Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

for

Dehydrogenative alkenylation of uracils *via* palladium-catalyzed regioselective C–H activation

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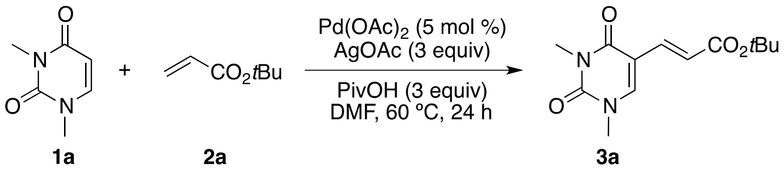
1. General experimental remarks

All reactions were carried out in clear 1-dram vials under air. Vials were used without drying. Palladium(II) acetate, the alkenes, all other chemicals and solvents were purchased and were directly used without further purification. Flash column chromatography was carried out on silica gel. TLC was conducted on 250 micron, F_{254} silica gel plates. ^1H NMR analyses were performed on a 400 MHz spectrometer and ^{13}C NMR spectra were recorded on a 100 MHz spectrometer with complete proton decoupling. Chemical shifts were reported as ppm relative to chloroform ($CHCl_3$: 7.26 ppm for ^1H, 77.16 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. IR spectra of solids were obtained by dissolving the sample in CH_2Cl_2 and letting the solvent evaporate on a NaCl plate. High-resolution mass spectrometry was performed on an ESI-TOF instrument. Melting points were uncorrected.

2. General Procedure for the dehydrogenative alkenylation reactions

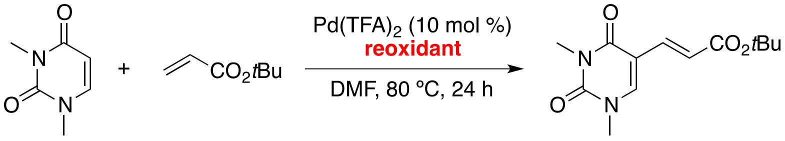


1,3-Dimethyluracil (**1**) (14.0 mg, 0.1 mmol) was mixed in a clear 1-dram vial with $Pd(OAc)_2$ (1.13 mg, 0.005 mmol), AgOAc (50.3 mg, 0.3 mmol), PivOH (30.6 mg, 0.3 mmol). To the mixture was added *tert*-butyl acrylate (**2a**) (29.3 μL, 0.2 mmol), followed by DMF (0.5 mL). The reaction vessel was then capped. After being stirred for 2 min, the reaction was heated at 60 °C for 24 h in dark. The reaction was then cooled, diluted with EtOAc (1 mL), and pressure-filtered over Celite. The filter cake was washed with EtOAc (20 mL). The filtrate was then concentrated under reduced pressure and purified by flash chromatography (30–40% EtOAc in hexanes) on silica gel to provide 24.3 mg (92%) of **3a** as an off-white solid (mp 140–142 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.19 (d, J = 15.8 Hz, 1H), 6.89 (d, J = 16.6 Hz, 1H), 3.47 (s, 3H), 3.38 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 161.5, 150.9, 144.2, 135.1, 121.4, 109.3, 80.5, 37.6, 28.3, 28.3; FTIR (NaCl, cm^{-1}) 3155, 2953, 1710, 1665, 1629, 1457, 1437, 1370, 1301, 1263, 1194, 1172, 1091, 984, 907; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{13}H_{18}N_2O_4Na$: 289.1159, found 289.1158.

3. Detailed optimization study

3.1 Reoxidant screening

Table S1 Reoxidant effect on the dehydrogenative alkenylation



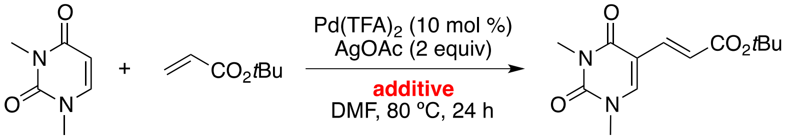
1a **2a** **3a**

Entry[a]	Reoxidant (equiv.)	Conversion (%)[b]	Yield (%)[c]
1	$Cu(OAc)_2$ (2.0)	74	52
2	$CuCl_2$ (2.0)	9	0
3	$Cu(OTf)_2$ (2.0)	8	6
4	$Cu(TFA)_2$ (2.0)	10	0
5	duroquinone (2.0)	15	4
6	$PhCO_3$*t*Bu (2.0)	60	45
7	Ag_2O (1.0)	26	11
8	Ag_2CO_3 (1.0)	37	20
9	AgF_2 (2.0)	-1	0
10	AgCl (2.0)	7	0
11	$AgNO_3$ (2.0)	10	3
12	$AgSbF_6$ (2.0)	32	0
13	AgOBz (2.0)	64	55
14	AgOTF (2.0)	27	0
15	**AgOAc (2.0)**	**86**	**68**

[a] Reaction conditions: uracil **1a** (0.2 M), acrylate **2a** (2.0 equiv.), $Pd(TFA)_2$ (10 mol%), oxidant, DMF (0.5 mL) under air at 80 °C, 24 h. [b] ^1H NMR % conversion of the starting enaminone with Ph_3SiMe (1.0 equiv) as the internal standard. [c] ^1H NMR % yield with Ph_3SiMe (1.0 equiv) as the internal standard.

