Electronic Supplementary Information

A CO_2-Mediated Conjugate Cyanide Addition to Chalcones

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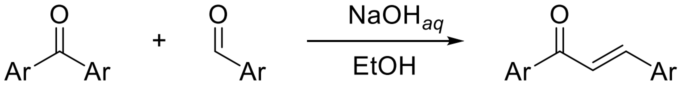
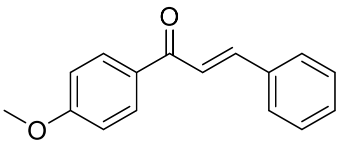
General procedure for chalcone ***1b*** *–* ***1m***

The chalcones **1b**-**1m** were synthesized in 2.40 mmol scale based on a general procedure:



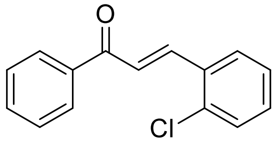
To a solution of 2.40 mmol of acetophenone derivate in EtOH (20 mL) an aqueous NaOH solution (0.50 M, 5 mL, 2.40 mmol) was added at 0 °C and stirred for 10 min. Next, 2.50 mmol of benzaldehyde derivate was added. The reaction mixture was allowed to warm up and stirred at room temperature for 24 – 48 h. On completion, the reaction was quenched with water (20 mL). The aqueous layer was extracted with ethyl acetate (3x 25 mL) and the combined organic layers were washed with brine (3x 25 mL), dried over $MgSO_4$, and concentrated under vacuum. The crude product was recrystallized from ethanol.

1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (**1b**)



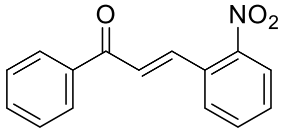
Yield: 62%, colourless crystals. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.05 (d, J=8.9, 2H), 7.81 (d, J=15.7, 1H), 7.68 – 7.62 (m, 2H), 7.55 (d, J=15.7, 1H), 7.42 (dq, J=4.9, 3.1, 2.4, 3H), 6.99 (d, J=8.8, 2H), 3.90 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 188.75, 163.45, 143.98, 135.12, 131.14, 130.83, 130.33, 128.94, 128.37, 121.93, 113.87, 55.52. HRMS (EI) calcd for [$C_{16}H_{14}O_2$] ([M + H$^+$]): 239.1067, found: 239.1075. Anal. calcd for $C_{16}H_{14}O_2$ C 80.65, H 5.95; found C 80.56, H 5.98

3-(2-chlorophenyl)-1-phenylprop-2-en-1-one (**1c**)



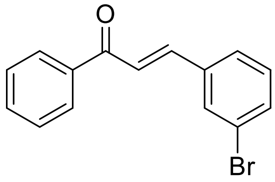
Yield: 12%, white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, J=15.8, 1H), 8.02 (d, J=8.5, 2H), 7.76 (dd, J=7.0, 2.4, 1H), 7.67 – 7.41 (m, 5H), 7.33 (tt, J=7.5, 5.5, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 190.51, 140.68, 137.96, 135.52, 133.31, 132.95, 131.18, 130.33, 128.68, 128.65, 127.81, 127.09, 124.89. HRMS (EI) calcd for [$C_{15}H_{11}ClO$] ([$M + H^+$]): 243.0571, found: 243.0573.

3-(2-nitrophenyl)-1-phenylprop-2-en-1-one (**1d**)



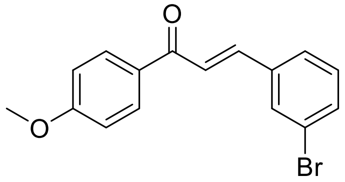
Yield: 14 %, pale white solid.^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.14 (d, J=15.8, 1H), 8.08 (dd, J=8.1, 1.3, 1H), 8.02 (dd, J=8.4, 1.3, 2H), 7.75 (dd, J=7.8, 1.5, 1H), 7.73 – 7.66 (m, 1H), 7.65 – 7.49 (m, 4H), 7.32 (d, J=15.7, 1H),. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 190.59, 140.24, 137.44, 133.56, 133.15, 131.41, 130.34, 129.28, 128.83, 128.75, 127.48, 125.04. HRMS (EI) calcd for [$C_{15}H_{11}NO_3$] ([$M + H^+$]): 254.0812, found: 254.0814.

3-(3-bromophenyl)-1-phenylprop-2-en-1-one (**1e**)

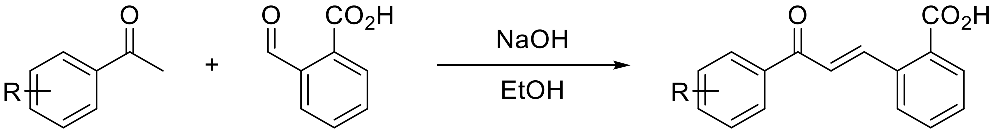


Yield 83%, colourless crystals. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.06 – 7.99 (m, 2H), 7.80 (s, 1H), 7.73 (d, J=15.8, 1H), 7.64 – 7.48 (m, 6H), 7.30 (t, J=7.9, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 190.08, 142.96, 137.92, 137.04, 133.26, 133.04, 130.84, 130.49, 128.72, 128.55, 127.26, 123.29, 123.11. HRMS (EI) calcd for [$C_{15}H_{11}BrO$] ([$M + H^+$]): 287.0066, found: 287.0068. Anal. calcd for $C_{15}H_{11}BrO$ C 62.74, H 3.86; found C 62.79, H 3.79.

3-(3-bromophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (**1f**)



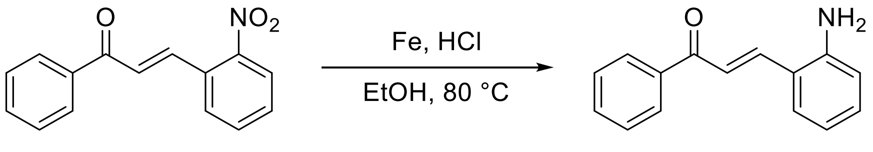
Yield: 56%, colourless crystals. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, J=8.9, 2H), 7.80 (t, J=1.9, 1H), 7.71 (d, J=15.6, 1H), 7.57 – 7.50 (m, 3H), 7.28 (d, J=7.9, 1H), 6.99 (d, J=8.8, 2H), 3.90 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 55.53, 58.50, 113.94, 123.07, 123.14, 127.22, 130.45, 130.71, 130.83, 130.90, 133.04, 137.25, 142.12, 163.64, 188.26. HRMS (EI) calcd for [$C_{16}H_{13}BrO_2$] ([$M + H^+$]): 317.0172, found: 317.0175.



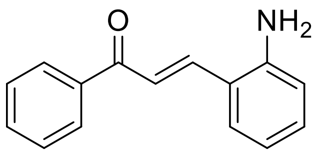
To a solution of acetophenone derivate (6.66 mmol) in EtOH (15 mL) NaOH (2.50 eq, 16.6 mmol, 0.67 g) was added at 0 °C and stirred for 10 min. Next, 2-carboxybenzaldehyde (6.66 mmol, 1.00 g) was added and stirred at room temperature for 72 h. On completion, the reaction was quenched with water and extracted with ethyl acetate. The aqueous phase was then adjusted to a pH of 2, using 0.5 M aqueous HCl and extracted with ethyl acetate. Those organic layers were combined, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was recrystallized from EtOH.

3-(2-aminophenyl)-1-phenylprop-2-en-1-one (**1g)**

2-Aminochalcone (**1g**) was synthesized in 2.00 mmol scale following a precedent literature procedure reported by Chen *et. al*.[30]

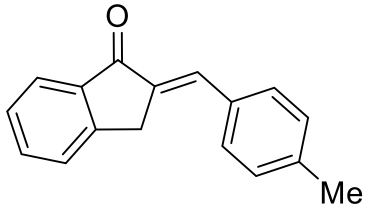


To a dispersion of 2-nitrochalcone **1d** (2.00 mmol, 0.51 g) and Fe powder (6.00 mmol, 0.34 g) in 30 mL EtOH 2.6 mL aqueous 1M HCl was added. The mixture was vigorously stirred at 80 °C for 2.5 h. The reaction cooled to room temperature and was extracted with ethyl acetate (3x 30 mL). The organic layers were combined, washed with saturated Na_2CO_3 solution (2x 30 mL) and brine (3x 30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The obtained crude product can be purified by recrystallization from EtOH.



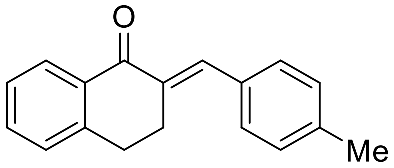
Yield: 58 %, yellow solid. ^{1}H-NMR (500 MHz, CDCl3): δ = 8.04 (d, *J* = 7.7, 1H), 8.00 (d, *J* = 15.4, 1H), 7.62 – 7.56 (m, 1H), 7.59 – 7.47 (m, 4H), 7.21 (t, *J* = 7.7, 1H), 6.80 (t, *J* = 7.4, 1H), 6.73 (d, *J* = 8.2, 1H), 4.08 (s, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 190.44, 146.39, 140.25, 138.48, 132.89, 131.83, 128.77, 128.66, 128.60, 128.29, 121.94, 120.43, 119.07, 116.95. HRMS (EI) calcd for [$C_{15}H_{13}NO$] ([M + H+]): 224.1070, found: 224.1078.

(*E*)-2-(4-methylbenzylidene)-2,3-dihydro-1H-inden-1-one (**1h)**



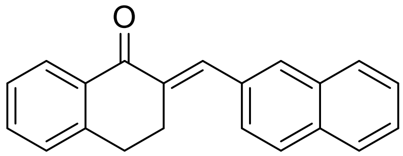
Yield: 80 %, off white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 7.3 Hz, 1H), 7.67 (br s, 1H), 7.64 – 7.52 (m, 5H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.28 (s, 1H), 4.03 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 194.55, 149.74, 140.31, 138.29, 134.62, 134.16, 133.92, 132.80, 130.93, 129.85, 127.76, 126.28, 124.52, 32.64, 21.65. HRMS (EI) calcd for [$C_{17}H_{14}O$] ([M + H$^+$]): 235.1117, found: 235.1121.

(*E*)-2-(4-methylbenzylidene)-3,4-dihydronaphthalen-1(2H)-one (**1i**)



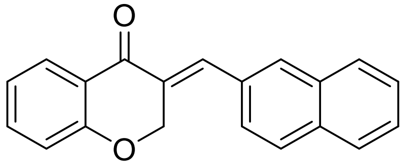
Yield: 84 %, off white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.14 (d, *J* = 7.9, 1H), 7.86 (s, 1H), 7.49 (td, *J* = 7.4, 1.5 Hz, 1H), 7.37 (m, 3H), 7.24 (t, *J* = 7.4 Hz, 3H), 3.15 (t, *J* = 6.5, 2H), 2.95 (t, *J* = 6.5 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 188.09, 143.34, 138.95, 136.96, 134.85, 133.72, 133.32, 133.14, 130.13, 129.33, 128.34, 128.27, 127.13, 29.00, 27.39, 21.55. HRMS (EI) calcd for [$C_{18}H_{16}O$] ([M + H$^+$]): 249,1274 found: 249.1283.

(*E*)-2-(naphthalen-2-ylmethylene)-3,4-dihydronaphthalen-1(2H)-one (**1j**)



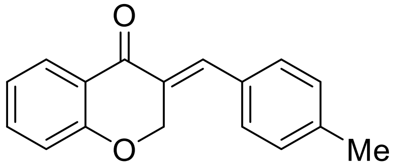
Yield: 86 %, pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.17 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.03 (s, 1H), 7.92 (s, 1H), 7.82-7.88 (m, 3H), 7.57 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.46-7.52 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.27 (d, overlapped with $CHCl_3$, *J* = 7.6 Hz, 1H), 3.22 (ddd, *J* = 6.8, 5.6, 1.9 Hz, 2H), 2.96 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 188.04, 143.37, 136.92, 135.88, 133.67, 133.54, 133.45, 133.26, 133.23, 129.74, 128.47, 128.41, 128.34, 128.18, 127.86, 127.42, 127.21, 126.95, 126.64, 29.05, 27.52. HRMS (EI) calcd for [$C_{21}H_{16}ONa$] ([M + Na$^+$]): 307.1093, found: 307.1101.

(*E*)-3-(naphthalen-2-ylmethylene)chroman-4-one (**1k**)



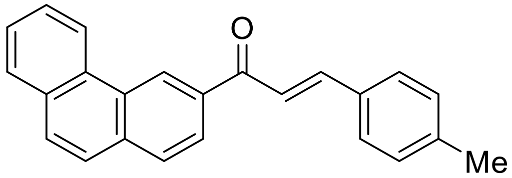
Yield: 47%, pale yellow solid,^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.08 – 8.01 (m, 2H), 7.85-7.91 (m, 3H), 7.76 (s, 1H), 7.56 (dqd, *J* = 6.9, 5.2, 2.5 Hz, 2H), 7.51 (tt, *J* = 7.1, 1.7 Hz, 1H), 7.44 (dt, *J* = 8.5, 1.7 Hz, 1H), 7.13 – 7.07 (m, 1H), 6.99 (d, *J* = 8.3, 1H), 5.47 (t, *J* = 1.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 182.40, 161.21, 137.78, 136.07, 133.49, 133.06, 131.97, 131.13, 130.19, 128.61, 128.59, 128.09, 127.91, 127.50, 127.09, 126.96, 122.13, 122.09, 118.07, 67.85. HRMS (EI) calcd for [$C_{20}H_{14}O_2$] ([M + H$^+$]): 287.1067, found: 278.1072.

(*E*)-3-(4-methylbenzylidene)chroman-4-one (**1l**)



Yield: 67 %, off white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.02 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.86 (br s, 1H), 7.51 – 7.47 (m, 1H), 7.19-7.28 (m, 4H), 7.09 – 7.05 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 5.37 (d, *J* = 2.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 182.45, 161.15, 140.10, 137.80, 135.94, 131.63, 130.29, 130.13, 129.60, 128.03, 122.14, 122.00, 118.00, 67.82, 21.63. HRMS (EI) calcd for [$C_{17}H_{14}O_2$] ([M + H$^+$]): 251.1067, found: 251.1079.

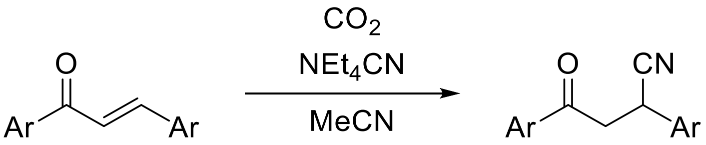
(*E*)-1-(phenanthren-3-yl)-3-(p-tolyl)prop-2-en-1-one (**1m**)



Yield: 83 %, pale yellow solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.37 (s, 1H), 8.82 (d, *J* = 8.2 Hz, 1H), 8.21 (dd, *J* = 8.2 Hz, 1.7 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.94 – 7.92 (m, 1H), 7.90 – 7.85 (m, 2H), 7.78 (m, 1H), 7.76 – 7.71 (m, 2H), 7.69 – 7.65 (m, 1H), 7.64 – 7.61 (m, 2H), 7.28 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.77, 145.23, 141.33, 136.14, 134.89, 132.29, 130.75, 129.97, 129.88 (quaternary carbon may be overlapped), 129.69, 129.05, 128.95, 128.72, 127.37, 127.30, 126.48, 125.85, 124.08, 122.95, 121.32, 21.74. HRMS (EI) calcd for [$C_{24}H_{18}O$] ([M + H$^+$]): 323.1430, found: 323.1435.

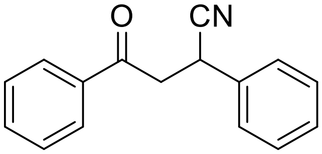
Cyanation

General procedure for cyanation using TEACN



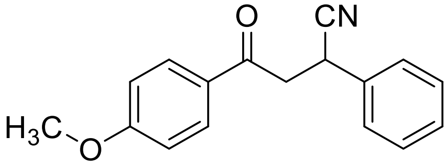
A solution of TEACN (0.80 mmol, 0.125 g) in 3 mL solvent was stirred for 10 min at room temperature under CO_2 atmosphere. To the clear solution, 0.40 mmol chalcone derivate was added and the mixture was stirred at room temperature under CO_2 atmosphere for 2 – 8 h. On completion, the reaction was quenched with water (5 mL). The aqueous layer was extracted with ethyl acetate (3x 8 mL) and the combined organic layers were washed with brine (3x 8 mL), dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by column chromatography [*V*(petroleum ether)/*V*(ethyl acetate)=10:1].

4-oxo-2,4-diphenylbutanenitrile (**2a**)



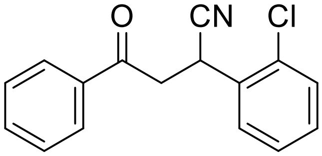
Yield: 85% colourless crystals. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.98 – 7.93 (m, 2H), 7.62 (td, *J* = 7.4, 1.3, 1H), 7.53 – 7.39 (m, 7H), 7.39 – 7.33 (m, 1H), 4.60 (dd, *J* = 7.8, 6.0, 1H), 3.76 (dd, *J* = 17.9, 7.9, 1H), 3.54 (dd, *J* = 17.9, 6.1, 1H). ^{13}C-NMR (126 MHz, CDCl$_3$): δ = 194.61, 135.70, 135.29, 133.92, 129.29, 128.85, 128.40, 128.11, 127.51, 120.62, 44.56, 31.91. HRMS (EI) calcd for [$C_{16}H_{13}NO$] ([M + H$^+$]): 236.1070, found: 236.1073. Anal. calcd for $C_{16}H_{13}NO$ C 81.68, H 5.57, N 5.95; found C 81.72, H 5.61, N 6.12. CCDC Deposit number: CCDC2047209

4-(4-methoxyphenyl)-4-oxo-2-phenylbutanenitrile (**2b**)



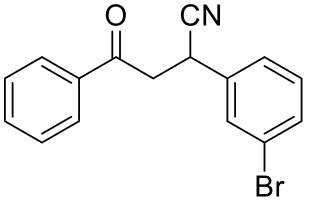
Yield: 73%, Oil. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.90 (d, *J* = 8.9, 2H), 7.46 – 7.40 (m, 2H), 7.38 (ddd, *J* = 7.8, 6.7, 1.4, 2H), 7.36 – 7.29 (m, 1H), 6.93 (d, *J* = 8.9, 2H), 4.57 (dd, *J* = 8.0, 6.0, 1H), 3.87 (s, 3H), 3.67 (dd, *J* = 17.6, 8.0, 1H), 3.45 (dd, *J* = 17.6, 6.0, 1H). ^{13}C-NMR (126 MHz, CDCl$_3$): 193.06, 164.11, 135.46, 130.46, 129.25, 128.81, 128.32, 127.51, 120.79, 114.00, 55.56, 44.18, 32.00. HRMS (EI) calcd for [$C_{17}H_{15}NO_2$] ([M + H$^+$]): 266.1176, found: 266.1181.

2-(2-chlorophenyl)-4-oxo-4-phenylbutanenitrile (**2c**)



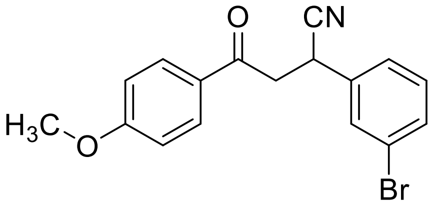
Yield: 63% colourless solid. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.98 – 7.92 (m, 2H), 7.68 (dd, *J* = 7.6, 1.8, 1H), 7.64 – 7.57 (m, 1H), 7.48 (t, *J* = 7.8, 2H), 7.43 (dd, J=7.7, 1.6, 1H), 7.40 – 7.29 (m, 2H), 4.93 (dd, *J* = 9.4, 4.4, 1H), 3.68 (dd, *J* = 18.0, 9.4, 1H), 3.54 (dd, *J* = 17.9, 4.4, 1H). ^{13}C-NMR (126 MHz, CDCl$_3$): δ = 194.42, 135.59, 133.94, 132.72, 132.70, 130.31, 129.90, 129.49, 128.86, 128.14, 127.79, 119.71, 42.44, 30.06. HRMS (EI) calcd for [$C_{16}H_{12}ClNO$] ([M + H$^+$]): 270.0680, found: 270.0683. Anal. calcd for $C_{16}H_{12}ClNO$ C 71.25, H 4.48, N 5.19; found C 71.59, H 4.60, N 5.16.

2-(3-bromophenyl)-4-oxo-4-phenylbutanenitrile (**2e**)



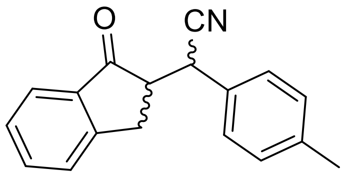
Yield: 59%, colourless solid. ^{1}H-NMR (500 MHz, DMSO): δ = 8.04 – 7.98 (m, 2H), 7.78 (t, *J* = 1.9, 1H), 7.70 – 7.64 (m, 1H), 7.59 – 7.51 (m, 4H), 7.39 (dd, *J* = 8.2, 7.5, 1H), 4.66 (dd, *J* = 9.1, 5.1, 1H), 4.04 (dd, *J* = 18.4, 9.1, 1H), 3.77 (dd, *J* = 18.4, 5.2, 1H). ^{13}C-NMR (126 MHz, DMSO): δ = 195.93, 138.41, 135.63, 133.74, 131.02, 130.92, 130.65, 128.78, 128.13, 126.99, 121.96, 120.93, 42.43, 30.72. HRMS (EI) calcd for [$C_{16}H_{12}BrNO$] ([M + Na$^+$]): 335.994, found: 336.001.

4-(4-methoxyphenyl)-4-oxo-2-(3-bromophenyl)butanenitrile (**2f**)



Yield: 64%, colourless oil. ^{1}H-NMR (500 MHz, CD$_2$Cl$_2$): δ = 7.91 (d, J=8.8, 2H), 7.62 (s, 1H), 7.50 (d, *J* = 8.0, 1H), 7.40 (d, *J* = 8.0, 1H), 7.29 (t, *J* = 7.9, 1H), 6.96 (d, *J* = 8.8, 2H), 4.51 (dd, *J* = 8.1, 5.9, 1H), 3.87 (s, 3H), 3.69 (dd, *J* = 17.8, 8.1, 1H), 3.47 (dd, *J* = 17.8, 5.8, 1H). ^{13}C-NMR (126 MHz, CD$_2$Cl$_2$): δ = 193.18, 164.63, 138.29, 131.83, 131.17, 131.05, 130.75, 129.07, 126.81, 123.33, 120.60, 114.37, 56.00, 44.23, 32.01. HRMS (EI) calcd for [$C_{17}H_{15}NO_2$] ([M + H$^+$]): 344.0281, found: 344.0285.

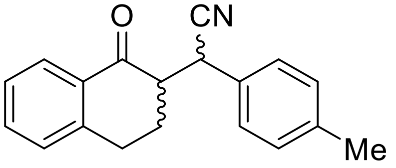
2-(1-oxo-2,3-dihydro-1H-inden-2-yl)-2-(p-tolyl)acetonitrile (**2h**)



Yield: 15%, colourless solid, ^{1}H-NMR (500 MHz, CD_2Cl_2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 0.4H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.55-7.43 (m, 3H), 7.38-7.33 (m, 2.7H), 7.22 – 7.32 (m, ?H), 7.22-7.18 (m, 0.37H), 7.11 (d, J = 7.8 Hz, 0.3H), 7.05 (d, *J* = 8.0 Hz, 0.7H), 6.99 (d, *J* = 7 Hz, 0.8H), 6.94 (d, J = 7 Hz, 0.5 H), 4.75 (d, *J* = 3.6 Hz, 1H), 4.67 – 4.59 (m, 0.35H), 4.47 (d, *J* = 10.5 Hz, 0.34H), 4.30 (d, *J* = 8.7 Hz, 0.32H), 3.29 – 3.14 (m, 2.65H), 3.13-3.08 (m, 1H), 2.81 (d, *J* = 17.1 Hz, 0.36H), 2.41 (s, 3H), 2.24 (d, *J* = 11.6 Hz, 2H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.47, 202.87, 201.69, 154.90, 153.05, 151.36, 138.86, 138.47, 137.65, 137.64, 136.56, 135.88, 135.80, 135.10, 132.27, 131.16, 130.67, 130.15, 129.52, 129.43, 128.90, 128.76, 128.17, 127.66, 127.47, 127.26, 126.78, 125.69, 125.17, 125.02, 124.69, 123.92, 118.81, 118.11, 70.43, 56.12, 55.40, 55.18, 52.16, 44.87, 37.49, 30.79, 29.66, 21.22, 21.09, 21.04. HRMS (EI) calcd for [$C_{18}H_{16}NO$] ([M + H$^+$]): 262.12264, found: 262.12307, calcd for [$C_{25}H_{19}NO$] ([M + Na$^+$]): 284,10459, found: 284.10505.

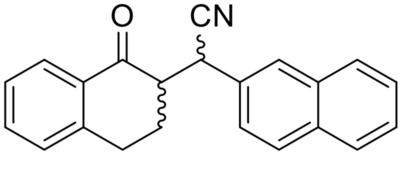
CCDC Deposit number: CCDC2047211

2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-2-(p-tolyl)acetonitrile (**2i**)



Yield: 37%, colourless solid, ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.11 (d, *J* = 8.0 Hz, 0.3H) 8.08 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.01 (dd, *J* = 7.9, 1.5 Hz, 0.5H), 7.85 (d, J = 8.0 Hz, 0.3iH), 7.65 – 7.59 (m, 0.6H), 7.52 – 7.41 (m, 3H), 7.36 – 7.25 (m, 6H), 7.23 (m, *J* = 1.2 Hz, 0.45 H), 7.23 – 7.19 (m, 3.3H), 7.17 (d, J = 7.8 Hz, 0.7H), 7.10 (d, *J* = 7.8 Hz, 1H), 4.99 (d, *J* = 3.5 Hz, 1H), 4.91 (d, *J* = 3.9 Hz, 0.5H), 3.11-3.08 (m, 0.7H), 3.08 – 2.85 (m, 4H), 2.82 – 2.76 (m, 1H), 2.40 (s, 0.7H), 2.35 (s, 3H), 2.27 (s, 2H), 2.26 – 2.08 (m, 3H), 1.67 (qd, *J* = 13.2, 4.4 Hiz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.52, 194.98, 143.80, 143.76, 138.21, 138.13, 134.15, 134.05, 132.01, 131.89, 131.23, 129.99, 129.91, 129.59, 129.52, 128.93, 128.91, 128.85, 128.01, 127.90, 127.69, 127.59, 127.08, 127.01, 123.52, 123.36, 121.26, 120.76, 119.01, 118.86, 117.58, 53.10, 52.07, 36.49, 35.82, 29.09, 28.90, 25.52, 24.61, 21.33, 21.17, 21.13. HRMS (EI) calcd for [$C_{19}H_{18}NO$] ([M + H$^+$]): 276.13829, found: 276.13933, calcd for [$C_{19}H_{17}NONa$] ([M + Na$^+$]): 298.12024, found: 298.12145.

