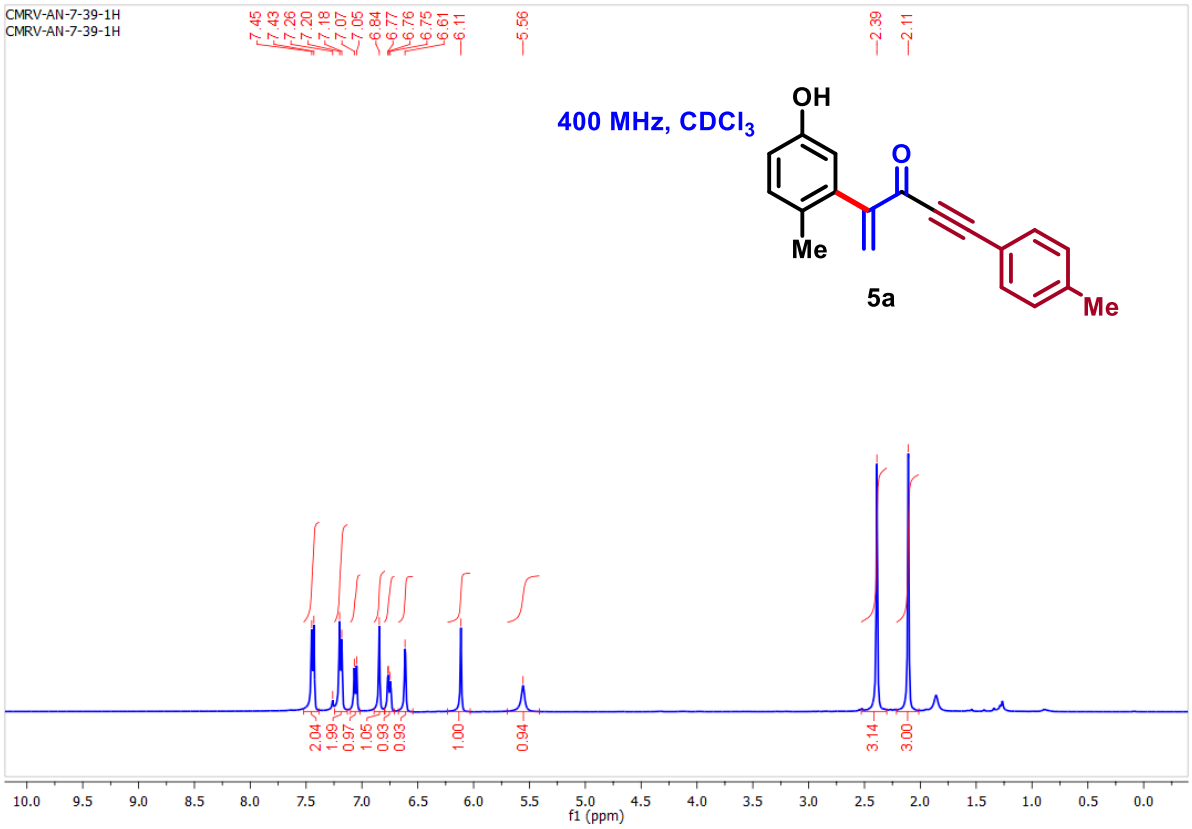

CMRV-AN-7-IPR-13C
CMRV-AN-7-IPR-13C
153.45
148.78
138.62
138.17
137.14
132.70
129.86
128.87
128.38
126.64
116.91
115.96
30.22
24.00
101 MHz, CDCl3
OH
O
i-Pr
3s
f1 (ppm)

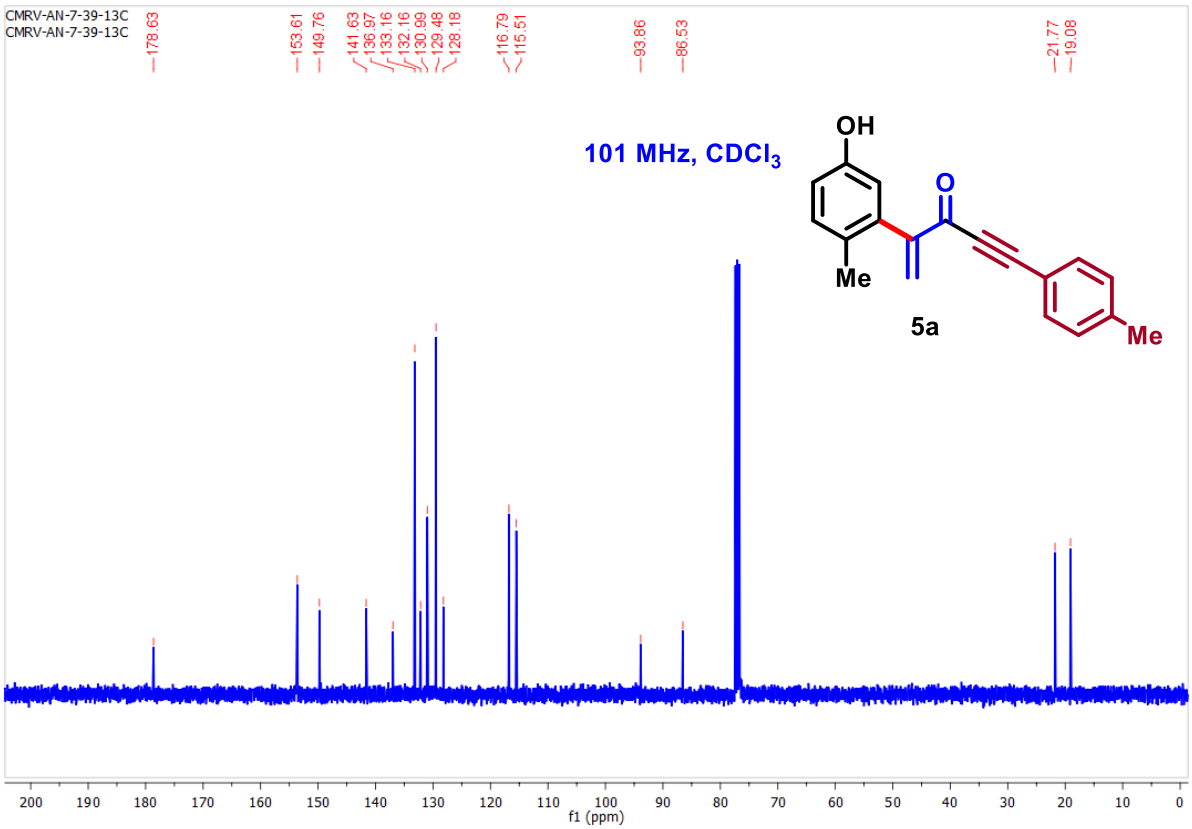

CMRV-AN-7-SEC-1H
CMRV-AN-7-SEC-1H
400 MHz, CDCl3
OH
O
s-Bu
3t
f1 (ppm)

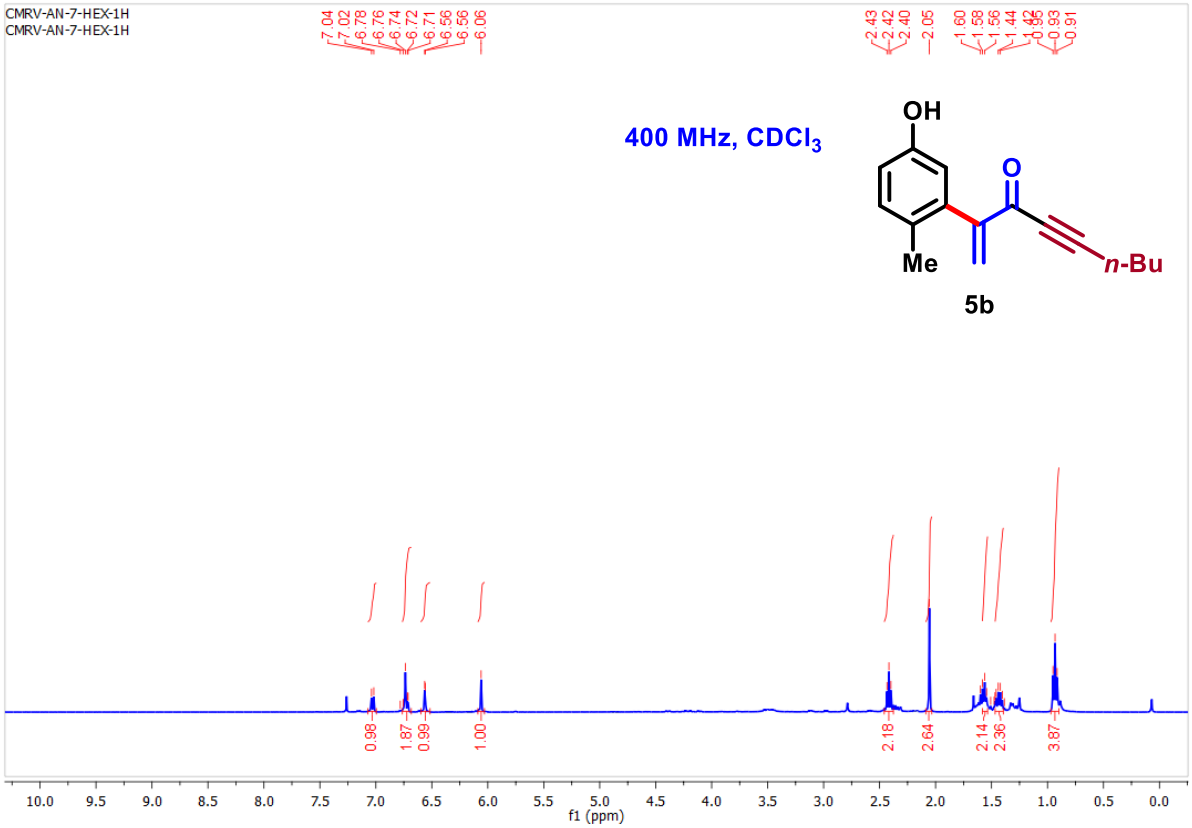

CMRV-AN-7-SEC-13C
CMRV-AN-7-SEC-13C
101 MHz, CDCl3
OH
O
s-Bu
3t
f1 (ppm)

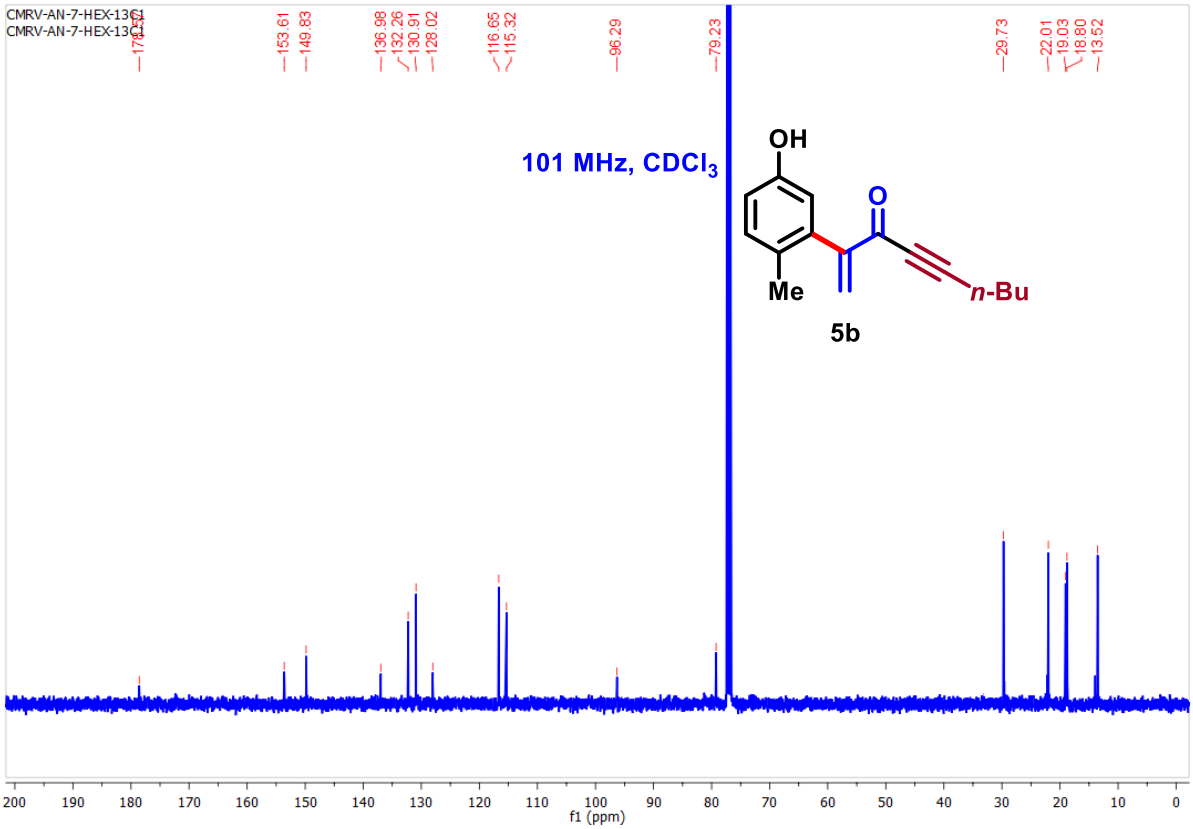

CMRV-IH-355-7-1H
CMRV-IH-355-7-1H
400 MHz, CDCl3
OH
O
MeO
3u
f1 (ppm)