3.2 Additive study

Table S2 Additive effect on the dehydrogenative alkenylation



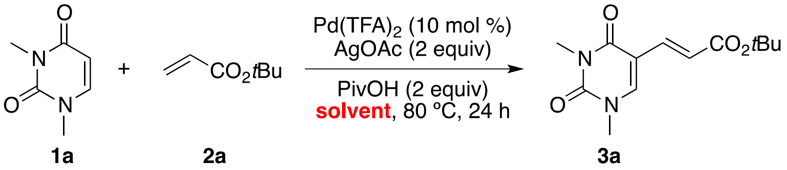
1a **2a** **3a**

Entry[a]	Reoxidant (equiv.)	Additive (equiv.)	Conversion (%)[b]	Yield (%)[c]
1	AgOAc (2.0)	K_2CO_3 (2.0)	37	19
2	AgOAc (2.0)	TFA (2.0)	34	24
3	AgOAc (2.0)	AcOH (2.0)	86	70
4	**AgOAc (2.0)**	**PivOH (2.0)**	**96**	**77**
5	Ag_2O (1.0)	PivOH (2.0)	88	74
6	AgOAc (2.0)	--	86	68

[a] Reaction conditions: uracil **1a** (0.2 M), acrylate **2a** (2.0 equiv.), $Pd(TFA)_2$ (10 mol%), AgOAc (2.0 equiv.), additive, DMF (0.5 mL) under air at 80 °C, 24 h. [b] ^1H NMR % conversion of the starting enaminone with Ph_3SiMe (1.0 equiv) as the internal standard. [c] ^1H NMR % yield with Ph_3SiMe (1.0 equiv) as the internal standard.

3.3 Solvent effect

Table S3 Solvent effect on the dehydrogenative alkenylation

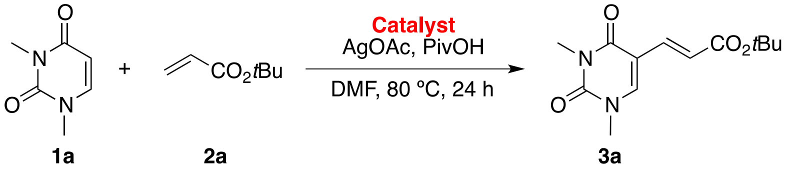


Entry[a]	Solvent (0.5 mL)	Conversion (%)[b]	Yield (%)[c]
1	DMSO	38	24
2	MeCN	76	62
3	NMP	92	64
4	**DMF**	**96**	**77**
5	THF	94	66
6	dioxane	100	58
7	*t*BuOH	78	52
8	DMA	90	72

[a] Reaction conditions: uracil **1a** (0.2 M), acrylate **2a** (2.0 equiv.), $Pd(TFA)_2$ (10 mol%), AgOAc (2.0 equiv.), PivOH (3.0 equiv.), solvent, under air at 80 °C, 24 h. [b] ^1H NMR % conversion of the starting enaminone with Ph_3SiMe (1.0 equiv) as the internal standard. [c] ^1H NMR % yield with Ph_3SiMe (1.0 equiv) as the internal standard.

3.4 Catalyst choice

Table S4 Catalyst efficiency on the dehydrogenative alkenylation

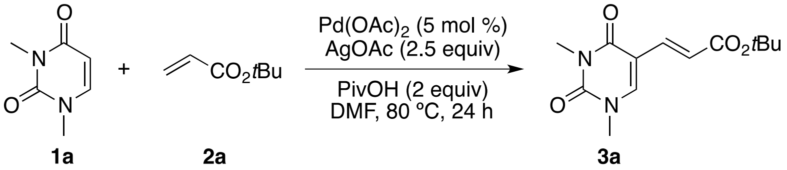


Entry[a]	Catalyst (mol%)	AgOAc (equiv.)	PivOH (equiv.)	Conversion (%)[b]	Yield (%)[c]
1	$Pd(TFA)_2$ (10)	2.0	2.0	86	68
2	$Pd(OAc)_2$ (10)	1.1	2.0	76	58
3	$Pd(OAc)_2$ (10)	2.0	2.0	95	80
4	$Pd(OAc)_2$ (10)	2.5	2.0	100	85
5	$Pd(OAc)_2$ (10)	3.0	2.0	100	85
6	$Pd(OAc)_2$ (1)	2.5	2.0	73	66
7	$Pd(OAc)_2$ (1)	4.0	2.0	65	57
8	$Pd(OAc)_2$ (5)	1.5	2.0	79	67
9	$Pd(OAc)_2$ (5)	2.0	2.0	93	83
10	**$Pd(OAc)_2$ (5)**	**2.5**	**2.0**	**100**	**84**
11	$Pd(OAc)_2$ (5)	3.0	2.0	100	82
12	$Pd(OAc)_2$ (5)	2.5	0.5	94	79
13	$Pd(OAc)_2$ (5)	2.5	2.5	100	83
14	$Pd(OAc)_2$ (5)	2.5	3.0	100	83

[a] Reaction conditions: uracil **1a** (0.2 M), acrylate **2a** (2.0 equiv.), catalyst, AgOAc, PivOH, DMF (0.5 mL) under air at 80 °C, 24 h. [b] ^1H NMR % conversion of the starting enaminone with Ph_3SiMe (1.0 equiv) as the internal standard. [c] ^1H NMR % yield with Ph_3SiMe (1.0 equiv) as the internal standard.