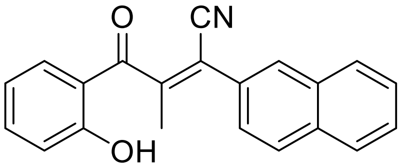
2-(naphthalen-2-yl)-2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acetonitrile (**2j**)



Yield: 73%, colourless solid, ^{1}H NMR (500 MHz, Chloroform-d) δ = 8.14 (dd, *J* = 7.9, 1.4 Hz, 0.7H), 8.07 (dd, *J* = 7.9, 1.4 Hz, 0.3H), 7.96 (s, 0.7H), 7.94 – 7.82 (m, 2.7H), 7.80 (d, J = 8.6 Hz, 0.7H), 7.59 – 7.40 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 0.7H), 7.30 (t, *J* = 7.6 Hz, 0.3 H), 7.23 (d, *J* = 7.6 Hz, 0.63 H), 7.17 (d, *J* = 7.7 Hz, 0.3 H), 5.23 (d, J = 3.4 Hz, 0.6H), 5.12 (d, *J* = 4.0 Hz, 0.3H), 3.23 (dt, *J* = 13.8, 4.2 Hz, 0.3H), 3.06 (ddd, *J* = 17.1, 12.7, 4.4

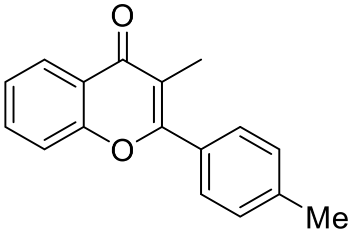
Hz, 0.5H), 3.01 – 2.84 (m, 2.3H), 2.35 – 2.21 (m, 1H), 2.14 (dtd, *J* = 12.8, 4.5, 2.7 Hz, 0.6H), 1.70 (qd, *J* = 13.2, 4.4 Hz, 0.3H). ^{13}C NMR (126 MHz, CDCl3) δ 195.32, 194.93, 143.76, 143.66, 134.14, 134.06, 133.28, 133.07, 132.88, 132.83, 131.87, 131.80, 131.50, 130.07, 129.23, 128.89, 128.79, 128.66, 128.34, 128.06, 127.95, 127.83, 127.79, 127.66, 127.05, 127.03, 126.96, 126.94, 126.72, 126.68, 126.66, 126.22, 124.95, 121.09, 118.70, 52.85, 52.07, 36.97, 36.27, 29.00, 28.81, 25.68, 24.59. HRMS (EI) calcd for [$C_{25}H_{19}NO$] ([$M + Na^+$]): 334.12024, found: 334.12171.

(*Z*)-4-(2-hydroxyphenyl)-3-methyl-2-(naphthalen-2-yl)-4-oxobut-2-enenitrile (**2k**)



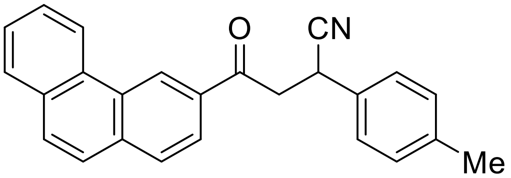
Yield: 24%, white solid,^{1}H NMR (500 MHz, Chloroform-d) δ = 8.29 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.14 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.90-7.96 (m, 2H), 7.73 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.66 (ddd, *J* = 8.5, 7.1, 1.8 Hz, 1H), 7.59 (m, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.41 (ddd, *J* = 8.1, 7.1, 1.8 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 178.99, 161.14, 156.33, 133.90, 133.48, 132.72, 130.88, 129.43, 128.75, 128.34, 127.93, 127.71, 126.99, 126.05, 125.67, 124.87, 122.68, 118.02, 117.93, 12.02. HRMS (EI) calcd for [$C_{17}H_{14}O_2$] ([$M + Na^+$]): 336.09950, found: 336.10086.

(Z)-4-(2-hydroxyphenyl)-3-methyl-4-oxo-2-(p-tolyl)but-2-enenitrile (**2l**)



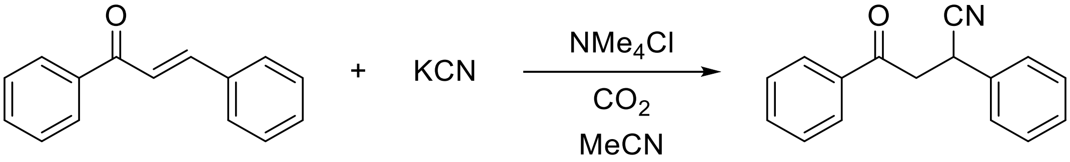
Yield: 41%, white solid,^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.25 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.63 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.37 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.17 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 178.96, 161.26, 156.20, 140.60, 133.32, 130.72, 129.20, 128.97, 125.94, 124.71, 122.59, 117.94, 117.34, 21.57, 11.90. HRMS (EI) calcd for [$C_{17}H_{14}O_2$] ([$M + H^+$]): 251.10666, found: 251.10716, calcd for [$C_{17}H_{14}O_2$] ([$M + Na^+$]): 273.08860, found: 273.08930.

4-oxo-4-(phenanthren-3-yl)-2-(p-tolyl)butanenitrile (**2m**)



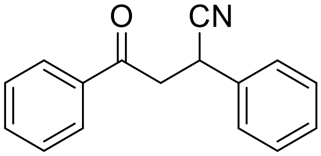
Yield 88%, white solid, ^{1}H NMR (500 MHz, Chloroform-d) δ = 9.23 (d, *J* = 1.7 Hz, 1H), 8.71 (d, *J* = 8.1 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.75 – 7.63 (m, 3H), 7.41 – 7.36 (m, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 4.63 (dd, *J* = 7.9, 6.1 Hz, 1H), 3.90 (dd, *J* = 17.7, 7.9 Hz, 1H), 3.69 (dd, *J* = 17.7, 6.1 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ = 194.85, 138.43, 135.52, 133.44, 132.46, 132.30, 130.63, 130.31, 130.08, 129.92, 129.24, 129.02, 127.56, 127.52, 126.29, 125.00, 123.90, 122.80, 121.02, 44.96, 31.87, 21.21. HRMS (EI) calcd for [C_{25}H20NO] ([$M + H^+$]): 350.15394, found: 350.15554, calcd for [$C_{25}H_{19}NONa$] ([$M + Na^+$]): 372.13589, found: 372.13771.

Cyanation using KCN



A solution of KCN (0.66 mmol, 43.2 mg) and NMe_4Cl (0.40 mmol, 43.8 mg) in 3 mL solvent was stirred for 30 min at room temperature under CO_2 atmosphere. To suspension *trans*-chalcone (0.20 mmol, 41.7 mg) was added and the mixture was stirred at room temperature under CO_2 atmosphere for 22 h. On completion, the reaction was quenched with water (5 mL). The aqueous layer was extracted with ethyl acetate (3x 8 mL) and the combined organic layers were washed with brine (3x 8 mL), dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by column chromatography [*V*(petroleum ether)/*V*(ethyl acetate)=10:1].

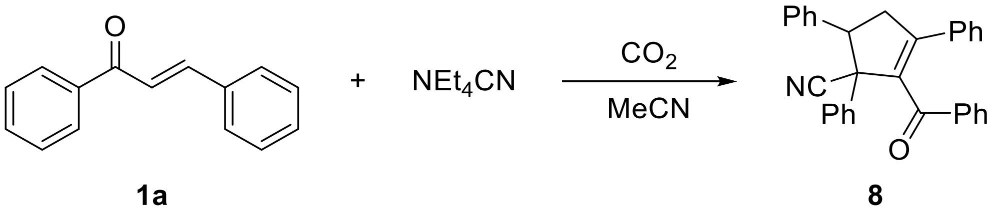
4-oxo-2,4-diphenylbutanenitrile (**2a**)



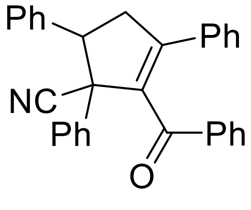
Yield: 78% colourless crystals. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.98 – 7.93 (m, 2H), 7.62 (td, J=7.4, 1.3, 1H), 7.53 – 7.39 (m, 7H), 7.39 – 7.33 (m, 1H), 4.60 (dd, J=7.8, 6.0, 1H), 3.76 (dd, J=17.9, 7.9, 1H), 3.54 (dd, J=17.9, 6.1, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 194.61, 135.70, 135.29, 133.92, 129.29, 128.85, 128.40, 128.11, 127.51, 120.62, 44.56, 31.91.

Large scale cyanation

2-benzoyl-1,3,5-triphenylcyclopent-2-ene-1-carbonitrile (**3a**)

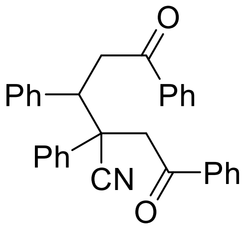


A solution of TEACN (72.0 mmol, 11.3 g) in 100 mL acetonitrile was stirred for 30 min at room temperature under CO_2 atmosphere. To the clear solution chalcone (36.0 mmol, 7.50g) was added. After 10 min the deep red solution was quenched with water and 100 mL ethyl acetate was added, resulting in the precipitation of a white foam. The mixture was filtered and the obtained solid was washed with water, ethyl acetate, and Et_2O. The obtained product can be recrystallized from acetone or MeOH.



8

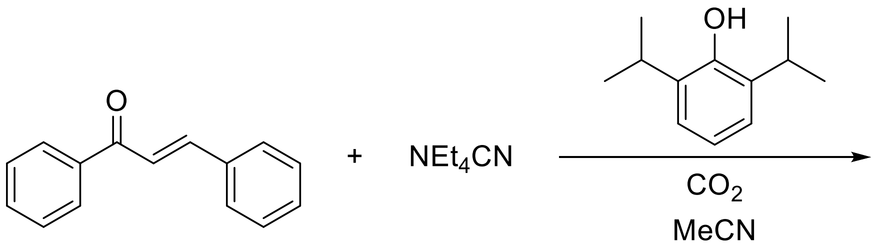
Yield: 50 %, colourless powder. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 7.66 (dd, *J* = 8.3, 1.4, 2H), 7.41 – 7.26 (m, 11H), 7.21 – 7.09 (m, 7H), 4.10 (dd, *J* = 10.9, 7.6, 1H), 3.67 (dd, *J* = 17.6, 10.9, 1H), 3.55 (dd, *J* = 17.6, 7.6, 1H). ^{13}C-NMR (126 MHz, CD_2Cl_2): δ = 193.24, 154.04, 137.44, 136.74, 135.72, 135.61, 134.48, 132.78, 129.52, 129.37, 128.93, 128.82, 128.79, 128.30, 128.29, 128.18, 128.17, 128.12, 126.49, 118.66, 63.52, 58.55, 41.19. HRMS (EI) calcd for [$C_{31}H_{23}NO$] ([M + H$^+$]): 426.1852, found: 426.1860. Anal. calcd for $C_{31}H_{23}NO$ C 87.50 H 5.45 N 3.29; found C 87.59 H 5.43 N 3.08. CCDC Deposit number: CCDC2047210



8-int

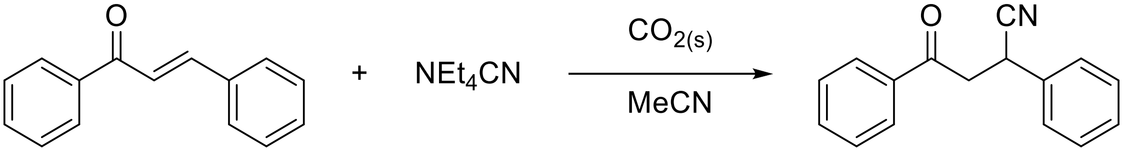
^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 7.79 – 7.70 (m, 4H), 7.70 – 7.64 (m, 4H), 7.53 – 7.46 (m, 2H), 7.45 – 7.34 (m, 8H), 7.34 – 7.30 (m, 1H), 7.30 – 7.26 (m, 1H), 4.06 (dd, *J* = 10.8, 2.5 Hz, 1H), 3.95 (dd, *J* = 17.3, 10.8 Hz, 1H), 3.80 (d, *J* = 17.8 Hz, 1H), 3.19 (d, *J* = 17.8 Hz, 1H), 2.96 (dd, *J* = 17.3, 2.5, 1H); ^{13}C-NMR (126 MHz, CD_2Cl_2): δ = 196.93, 194.11, 138.58, 137.71, 136.49, 136.22, 133.62, 133.42, 129.26, 129.14, 128.72, 128.66, 128.40, 128.34, 128.07, 127.90, 126.53, 121.06, 50.11, 48.81, 46.94, 40.19.

In situ quenching



A solution of TEACN (4.80 mmol, 0.75 g) in 20 mL acetonitrile was stirred for 30 min at room temperature under CO_2 atmosphere. To the clear solution chalcone (2.40 mmol, 0.50 g) and 2,6-diisopropylphenol (2.40 mmol, 0,43 g) were added and the mixture was stirred at room temperature under CO_2 atmosphere. On completion, the reaction was quenched with water (100 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by column chromatography [*V*(petroleum ether)/*V*(ethyl acetate)=10:1]. Yield 81%, colourless solid.

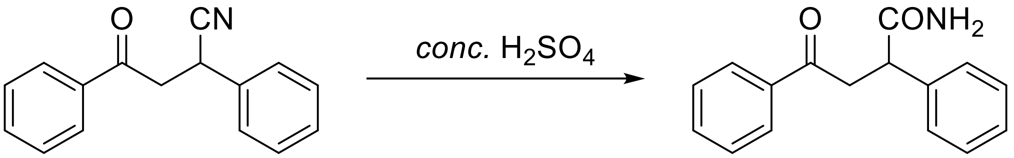
Dry ice method



To a solution of TEACN (4.80 mmol, 0.75 g) in 20 mL acetonitrile, 25 g dry ice was added and stirred for 1h. To the clear solution *trans*-chalcone (2.40 mmol, 0.50 g) was added and the mixture was stirred at room temperature under CO_2 atmosphere. On completion, the reaction was quenched with water (100 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by column chromatography [*V*(petroleum ether)/*V*(ethyl acetate)=15:1]. Yield 78%, colourless solid.

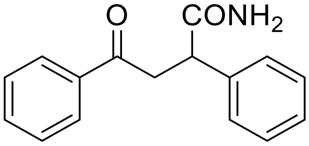
Synthetic applications

Hydrolysis to amide



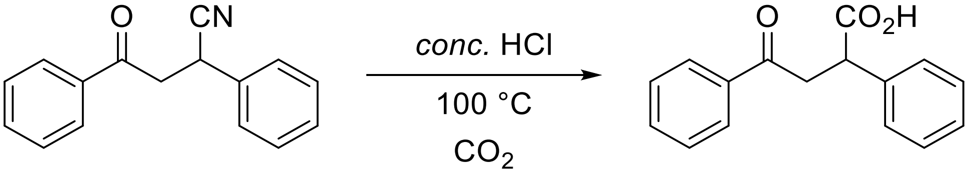
To a dried vial chalcone (0.40 mmol, 94.1 mg) and 2.0 mL conc. H_2SO_4 was added. The mixture was stirred at room temperature for 2 h. On completion, the reaction was quenched with water (30 mL) and extracted with ethyl acetate (3 x 8 mL). The combined organic layers were washed with water and brine, dried over MgSO4, and concentrated under vacuum.

4-oxo-2,4-diphenylbutanamide (**4a**)



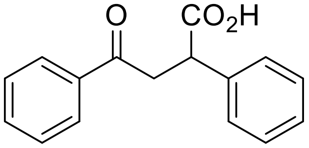
Yield: 71%, off-white solid. 1H-NMR (500 MHz, CDCl3): δ = 7.97 (dd, J=8.4, 1.3, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 7.44 – 7.36 (m, 2H), 7.35 (ddd, J=7.7, 6.7, 1.4, 2H), 7.32 – 7.25 (m, 1H), 5.65 (d, J=14.2, 2H), 4.23 (dd, J=9.0, 4.6, 1H), 4.06 (dd, J=18.0, 9.1, 1H), 3.23 (dd, J=18.0, 4.6, 1H). 13C-NMR (126 MHz, CDCl3): δ = 198.17, 175.06, 139.39, 136.45, 133.34, 129.11, 128.61, 128.17, 127.96, 127.68, 47.19, 42.58. HRMS (EI) calcd for [C16H15NO2] ([M + Na+]): 276.0995, found: 276.1004.

Hydrolysis to carboxylic acid



A dispersion of **2a** (0.40 mmol, 94.1 mg) in 3.0 mL *conc.* HCl was heated at 100 °C for 3 h under CO_2 atmosphere. The reaction cooled to room temperature, was quenched with water, and extracted with ethyl acetate (3x10 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure.

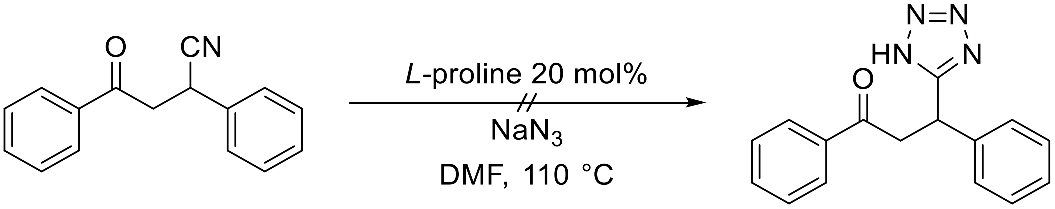
4-oxo-2,4-diphenylbutanoic acid (**5a**)



Yield: 70%, white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.80 (s, 1H), 8.00 – 7.94 (m, 2H), 7.61 – 7.54 (m, 1H), 7.46 (t, *J* = 7.8, 2H), 7.41 – 7.29 (m, 4H), 4.33 (dd, *J* = 10.2, 4.1, 1H), 3.92 (dd, *J* = 18.1, 10.3, 1H), 3.30 (dd, *J* = 18.1, 4.1, 1H). HRMS (EI) calcd for [$C_{16}H_{14}O_3$] ([$M + H^+$]): 255.1016, found: 255.1023.

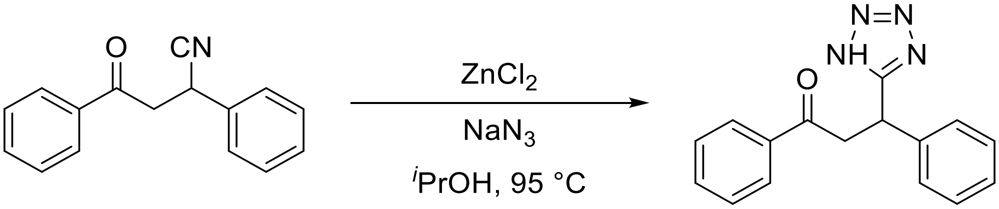
Tetrazole

With L-proline as catalyst



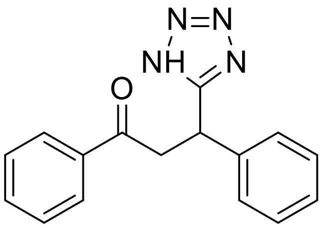
In a vial **2a** (0.40 mmol, 94.1 mg), NaN_3 (1.25 eq, 0.50 mmol, 32.5 mg) and L-proline (30 mol%, 0.12 mmol, 13.8 mg) were dissolved in 4 mL DMF and stirred at 110 °C for 2h. Next, the reaction was stirred at room temperature for 20h. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. ^{1}H-NMR only shows the starting material.

With $ZnCl_2$ as catalyst



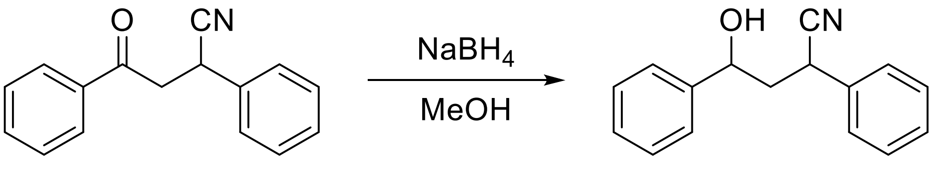
In a vial **2a** (0.43 mmol, 0.10 g), NaN_3 (2.0 eq, 0.85 mmol, 55.0 mg) and $ZnCl_2$ (1.25 eq, 0.44 mmol, 55.5 mg) were stirred in 1.5 mL *n*PrOH 95 °C for 3h and afterwards for 12h at room temperature. Next, the solvent was removed under reduced pressure and the obtained green residue was stirred in 5 mL 5% *aqueous* NaOH for 30 min. The formed $Zn(OH)_2$ was filtered, washed with additional 5% *aqueous* NaOH. The obtained clear filtrate was adjusted to a pH of 1 using 5 M HCl, resulting in precipitation of a white solid. The mixture was cooled to 0°C, filtered, washed with water, and dried under reduced pressure.

1,3-diphenyl-3-(1H-tetrazol-5-yl)propan-1-one (**6a**)



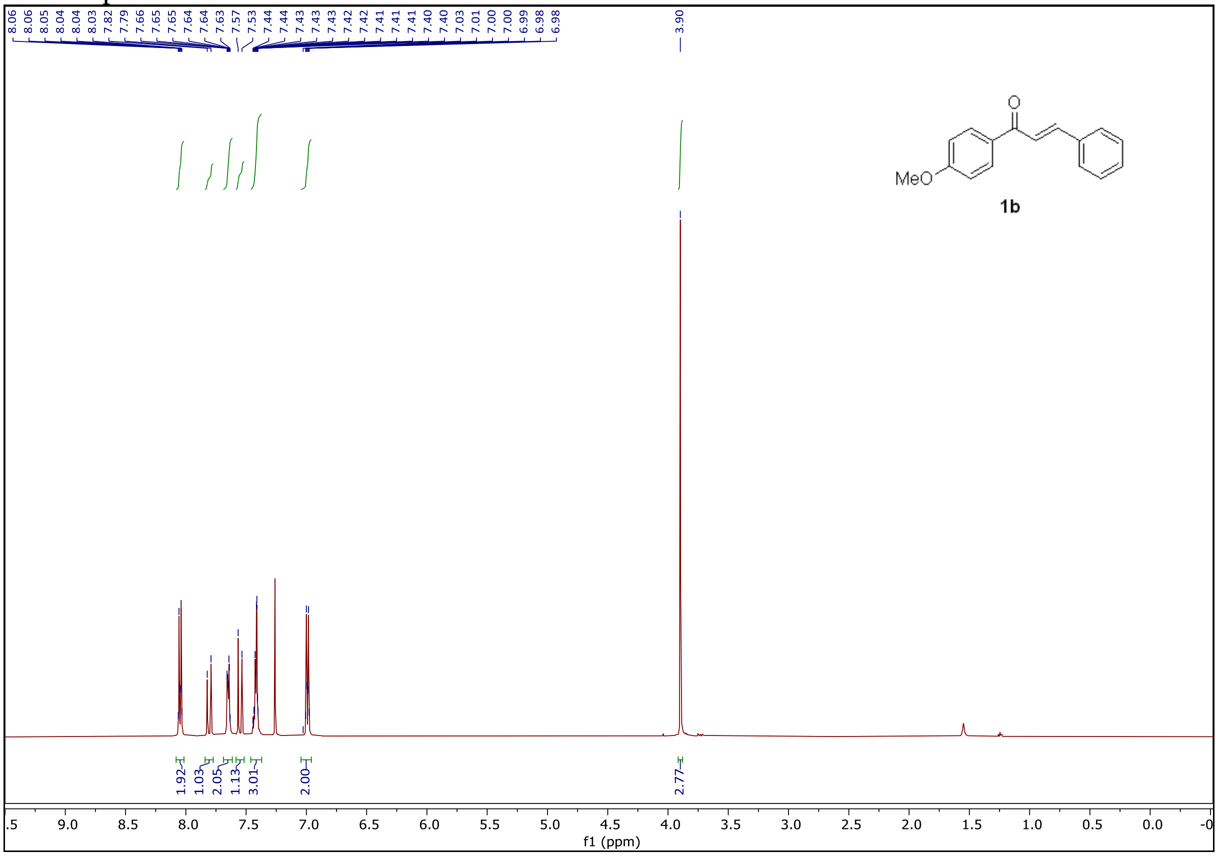
Yield: 39%, off-white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 8.03 – 7.97 (m, 2H), 7.65 (dd, *J* = 8.2, 6.5, 1H), 7.53 (t, *J* = 7.7, 2H), 7.37 – 7.31 (m, 4H), 7.27 (dt, *J* = 5.6, 3.0, 1H), 4.98 (dd, *J* = 9.9, 4.9, 1H), 4.23 (dd, *J* = 18.3, 9.9, 1H), 3.79 (dd, *J* = 18.3, 4.9, 1H). ^{13}C-NMR (126 MHz, DMSO): δ = 197.19, 140.12, 136.12, 133.64, 128.92, 128.87, 128.60, 128.54, 128.15, 127.86, 127.43. HRMS (EI) calcd for [$C_{16}H_{14}N_4O$] ([M + H$^+$]): 279.1240, found: 279.1244.

Reduction with $NaBH_4$



To a flame dried vial **2a** (0.40 mmol 94.1 mg), $NaBH_4$ (0.80 mmol, 30.3 mg) and 2 mL MeOH were added and stirred at 0 °C for 10 minutes. Next, the reaction was stirred at room temperature for 16h. On completion, the reaction was quenched with brine (8 mL) and extracted with CH_2Cl_2. The organic layers were combined, washed with brine and water, and dried over Na_2SO_4. The solvent was removed under reduced pressure.