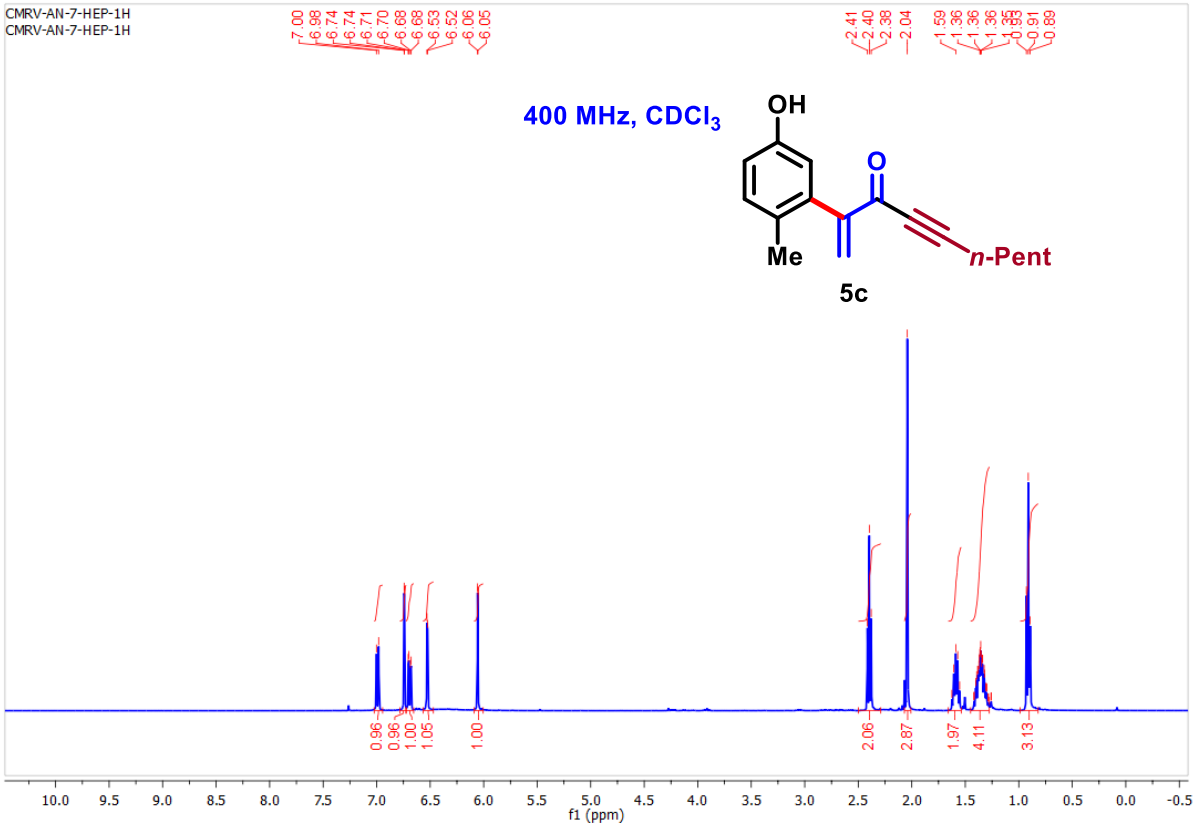

CMRV-IH-355-7-13C
CMRV-IH-355-7-13C
101 MHz, CDCl3
OH
O
MeO
3u
f1 (ppm)

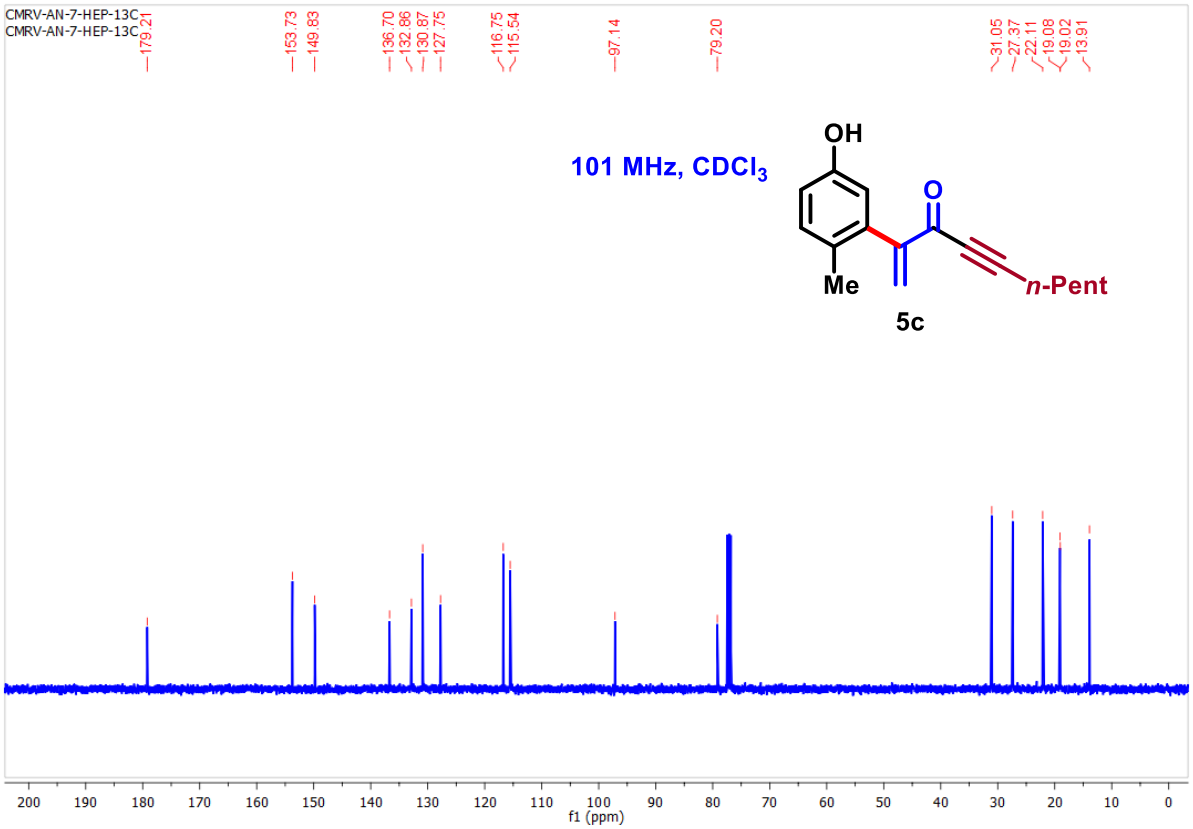

CMRV-AN-7-39-1H
CMRV-AN-7-39-1H
400 MHz, CDCl3
OH
O
Me
5a
Me
f1 (ppm)

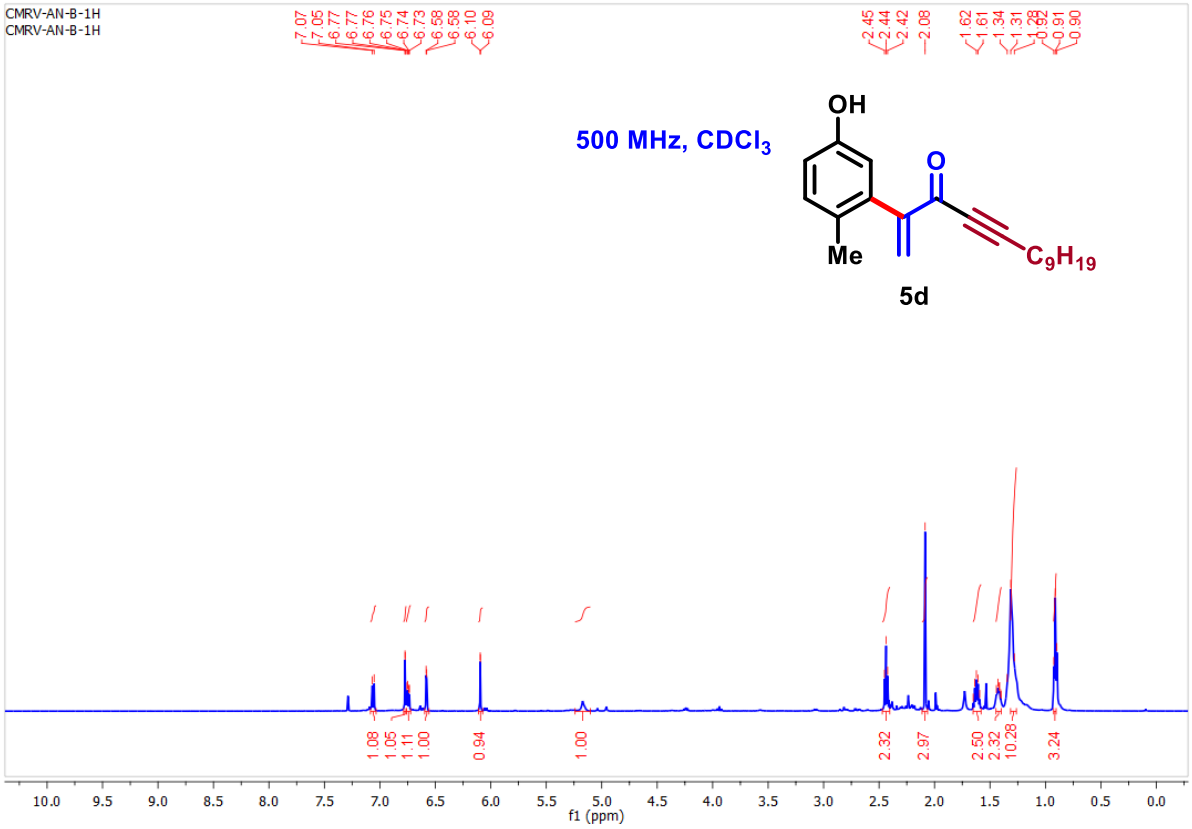

CMRV-AN-7-39-13C
CMRV-AN-7-39-13C
101 MHz, CDCl3
OH
O
Me
5a
Me
f1 (ppm)

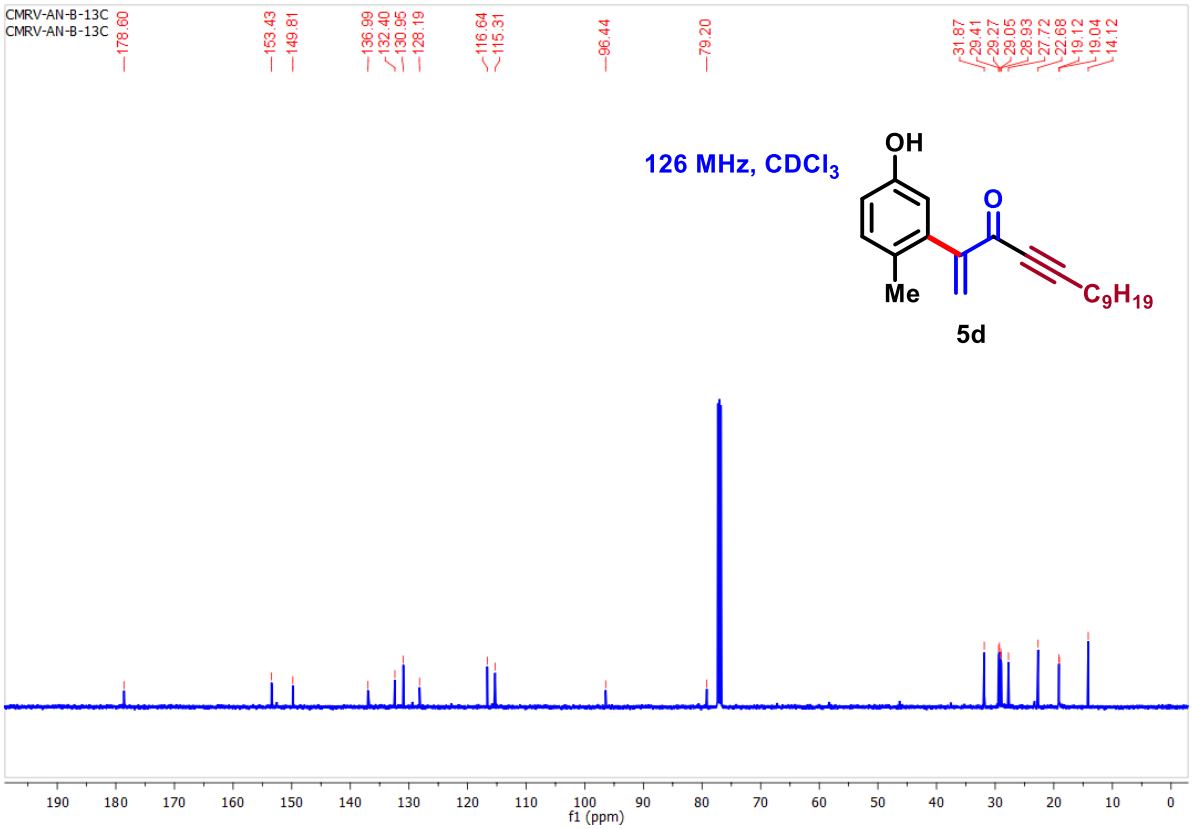

CMRV-AN-7-HEX-1H
CMRV-AN-7-HEX-1H
400 MHz, CDCl3
OH
O
Me
n-Bu
5b
f1 (ppm)