3.5 Reaction scale

Table S5 Reaction scale of the dehydrogenative alkenylation

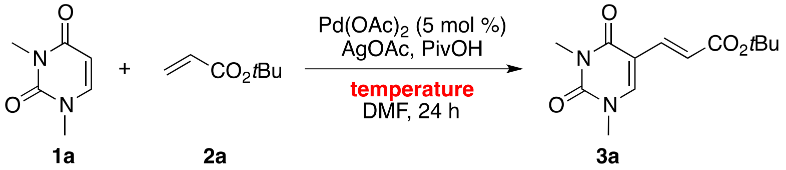


Entry[a]	**1a** (M)	**2a** (equiv.)	Conversion (%)[b]	Yield (%)[c]
1	0.2	1.1	100	78
2	**0.2**	**2.0**	**100**	**84**
3	0.2	3.0	97	81
4	0.1	2.0	100	84
5	0.5	2.0	100	82

[a] Reaction conditions: uracil **1a** (0.1 mmol), acrylate **2a** (2.0 equiv.), $Pd(OAc)_2$ (5 mol%), AgOAc (2.5 equiv.), PivOH (2.0 equiv.), DMF (0.2–1.0 mL) under air at 80 °C, 24 h. [b] ^{1}H NMR % conversion of the starting enaminone with Ph_3SiMe (1.0 equiv) as the internal standard. [c] ^{1}H NMR % yield with Ph_3SiMe (1.0 equiv) as the internal standard.

3.6 Temperature effect

Table S6 Temperature effect on the dehydrogenative alkenylation

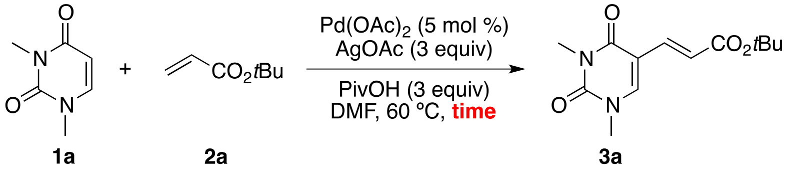


Entry[a]	AgOAc (equiv.)	PivOH (equiv.)	Temp (°C)	Conversion (%)[b]	Yield (%)[c]
1	2.5	2.0	50	86	80
2	2.5	2.0	50	86	78
3	3.0	3.0	50	92	87
4	2.5	2.0	60	100	86
5	3.0	2.0	60	100	91
6	2.5	2.5	60	100	87
7	2.5	3.0	60	100	91
8	**3.0**	**3.0**	**60**	**100**	**91**
9	2.5	2.0	70	100	88
10	3.0	3.0	70	100	87
11	2.5	2.0	80	100	84
12	2.5	2.0	100	100	74

[a] Reaction conditions: uracil **1a** (0.2 M), acrylate **2a** (2.0 equiv.), $Pd(OAc)_2$ (5 mol%), AgOAc, PivOH, DMF (0.5 mL) under air, 24 h. [b] ^{1}H NMR % conversion of the starting enaminone with Ph_3SiMe (1.0 equiv) as the internal standard. [c] ^{1}H NMR % yield with Ph_3SiMe (1.0 equiv) as the internal standard.

3.7 Reaction time

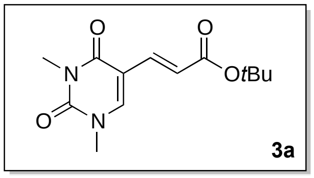
Table S7 Effect of reaction time on the dehydrogenative alkenylation



Entry[a]	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	0.5	31	25
2	1	40	37
3	2	60	53
4	4	75	66
5	8	88	81
6	12	92	88
7	18.5	100	91
8	**24**	**100**	**91(92)[d]**

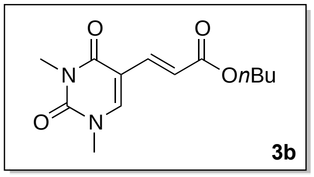
[a] Reaction conditions: uracil **1a** (0.2 M), acrylate **2a** (2.0 equiv.), $Pd(OAc)_2$ (5 mol%), AgOAc (3.0 equiv.), PivOH (3.0 equiv.), DMF (0.5 mL), under air at 60 °C, 0–24 h. [b] ^1H NMR % conversion of the starting enaminone with Ph_3SiMe (1.0 equiv) as the internal standard. [c] ^1H NMR % yield with Ph_3SiMe (1.0 equiv) as the internal standard. [d] Isolated yield in parenthesis.

4. Characterization data for new compounds



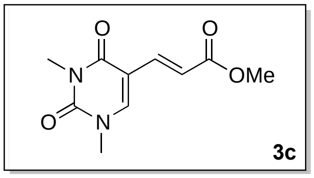
3a

(*E*)-1,3-Dimethyl-5-(2’-*t*-butoxycarbonylvinyl)uracil (3a). 3a was prepared by the general procedure described above and purified by flash chromatography (30–40% EtOAc in hexanes) on silica gel to provide 24.3 mg (92%) as an off-white solid (mp 140–142 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.19 (d, *J* = 15.8 Hz, 1H), 6.89 (d, *J* = 16.6 Hz, 1H), 3.47 (s, 3H), 3.38 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 161.5, 150.9, 144.2, 135.1, 121.4, 109.3, 80.5, 37.6, 28.3, 28.3; FTIR (NaCl, cm^{-1}) 3155, 2953, 1710, 1665, 1629, 1457, 1437, 1370, 1301, 1263, 1194, 1172, 1091, 984, 907; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{13}H_{18}N_2O_4Na$: 289.1159, found 289.1158.