NMR Spectra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O
1b
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2.00
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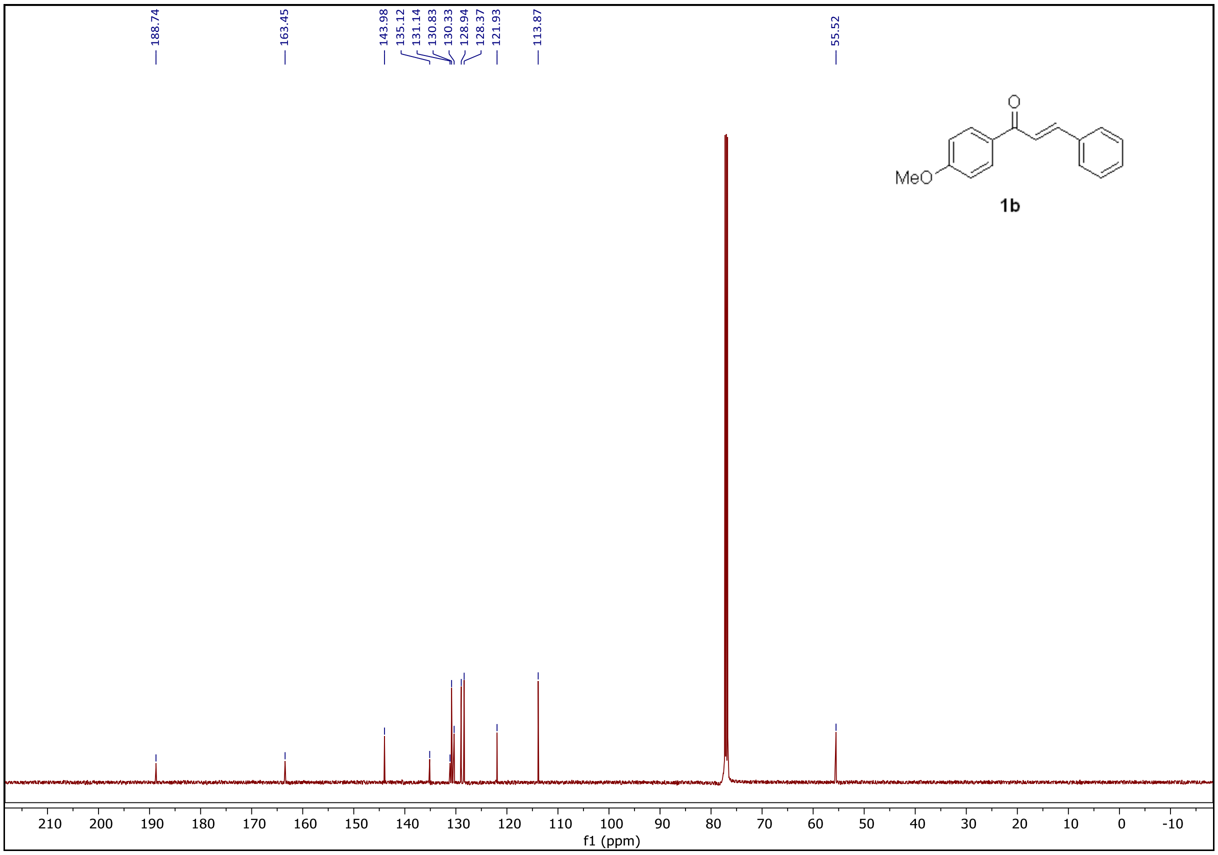
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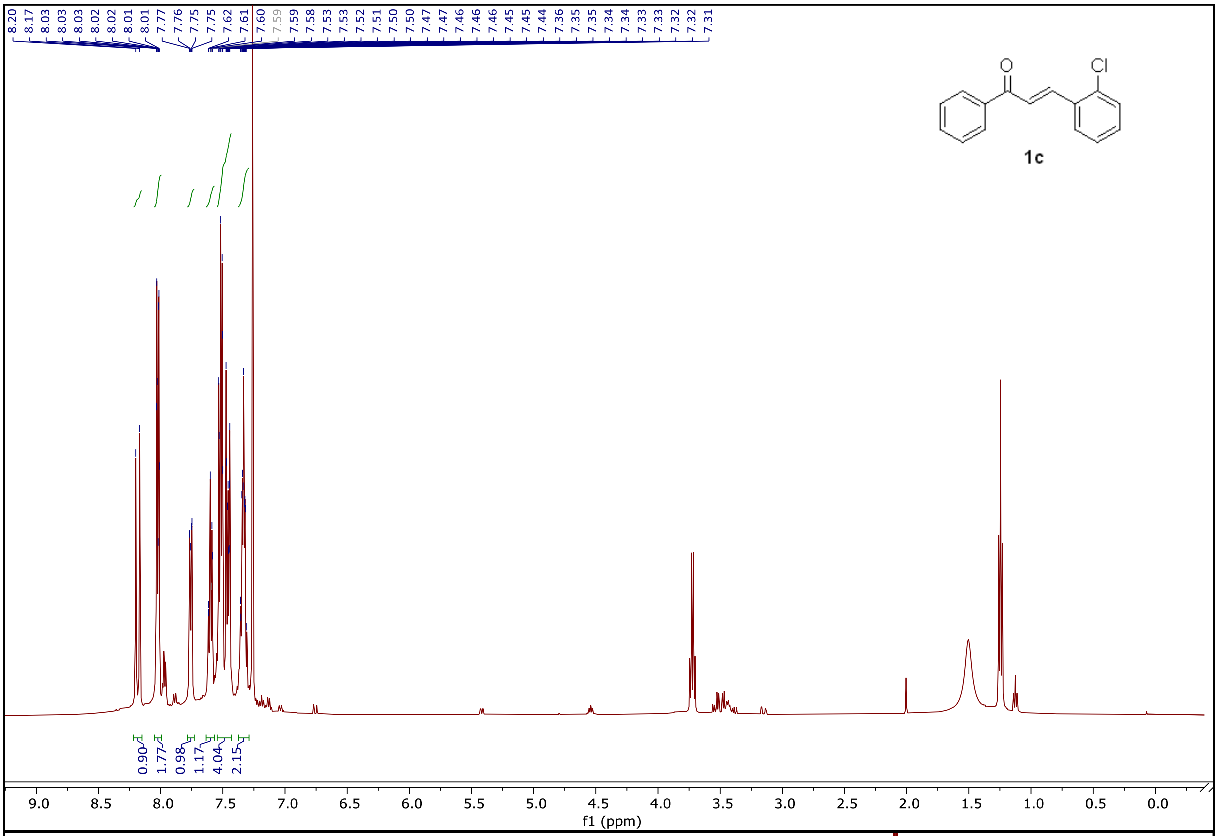
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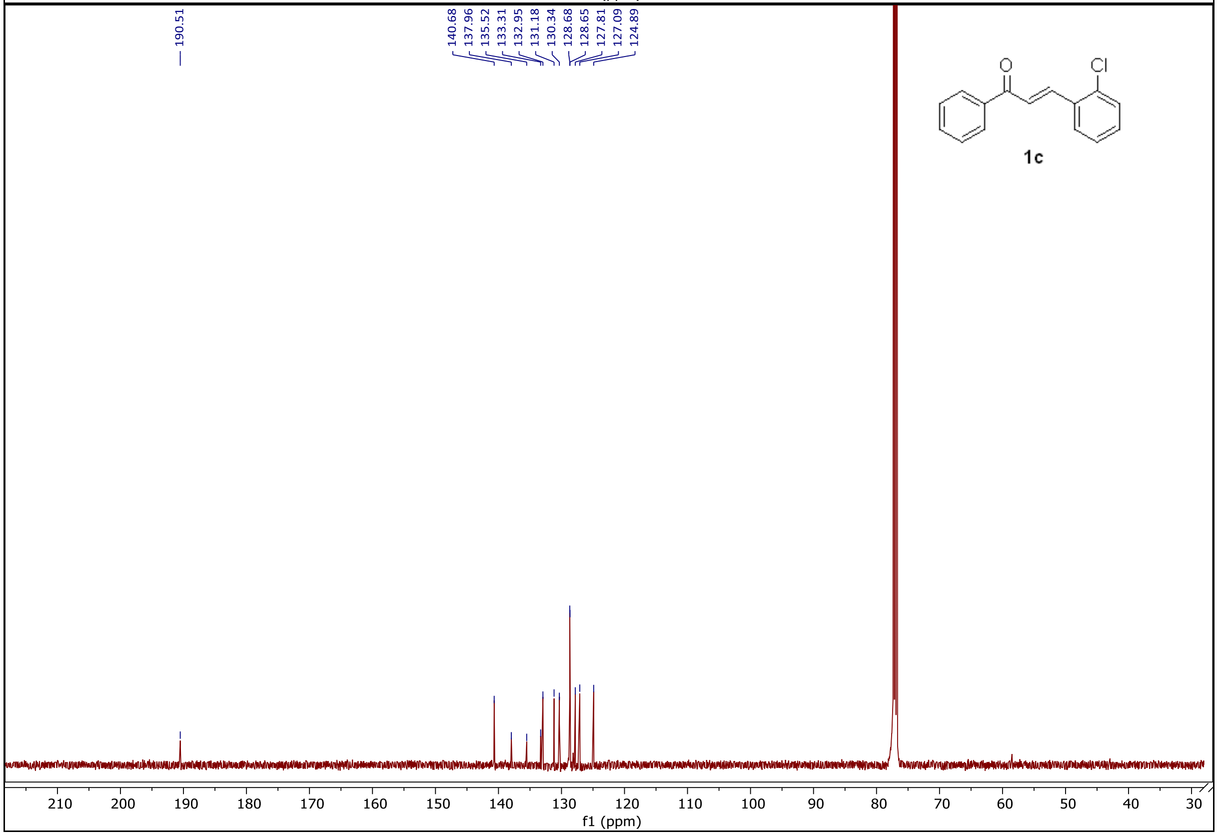
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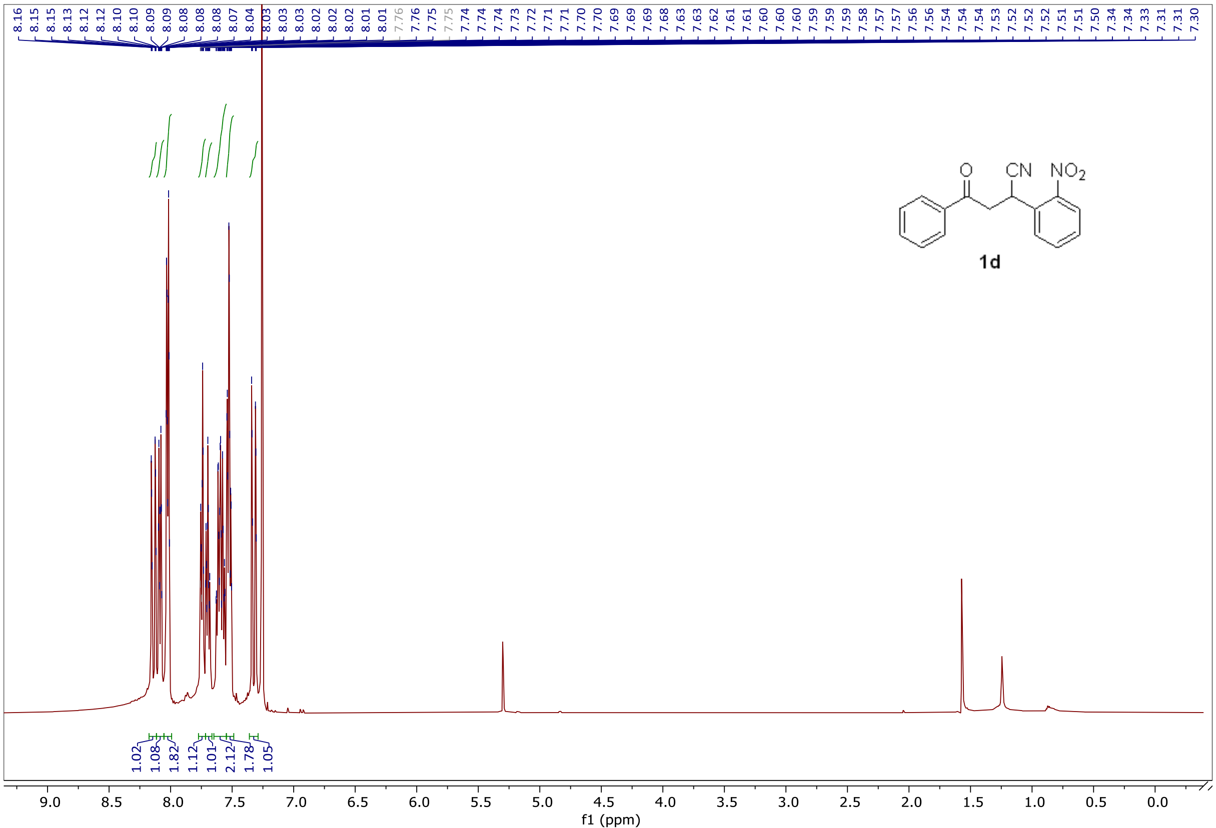
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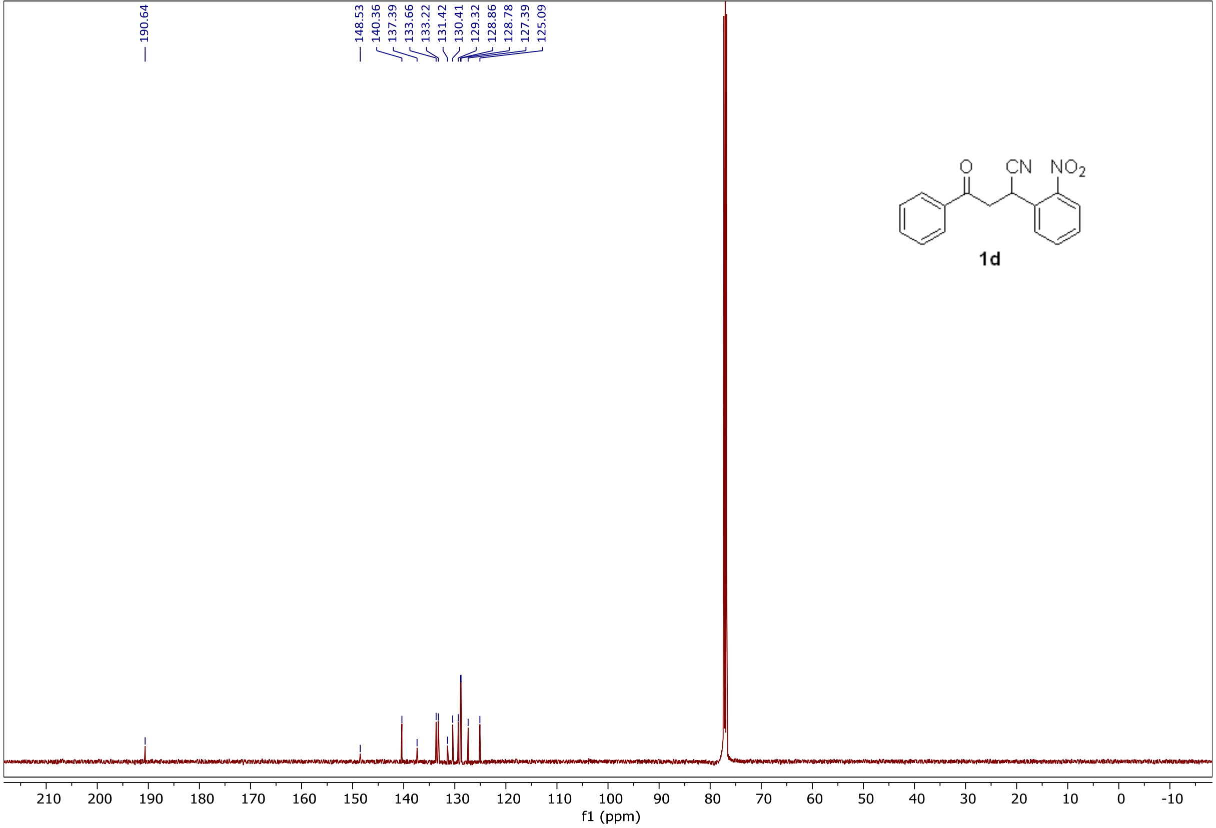
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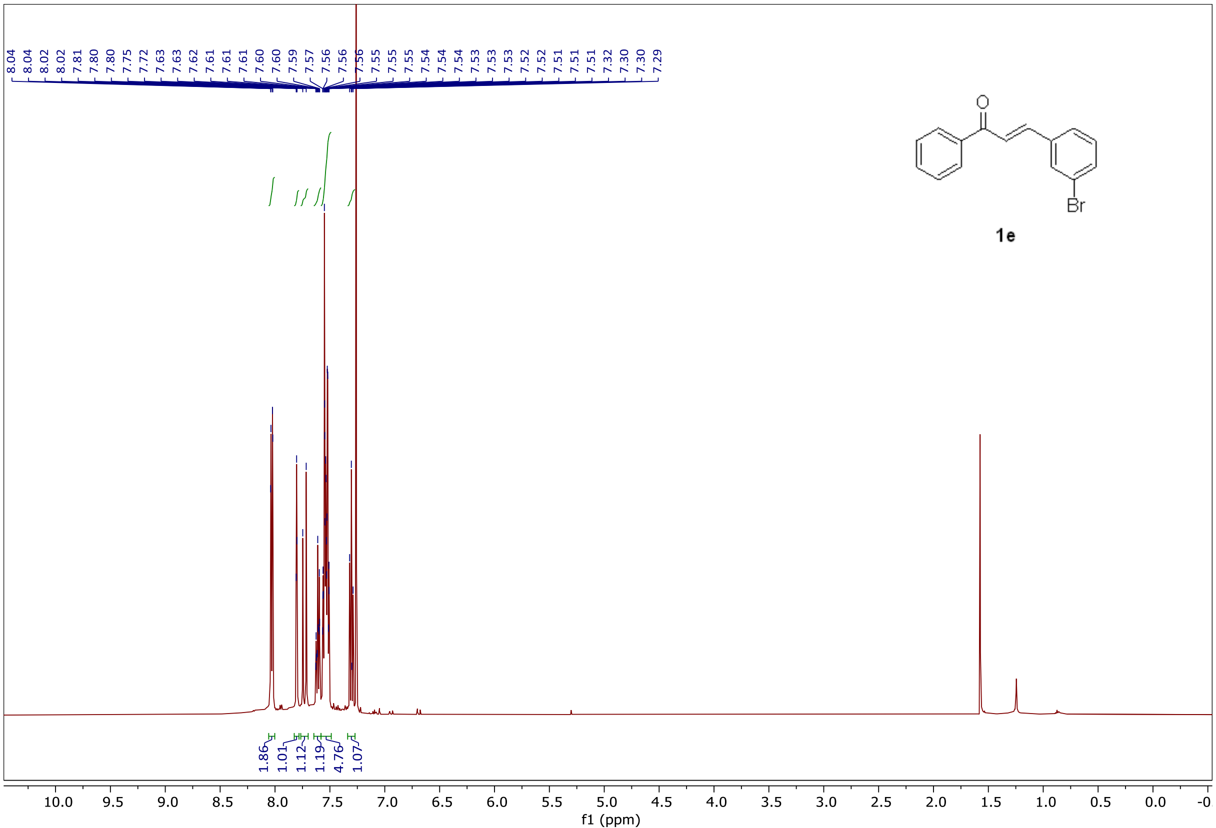
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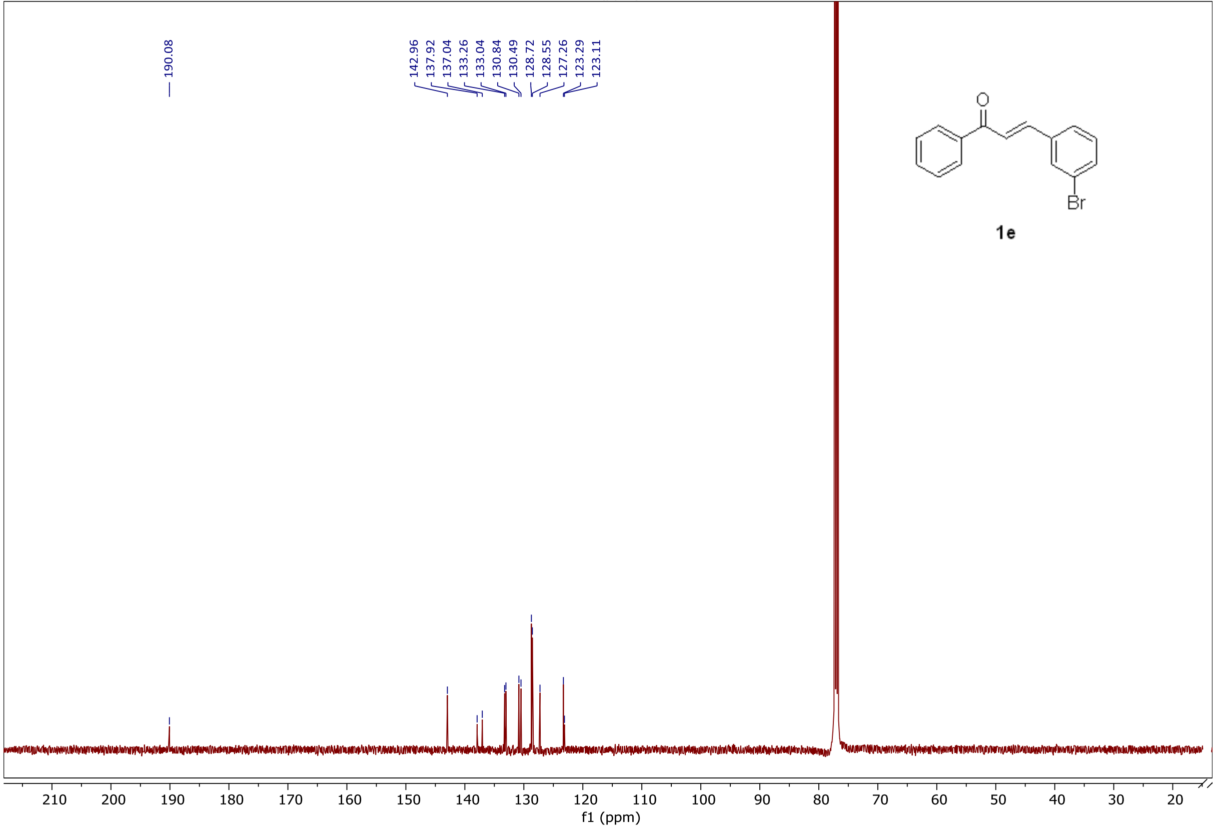
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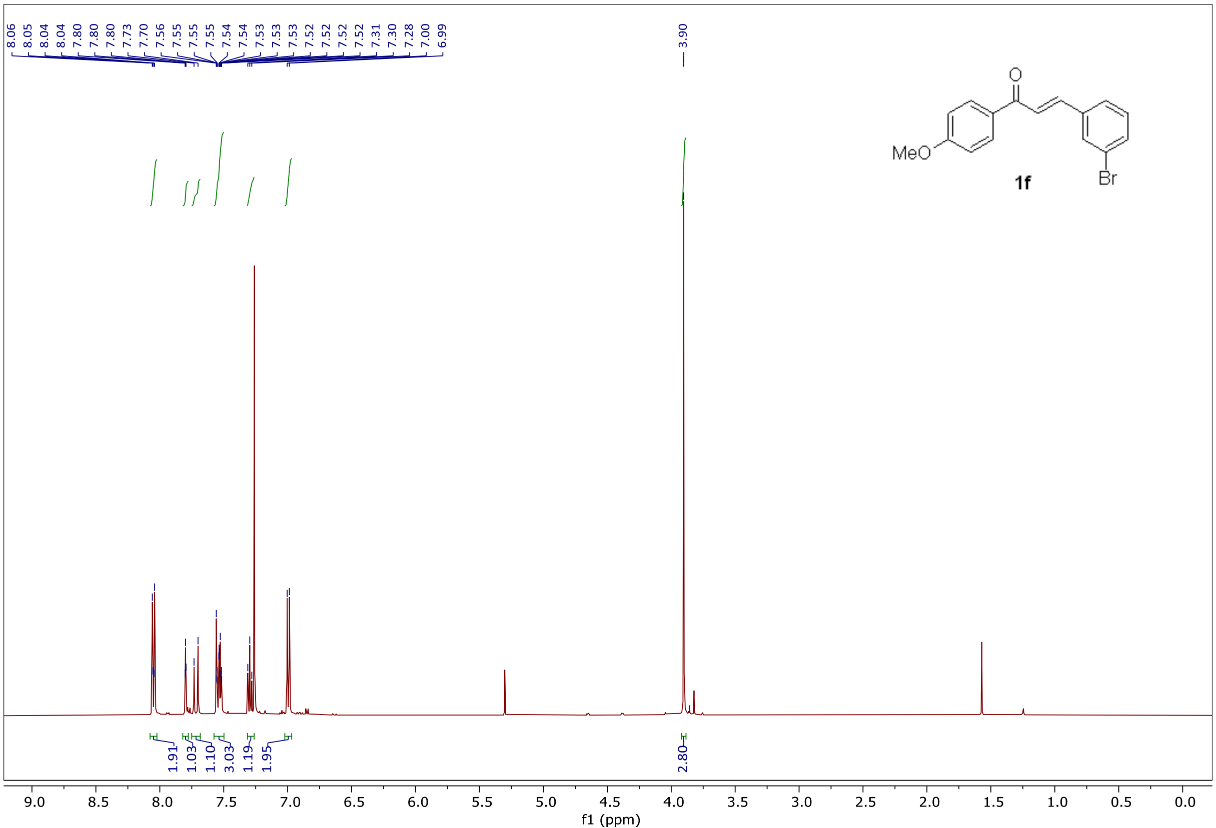
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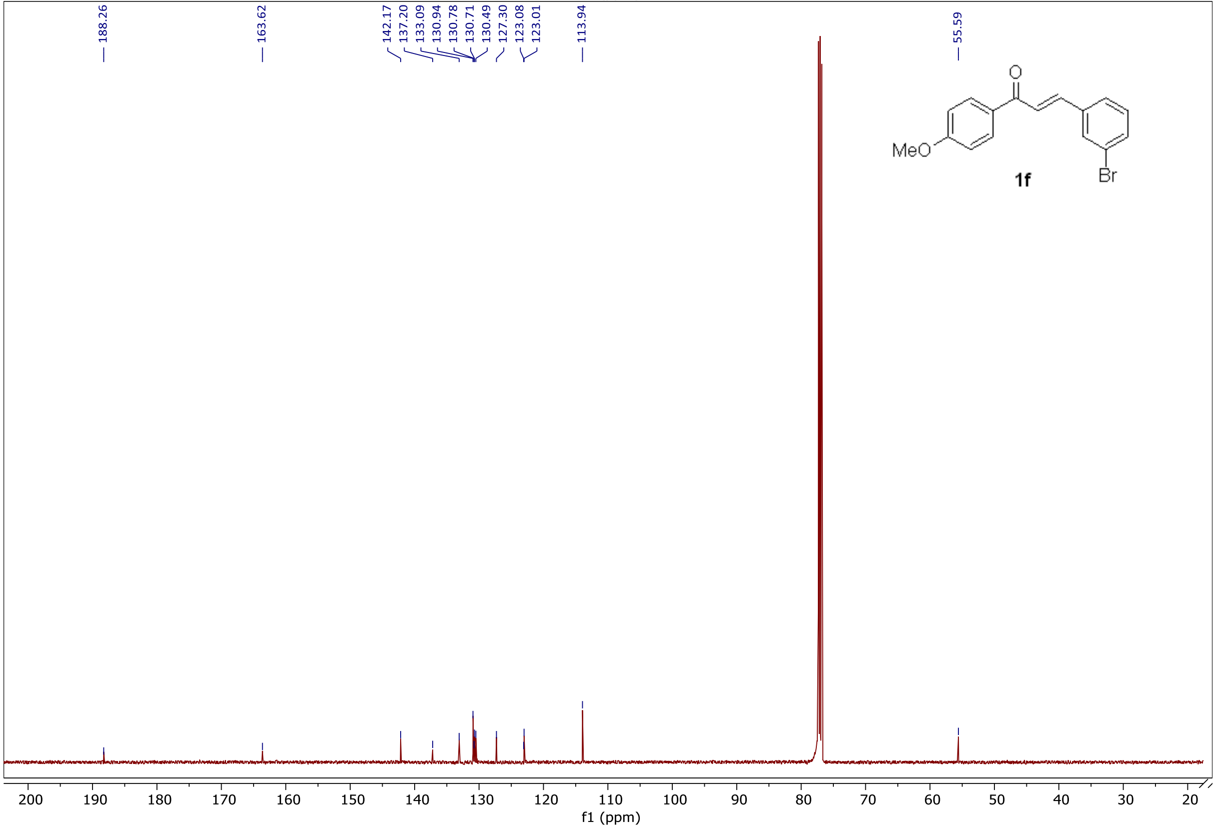
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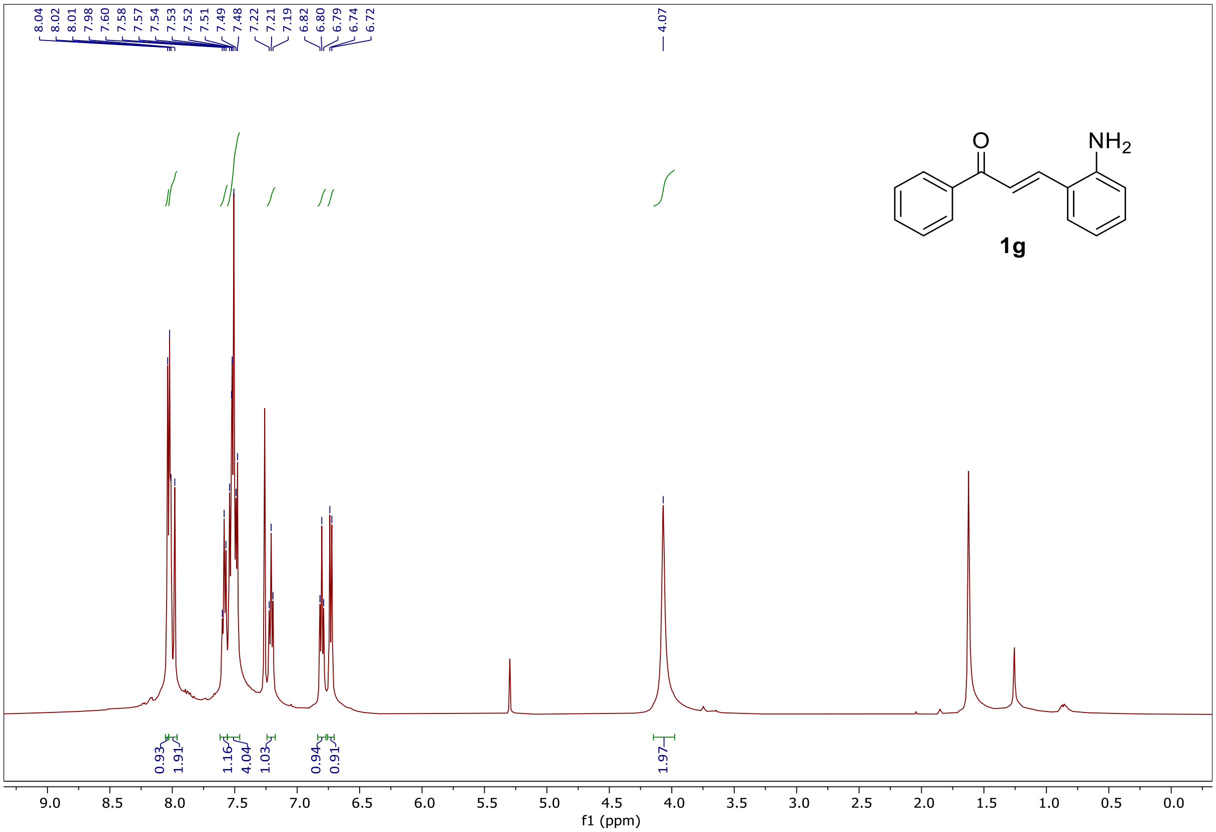
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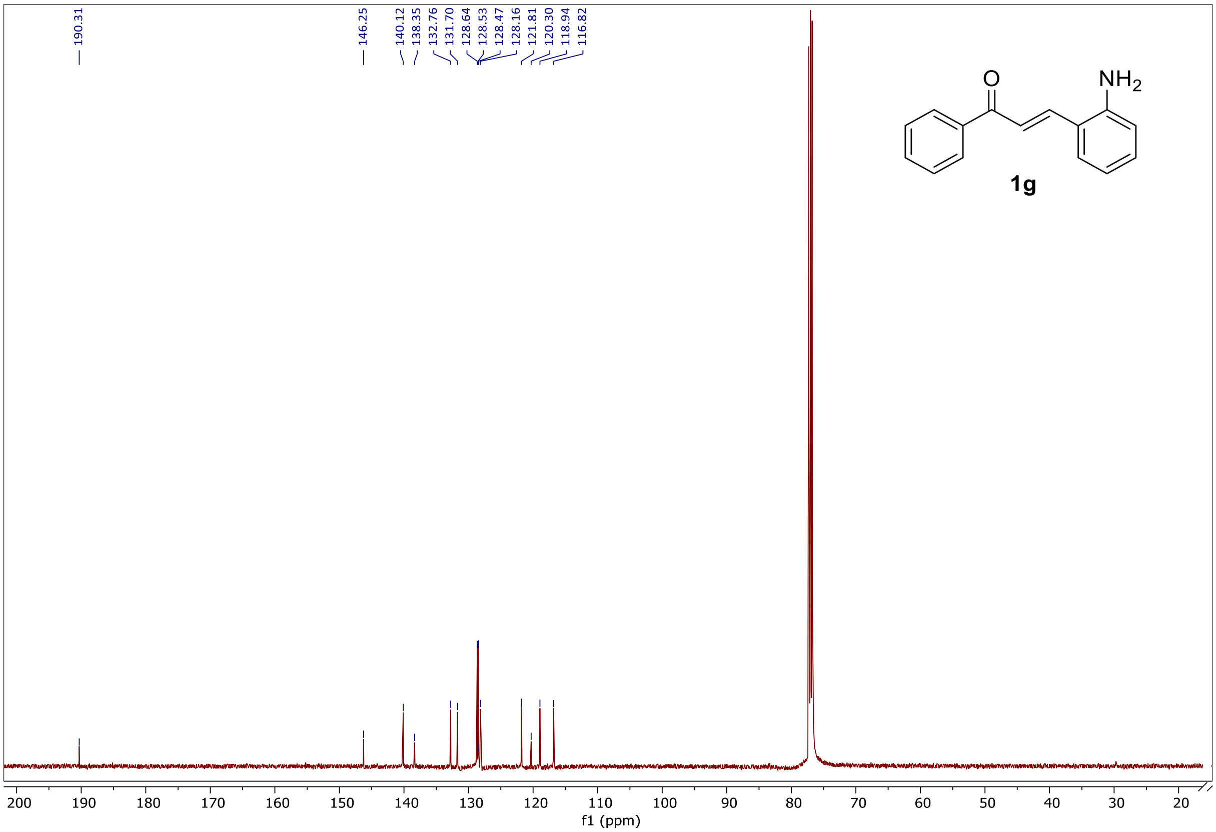
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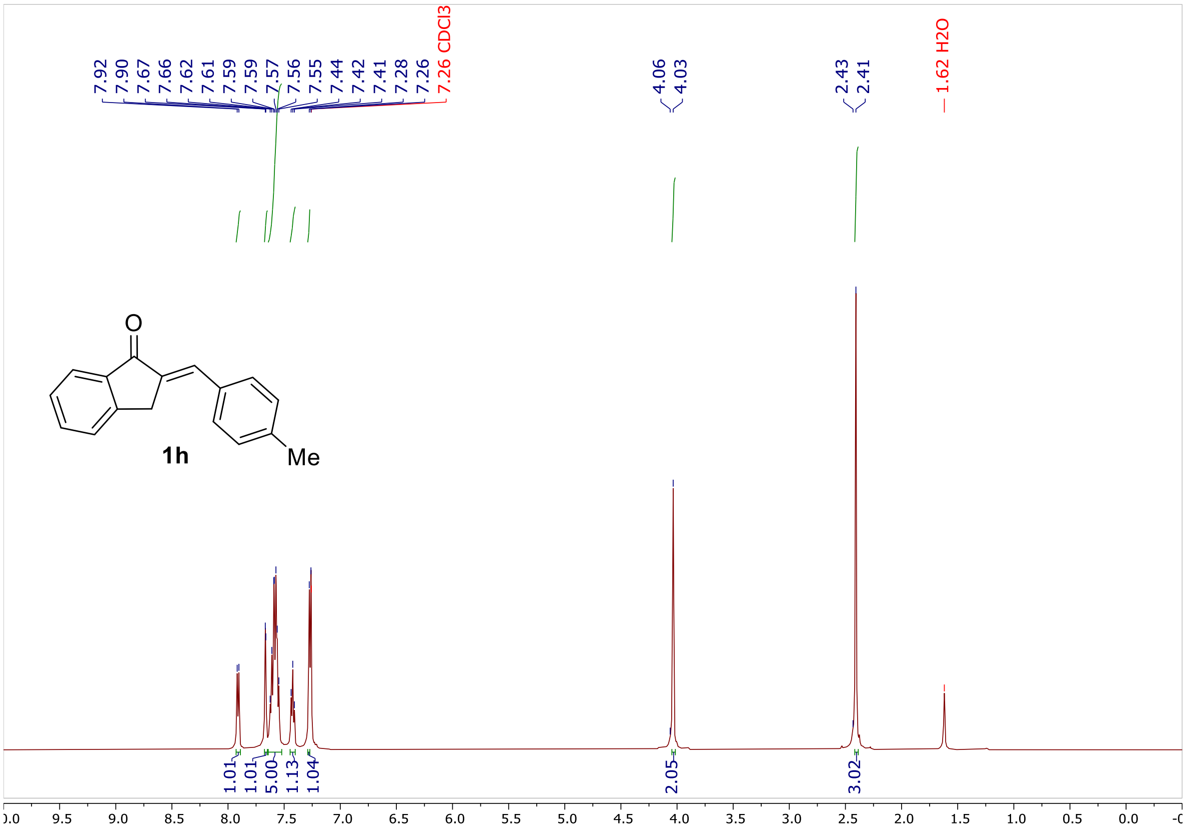
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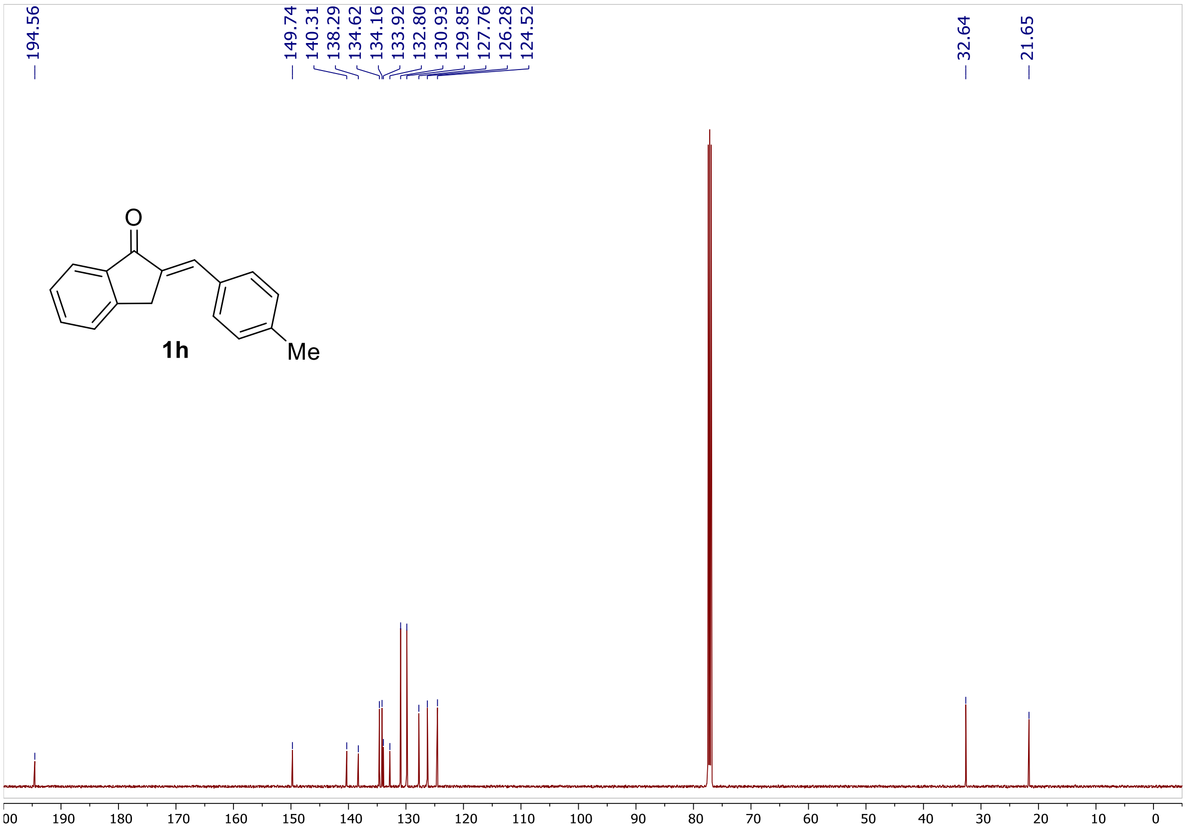
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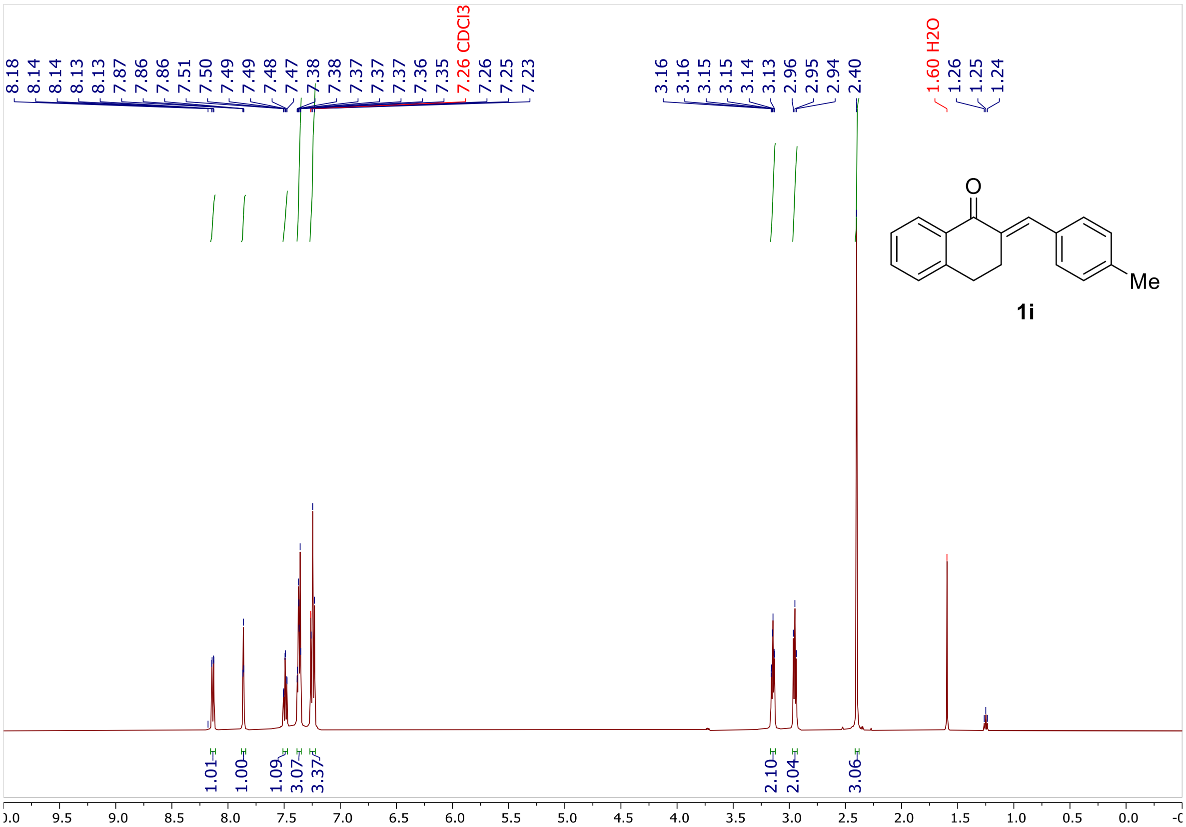
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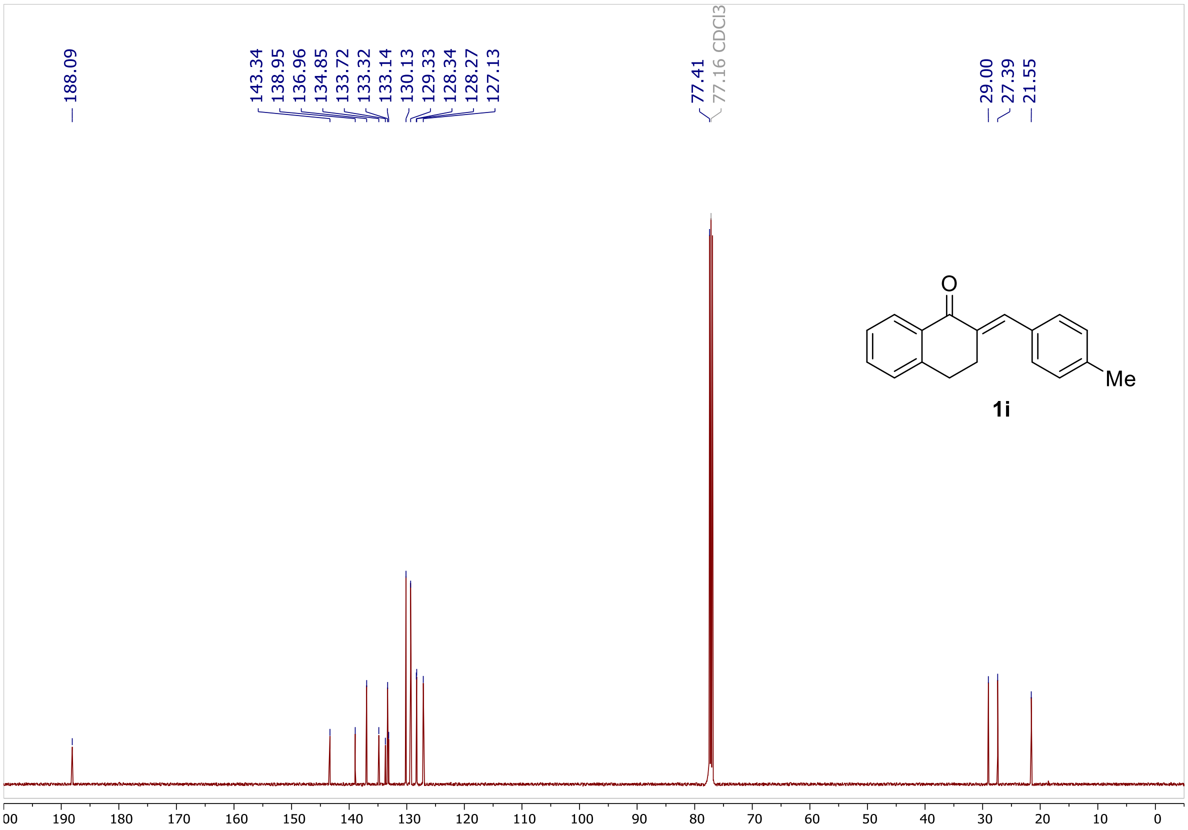
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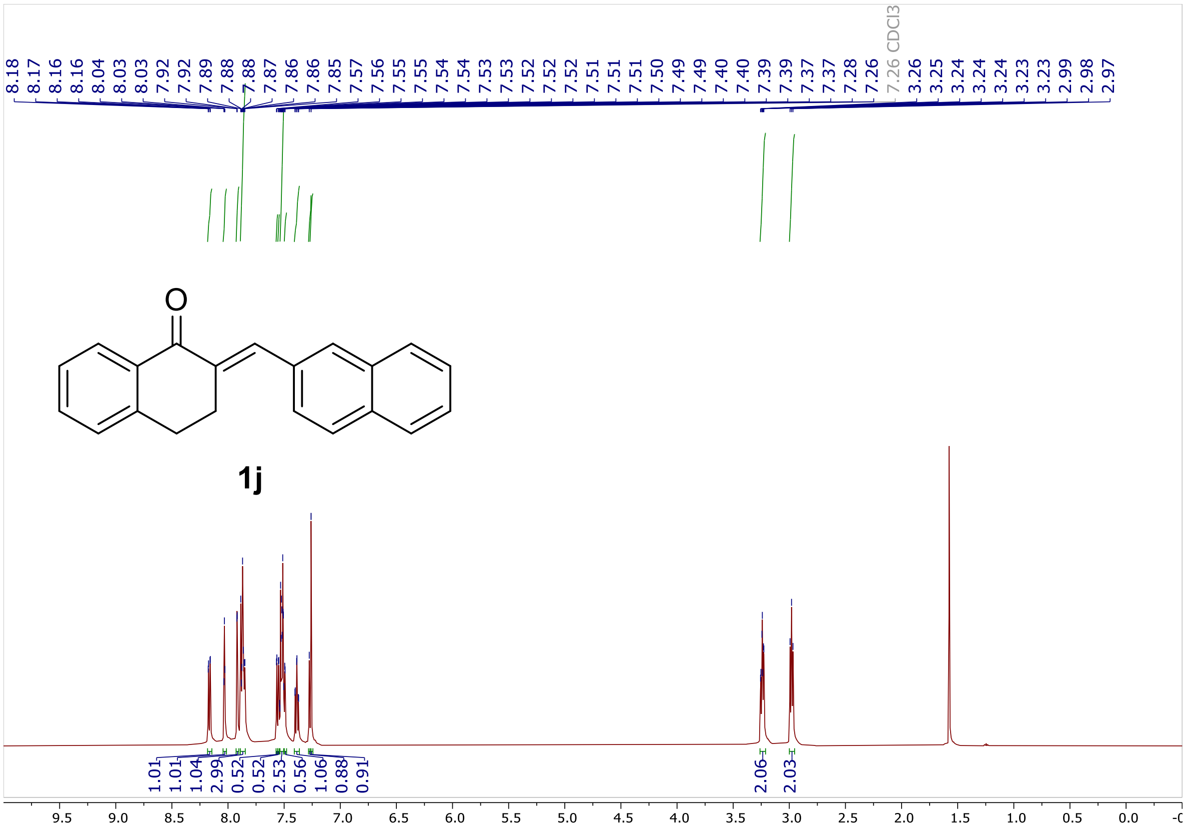
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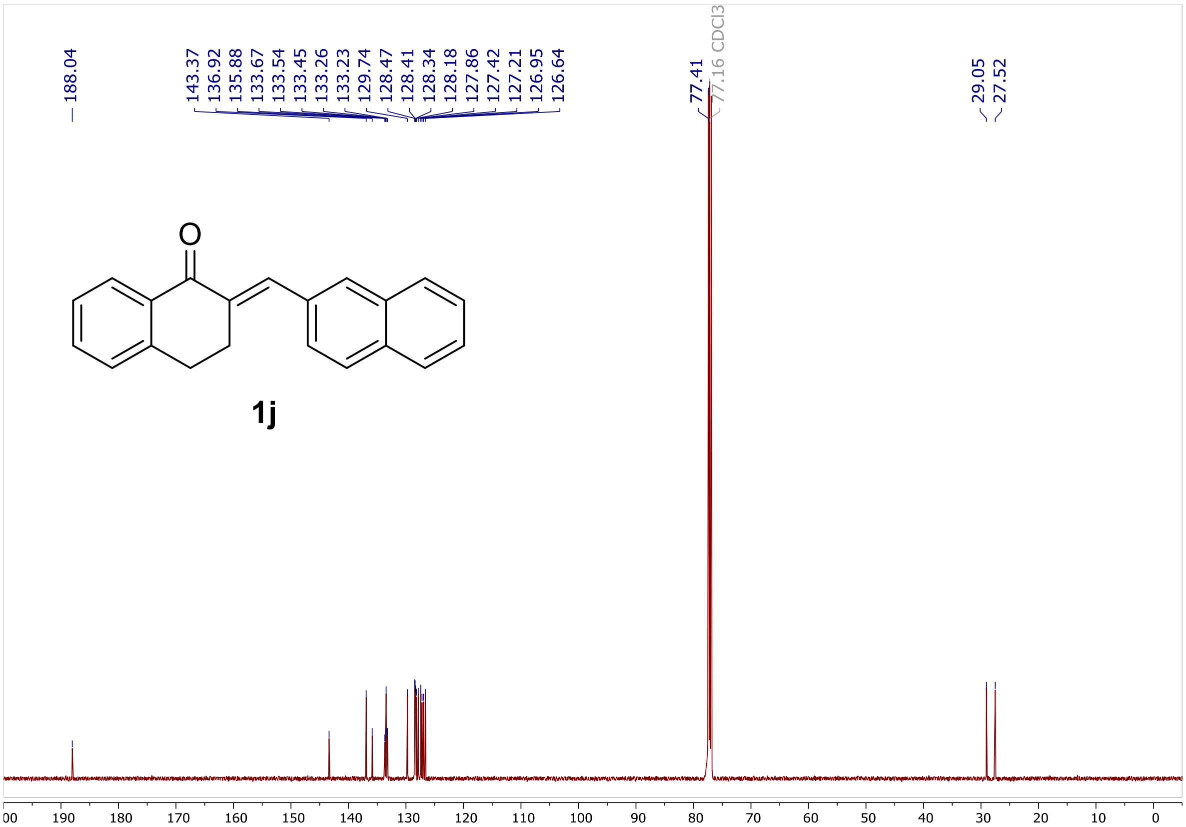
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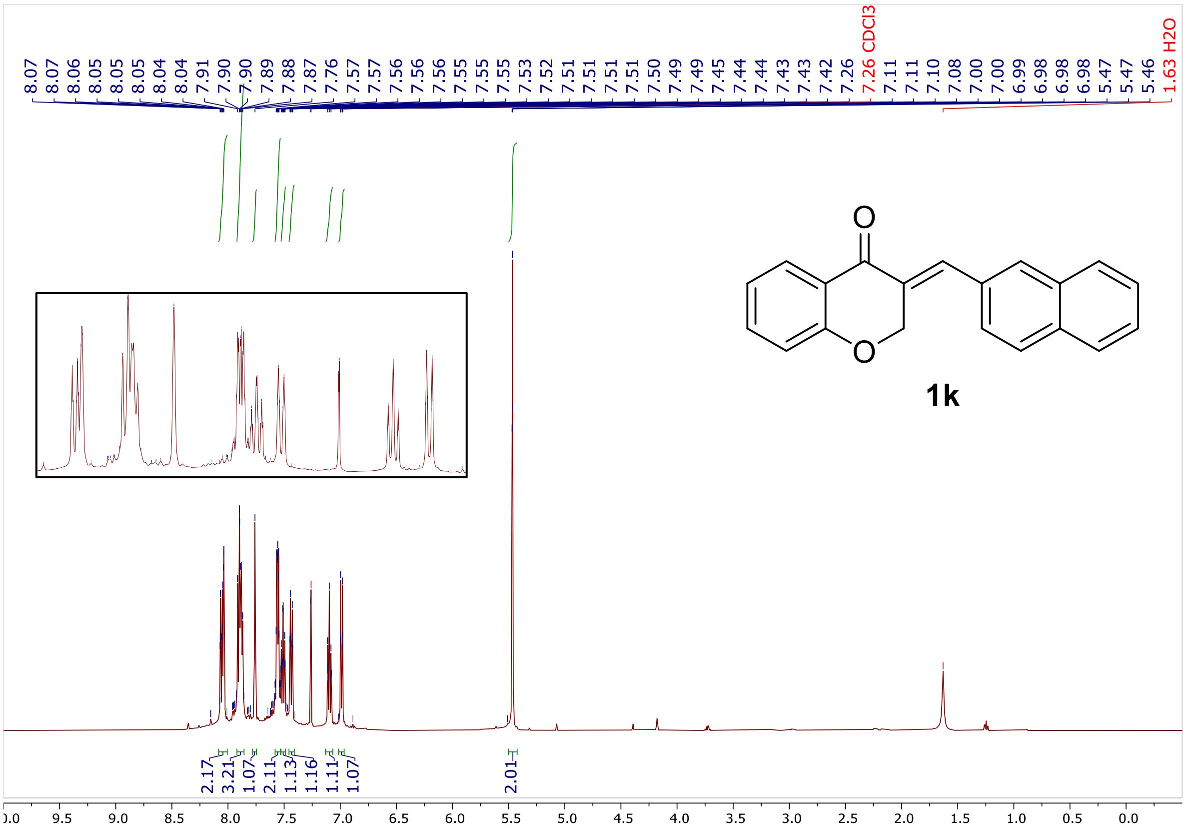