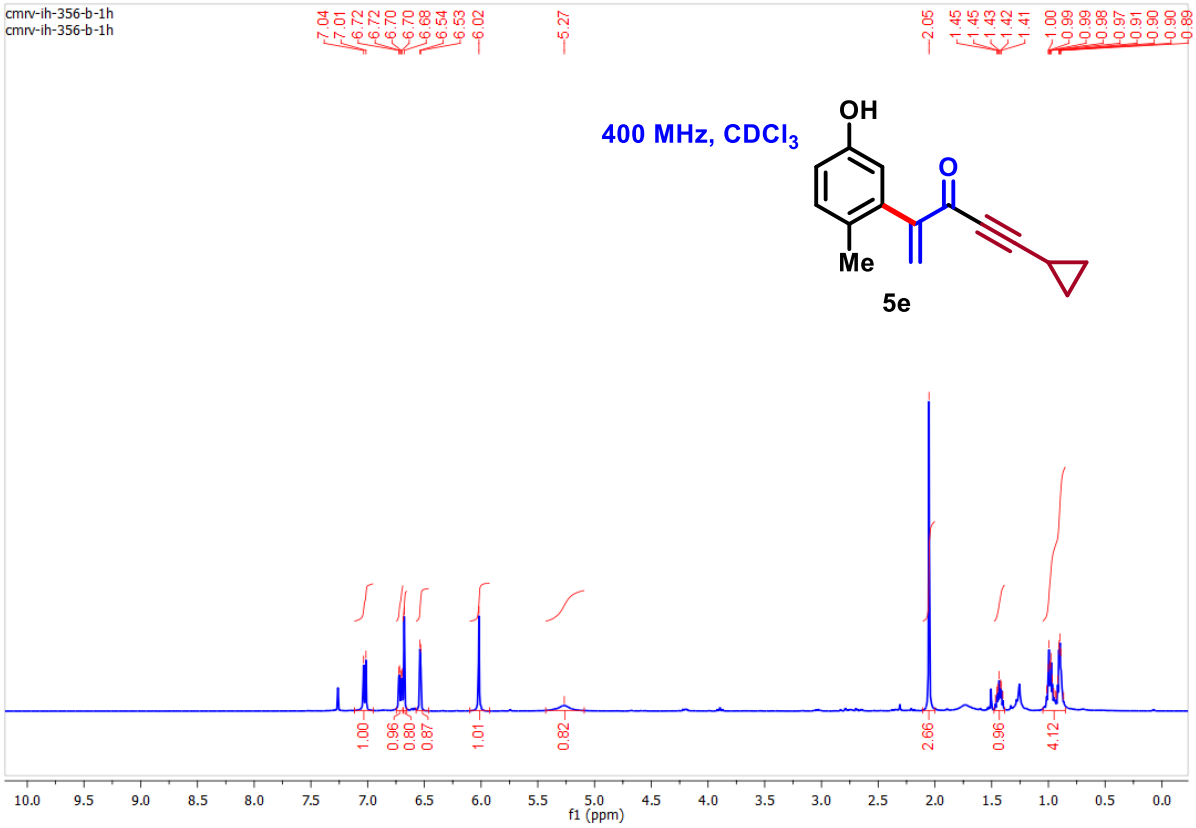

CMRV-AN-7-HEX-13C1
CMRV-AN-7-HEX-13C1
101 MHz, CDCl3
OH
O
Me
n-Bu
5b
f1 (ppm)

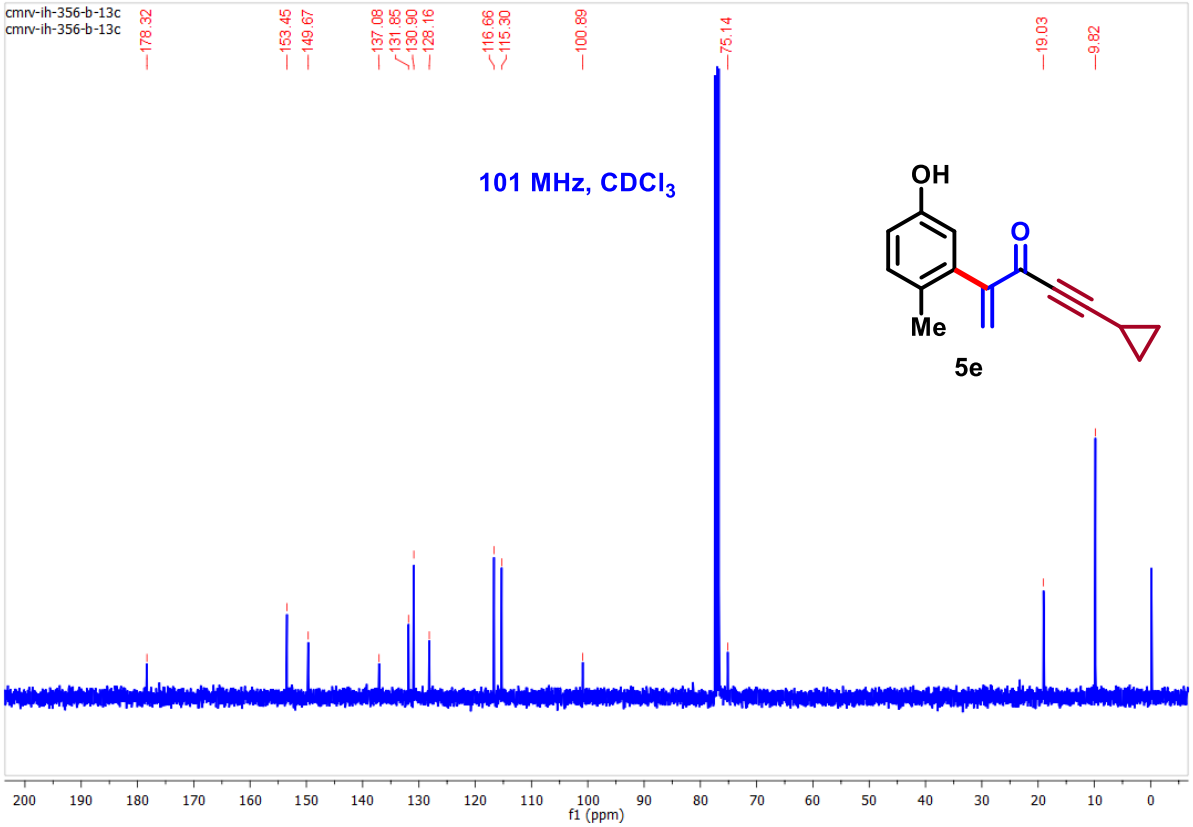

CMRV-AN-7-HEP-1H
CMRV-AN-7-HEP-1H
400 MHz, CDCl3
OH
O
Me
n-Pent
5c
f1 (ppm)

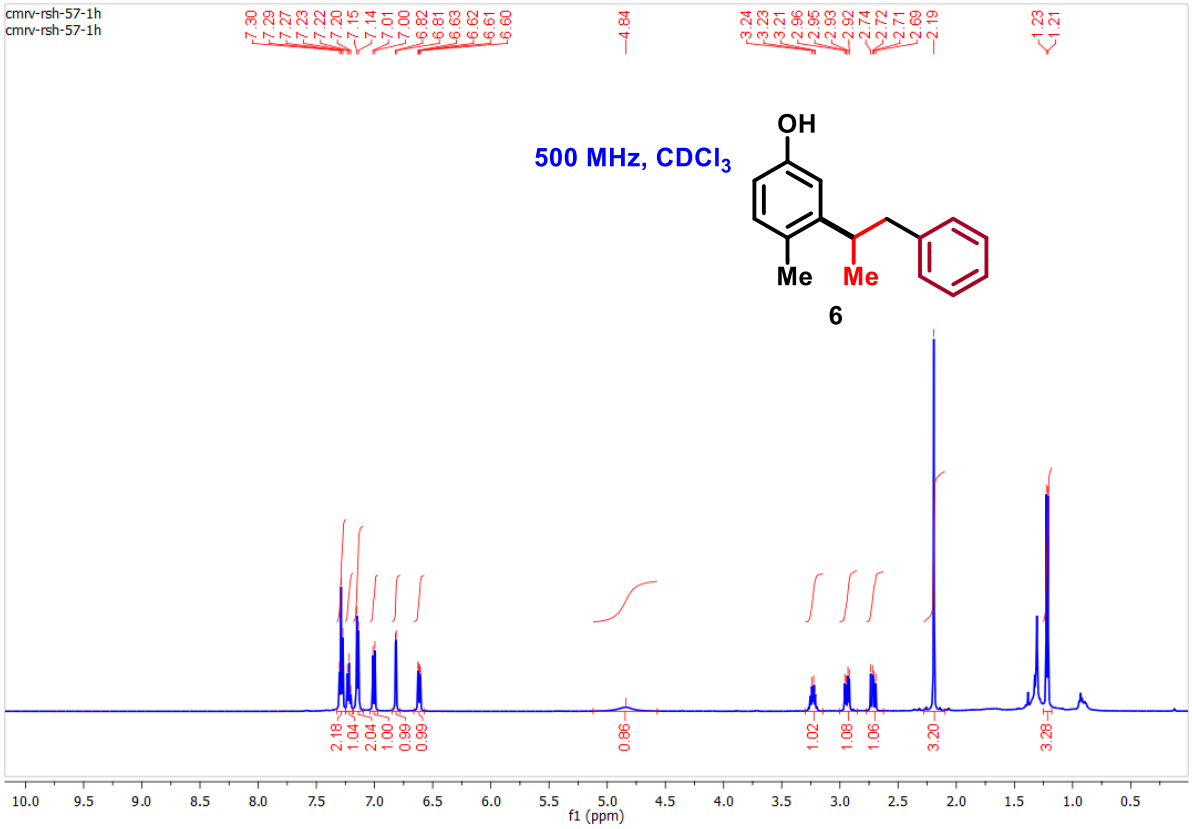

CMRV-AN-7-HEP-13C
CMRV-AN-7-HEP-13C
101 MHz, CDCl3
OH
O
Me
n-Pent
5c
f1 (ppm)