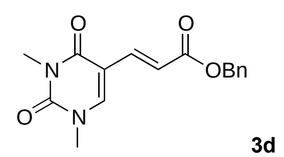
3b

(*E*)-1,3-Dimethyl-5-(2’-*n*-butoxycarbonylvinyl)uracil (3b). 3b was prepared by the general procedure described above and purified by flash chromatography (40% EtOAc in hexanes) on silica gel to provide 24.1 mg (91%) as a white solid (mp 138–140 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.28 (d, *J* = 16.3 Hz, 1H), 6.99 (d, *J* = 15.8 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.47 (s, 3H), 3.38 (s, 3H), 1.65 (m, 2H), 1.41 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 161.4, 150.8, 144.8, 136.3, 119.3, 109.0, 64.4, 37.6, 30.9, 28.3, 19.3, 13.8; FTIR (NaCl, cm^{-1}) 3055, 2987, 2963, 1708, 1665, 1628, 1454, 1422, 1355, 1299, 1173, 1090, 1063, 985, 867; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{13}H_{18}N_2O_4Na$: 289.1159, found 289.1159.



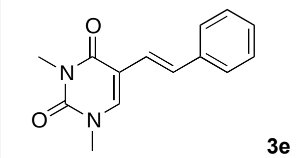
3c

(*E*)-5-(2’-Methoxycarbonylvinyl)-1,3-dimethyluracil (3c). 3c was prepared by the general procedure described above and purified by flash chromatography (50% EtOAc in hexanes) on silica gel to provide 21.0 mg (94%) as a white solid (mp 163–165 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.30 (d, *J* = 15.8 Hz, 1H), 7.00 (d, *J* = 15.8 Hz, 1H), 3.77 (s, 3H), 3.48 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 161.4, 150.8, 144.9, 136.6, 118.9, 109.0, 51.8, 37.7, 28.3; FTIR (NaCl, cm^{-1}) 3424, 2953, 1710, 1666, 1630, 1456, 1437, 1369, 1301, 1262, 1172, 1091, 984, 908; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{10}H_{12}N_2O_4Na$: 247.0689, found 247.0695.



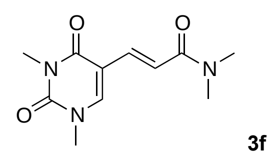
3d

(*E*)-5-(2'-Benzoxycarbonylvinyl)-1,3-dimethyluracil (3d). 3d was prepared by the general procedure described above and purified by flash chromatography (50% EtOAc in hexanes) on silica gel to provide 15.7 mg (52%) as a white solid (mp 180–182 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42—7.30 (m, 7H), 7.06 (d, *J* = 15.7 Hz, 1H), 5.22 (s, 2H), 3.47 (s, 3H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.5, 161.4, 150.8, 145.0, 136.9, 136.3, 128.7, 128.3, 128.2, 119.0, 109.0, 66.4, 37.7, 28.3; FTIR (NaCl, cm^{-1}) 3367, 2956, 1710, 1666, 1629, 1456, 1380, 1299, 1166, 1093, 985, 907; HRMS (ESI+) *m/e* calculated for [M+Na]$^+$ $C_{16}H_{16}N_2O_4Na$: 323.1002, found 323.1003.



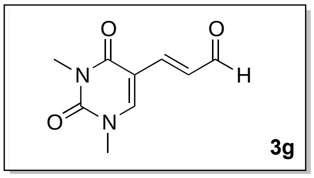
3e

(*E*)-1,3-Dimethyl-5-styryluracil (3e). 3e was prepared by the general procedure described above and purified by flash chromatography (40% EtOAc in hexanes) on silica gel to provide 24.0 mg (98%) as a yellowish solid (mp 139–141 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 16.4 Hz, 1H), 7.28 (m, 4H), 6.84 (d, *J* = 16.3 Hz, 1H), 3.46 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.4, 151.2, 139.4, 137.5, 129.5, 128.8, 127.8, 126.5, 120.1, 111.6, 37.4, 28.3; FTIR (NaCl, cm^{-1}) 3055, 2987, 1702, 1659, 1459, 1369, 1087, 968; HRMS (ESI+) *m/e* calculated for [M+Na]$^+$ $C_{14}H_{14}N_2O_2Na$: 265.0947, found 265.0943.



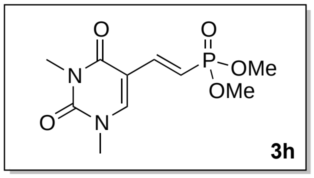
3f

(*E*)-1,3-Dimethyl-5-(2'-dimethylcarbamoylvinyl)uracil (3f). 3f was prepared by the general procedure described above and purified by flash chromatography (100% acetone) on silica gel to provide 23.5 mg (100%) as a yellowish solid (mp 208–210 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, *J* = 15.0 Hz, 1H), 7.13 (s, 1H), 7.07 (d, *J* = 15.0 Hz, 1H), 3.33 (s, 3H), 3.25 (s, 3H), 3.01 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.3, 161.9, 150.8, 145.3, 134.3, 118.8, 109.5, 37.5, 36.0, 28.2; FTIR (NaCl, cm^{-1}) 3155, 2929, 1709, 1663, 1599, 1454, 1398, 1354, 1146, 1090, 980, 908; HRMS (ESI+) *m/e* calculated for [M+Na]$^+$ $C_{11}H_{15}N_3O_3Na$: 260.1006, found 260.1011.