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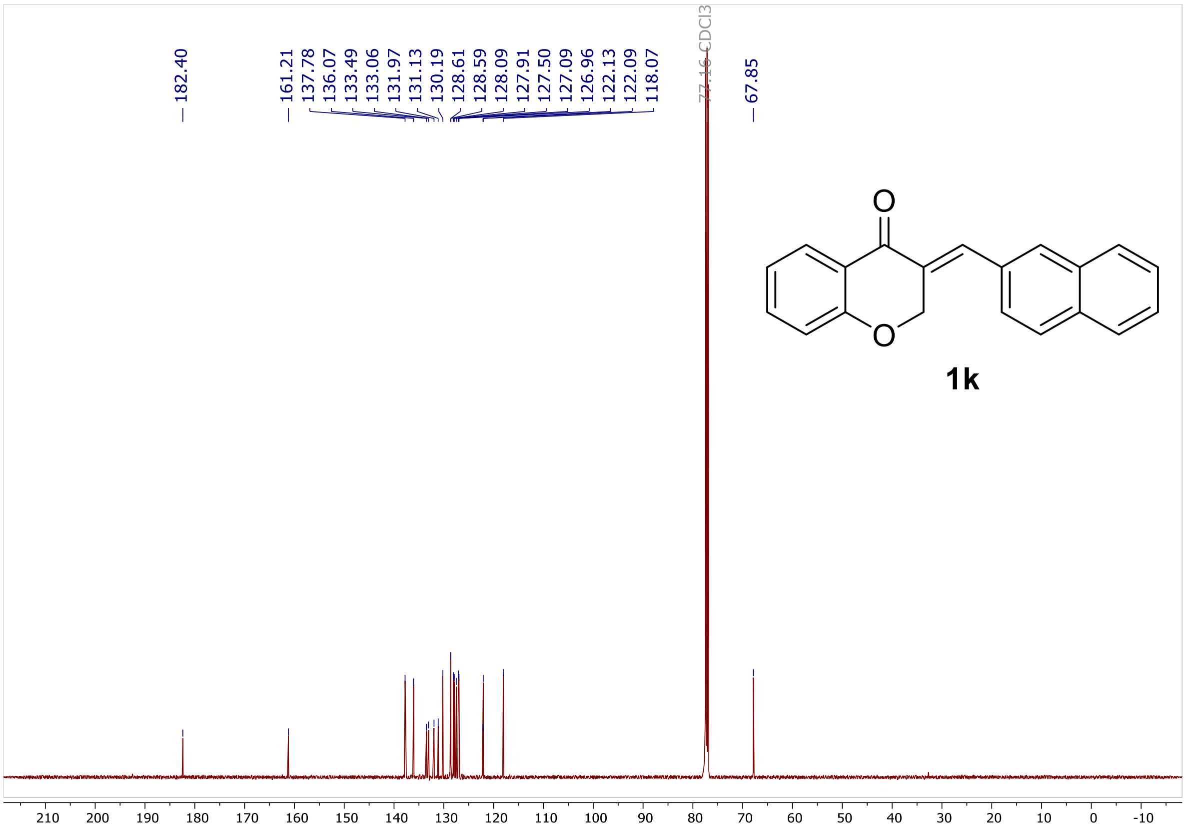
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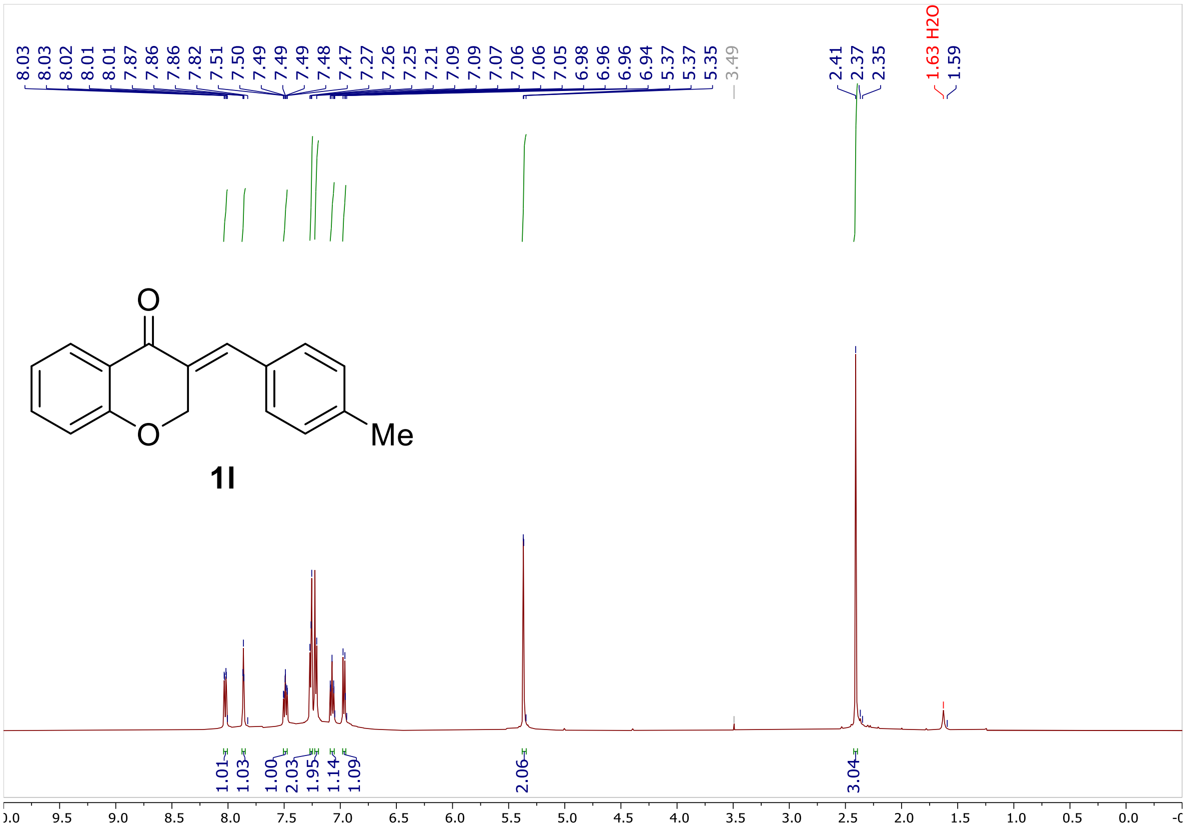
1k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7.25
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7.09
7.07
7.06
7.06
7.05
6.98
6.96
6.96
6.94
5.37
5.37
5.35
3.49
2.41
2.37
2.35
1.63 H2O
1.59
O
O
Me
1l
1.01
1.03
1.00
2.03
1.95
1.14
1.09
2.06
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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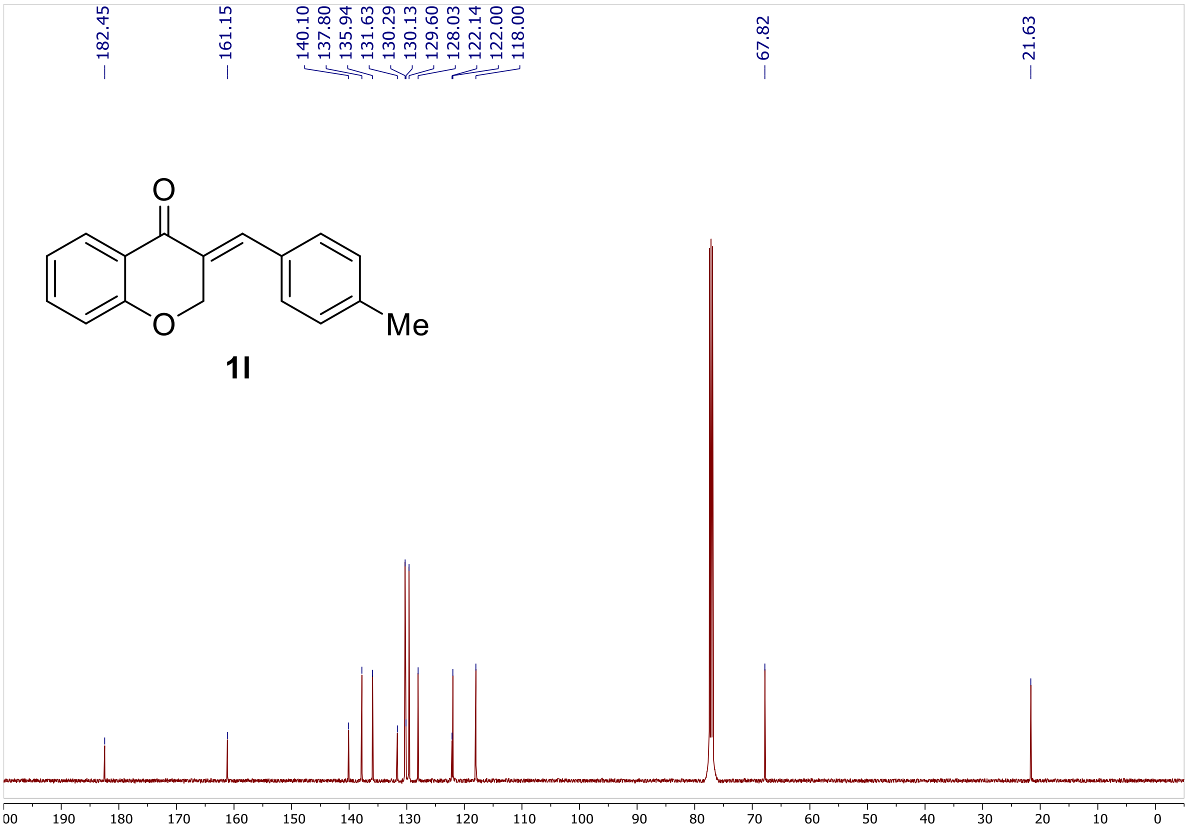
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130.13
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128.03
122.14
122.00
118.00
67.82
21.63
O
O
Me
1l
200
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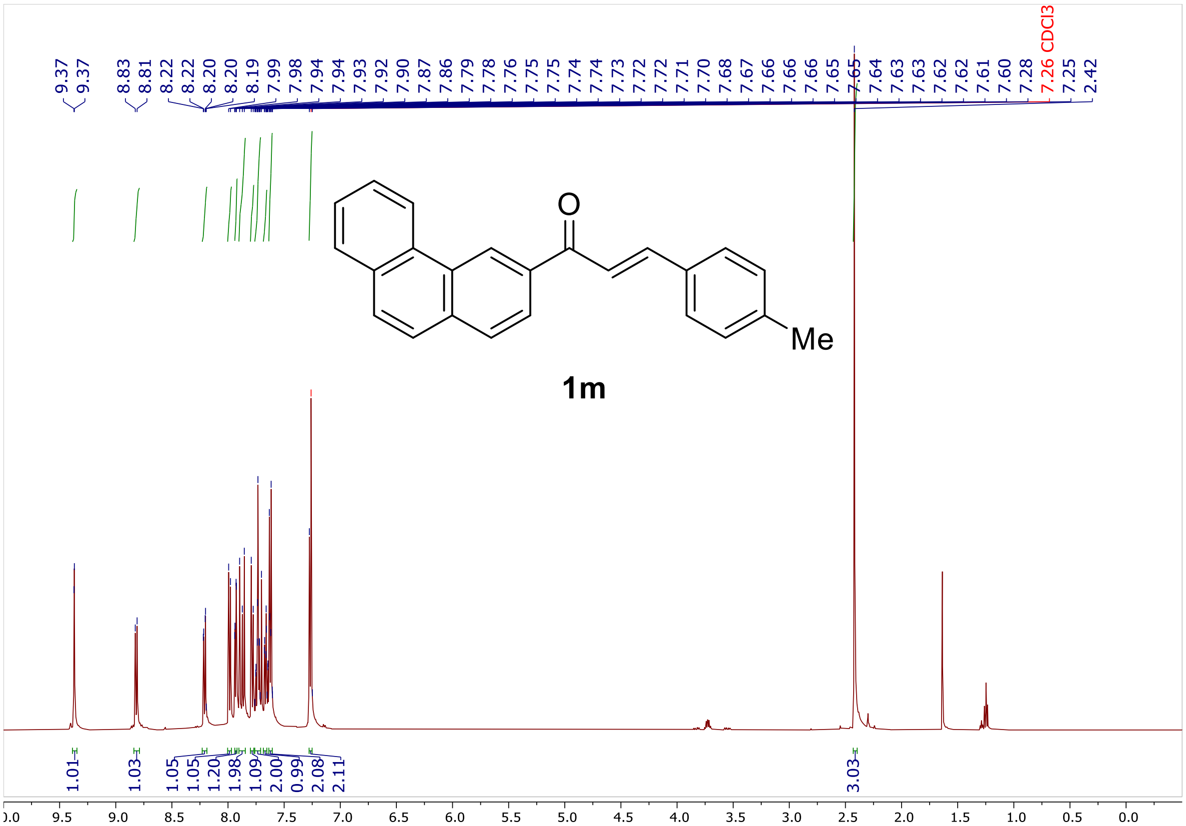
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7.93
7.92
7.90
7.87
7.86
7.79
7.78
7.76
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7.75
7.74
7.74
7.73
7.72
7.72
7.71
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7.68
7.67
7.66
7.66
7.66
7.65
7.65
7.64
7.63
7.63
7.62
7.62
7.61
7.60
7.28
7.26 CDCl3
7.25
2.42
O
Me
1.01
1.03
1.05
1.05
1.20
1.98
1.09
2.00
0.99
2.08
2.11
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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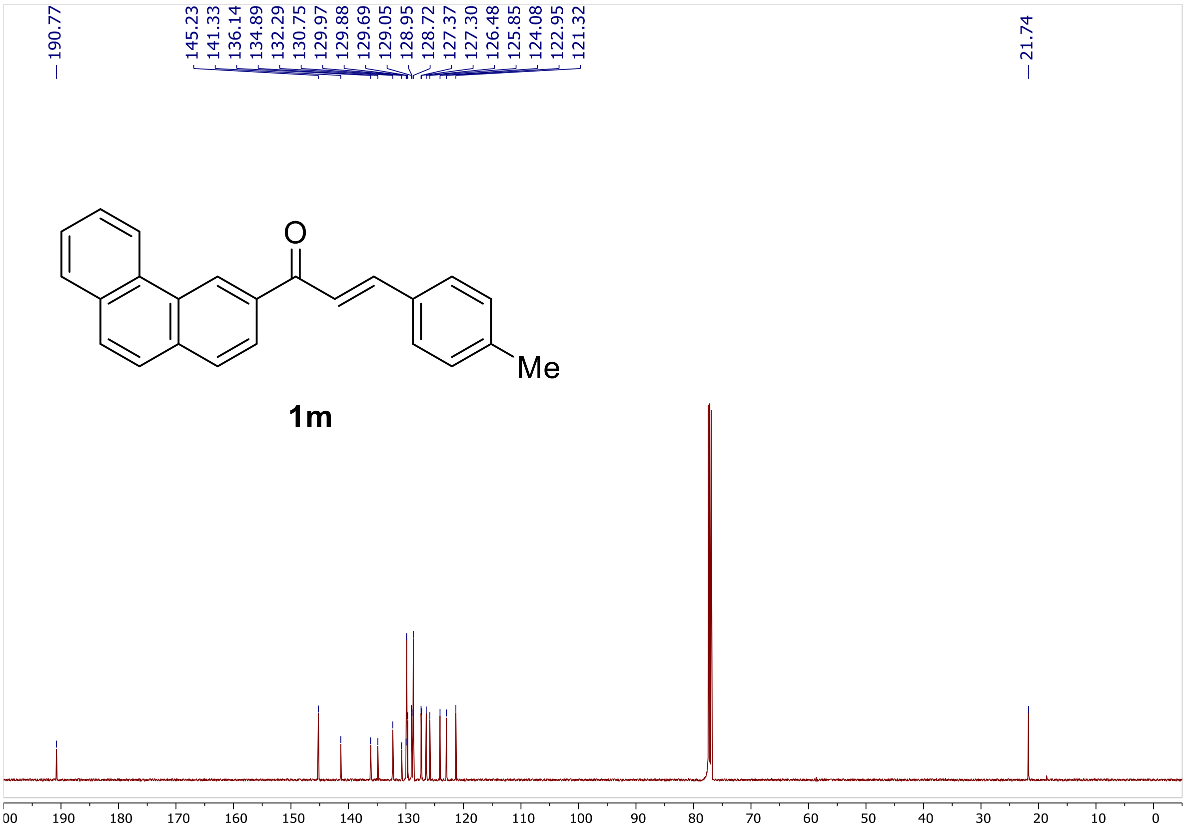
1m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129.69
129.05
128.95
128.72
127.37
127.30
126.48
125.85
124.08
122.95
121.32
21.74
O
Me
190
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140
130
120
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100
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50
40
30
20
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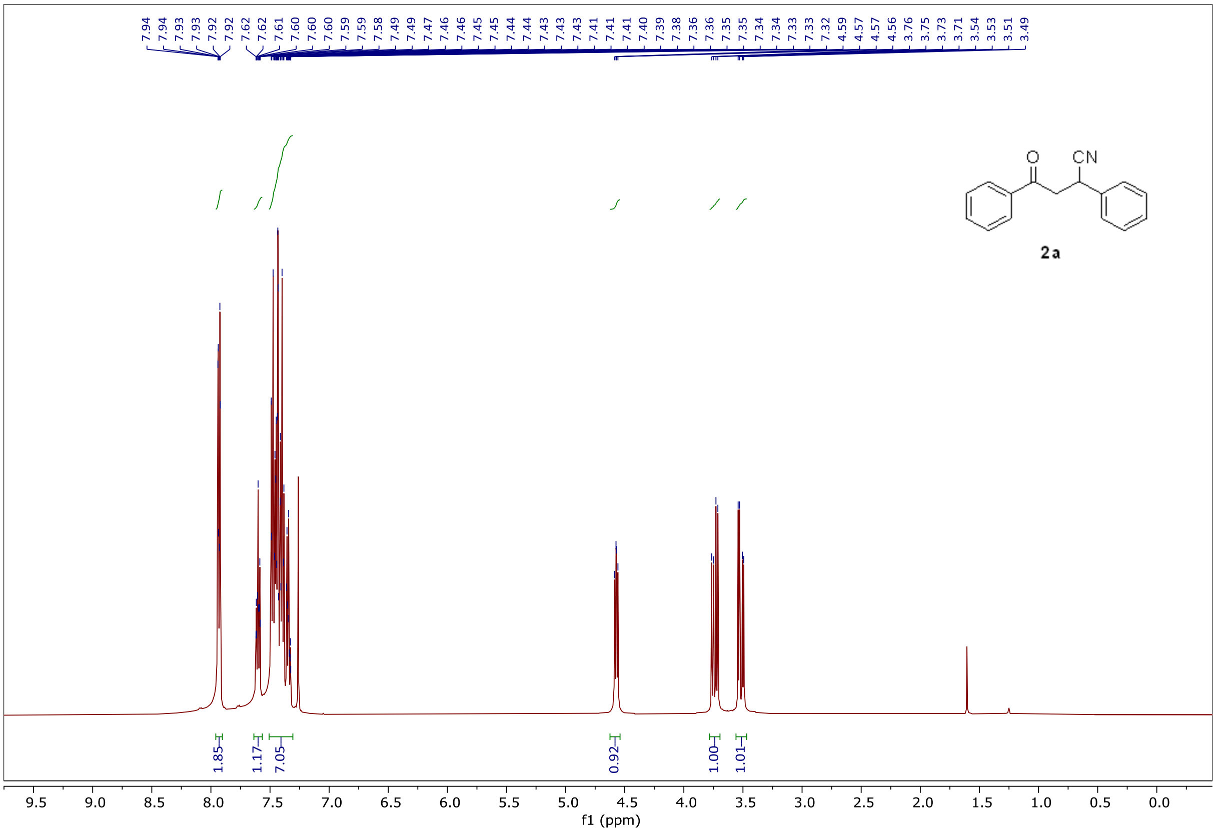
0