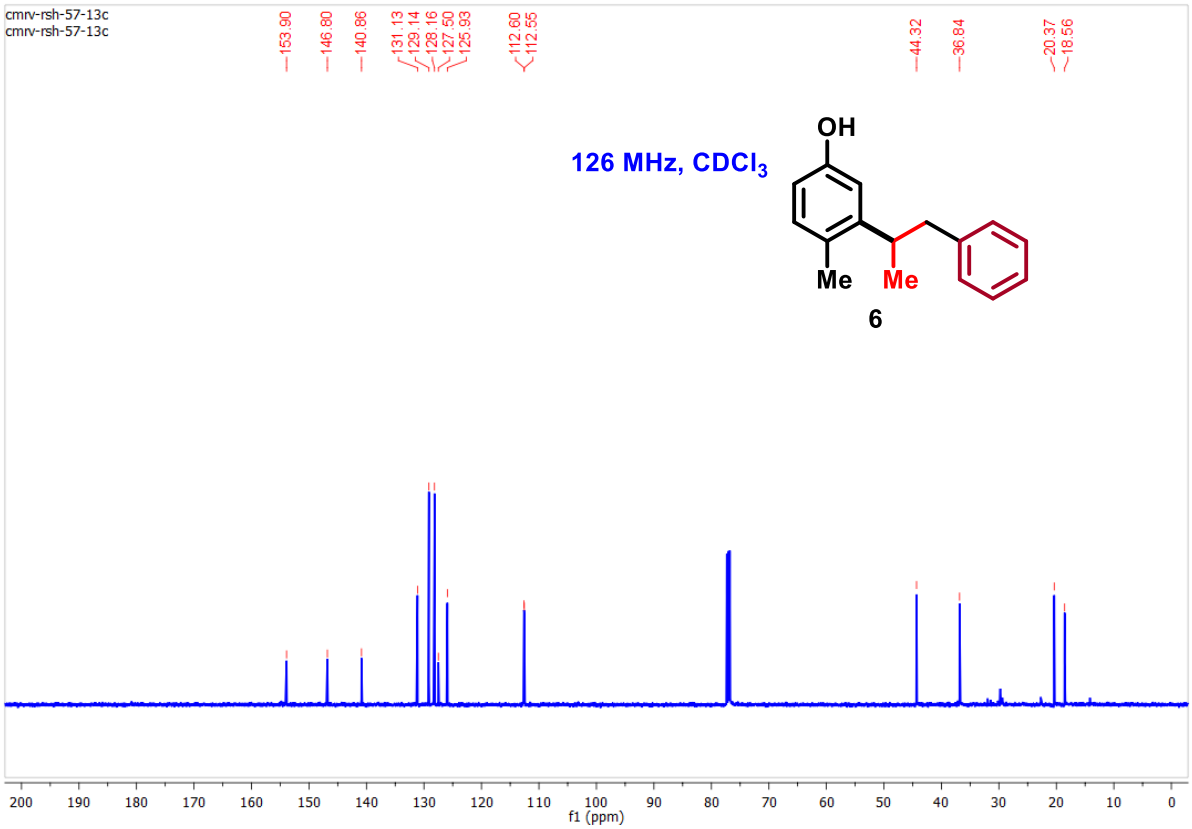

CMRV-AN-B-1H
CMRV-AN-B-1H
500 MHz, CDCl3
OH
O
Me
C9H19
5d
f1 (ppm)

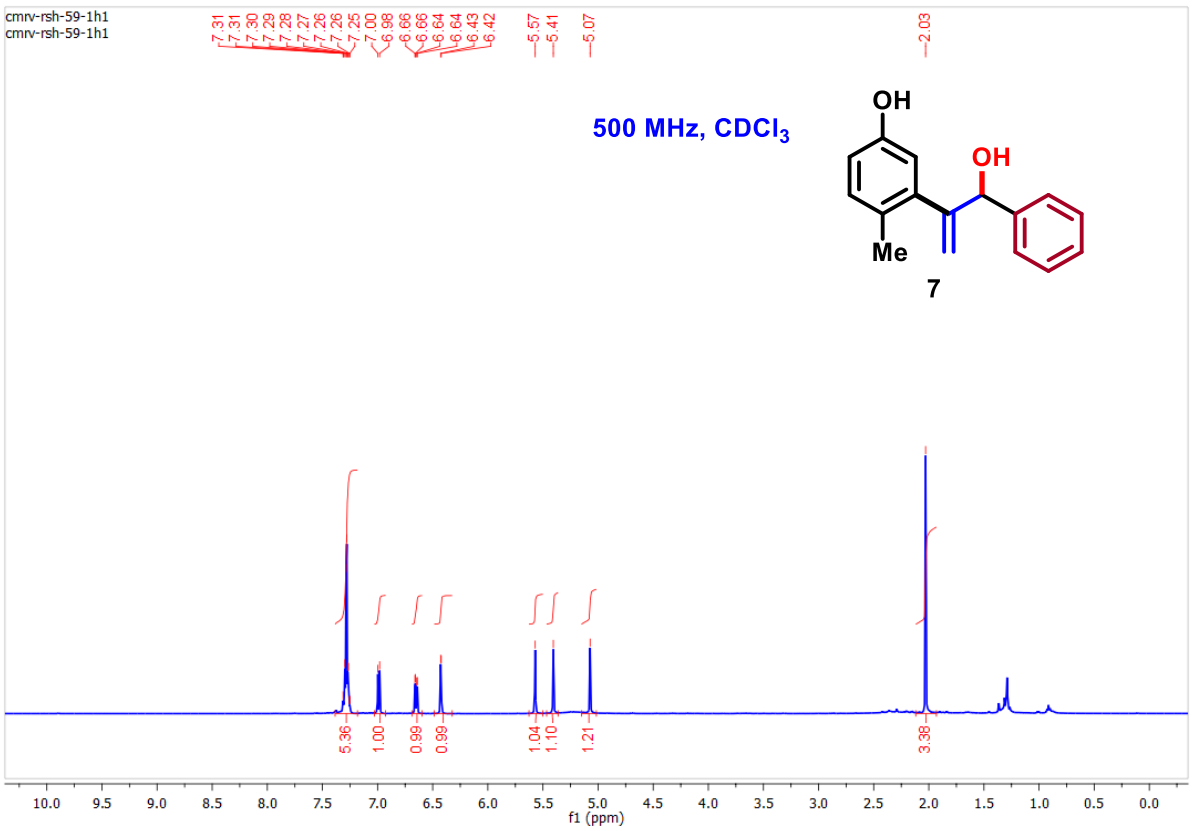

CMRV-AN-B-13C
CMRV-AN-B-13C
126 MHz, CDCl3
OH
O
Me
C9H19
5d
f1 (ppm)

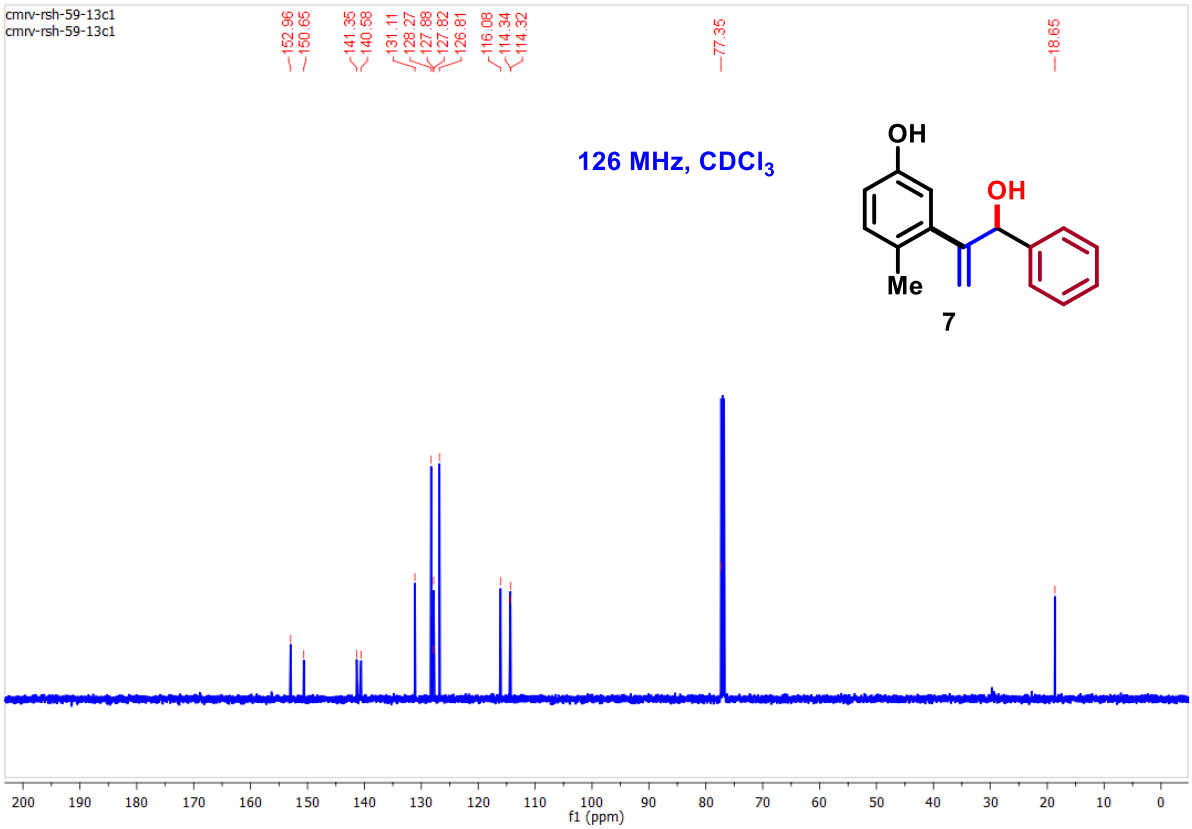

cmrv-ih-356-b-1h
cmrv-ih-356-b-1h
400 MHz, CDCl3
OH
O
Me
5e
f1 (ppm)

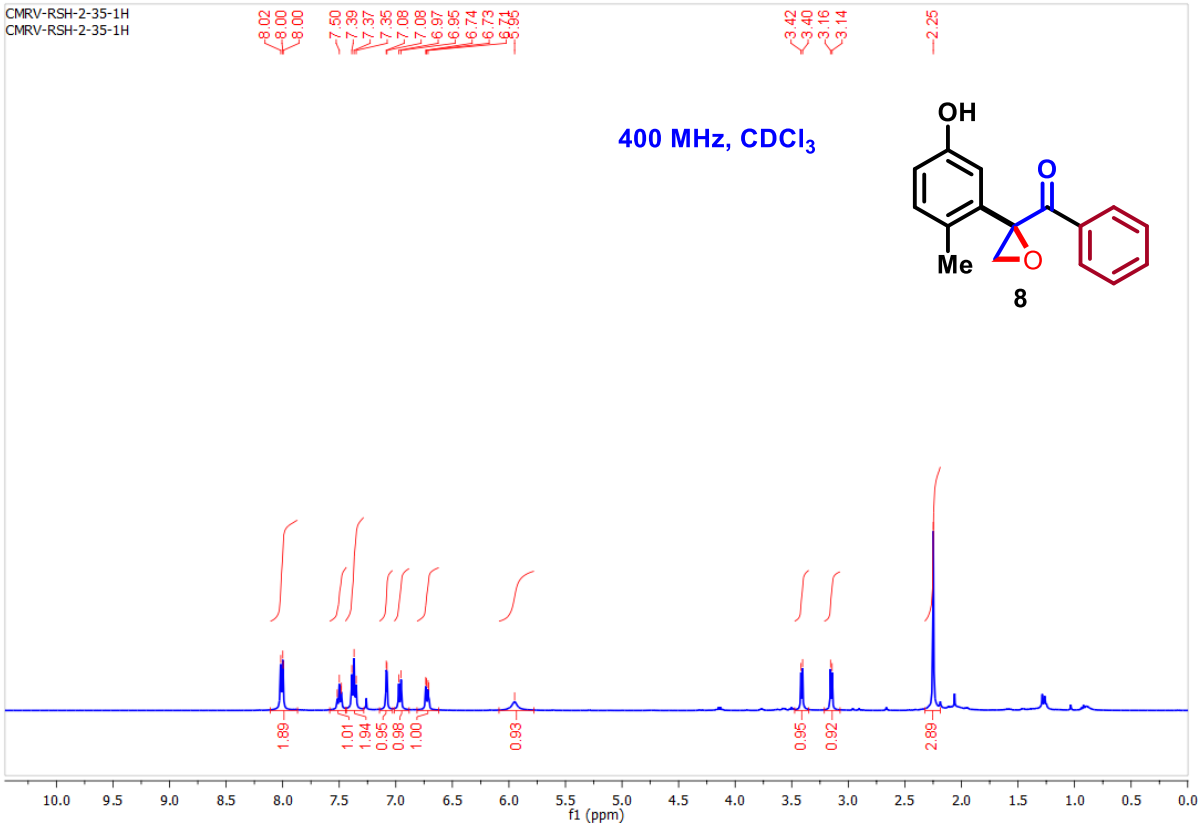

cmrv-ih-356-b-13c
cmrv-ih-356-b-13c
101 MHz, CDCl3
OH
O
Me
5e
f1 (ppm)