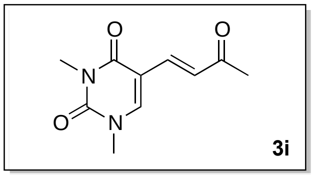
3g

(*E*)-5-(2'-Formylvinyl)-1,3-dimethyluracil (3g). 3g was prepared by the general procedure described above and purified by flash chromatography (100% EtOAc) on silica gel to provide 15.3 mg (79%) as a white solid (mp 175–177 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.59 (d, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 7.23 (d, *J* = 15.9 Hz, 1H), 7.02 (dd, *J* = 15.9, 7.6 Hz, 1H), 3.52 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.9, 161.1, 150.8, 144.6, 144.2, 128.5, 108.8, 37.9, 28.4; FTIR (NaCl, cm^{-1}) 3155, 2949, 2847, 1716, 1665, 1630, 1455, 1372, 1127, 1092, 908; HRMS (ESI+) *m/e* calculated for [M+Na]$^+$ $C_9H_{10}N_2O_3Na$: 217.0584, found 217.0580.



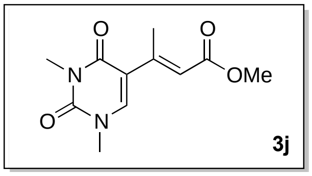
3h

(*E*)-5-(2'-Dimethoxyphosphinylvinyl)-1,3-dimethyluracil (3h). 3h was prepared by the general procedure described above and purified by flash chromatography (100% acetone) on silica gel to provide 23.0 mg (84%) as a yellow solid (mp 155–157 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (s, 1H), 7.10 (dd, *J* = 24.1, 17.3 Hz, 1H), 6.91 (dd, *J* = 17.3, 20.1 Hz, 1H), 3.73 (d, *J* = 11.1 Hz, 6H), 3.47 (s, 3H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.6, 150.7, 145.6, 141.7 (d, *J* = 7.1 Hz), 113.6 (d, *J* = 185.8 Hz), 109.0 (d, *J* = 23.2 Hz), 52.6 (d, *J* = 13.9 Hz), 37.7, 28.2; FTIR (NaCl, cm^{-1}) 3055, 2987, 2954, 1711, 1664, 1454, 1422, 1356, 1266, 1196, 1057, 1034, 989, 863, 838; HRMS (ESI+) *m/e* calculated for [M+Na]$^+$ $C_{10}H_{15}N_2O_5PNa$: 297.0611, found 297.0607.



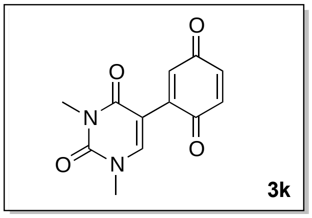
3i

(*E*)-1,3-Dimethyl-5-(3'-oxobut-1'-enyl)uracil (3i). 3i was prepared by the general procedure described above and purified by flash chromatography (100% EtOAc) on silica gel to provide 15.8 mg (75%) as an off-white solid (mp 164–166 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 (s, 1H), 7.22 (s, 2H), 3.49 (s, 3H), 3.39 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 198.6, 161.6, 150.8, 145.0, 134.7, 126.7, 109.0, 37.8, 28.9, 28.3; FTIR (NaCl, cm^{-1}) 3155, 2980, 2938, 2834, 1727, 1703, 1676, 1634, 1456, 1393, 1368, 1318, 1288, 1155, 1100, 1057, 983, 908, 870; HRMS (ESI+) *m/e* calculated for [M+Na]$^+$ $C_{10}H_{12}N_2O_3Na$: 231.0740, found 231.0742.



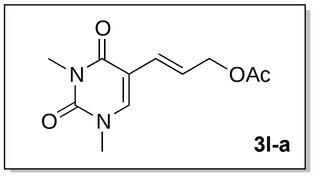
3j

(*E*)-5-(2’-Methoxycarbonyl-1’-methylvinyl)-1,3-dimethyluracil (3j). 3j was prepared by the general procedure described above and purified by flash chromatography (40% EtOAc in hexanes) on silica gel to provide 13.9 mg (59%) as a white solid (mp 108–110 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 6.39 (s, 1H), 3.72 (s, 3H), 3.45 (s, 3H), 3.36 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 161.5, 151.2, 148.5, 141.1, 118.8, 115.5, 51.4, 37.5, 28.3, 17.7; FTIR (NaCl, cm^{-1}) 3208, 2951, 1702, 1655, 1450, 1363, 1341, 1291, 1214, 1175, 1040; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{11}H_{14}N_2O_4Na$: 261.0846, found 261.0852.