1m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7.58
7.49
7.49
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.43
7.41
7.41
7.41
7.40
7.39
7.38
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
4.59
4.57
4.57
4.56
3.76
3.75
3.73
3.71
3.54
3.53
3.51
3.49
O
CN
2a
1.85
1.17
7.05
0.92
1.00
1.01
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
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1.0
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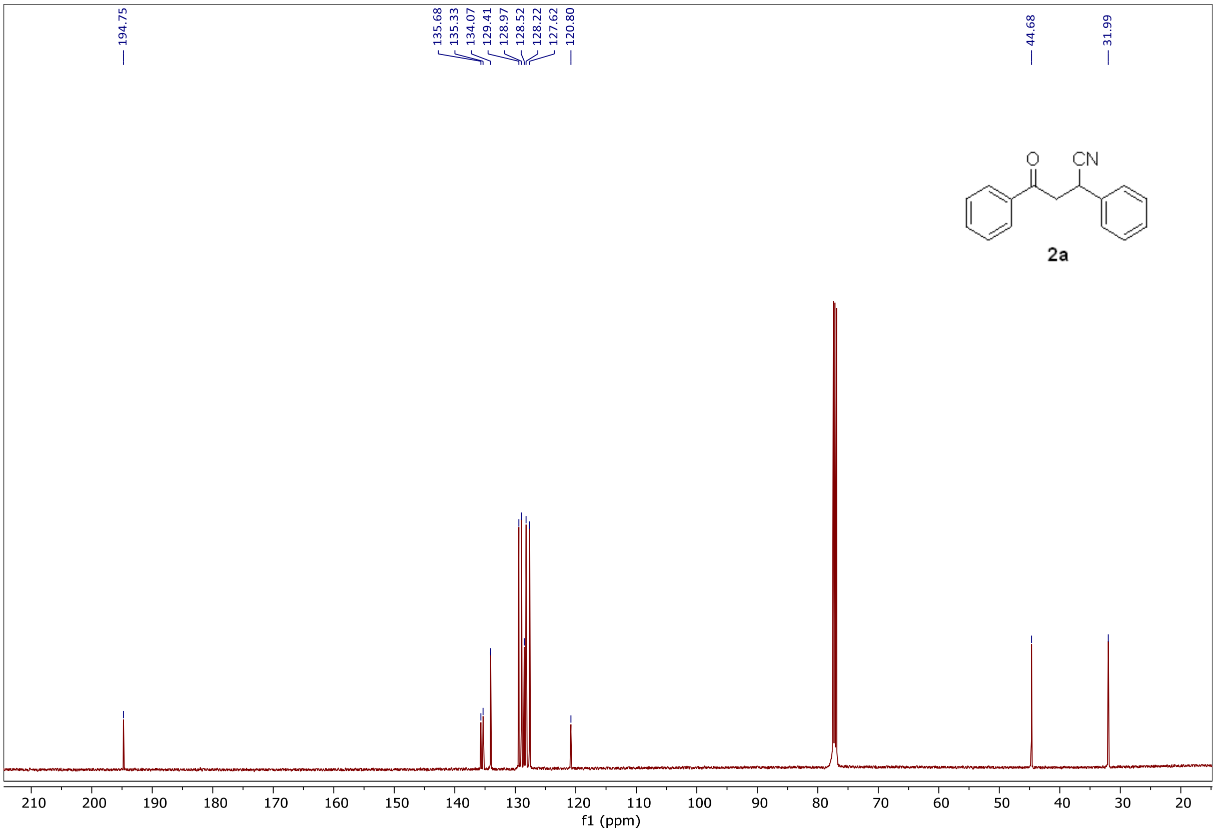
0.0
f1 (ppm)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135.68
135.33
134.07
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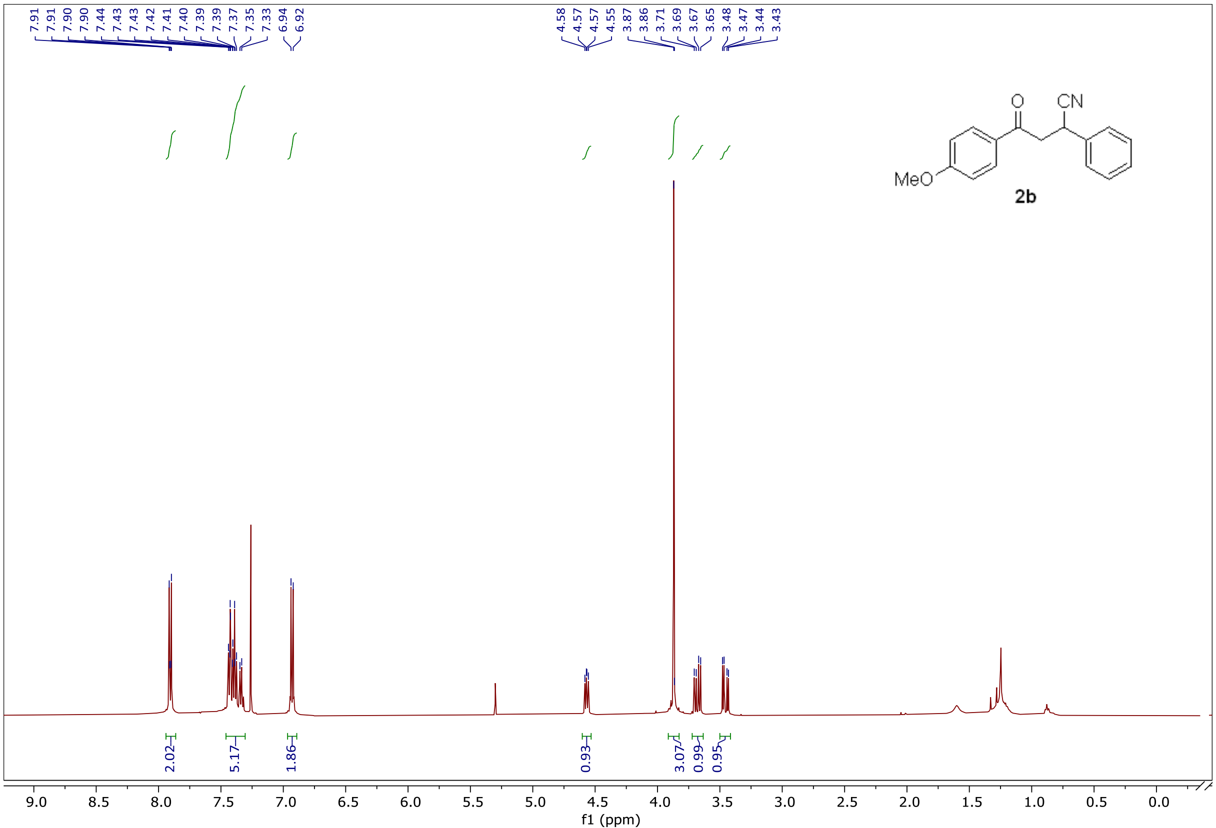
128.97
128.52
128.22
127.62
120.80
44.68
31.99
O
CN
2a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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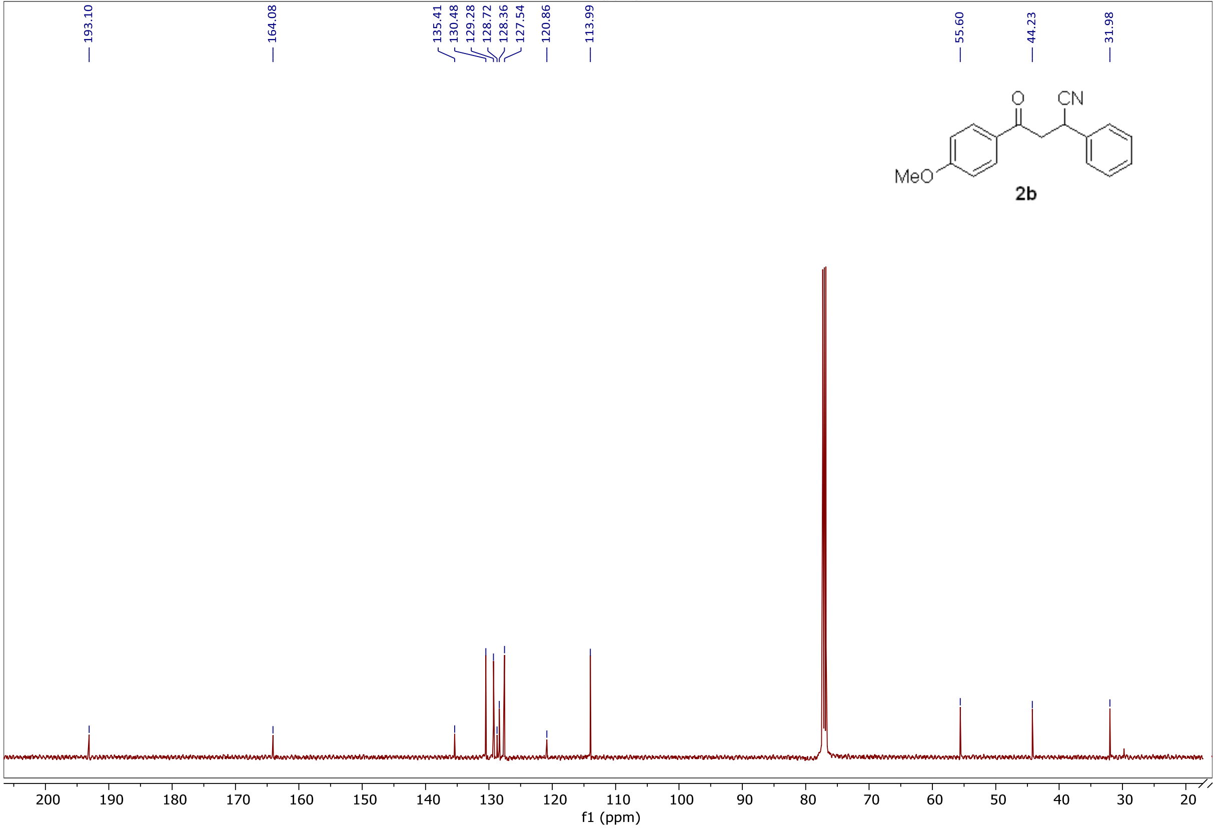
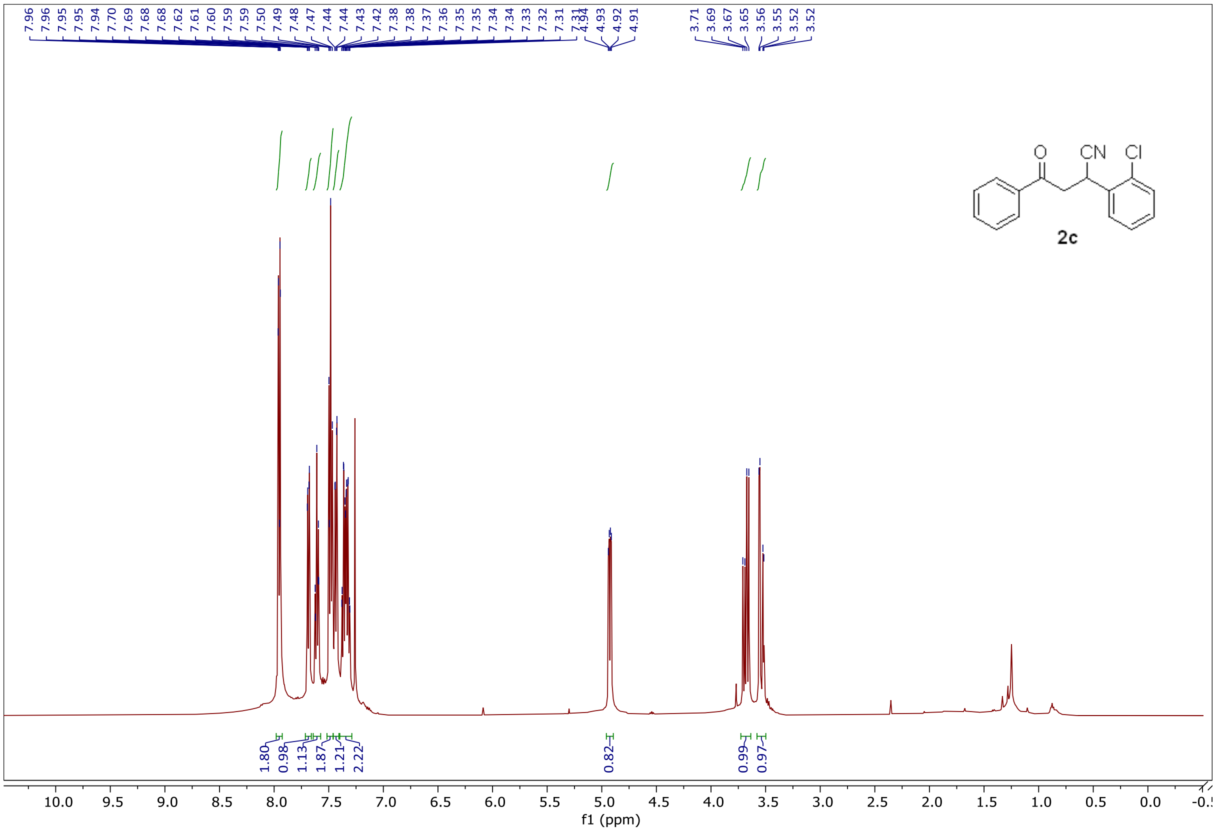
7.39
7.39
7.37
7.35
7.33
6.94
6.92
4.58
4.57
4.57
4.55
3.87
3.86
3.71
3.69
3.67
3.65
3.48
3.47
3.44
3.43
O
CN
MeO
2b
2.02
5.17
1.86
0.93
3.07
0.99
0.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