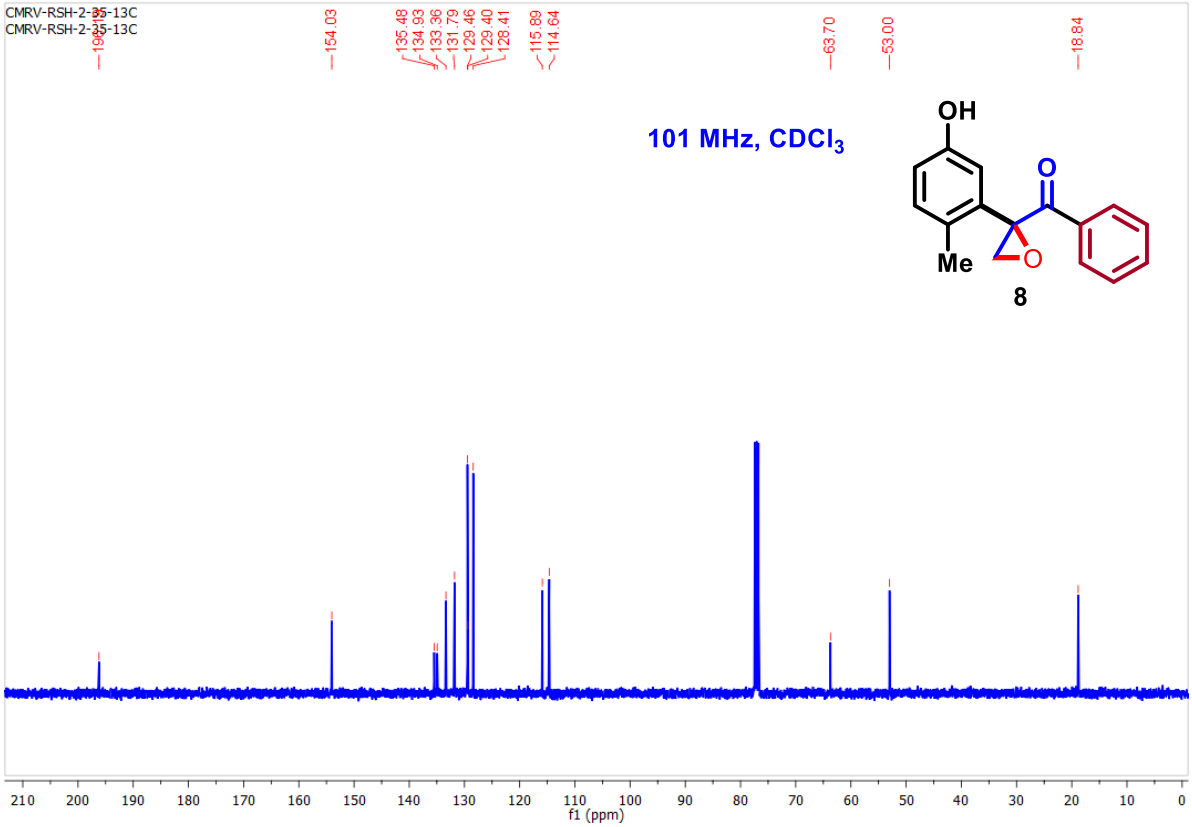

cmrv-rsh-57-1h
cmrv-rsh-57-1h
500 MHz, CDCl3
OH
Me
Me
6
f1 (ppm)

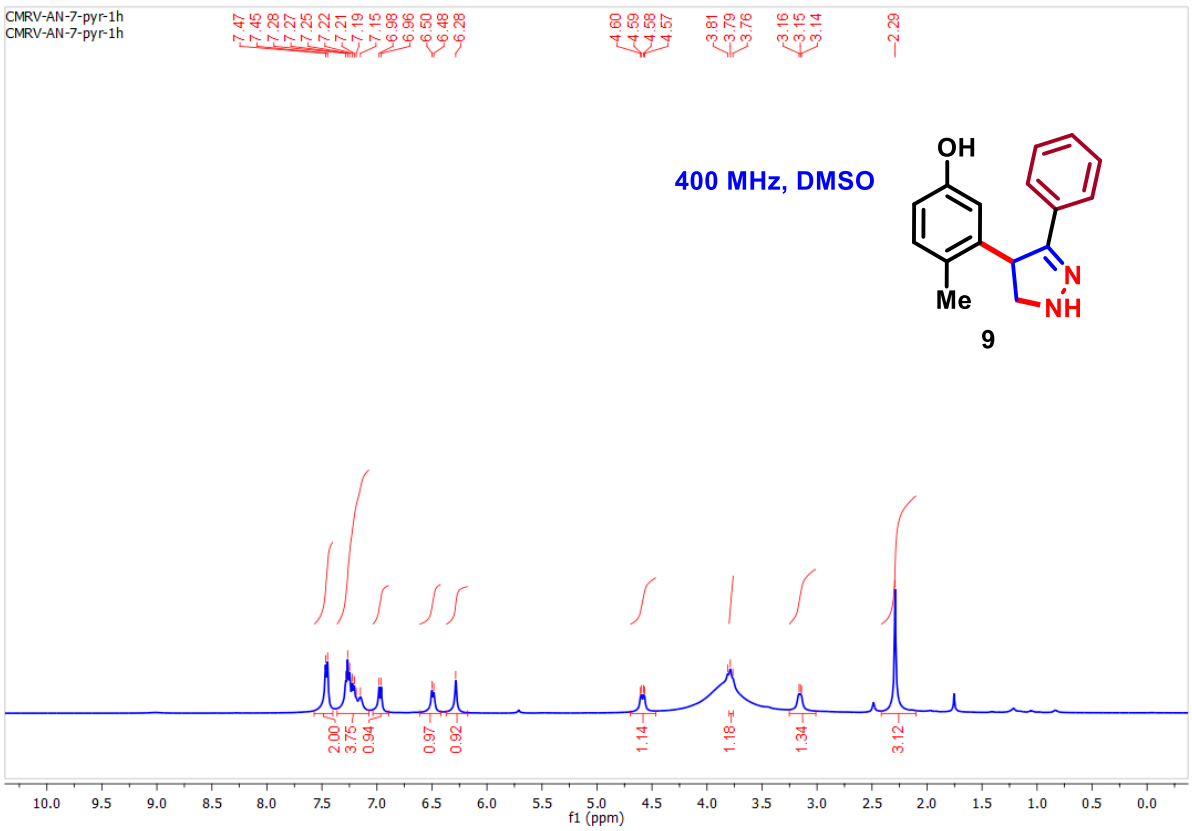

cmrv-rsh-57-13c
cmrv-rsh-57-13c
126 MHz, CDCl3
OH
Me
Me
6
f1 (ppm)

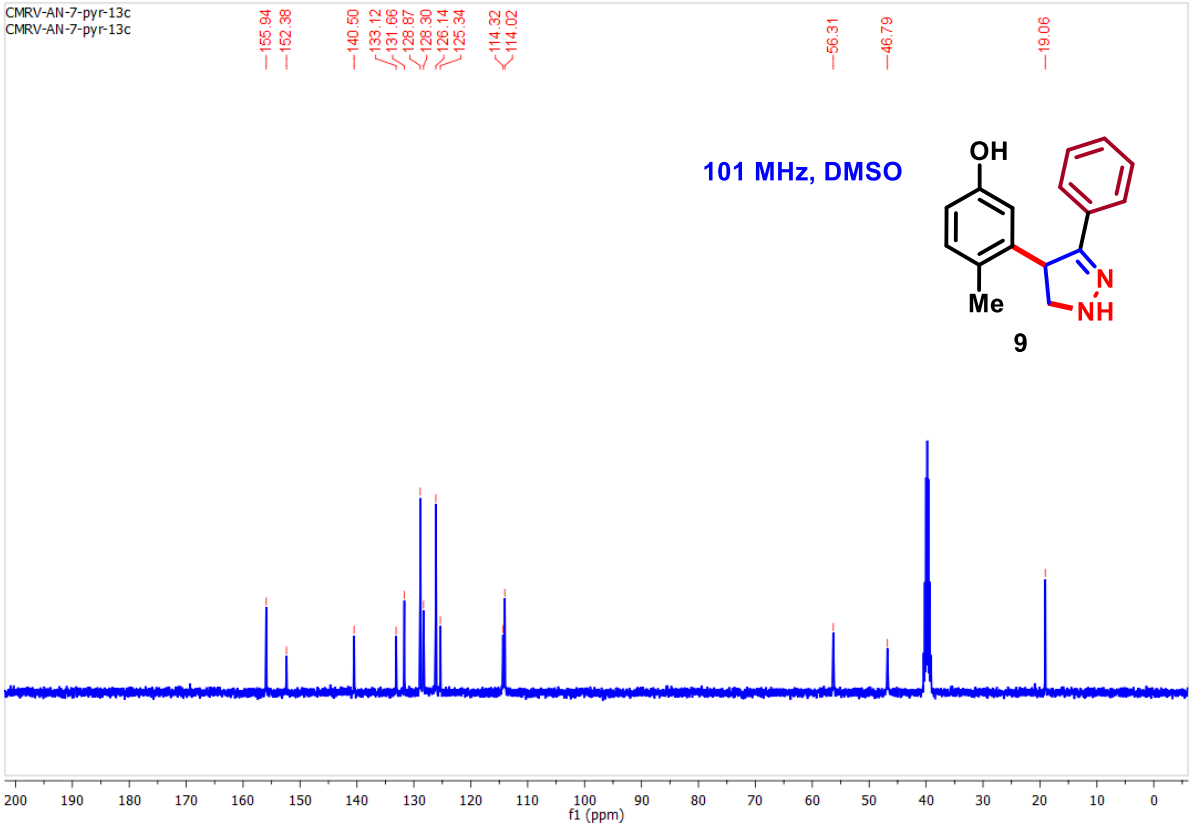

cmrv-rsh-59-1h1
cmrv-rsh-59-1h1
7.31
7.31
7.30
7.29
7.28
7.27
7.26
7.26
7.25
7.00
6.98
6.66
6.66
6.64
6.64
6.43
6.42
5.57
5.41
5.07
2.03
500 MHz, CDCl3
OH
OH
Me
7
5.36
1.00
0.99
0.99
1.04
1.10
1.21
3.38
f1 (ppm)

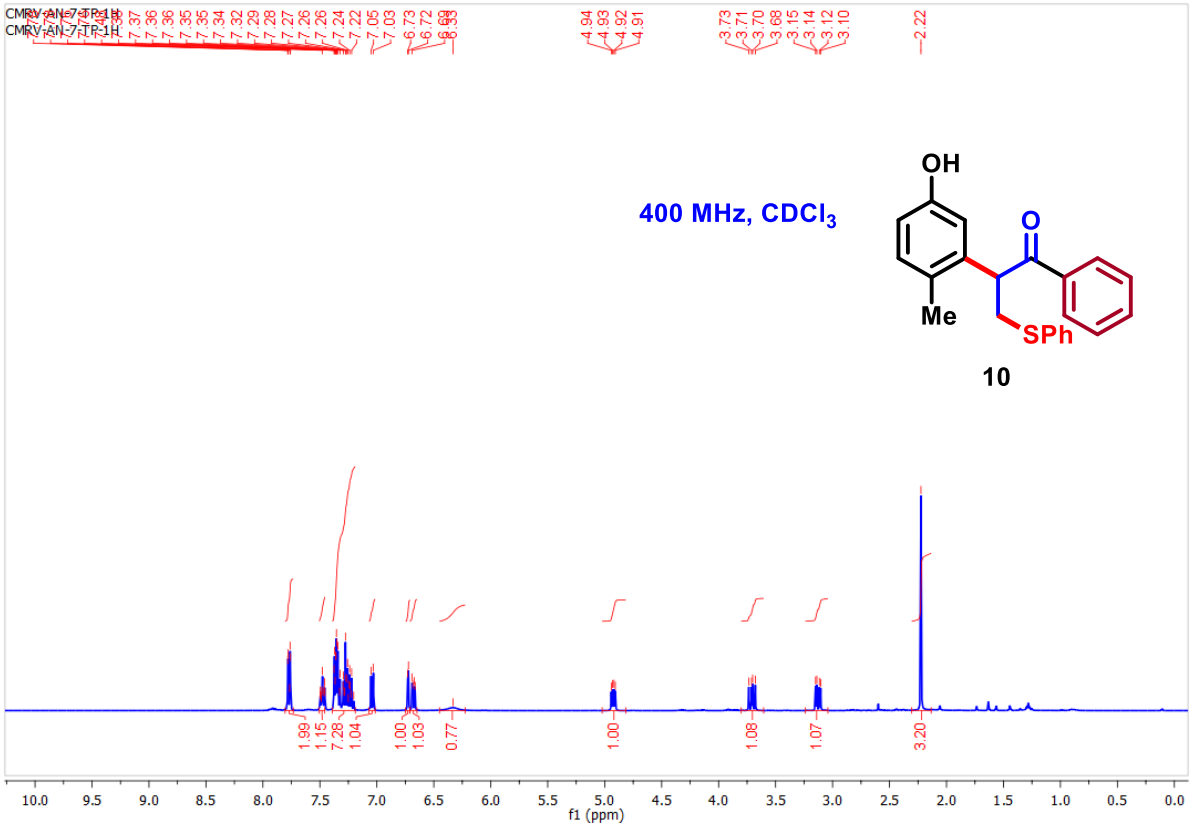

cmrv-rsh-59-13c1
cmrv-rsh-59-13c1
152.96
150.65
141.35
140.58
131.11
128.27
127.88
127.82
126.81
116.08
114.34
114.32
77.35
18.65
126 MHz, CDCl3
OH
OH
Me
7
f1 (ppm)