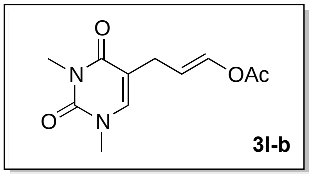


3k

1,3-Dimethyl-5-*p*-quinonyluracil (3k). 3k was prepared by the general procedure described above and purified by flash chromatography (50% EtOAc in hexanes) on silica gel to provide 13.7 mg (56%) as an orange solid (mp 159–161 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.46 (d, *J* = 2.1 Hz, 1H), 6.83–6.76 (m, 2H), 3.51 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 186.7, 161.4, 150.7, 146.2, 137.0, 136.9, 136.6, 134.1, 104.3, 38.0, 28.6; FTIR (NaCl, cm^{-1}) 3055, 2087, 1710, 1655, 1422, 1357, 1109, 996; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{12}H_{10}N_2O_4Na$: 269.0533, found 269.0536.

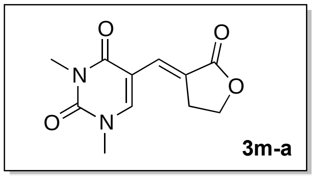


3l-a

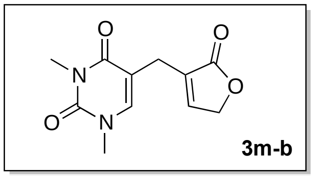


3l-b

(*E*)-5-(3’-Acetoxyprop-1’-enyl)-1,3-dimethyluracil (3l-a) and **(*E*)-5-(3’-acetoxyprop-2’-enyl)-1,3-dimethyluracil (3l-b). 3l-a** and **3l-b** were prepared by the general procedure described above and purified by flash chromatography (60% EtOAc in hexanes) on silica gel to provide 12.5 mg (53%) of an inseparable mixture as a white solid (mp 108–110 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H, **3l-b**), 7.22 (s, 1H, **3l-a**), 6.58 (dt, *J* = 15.8, 6.3 Hz, 1H, **3l-a**), 6.43 (d, *J* = 12.2 Hz, 1H, **3l-b**), 6.35 (d, *J* = 15.9 Hz, 1H, **3l-a**), 5.83 (dt, *J* = 7.0, 11.6 Hz, 1H, **3l-b**), 4.70 (d, *J* = 7.0 Hz, 2H, **3l-b**), 4.65 (d, *J* = 6.3 Hz, 2H, **3l-a**), 3.44 (s, 3H, **3l-b**), 3.43 (s, 3H, **3l-a**), 3.37 (s, 3H, **3l-a**), 3.37 (s, 3H, **3l-b**), 2.08 (s, 3H, **3l-b**), 2.07 (s, 3H, **3l-a**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9 (**3l-a**), 162.2 (**3l-a**), 151.2 (**3l-a**), 140.3 (**3l-a**), 125.3 (**3l-a**), 124.6 (**3l-a**), 110.4 (**3l-a**), 65.3 (**3l-a**), 37.3 (**3l-a**), 28.2 (**3l-a**), 21.1 (**3l-a**); FTIR (NaCl, cm^{-1}) 3055, 2087, 1735, 1707, 1655, 1458, 1421, 1369, 1089, 1025, 970; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{11}H_{14}N_2O_4Na$: 261.0846, found 261.0848.

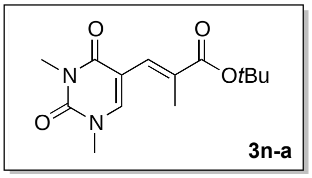


3m-a

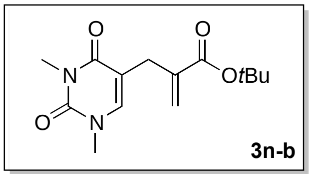


3m-b

(*E*)-1,3-Dimethyl-5-((2-oxodihydrofuran-3(2*H*)-ylidene)methyl)uracil (3m-a) and **1,3-dimethyl-5-((2-oxo-2,5-dihydrofuran-3-yl)methyl)uracil (3m-b). 3m-a** and **3m-b** were prepared by the general procedure described above and purified by flash chromatography (60% acetone in hexanes) on silica gel to provide 22.4 mg (96%) of an inseparable mixture as a yellow solid (mp 130–132 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 (t, *J* = 2.9 Hz, 1H, **3m-a**), 7.42 (s, 1H, **3m-a**), 7.36 (s, 1H, **3m-b**), 7.31 (s, 1H, **3m-b**), 4.76 (d, *J* = 1.4 Hz, 2H, **3m-b**), 4.40 (t, *J* = 7.2 Hz, 2H, **3m-a**), 3.49 (s, 3H, **3m-a**), 3.38 (s, 3H, **3m-a**), 3.38 (s, 3H, **3m-b**), 3.33 (s, 3H, **3m-b**), 3.31 (s, 2H, **3m-b**), 3.13 (td, *J* = 7.1, 2.7 Hz, 2H, **3m-a**); ^{13}C NMR (100 MHz, CDCl$_3$) δ 174.3 (**3m-b**), 171.9 (**3m-a**), 163.4 (**3m-b**), 161.4 (**3m-a**), 151.7 (**3m-b**), 150.9 (**3m-a**), 147.2 (**3m-b**), 143.8 (**3m-a**), 141.6 (**3m-b**), 130.5 (**3m-b**), 127.9 (**3m-a**), 123.3 (**3m-a**), 109.6 (**3m-a**), 108.8 (**3m-b**), 70.3 (**3m-b**), 65.3 (**3m-a**), 37.9 (**3m-a**), 37.1 (**3m-b**), 28.5 (**3m-a**), 28.2 (**3m-a**), 28.1 (**3m-b**), 23.5 (**3m-b**); FTIR (NaCl, cm^{-1}) 3224, 2930, 1752, 1702, 1664, 1459, 1375, 1343, 1205, 1171, 1081, 1052, 907, 833, 312; HRMS (ESI+) *m/e* calculated for [M+Na]$^+$ $C_{11}H_{12}N_2O_4Na$: 259.0689, found 259.0686.