193.10
164.08
135.41
130.48
129.28
128.72
128.36
127.54
120.86
113.99
55.60
44.23
31.98
O
CN
MeO
2b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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7.62
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7.60
7.59
7.50
7.49
7.48
7.47
7.44
7.44
7.43
7.42
7.38
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.31
4.94
4.93
4.92
4.91
3.71
3.69
3.67
3.65
3.56
3.55
3.52
3.52
O
CN
Cl
2c
1.80
0.98
1.13
1.87
1.21
2.22
0.82
0.99
0.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
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1.0
0.5
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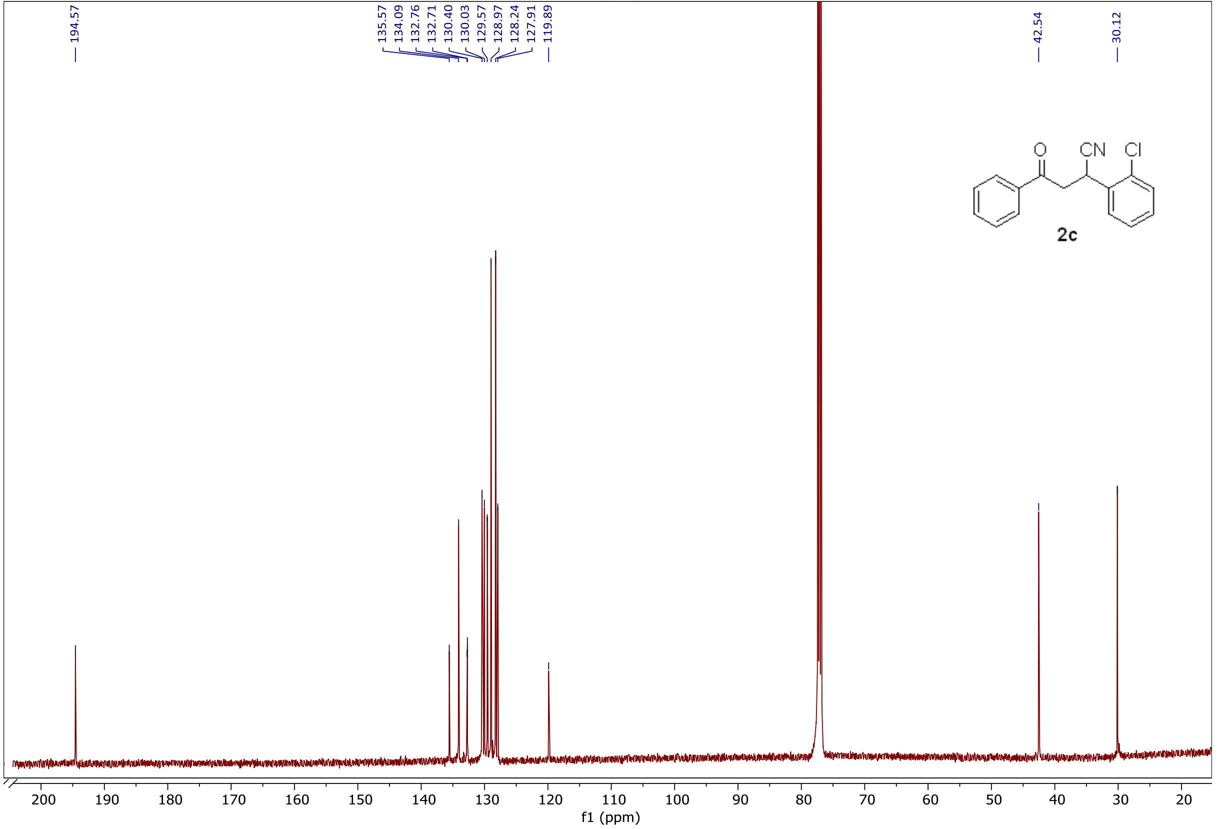
-0.
f1 (ppm)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130.03
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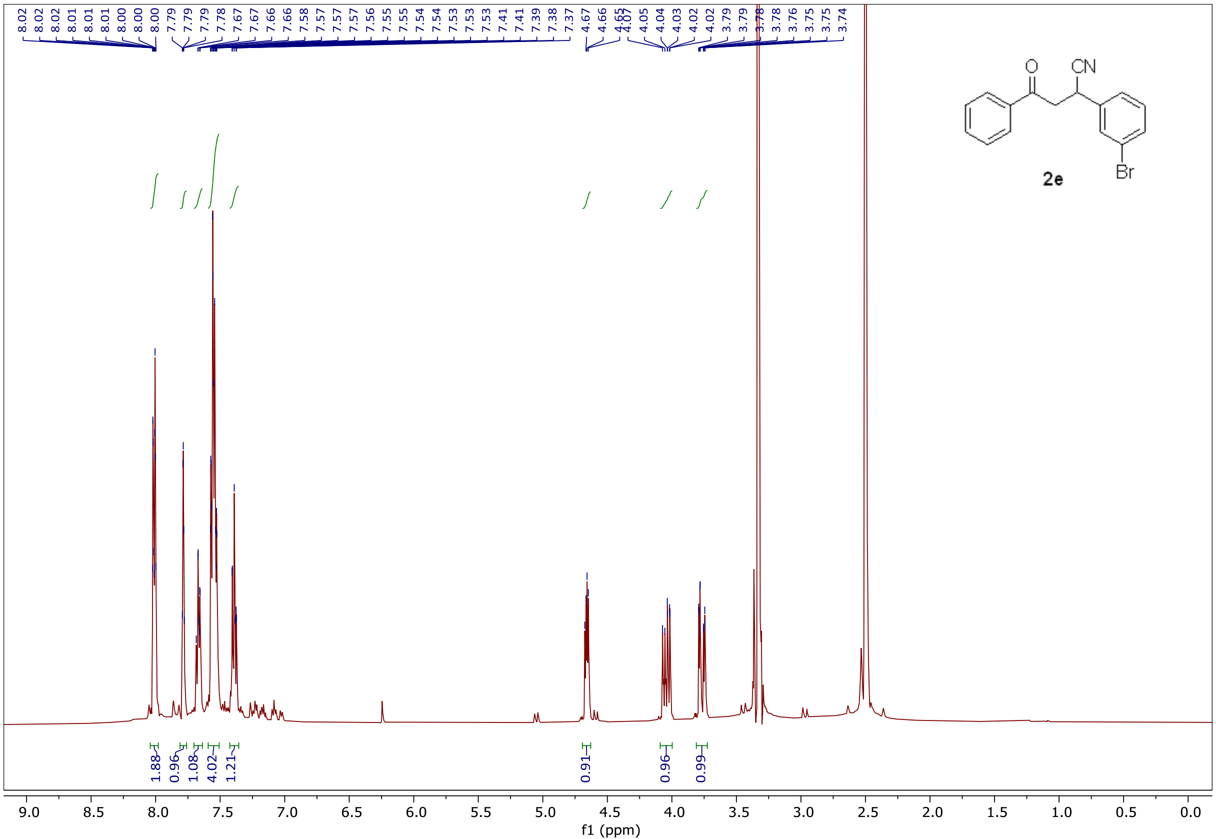
127.91
119.89
42.54
30.12
O
CN
Cl
2c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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8.00
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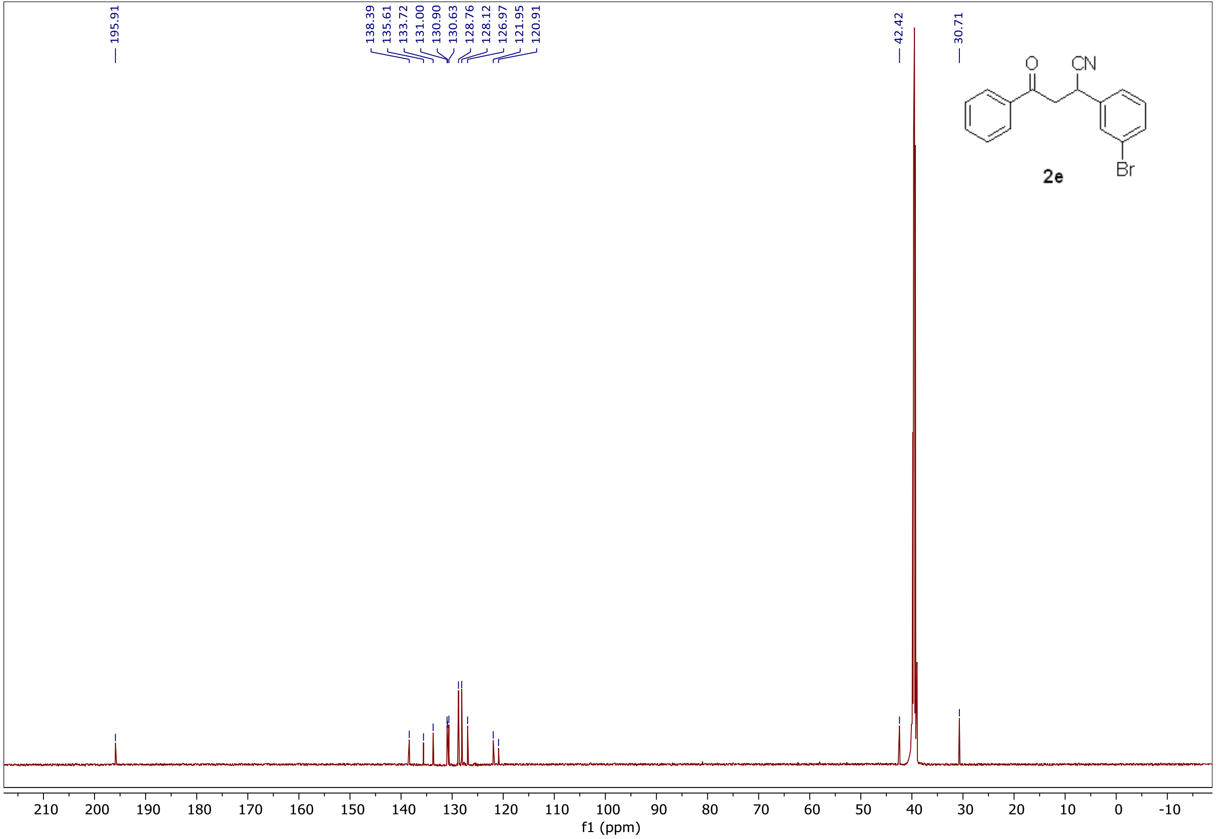
7.79
7.78
7.67
7.67
7.66
7.66
7.58
7.57
7.57
7.57
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.41
7.41
7.39
7.38
7.37
4.67
4.66
4.65
4.07
4.05
4.04
4.03
4.02
4.02
3.79
3.79
3.78
3.78
3.76
3.75
3.75
3.74
O
CN
Br
1.88
0.96
1.08
4.02
1.21
0.91
0.96
0.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2e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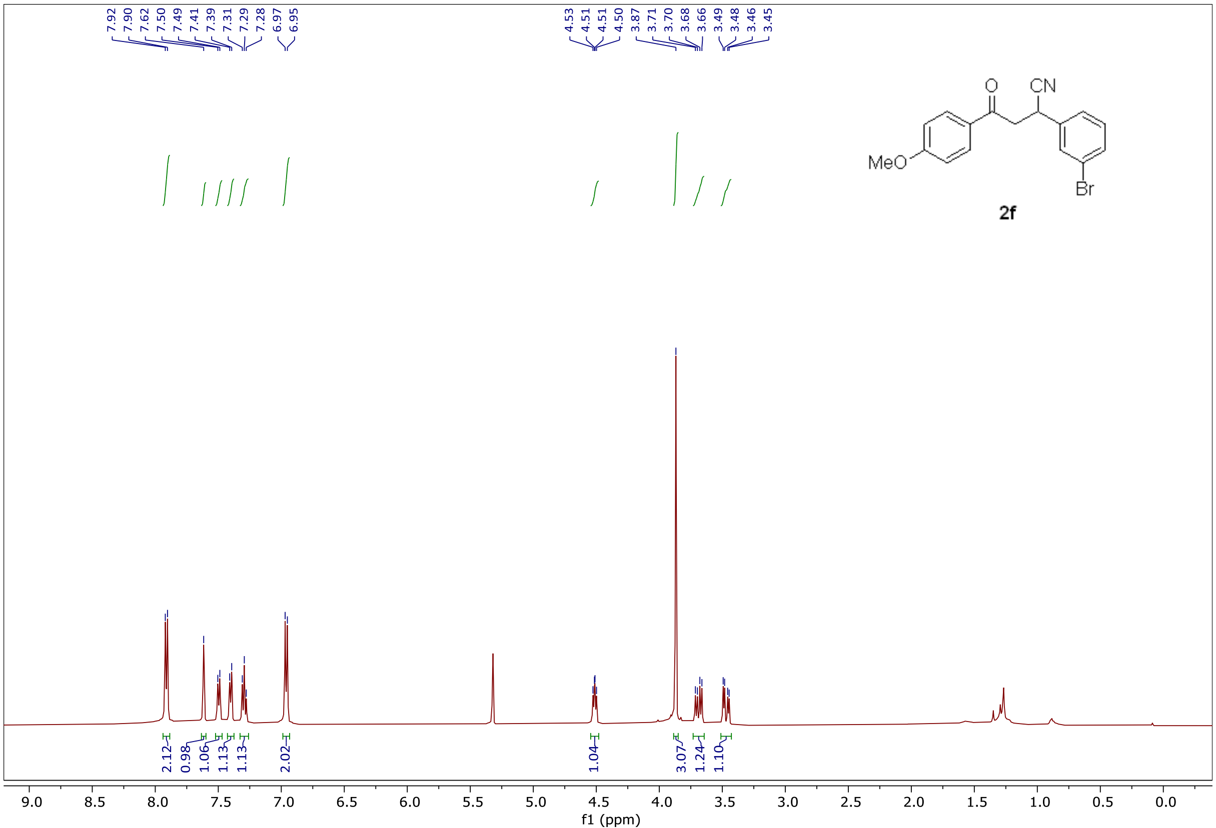
130.90
130.63
128.76
128.12
126.97
121.95
120.91
42.42
30.71
O
CN
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2e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7.28
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6.95
4.53
4.51
4.51
4.50
3.87
3.71
3.70
3.68
3.66
3.49
3.48
3.46
3.45
O
CN
MeO
Br
2f
2.12
0.98
1.06
1.13
1.13
2.02
1.04
3.07
1.24
1.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
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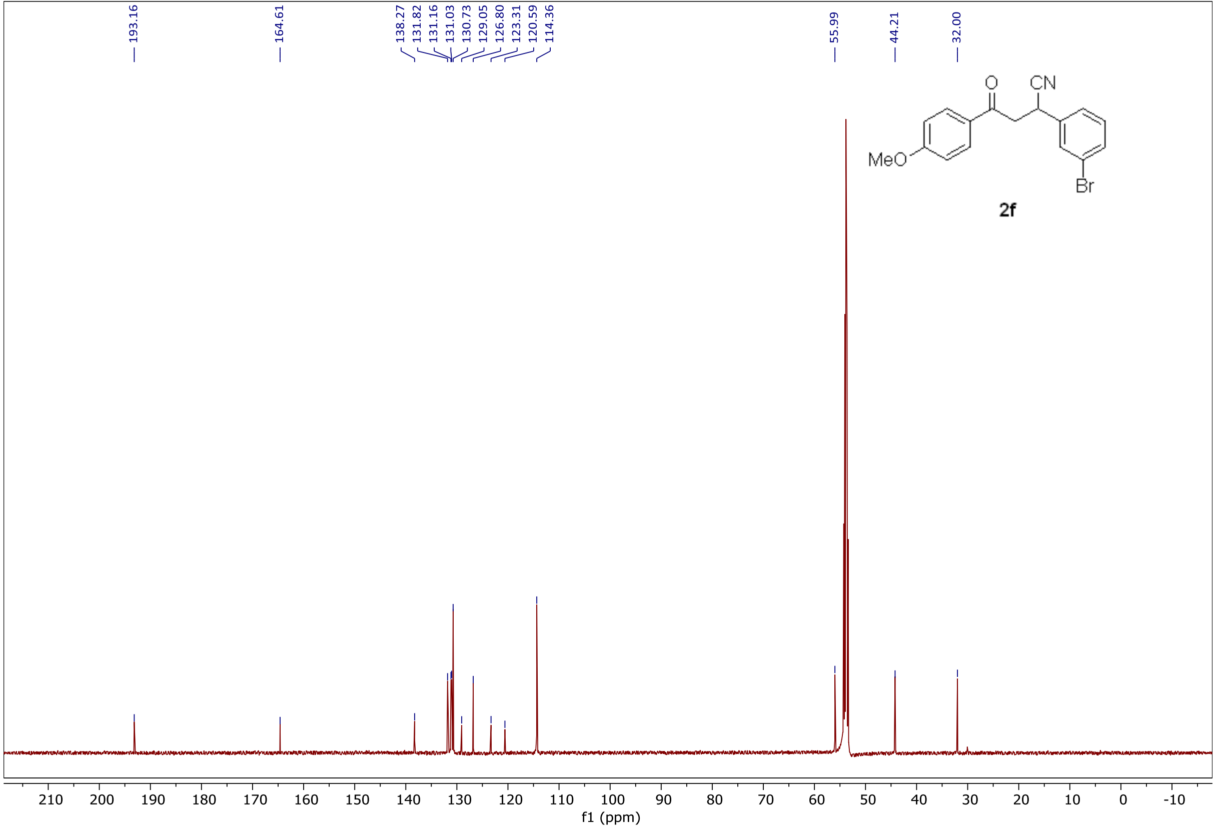
1.0
0.5
0.0
f1 (ppm)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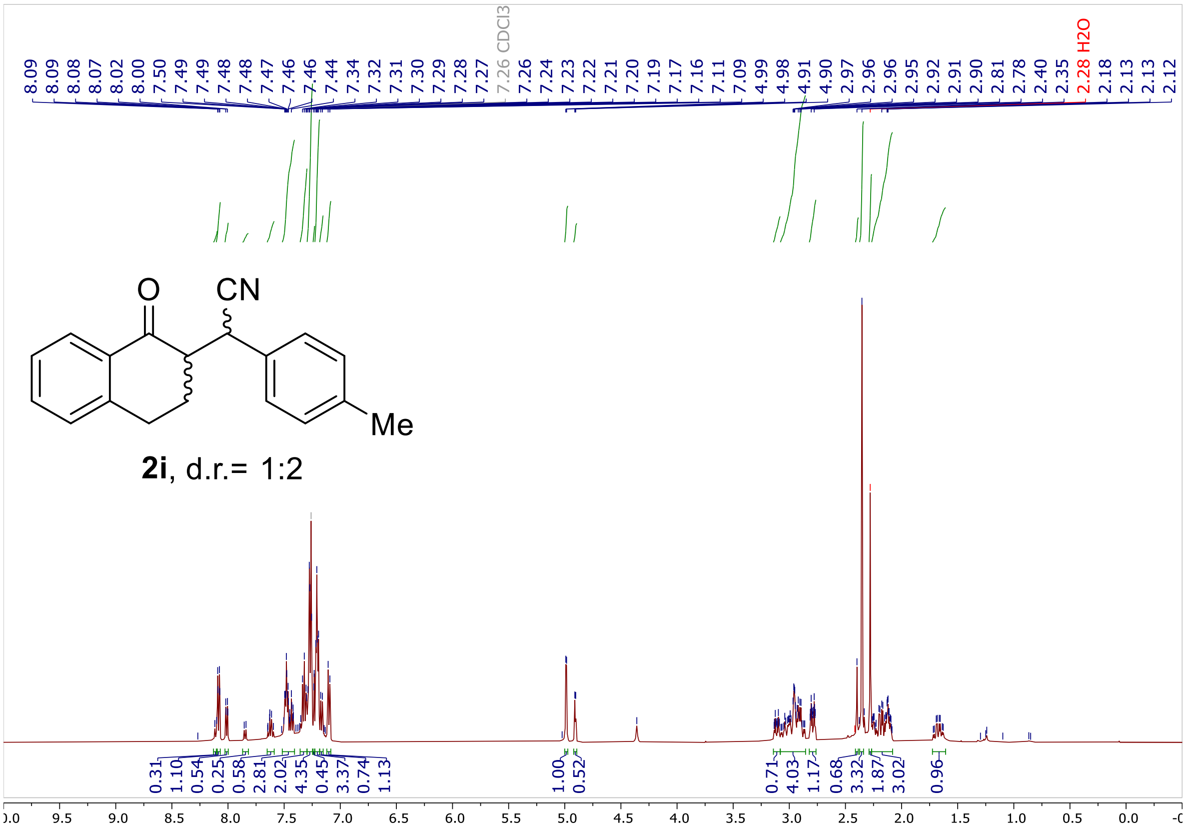
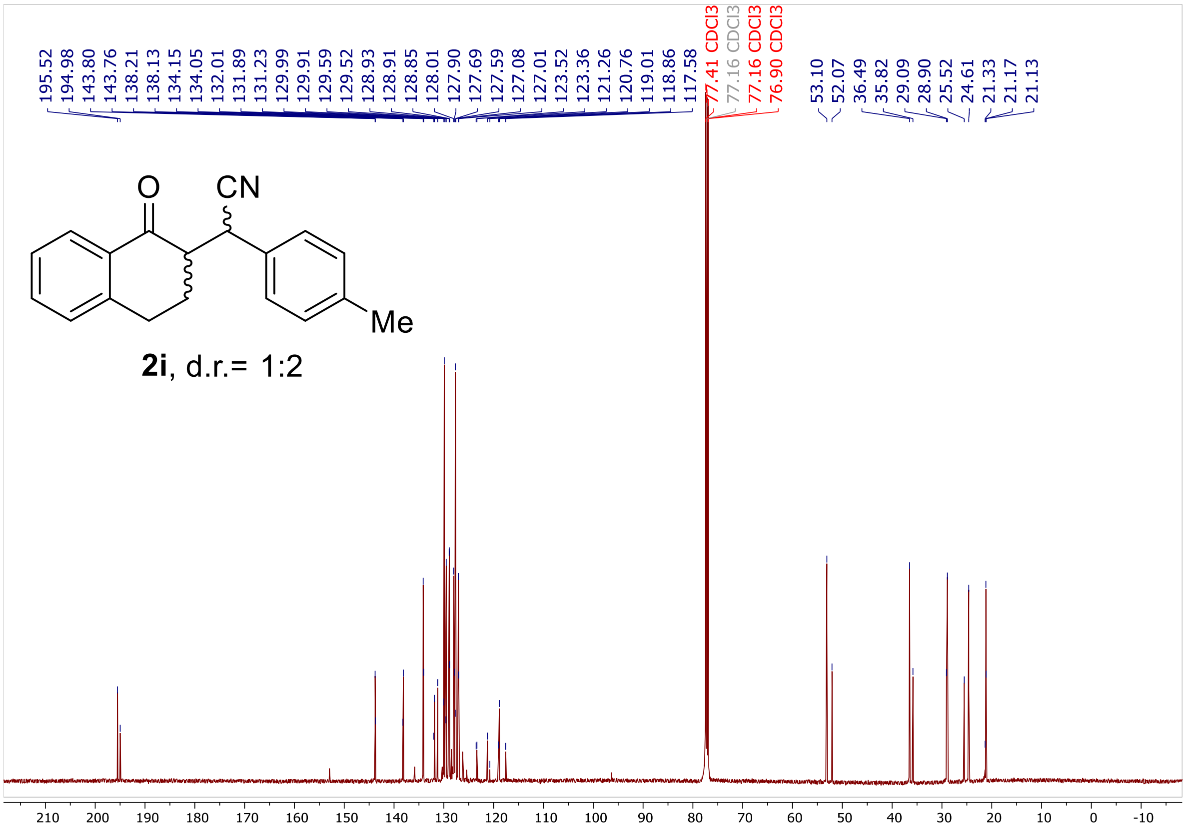
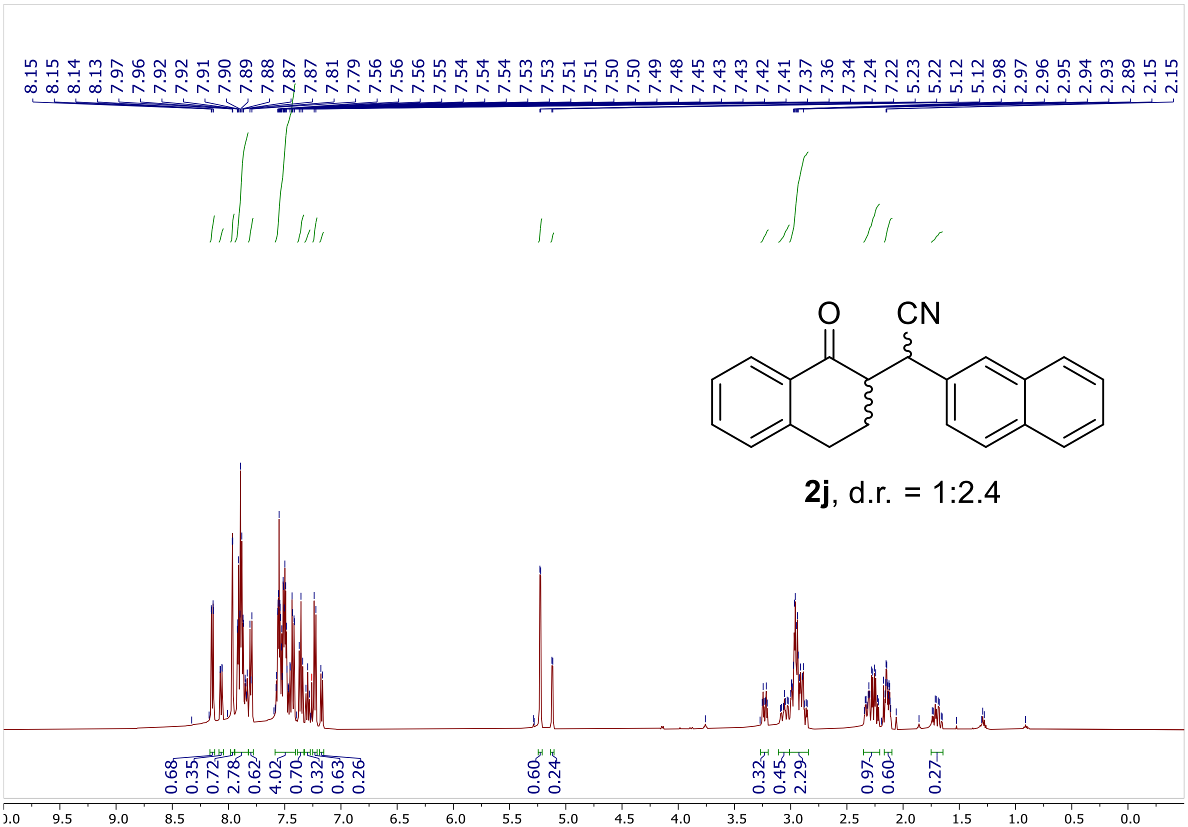
129.05
126.80
123.31
120.59
114.36
55.99
44.21
32.00
O
CN
MeO
Br
2f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2i, d.r.= 1:2