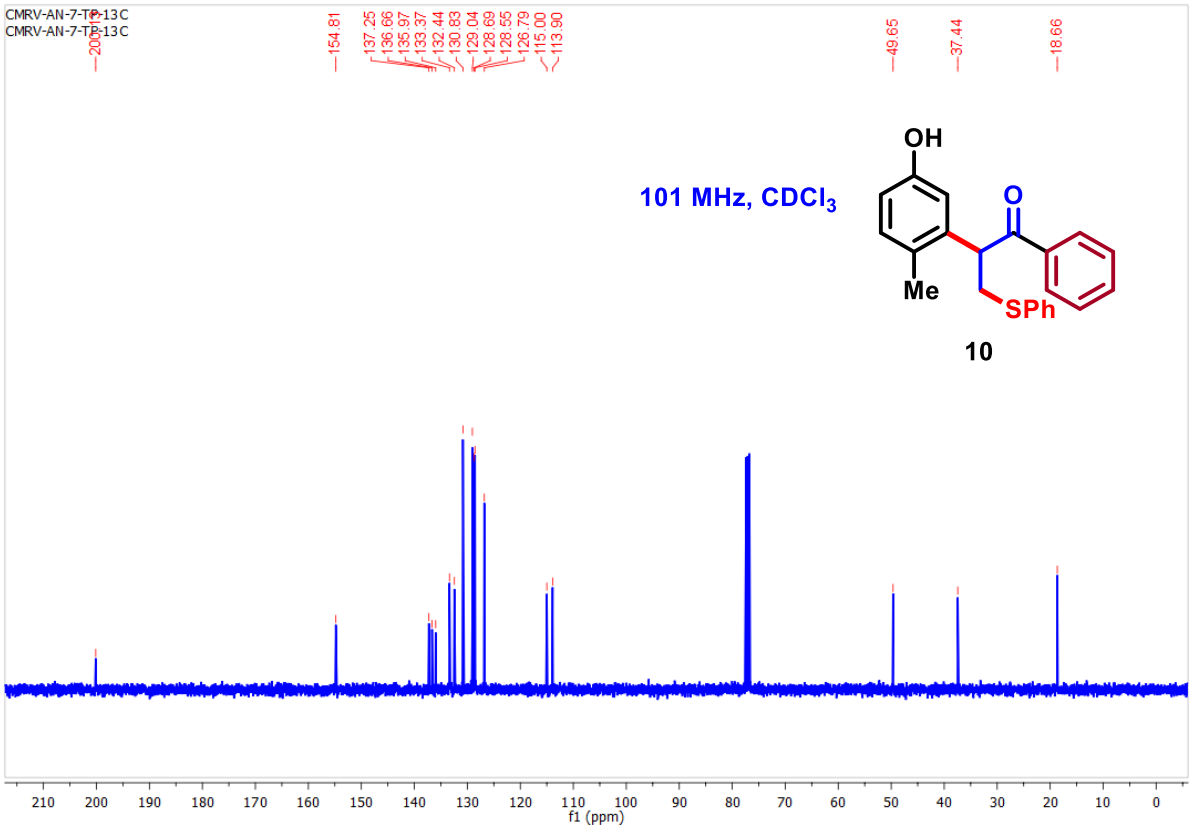

CMRV-RSH-2-35-1H
CMRV-RSH-2-35-1H
8.02
8.00
8.00
7.50
7.39
7.37
7.35
7.08
7.08
6.97
6.95
6.74
6.73
5.71
5.95
3.42
3.40
3.16
3.14
2.25
400 MHz, CDCl3
OH
O
Me
O
8
1.89
1.01
1.94
0.95
0.98
1.00
0.93
0.95
0.92
2.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

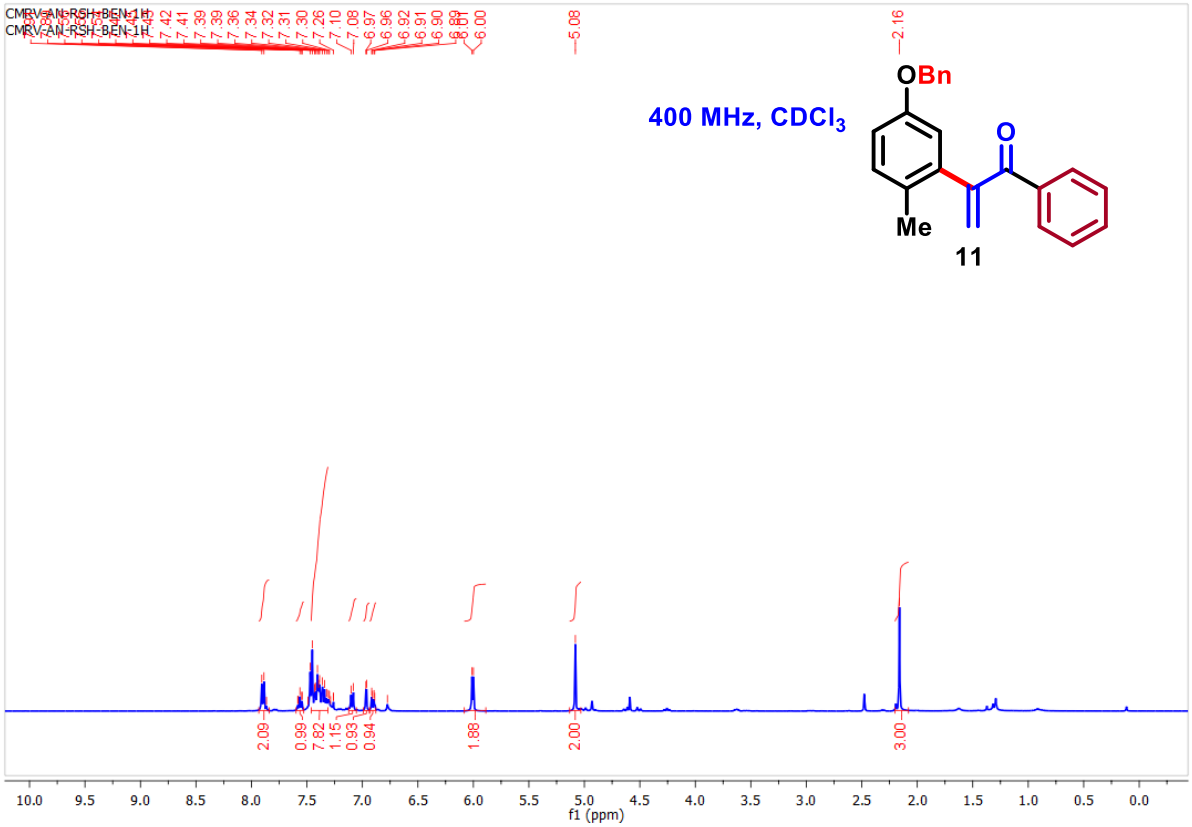

CMRV-RSH-2-35-13C
CMRV-RSH-2-35-13C
154.03
135.48
134.93
133.36
131.79
129.46
129.40
128.41
115.89
114.64
63.70
53.00
18.84
101 MHz, CDCl3
OH
O
Me
O
8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

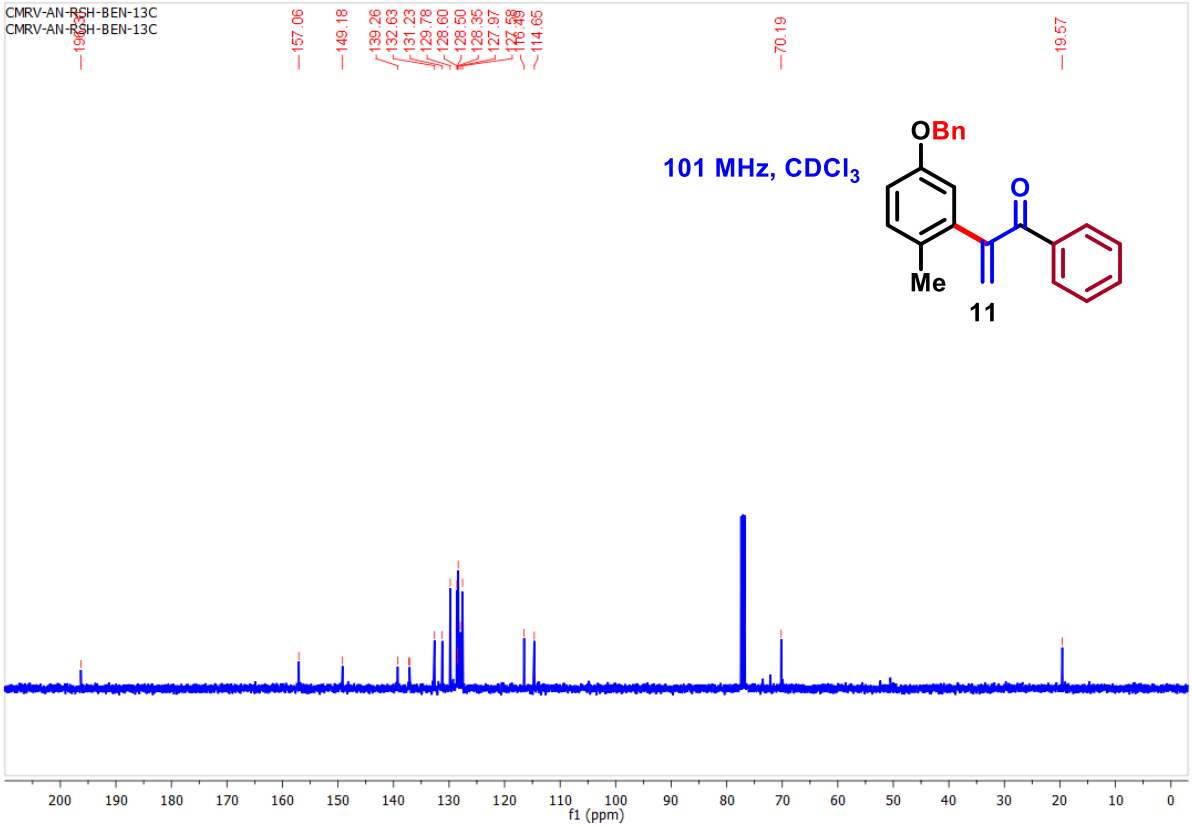

CMRV-AN-7-pyr-1h
CMRV-AN-7-pyr-1h
400 MHz, DMSO
OH
Me
N
NH
9
f1 (ppm)

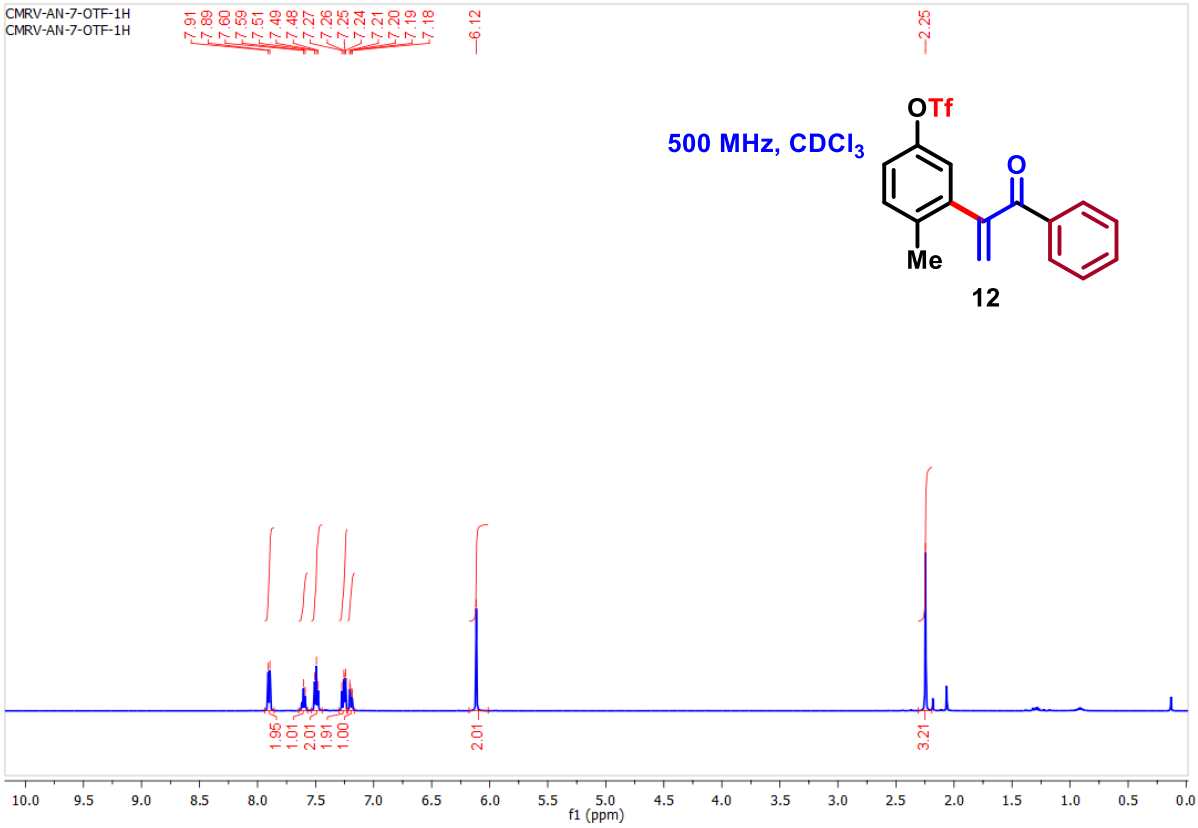

CMRV-AN-7-pyr-13c
CMRV-AN-7-pyr-13c
101 MHz, DMSO
OH
Me
N
NH
9
f1 (ppm)