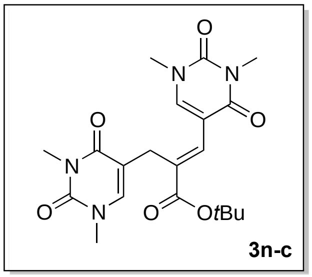


3n-a



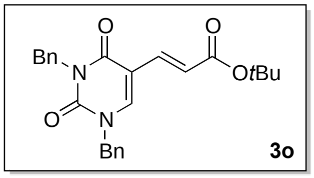
3n-b

(*E*)-1,3-Dimethyl-5-(2’-*t*-butoxycarbonylpropenyl)uracil (3n-a) and **1,3-dimethyl-5-(2’-*t*-butoxycarbonylallyl) uracil (3n-b). 3n-a** and **3n-b** were prepared by the general procedure described above and purified by flash chromatography (50% EtOAc in hexanes) on silica gel to provide 13.2 mg (47%) of an inseparable mixture as colorless crystals (mp 93–95 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (s, 1H, **3n-a**), 7.28 (s, 1H, **3n-a**), 7.10 (s, 1H, **3n-b**), 6.15 (s, 1H, **3n-b**), 5.69 (s, 1H, **3n-b**), 3.46 (s, 3H, **3n-a**), 3.38 (s, 3H, **3n-a**), 3.37 (s, 3H, **3n-b**), 3.35 (s, 3H, **3n-b**), 3.29 (s, 2H, **3n-b**), 1.98 (s, 3H, **3n-a**), 1.51 (s, 9H, **3n-a**), 1.47 (s, 9H, **3n-b**); ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.1 (**3n-a**), 166.1 (**3n-b**), 163.5 (**3n-b**), 162.5 (**3n-a**), 151.9 (**3n-b**), 151.2 (**3n-a**), 142.2 (**3n-a**), 140.8 (**3n-b**), 138.6 (**3n-b**), 130.3 (**3n-a**), 128.6 (**3n-a**), 126.7 (**3n-b**), 111.0 (**3n-b**), 110.1 (**3n-a**), 81.1 (**3n-b**), 81.0 (**3n-a**), 37.6 (**3n-a**), 37.0 (**3n-a**, **3n-b**), 29.6 (**3n-a**, **3n-b**), 28.2 (**3n-a**, **3n-b**), 14.9 (**3n-a**); FTIR (NaCl, cm^{-1}) 3055, 2086, 1702, 1660, 1457, 1422, 1369, 1341, 1143, 1085, 1049, 954, 849; HRMS (ESI+) *m/e* calculated for [M+Na]$^+$ $C_{14}H_{20}N_2O_4Na$: 303.1315, found 303.1316.



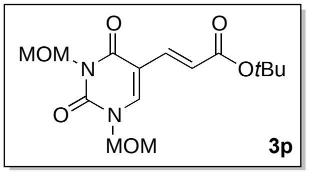
3n-c

(*E*)-1,3-Dimethyl-5-(3'-(1,3-dimethyluracil-5-yl)-2'-*t*-butoxycarbonylallyl)uracil (3n-c). 3n-c was prepared by the general procedure described above and purified by flash chromatography (100% EtOAc) on silica gel to provide 6.6 mg (24%) as a white wax. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.50 (s, 1H), 7.37 (s, 1H), 3.50 (s, 3H), 3.44 (s, 2H), 3.38 (s, 6H), 3.36 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 164.3, 162.8, 151.6, 151.4, 144.3, 143.1, 131.1, 130.7, 109.6, 108.5, 81.6, 37.6, 37.2, 37.2, 28.3, 25.4; FTIR (NaCl, cm^{-1}) 3054, 2987, 1702, 1659, 1552, 1422, 1370, 1344, 1157, 1102; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{20}H_{26}N_4O_6Na$: 441.1745, found 441.1751.



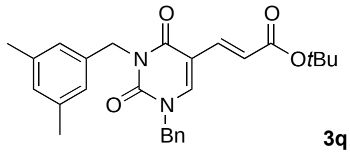
3o

(*E*)-1,3-Dibenzyl-5-(2'-*t*-butoxycarbonylvinyl)uracil (3o). 3o was prepared by the general procedure described above and purified by flash chromatography (20% EtOAc in hexanes) on silica gel to provide 38.4 mg (94%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.7 Hz, 2H), 7.42–7.26 (m, 9H), 7.12 (d, *J* = 15.8 Hz, 1H), 6.88 (d, *J* = 15.7 Hz, 1H), 5.18 (s, 2H), 4.97 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 161.1, 150.8, 143.3, 136.6, 135.2, 134.7, 129.4, 129.3, 129.0, 128.6, 128.4, 127.9, 121.6, 109.9, 80.5, 52.8, 45.0, 28.3; FTIR (NaCl, cm^{-1}) 3055, 2983, 2933, 1708, 1664, 1629, 1496, 1452, 1384, 1368, 1317, 1155, 1080, 1030, 984, 910; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{25}H_{26}N_2O_4Na$: 441.1785, found 441.1790.