2i, d.r.= 1:2



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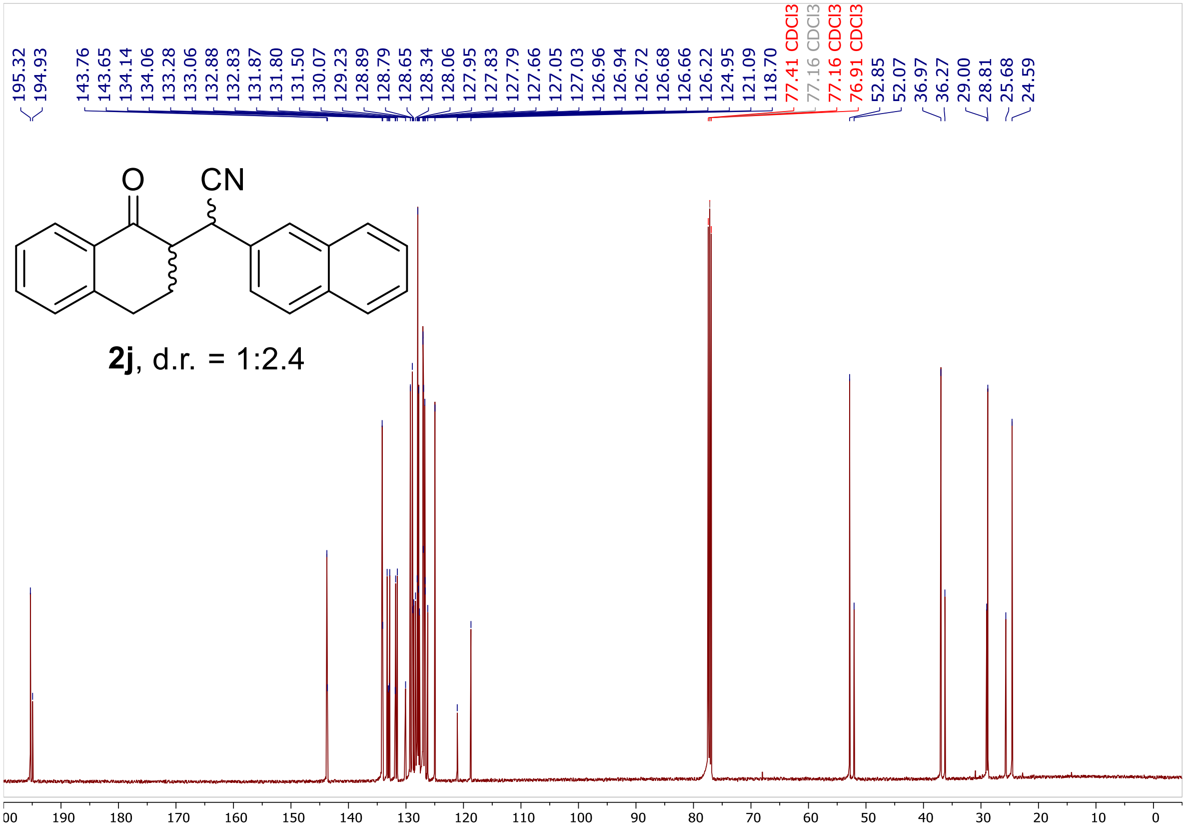

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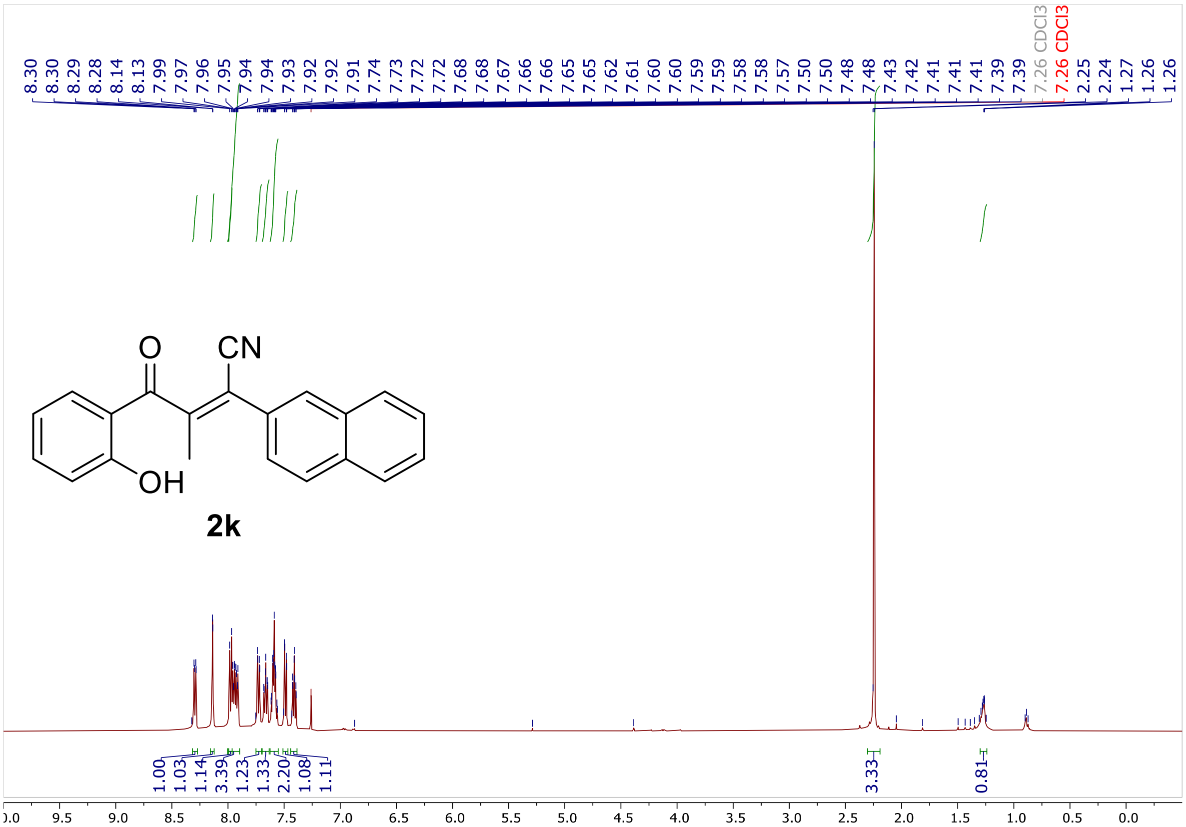
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7.93
7.92
7.92
7.91
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7.67
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7.60
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7.58
7.58
7.57
7.50
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7.48
7.43
7.42
7.41
7.41
7.41
7.39
7.26 CDCl3
7.26 CDCl3
2.25
2.24
1.27
1.26
1.26
O
CN
OH
2k
1.00
1.03
1.14
3.39
1.23
1.33
2.20
1.08
1.11
3.33
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7.0
6.5
6.0
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2.0
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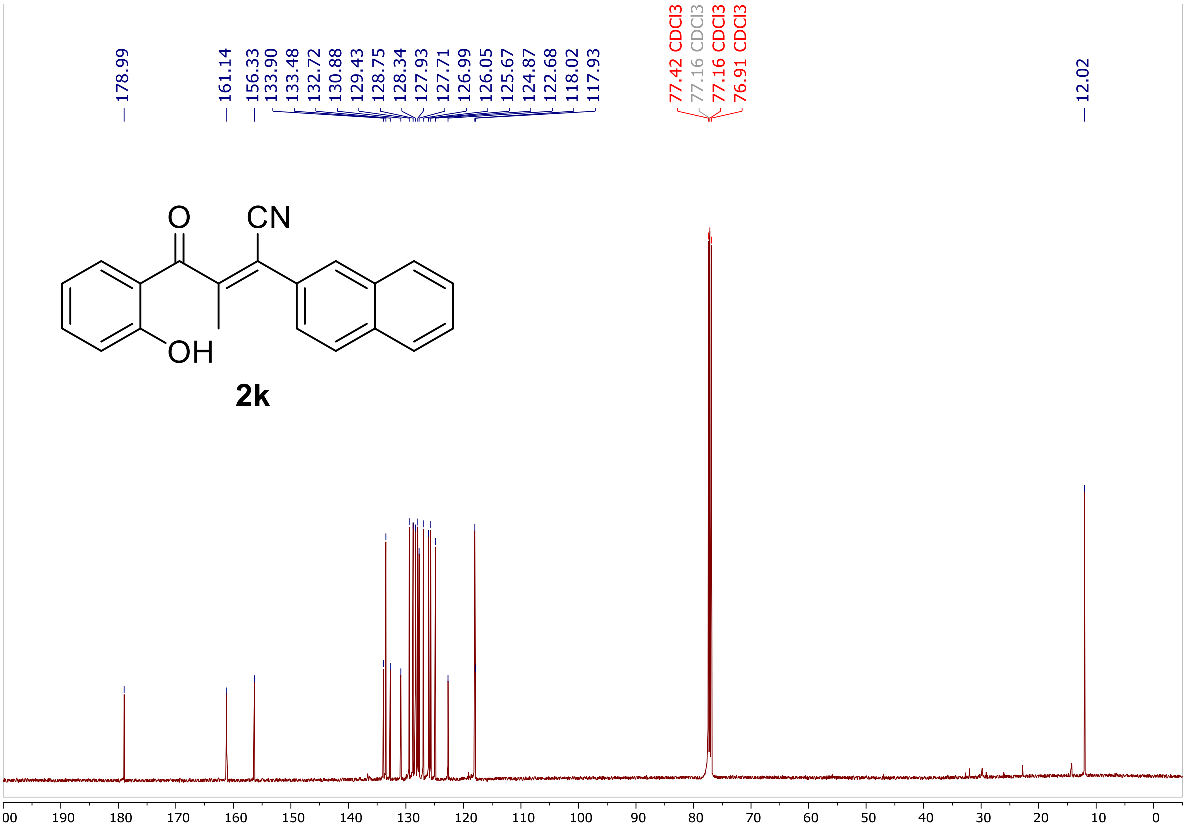
1.0
0.5
0.0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128.34
127.93
127.71
126.99
126.05
125.67
124.87
122.68
118.02
117.93
77.42 CDCl3
77.16 CDCl3
77.16 CDCl3
76.91 CDCl3
12.02
O
CN
OH
2k
190
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150
140
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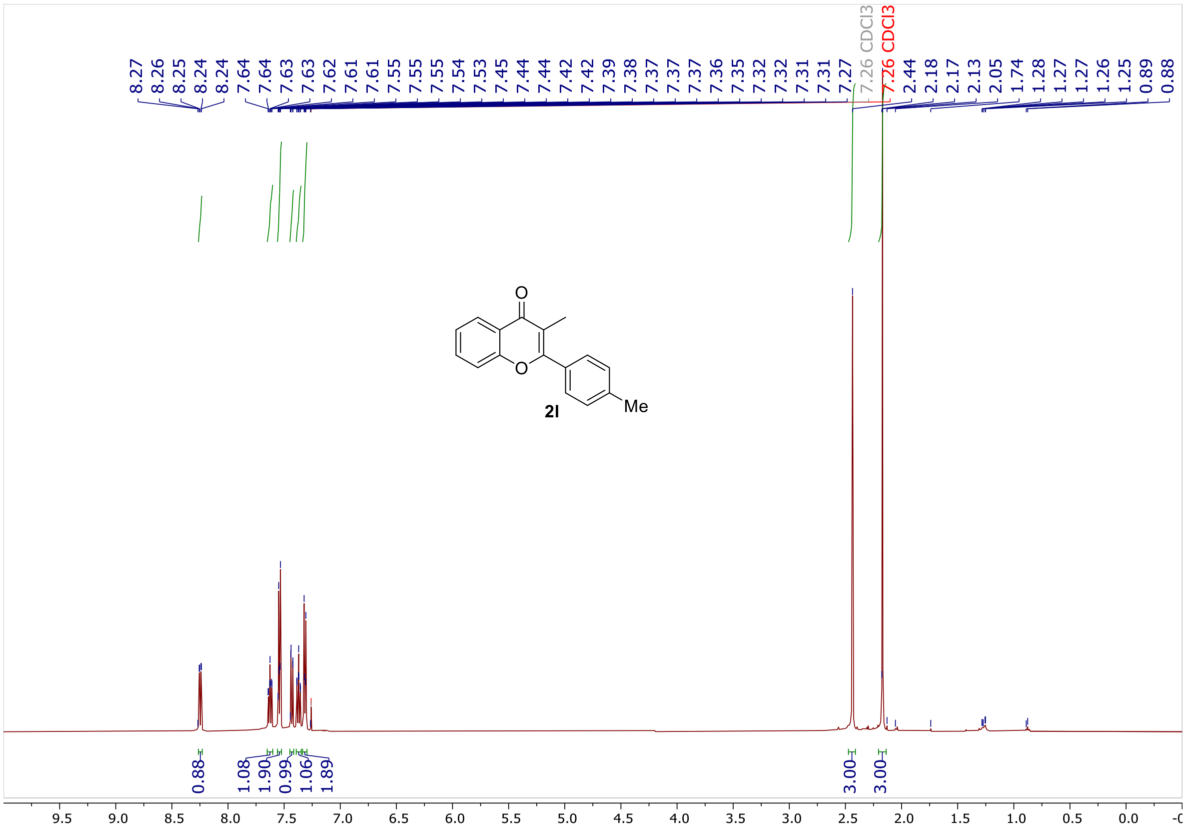
20
10
0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7.62
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7.55
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7.55
7.54
7.53
7.45
7.44
7.44
7.42
7.42
7.39
7.38
7.37
7.37
7.37
7.36
7.35
7.32
7.32
7.31
7.31
7.27
7.26 CDCl3
7.26 CDCl3
2.44
2.18
2.17
2.13
2.05
1.74
1.28
1.27
1.27
1.26
1.25
0.89
0.88
O
O
Me
2l
0.88
1.08
1.90
0.99
1.06
1.89
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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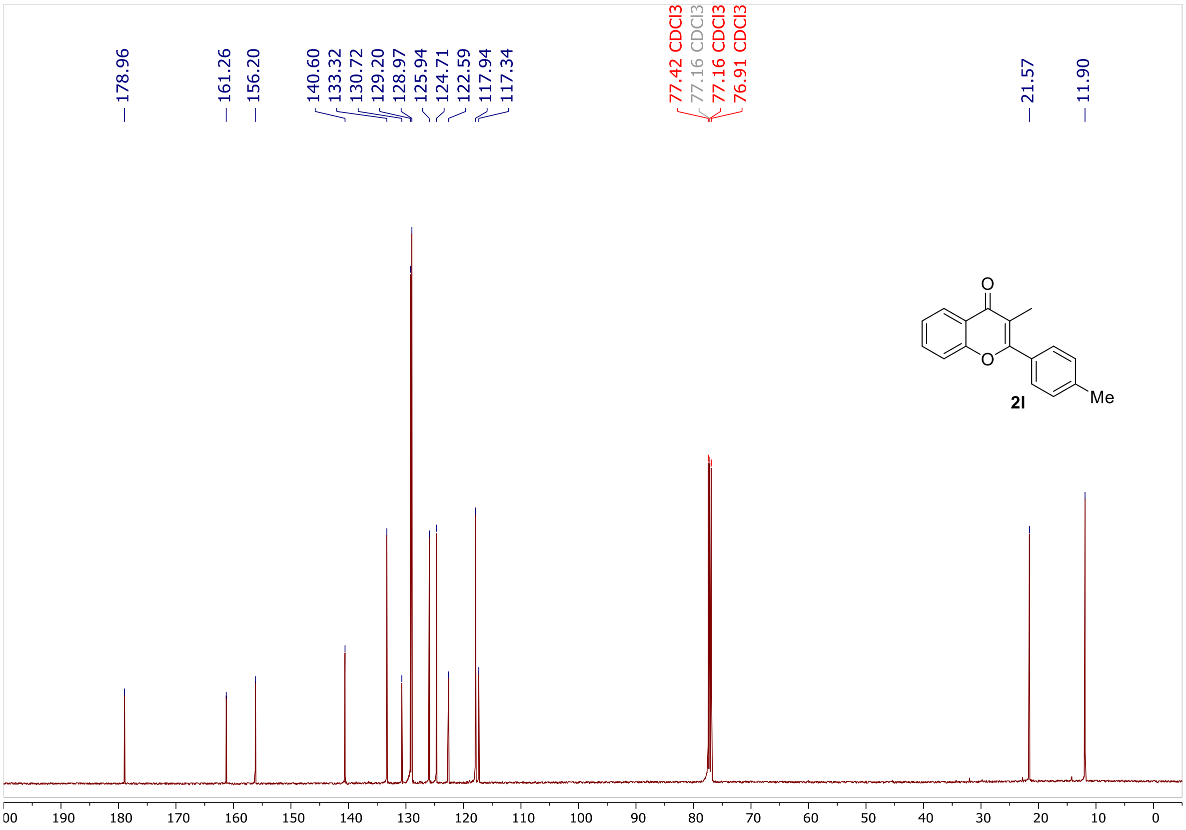
0.0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129.20
128.97
125.94
124.71
122.59
117.94
117.34
77.42 CDCl3
77.16 CDCl3
77.16 CDCl3
76.91 CDCl3
21.57
11.90
O
O
Me
2l
190
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150
140
130
120
110
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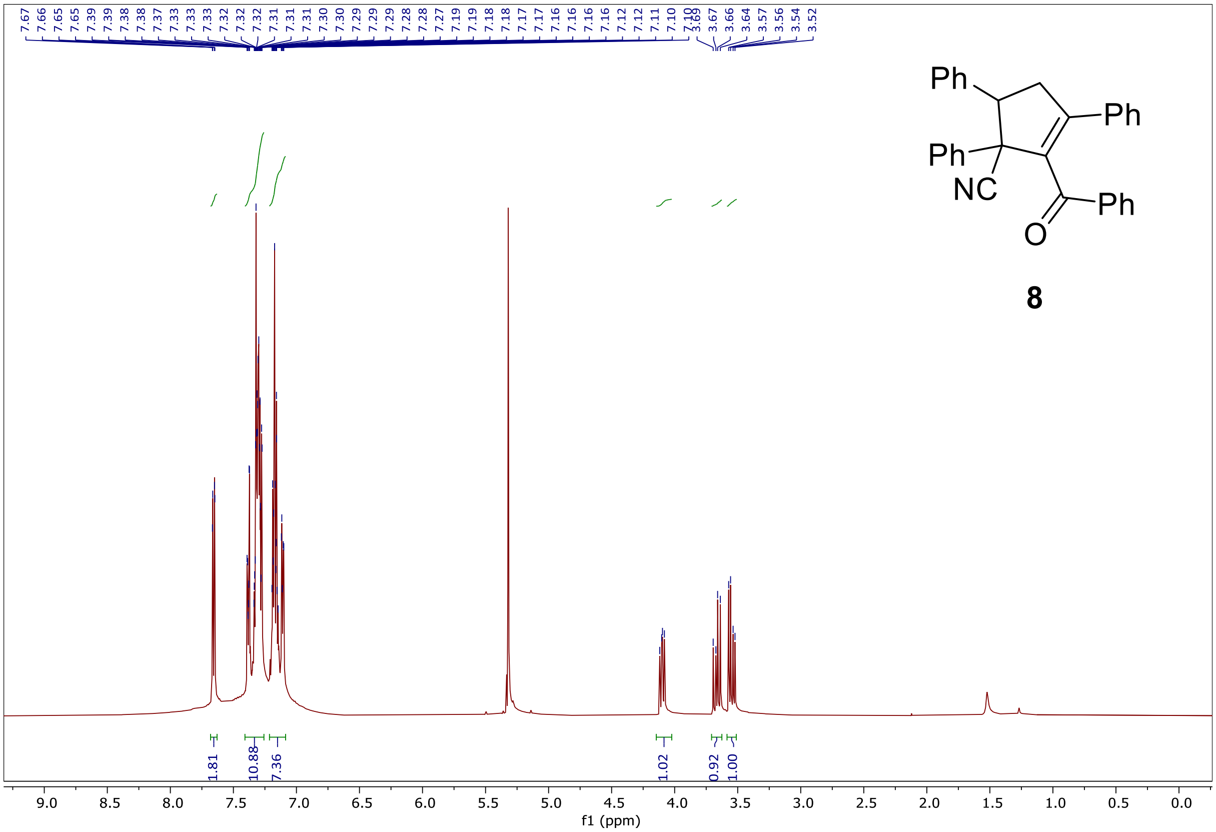
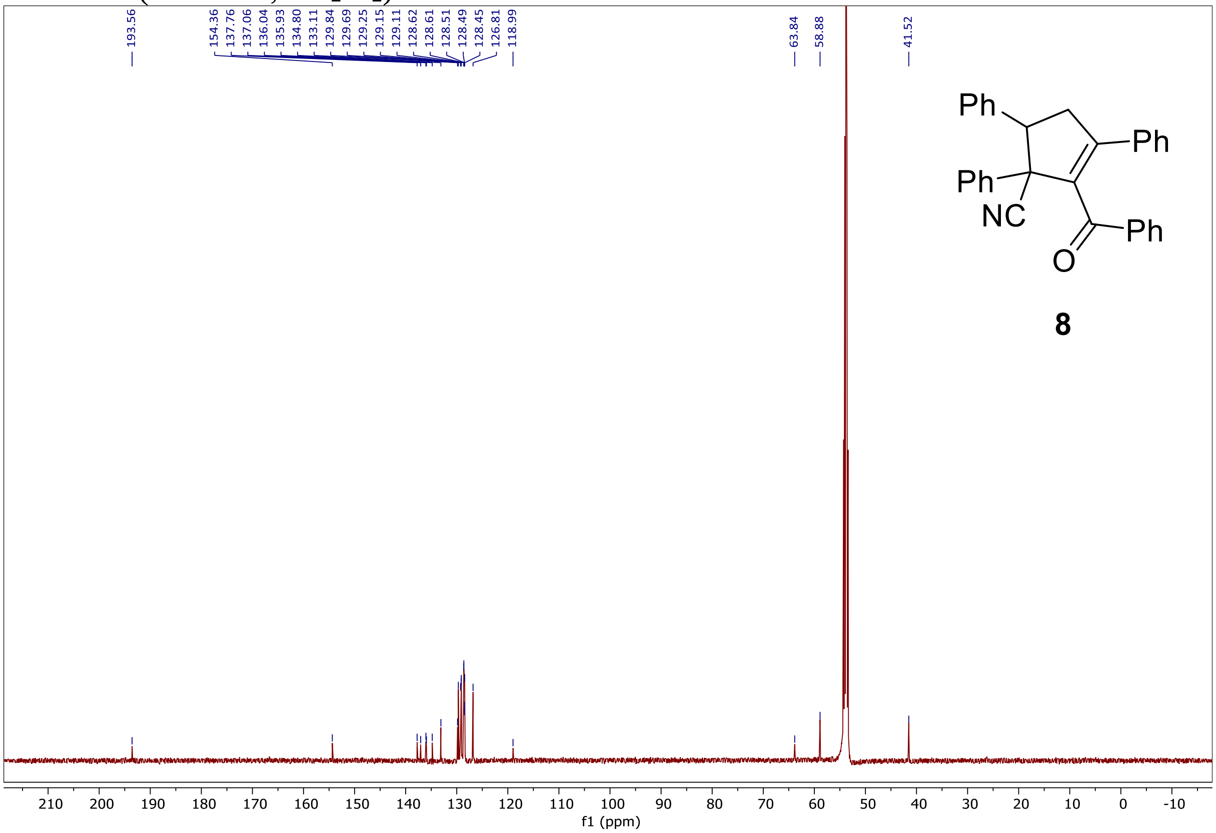
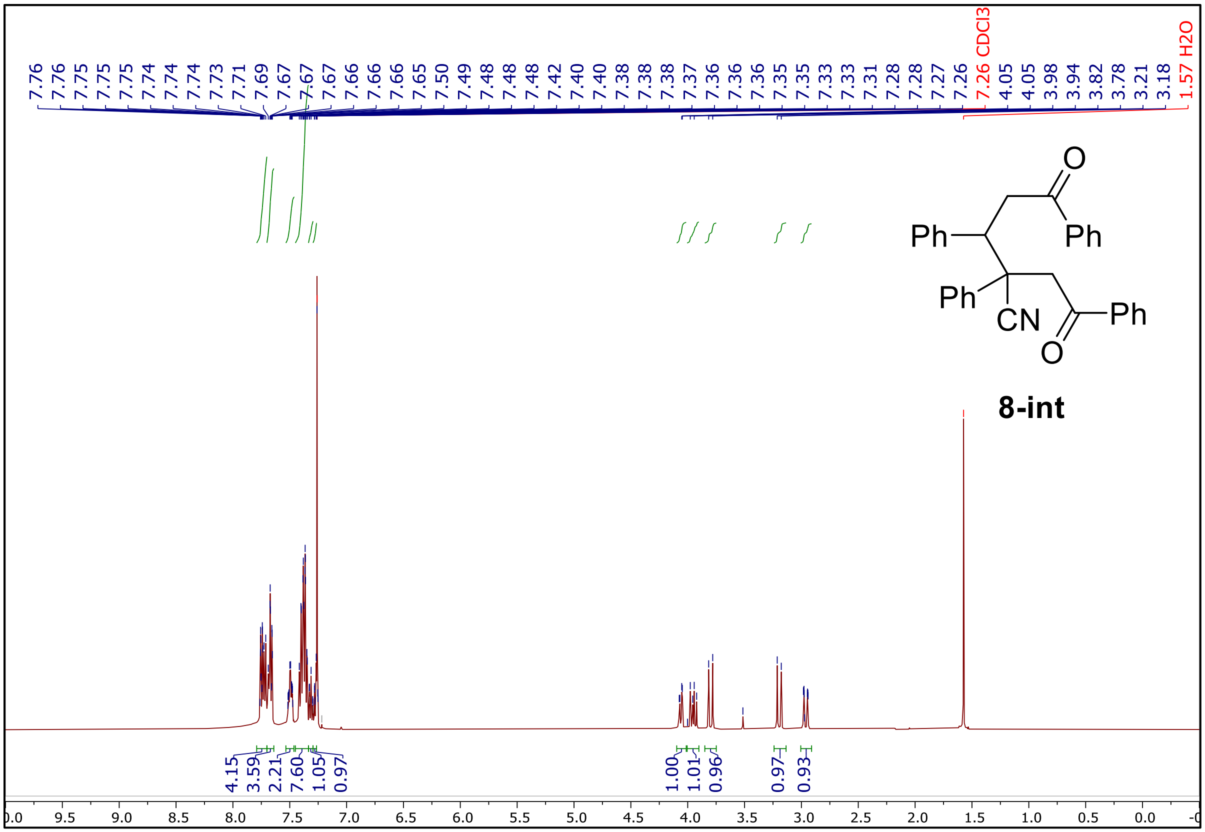
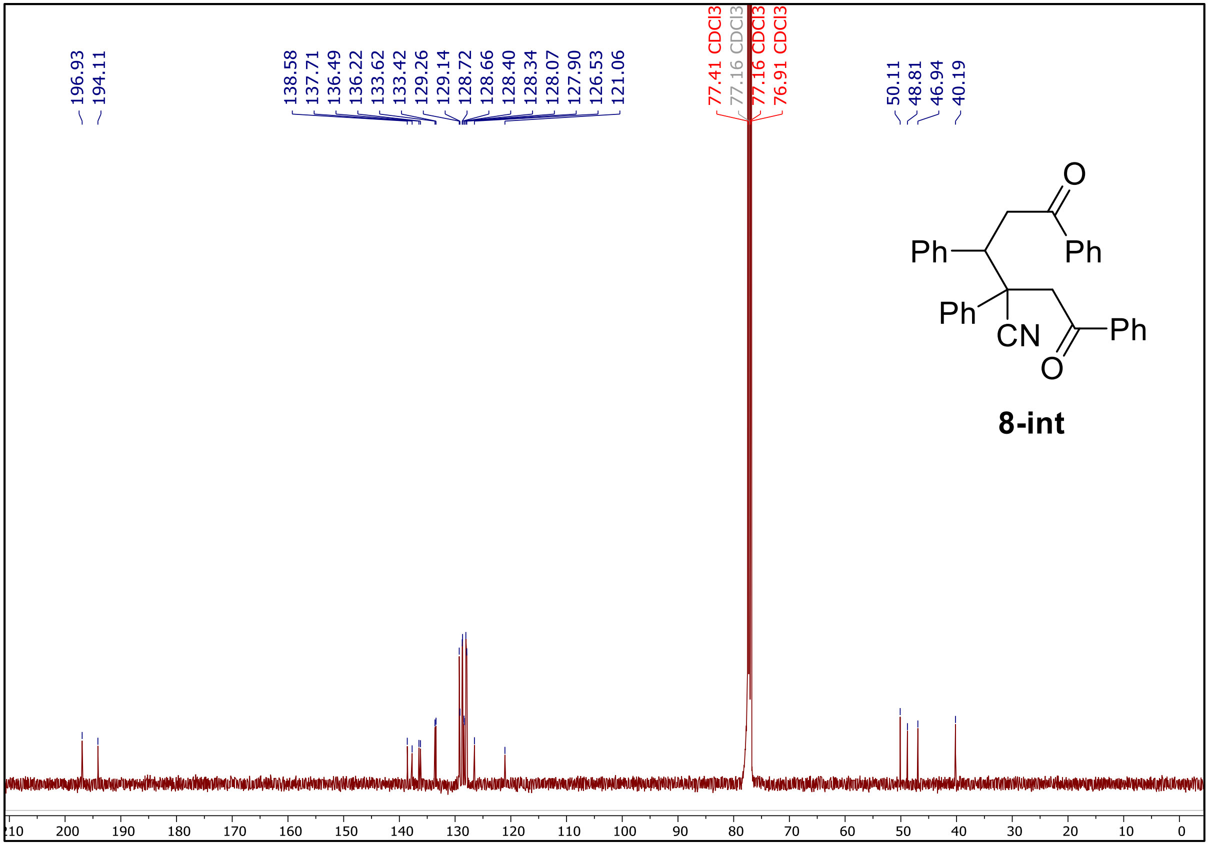
30
20
10
0