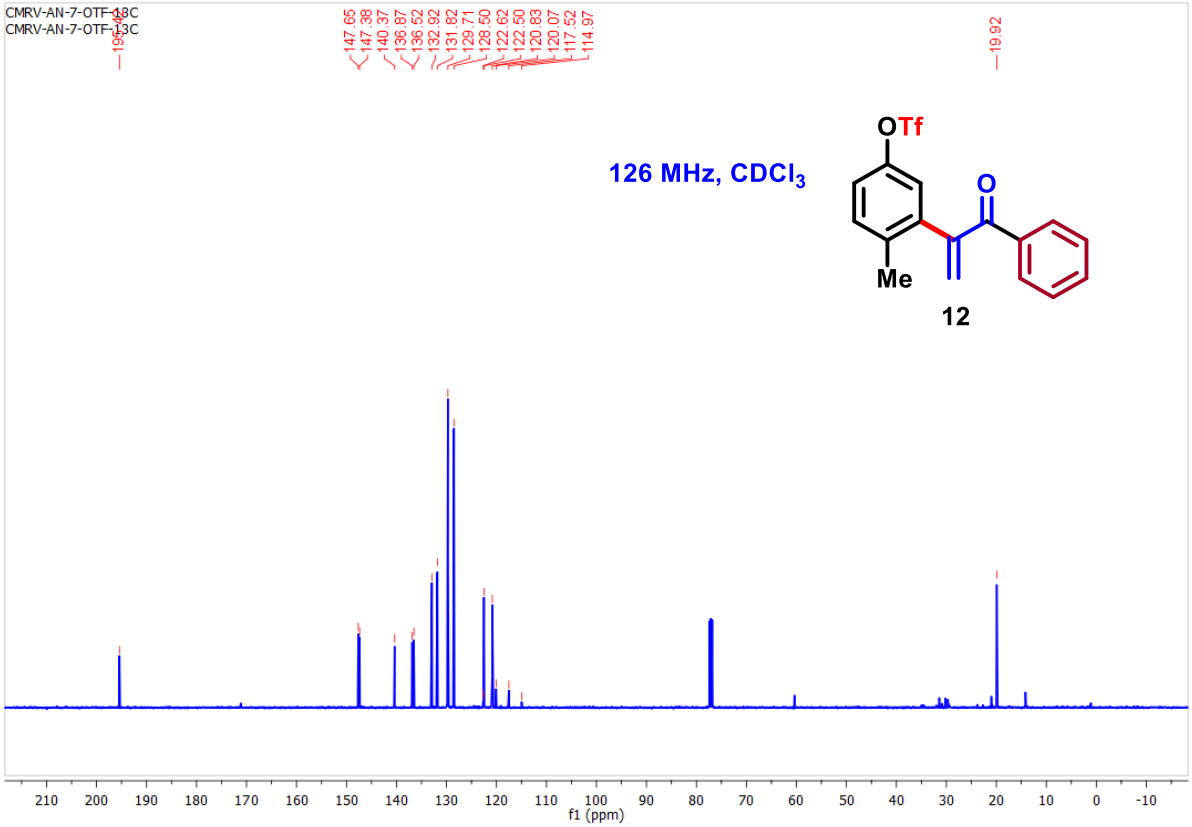

CMRV-AN-7-TP-1H
CMRV-AN-7-TP-1H
7.37
7.36
7.36
7.35
7.35
7.34
7.32
7.29
7.28
7.27
7.26
7.26
7.24
7.22
7.05
7.03
6.73
6.72
6.69
6.68
4.94
4.93
4.92
4.91
3.73
3.71
3.70
3.68
3.15
3.14
3.12
3.10
2.22
400 MHz, CDCl3
OH
O
Me
SPh
10
1.99
1.15
7.28
1.04
1.00
1.03
0.77
1.00
1.08
1.07
3.20
f1 (ppm)

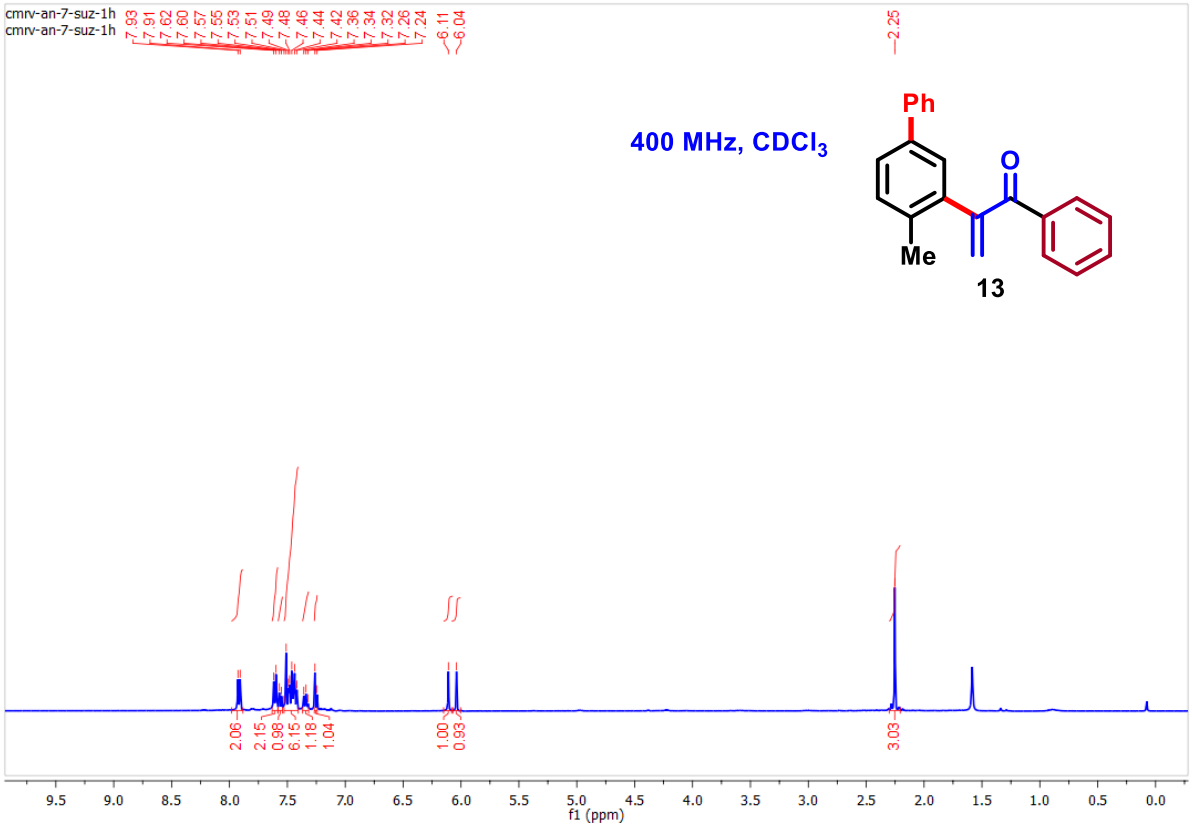

CMRV-AN-7-TP-13C
CMRV-AN-7-TP-13C
154.81
137.25
136.66
135.97
133.37
132.44
130.83
129.04
128.69
128.55
126.79
115.00
113.90
49.65
37.44
18.66
101 MHz, CDCl3
OH
O
Me
SPh
10
f1 (ppm)

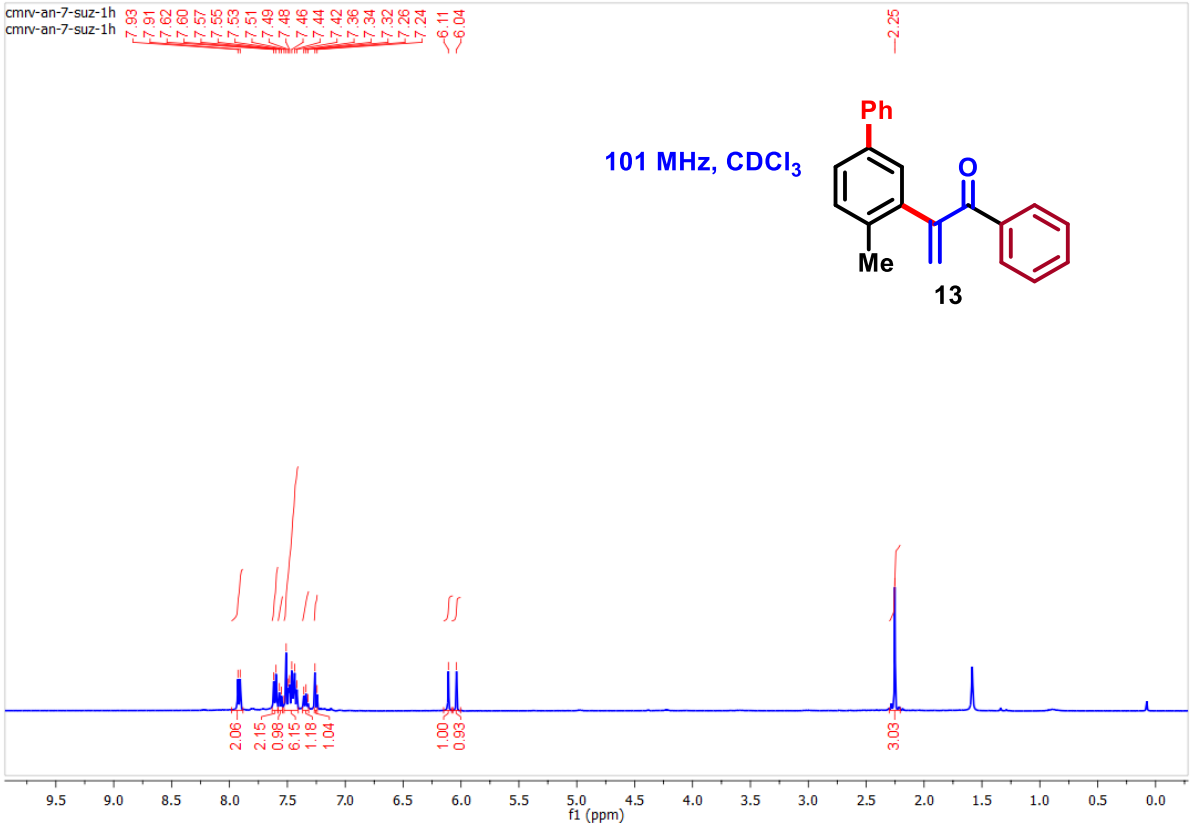

CMRV-AN-RSH-BEN-1H
CMRV-AN-RSH-BEN-1H
7.42
7.41
7.39
7.39
7.36
7.34
7.32
7.31
7.30
7.26
7.10
7.08
6.97
6.96
6.92
6.91
6.90
6.89
6.88
6.00
5.08
2.16
400 MHz, CDCl3
OBn
O
Me
11
2.09
0.99
7.82
1.15
0.93
0.94
1.88
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