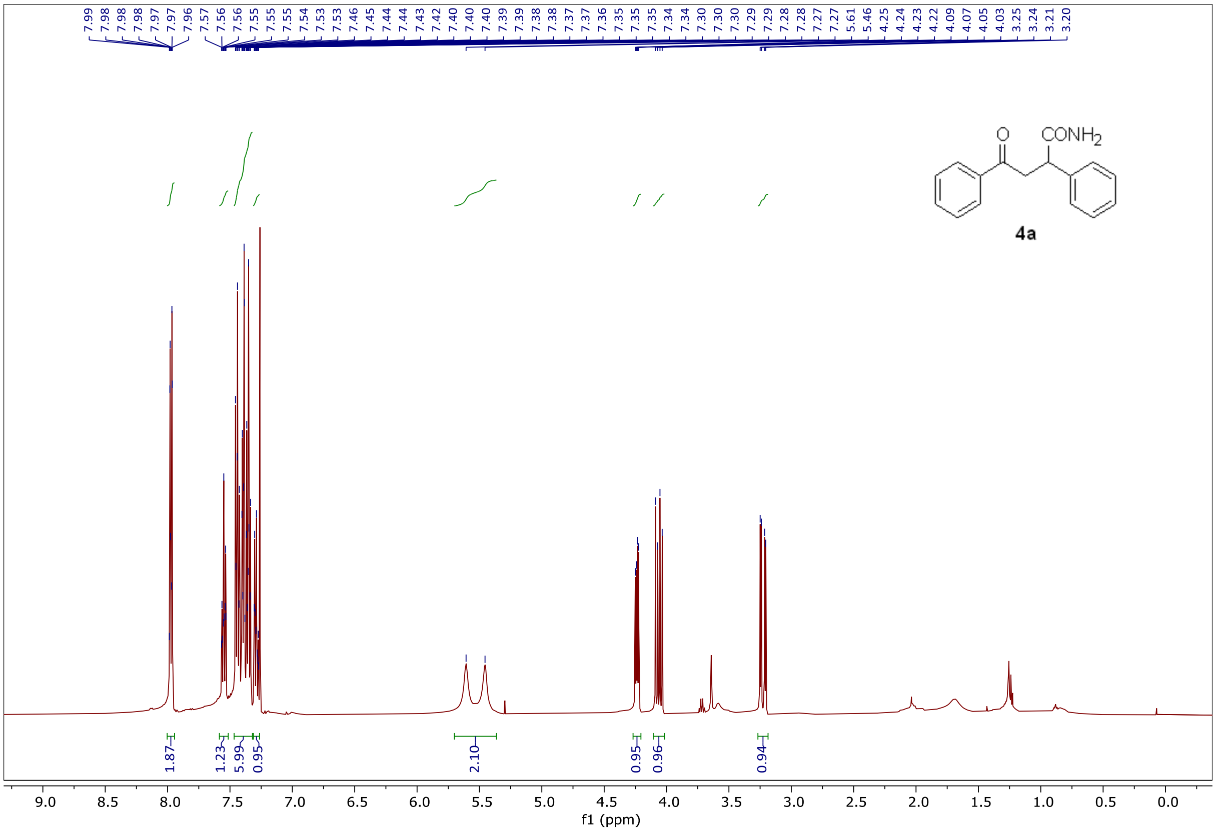


^{13}C-NMR (126 MHz, CD_2Cl_2) – **3a**




7.76 7.76 7.75 7.75 7.75 7.74 7.74 7.74 7.73 7.71 7.69 7.67 7.67 7.67 7.66 7.66 7.65 7.50 7.49 7.48 7.48 7.48 7.42 7.40 7.40 7.38 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.35 7.33 7.33 7.31 7.28 7.28 7.27 7.26
7.26 CDCl3
4.05 4.05 3.98 3.94 3.82 3.78 3.21 3.18
1.57 H2O
4.15 3.59 2.21 7.60 1.05 0.97
1.00 1.01 0.96
0.97 0.93
O
Ph
Ph
Ph
CN
Ph
O
8-int
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


196.93 194.11
138.58 137.71 136.49 136.22 133.62 133.42 129.26 129.14 128.72 128.66 128.40 128.34 128.07 127.90 126.53 121.06
77.41 CDCl3 77.16 CDCl3 77.16 CDCl3 76.91 CDCl3
50.11 48.81 46.94 40.19
O
Ph
Ph
Ph
CN
Ph
O
8-int
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.97
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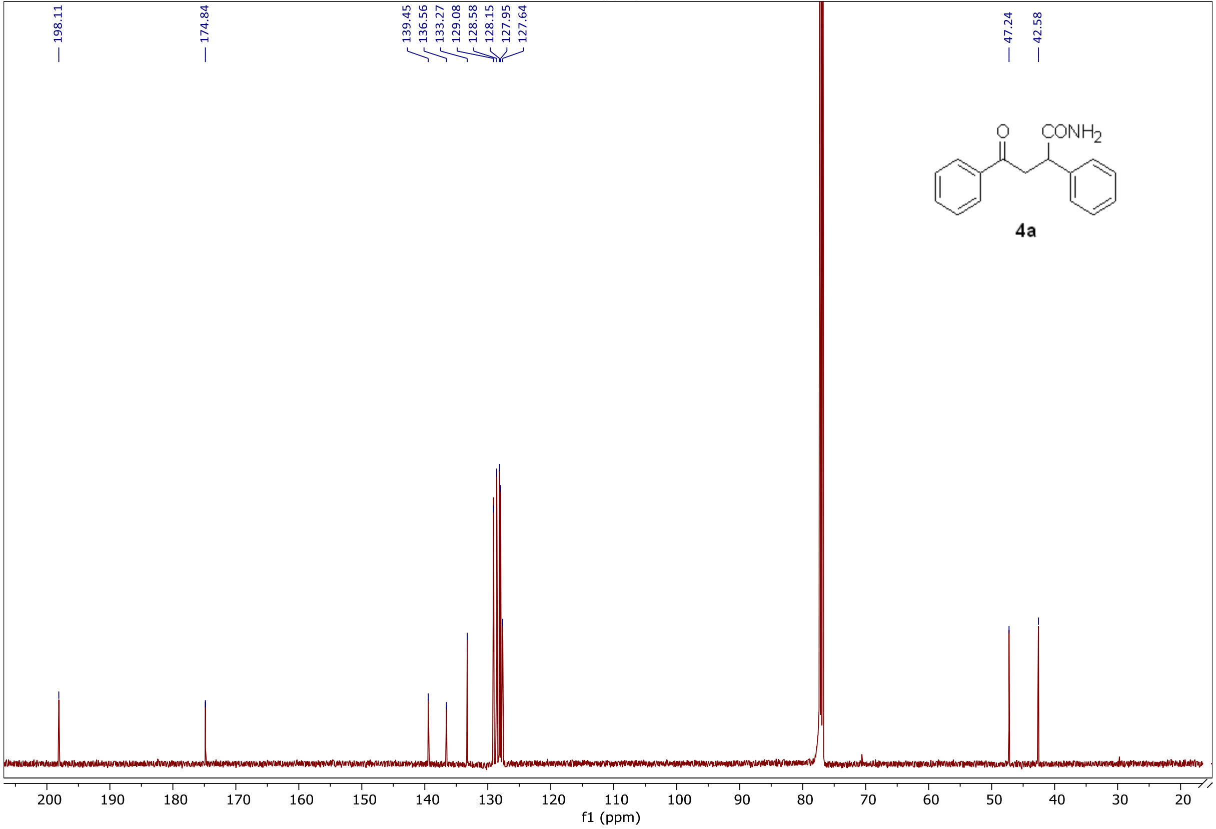
7.56
7.55
7.55
7.54
7.53
7.53
7.46
7.45
7.44
7.43
7.42
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.34
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
5.61
5.46
4.25
4.24
4.23
4.22
4.09
4.07
4.05
4.03
3.25
3.24
3.21
3.20
O
CONH2
4a
1.87
1.23
5.99
0.95
2.10
0.95
0.96
0.94
9.0
8.5
8.0
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)


198.11
174.84
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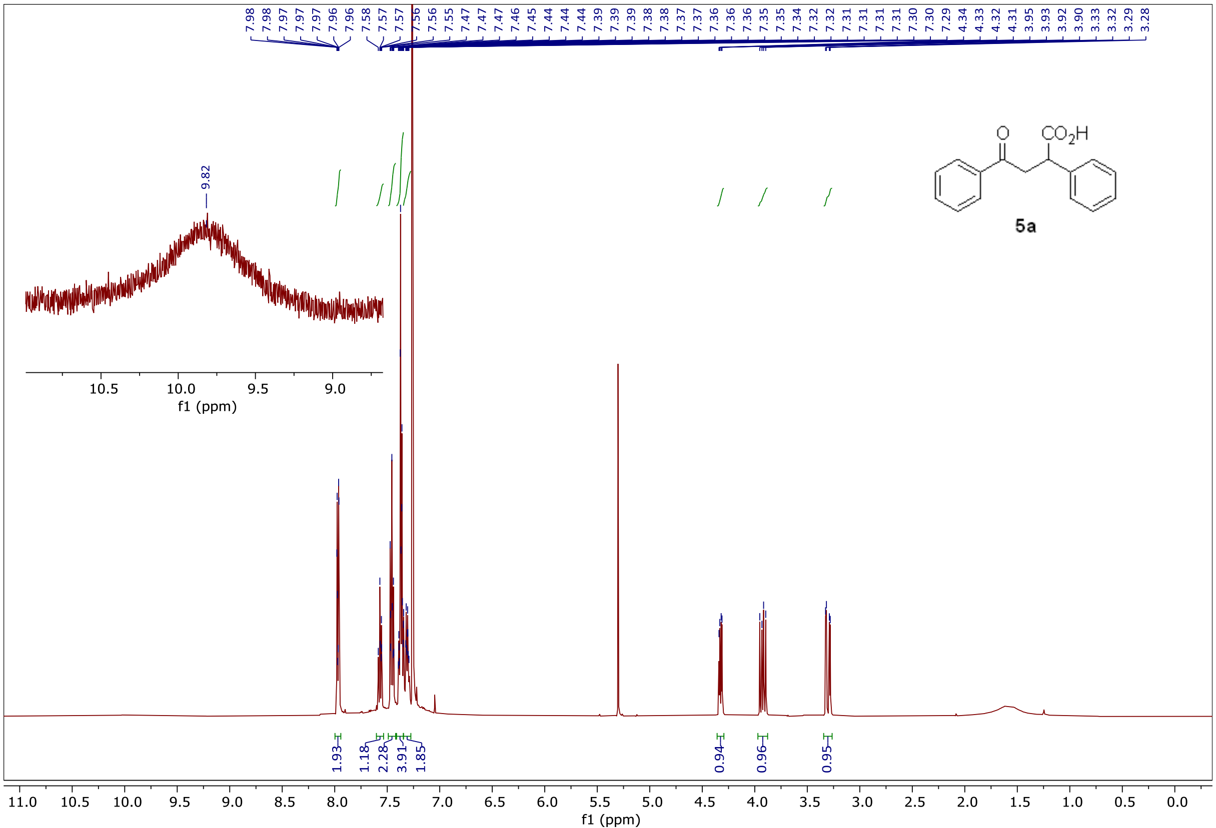
136.56
133.27
129.08
128.58
128.15
127.95
127.64
47.24
42.58
O
CONH2
4a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.98
7.98
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7.96
7.58
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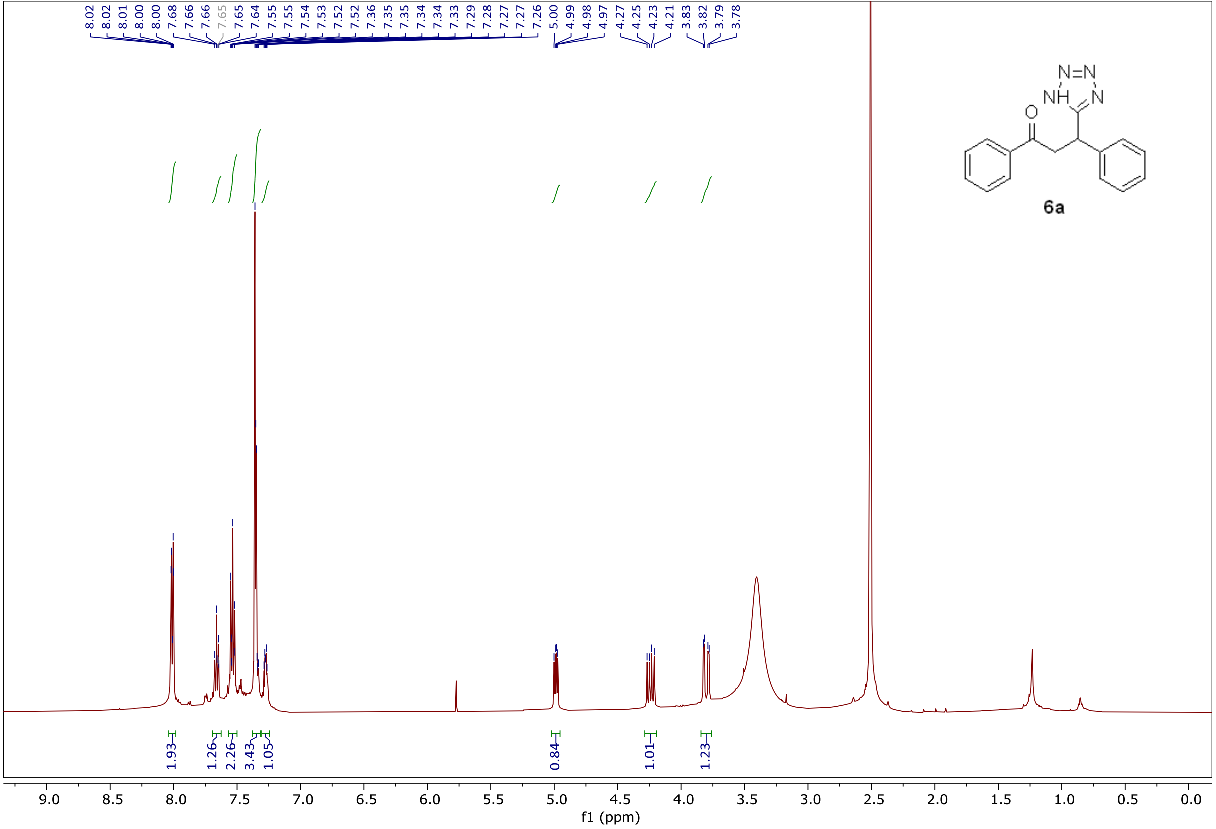
7.47
7.47
7.46
7.45
7.44
7.44
7.39
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.32
7.31
7.31
7.31
7.31
7.30
7.29
4.34
4.33
4.32
4.31
3.95
3.93
3.92
3.90
3.33
3.32
3.29
3.28
O
CO2H
5a
9.82
10.5
10.0
9.5
9.0
f1 (ppm)
1.93
1.18
2.28
3.91
1.85
0.94
0.96
0.95
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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)


8.02
8.02
8.01
8.00
8.00
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7.65
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7.64
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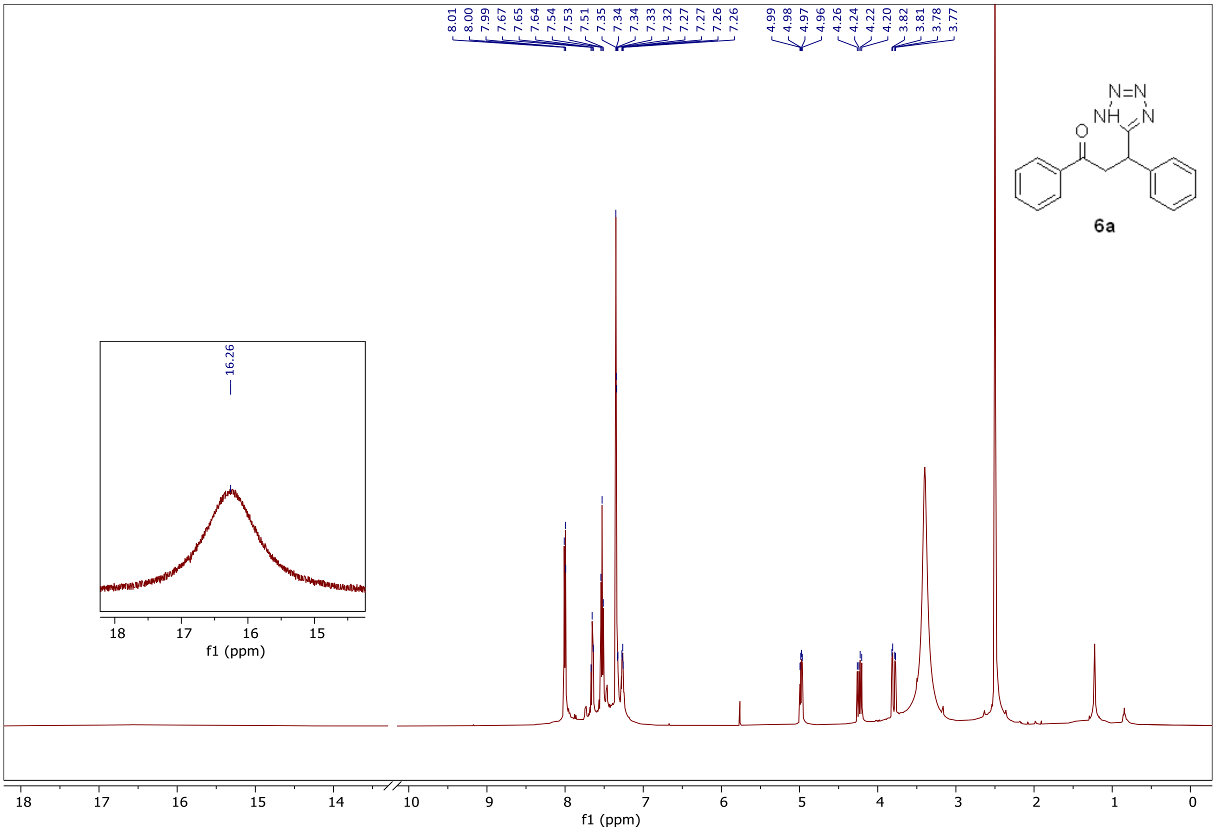
7.54
7.53
7.52
7.52
7.36
7.35
7.35
7.34
7.33
7.29
7.28
7.27
7.27
7.26
5.00
4.99
4.98
4.97
4.27
4.25
4.23
4.21
3.83
3.82
3.79
3.78
N=N
NH
N
O
6a
1.93
1.26
2.26
3.43
1.05
0.84
1.01
1.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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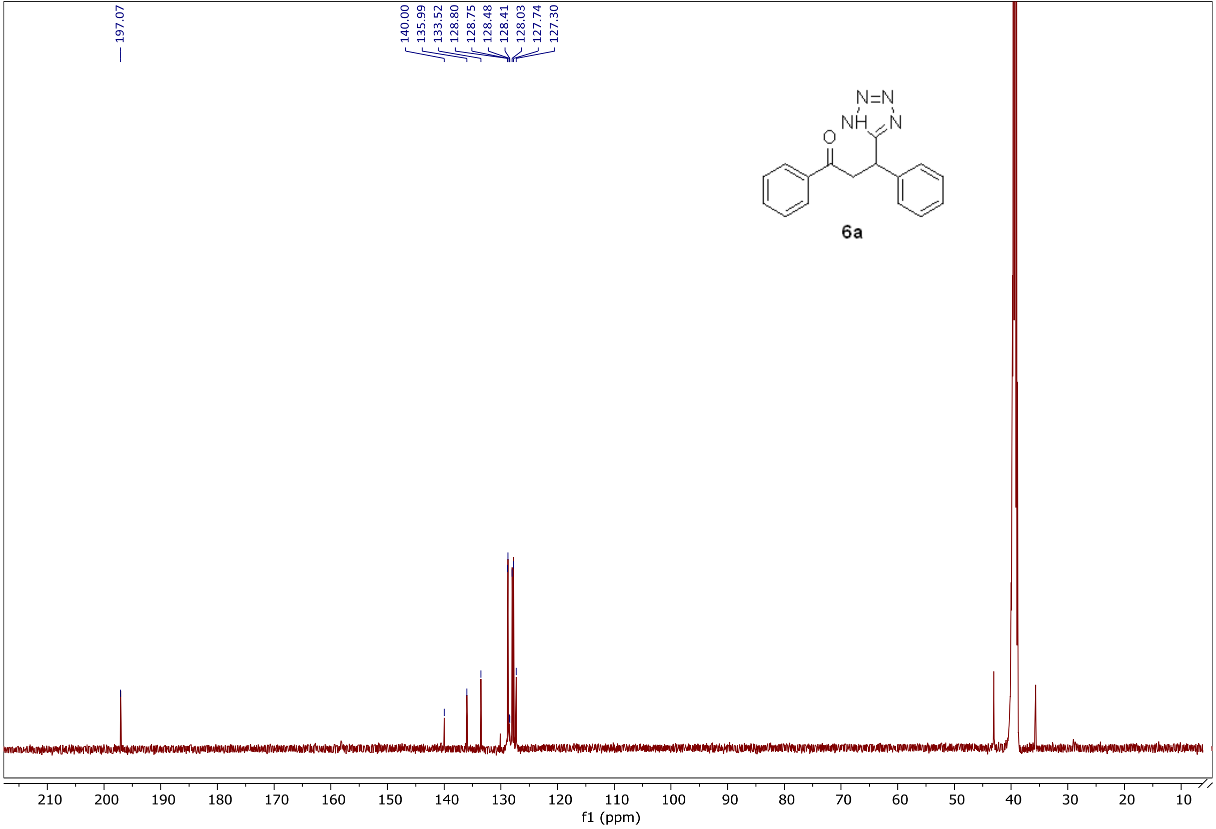
8.00
7.99
7.67
7.65
7.64
7.54
7.53
7.51
7.35
7.34
7.34
7.33
7.32
7.27
7.27
7.26
7.26
4.99
4.98
4.97
4.96
4.26
4.24
4.22
4.20
3.82
3.81
3.78
3.77
16.26
18
17
16
15
f1 (ppm)
N=N
NH
N
O
6a
18
17
16
15
14
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


197.07
140.00
135.99
133.52
128.80
128.75
128.48
128.41
128.03
127.74
127.30
N=N
NH
N
O
6a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)