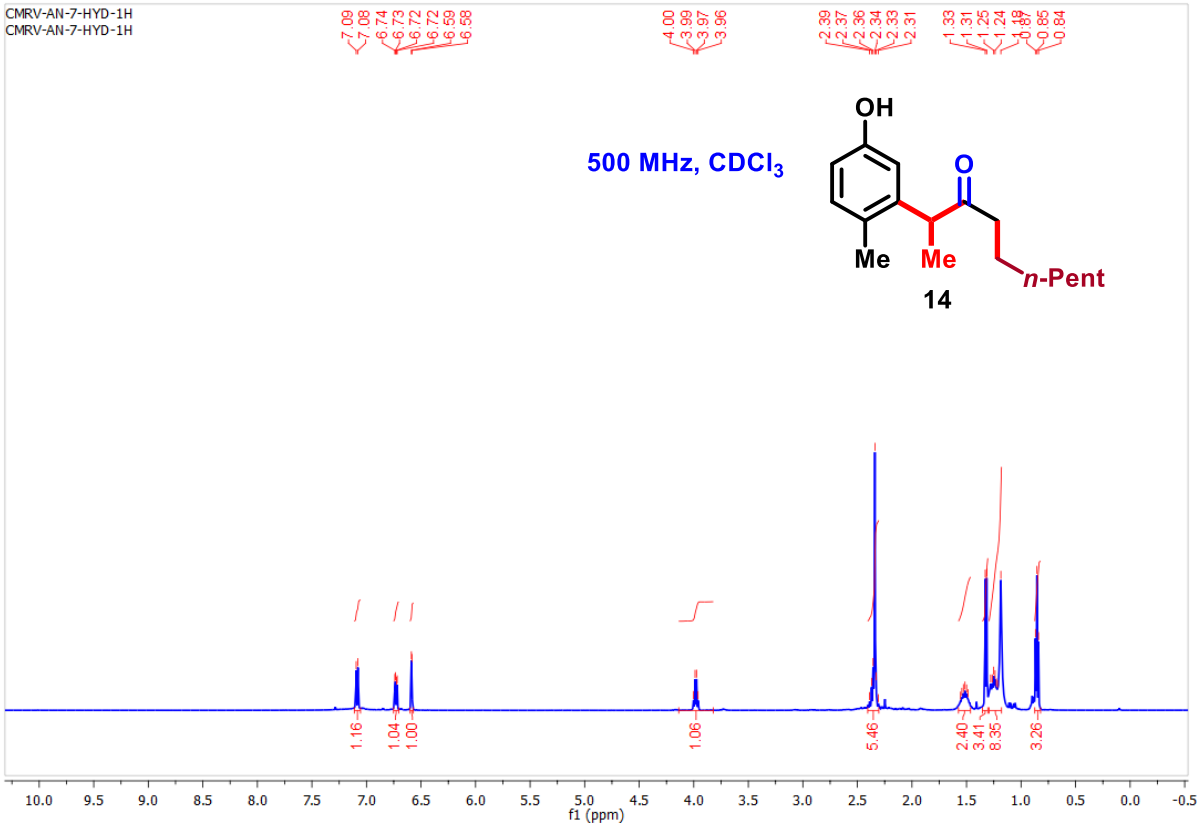

CMRV-AN-RSH-BEN-13C
CMRV-AN-RSH-BEN-13C
193.43
157.06
149.18
139.26
132.63
131.23
129.78
128.60
128.50
128.35
127.97
127.58
116.49
114.65
70.19
19.57
101 MHz, CDCl3
OBn
O
Me
11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

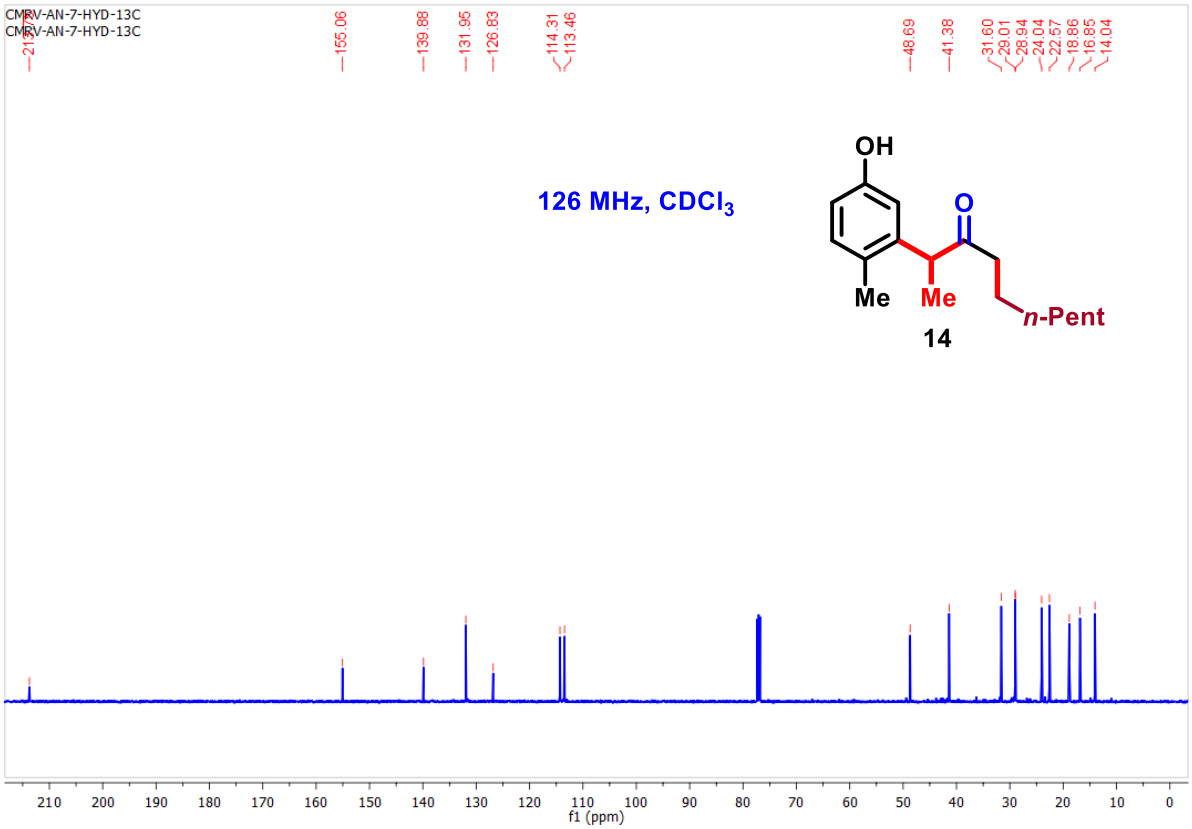

CMRV-AN-7-OTF-1H
CMRV-AN-7-OTF-1H
500 MHz, CDCl3
OTf
O
Me
12
f1 (ppm)

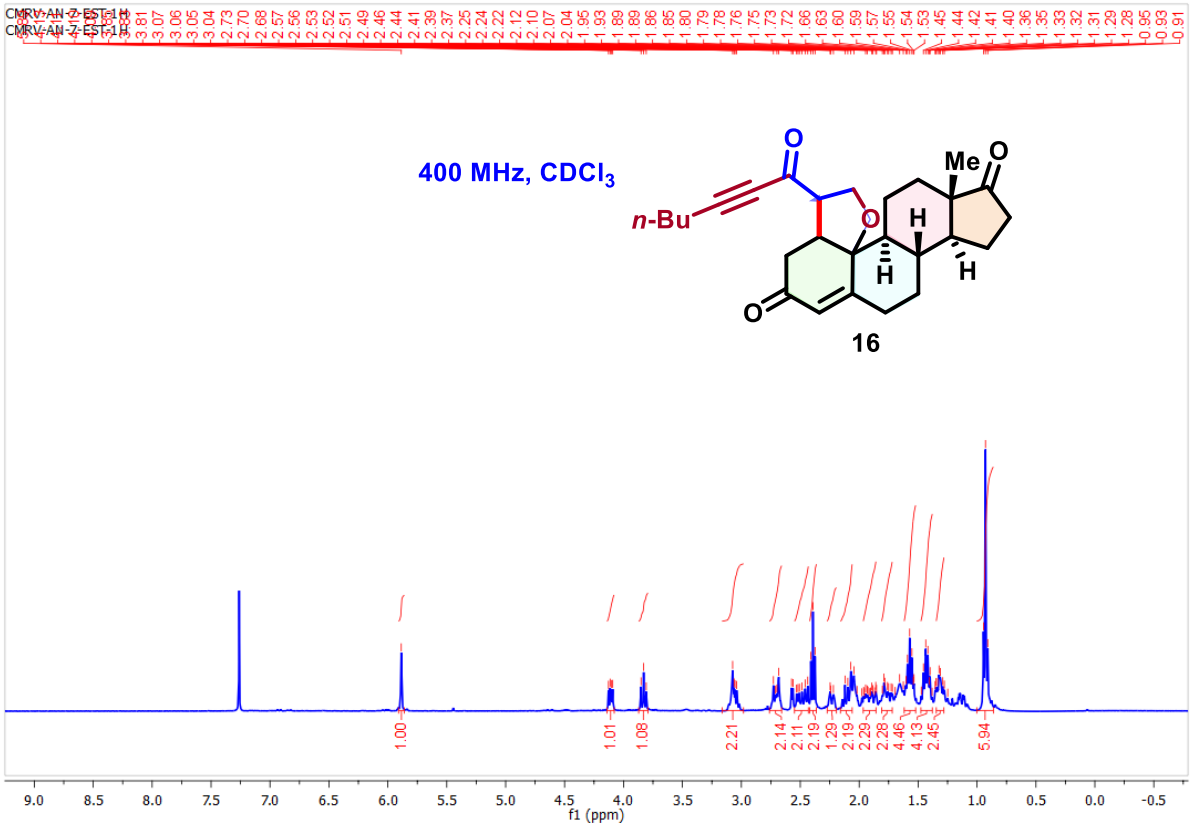

CMRV-AN-7-OTF-13C
CMRV-AN-7-OTF-13C
126 MHz, CDCl3
OTf
O
Me
12
f1 (ppm)

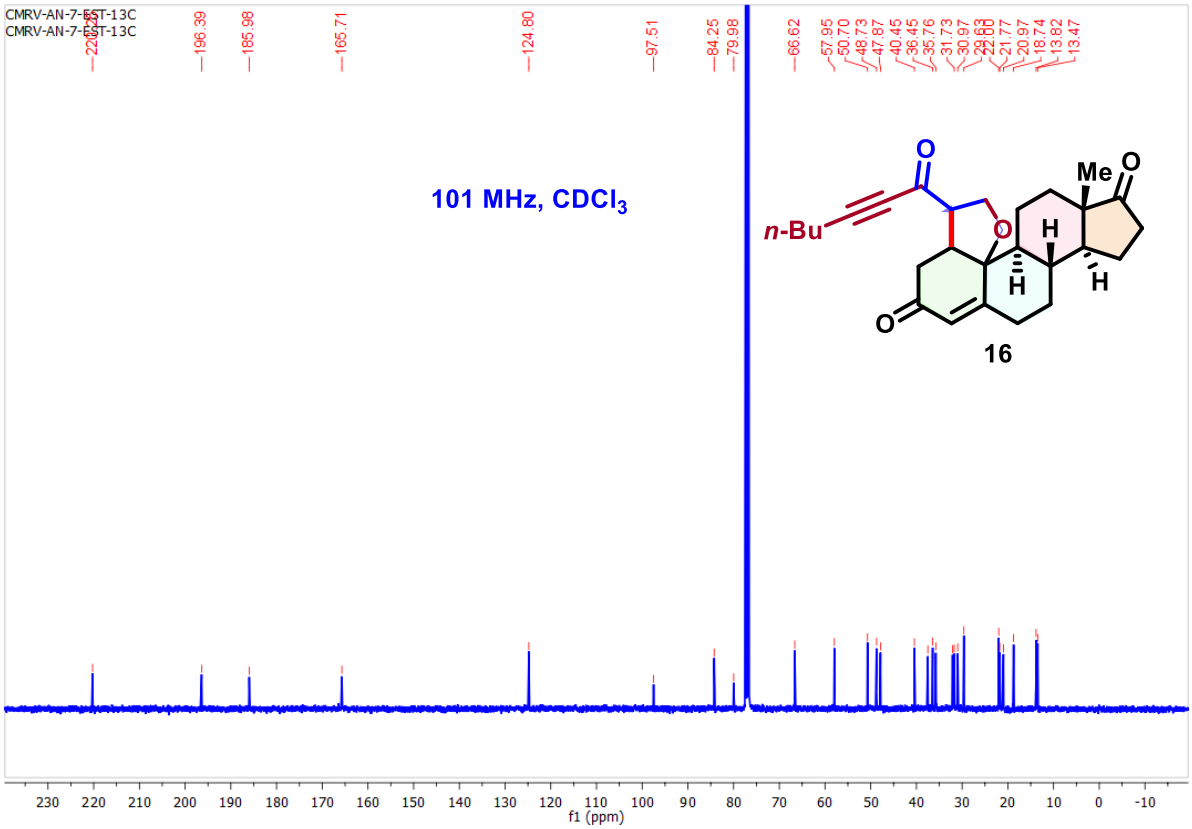

cmrv-an-7-suz-1h
cmrv-an-7-suz-1h
400 MHz, CDCl3
Ph
O
Me
13
f1 (ppm)


cmrv-an-7-suz-1h
cmrv-an-7-suz-1h
101 MHz, CDCl3
Ph
O
Me
13
f1 (ppm)


CMRV-AN-7-HYD-1H
CMRV-AN-7-HYD-1H
500 MHz, CDCl3
OH
O
Me
Me
n-Pent
14
f1 (ppm)


CMRV-AN-7-HYD-13C
CMRV-AN-7-HYD-13C
126 MHz, CDCl3
OH
O
Me
Me
n-Pent
14
f1 (ppm)


400 MHz, CDCl3
n-Bu
Me
H
H
H
16
f1 (ppm)


101 MHz, CDCl3
n-Bu
Me
H
H
H
16
f1 (ppm)