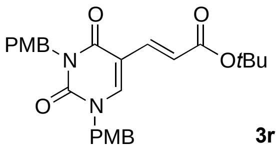
3p

(*E*)-1,3-Bis(methoxymethyl)-5-(2'-*t*-butoxycarbonylvinyl)uracil (3p). 3p was prepared by the general procedure described above and purified by flash chromatography (50% EtOAc in hexanes) on silica gel to provide 21.7 mg (68%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.21 (d, *J* = 15.8 Hz, 1H), 6.88 (d, *J* = 15.8 Hz, 1H), 5.42 (s, 2H), 5.18 (s, 2H), 3.45 (s, 3H), 3.41 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 161.1, 150.9, 142.7, 134.7, 122.4, 110.4, 80.6, 79.3, 72.5, 58.2, 57.5, 28.3; FTIR (NaCl, cm^{-1}) 3155, 2980, 2938, 1724, 1676, 1634, 1456, 1368, 1318, 1288, 1155, 1100, 984, 908; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{15}H_{21}N_2O_6Na$: 349.1370, found 349.1367.



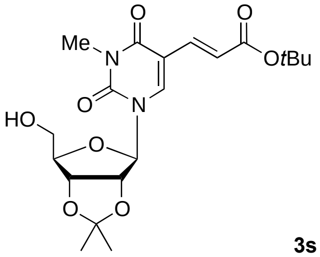
3q

(*E*)-1-Benzyl-3-(3’,5’-dimethylbenzyl)-5-(2’-*t*-butoxycarbonylvinyl)uracil (3q). 3q was prepared by the general procedure described above and purified by flash chromatography (20% EtOAc in hexanes) on silica gel to provide 33.3 mg (76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.27 (m, 6H), 7.13 (d, *J* = 15.8 Hz, 1H), 7.06 (s, 2H), 6.90–6.87 (m, 2H), 5.11 (s, 2H), 4.98 (s, 2H), 2.28 (s, 6H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 161.0, 150.8, 143.3, 138.1, 136.4, 135.3, 134.8, 129.5, 129.4, 129.0, 128.3, 126.7, 121.5, 109.9, 80.5, 52.8, 44.9, 28.3, 21.4; FTIR (NaCl, cm^{-1}) 3156, 2079, 2948, 2869, 1704, 1660, 1466, 1368, 1329, 1297, 1153, 1116, 1041, 993, 908; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{27}H_{30}N_2O_4Na$: 469.2098, found 469.2097.



3r

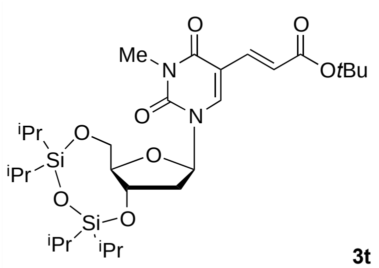
(*E*)-1,3-Bis(*p*-methoxybenzyl)-5-(2’-*t*-butoxycarbonylvinyl)uracil (3r). 3r was prepared by the general procedure described above and purified by flash chromatography (50% EtOAc in hexanes) on silica gel to provide 46.1 mg (96%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.28 (s, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 15.8 Hz, 1H), 6.92–6.80 (m, 5H), 5.10 (s, 2H), 4.88 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 161.0, 160.1, 159.3, 150.8, 143.1, 135.4, 130.9, 130.1, 128.9, 126.5, 121.3, 114.8, 113.8, 109.7, 80.4, 55.4, 52.3, 44.4, 28.3; FTIR (NaCl, cm^{-1}) 3055, 2987, 2839, 1706, 1663, 1628, 1623, 1514, 1456, 1422, 1368, 1178, 1155, 1034, 985, 896; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{27}H_{30}N_2O_6Na$: 501.1996, found 501.1995.



3s

(*E*)-2′,3′-*O*-Isopropylidene-3-methyl-5-(2’-*t*-butoxycarbonylvinyl)uridine (3s). 3s was prepared by the general procedure described above and purified by flash chromatography (35% EtOAc in hexanes) on silica gel to provide 27.1 mg (66%) as a white wax. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.19 (d, *J* = 15.8 Hz, 1H), 6.81 (d, *J* = 15.8 Hz, 1H), 5.76 (d, *J* = 1.4 Hz, 1H), 4.96–4.89 (m, 2H), 4.42–4.34 (m, 1H), 3.96 (dd, *J* = 11.8, 2.3 Hz, 1H), 3.83 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.34 (s, 3H), 2.95 (br, 1H), 1.58 (s, 3H), 1.48 (s, 9H), 1.35 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 167.1, 161.1, 150.1, 141.2, 135.4, 121.3, 114.4, 109.2, 96.0, 87.2, 84.9, 80.7, 62.8, 28.3, 28.1, 27.3, 25.4; FTIR (NaCl, cm^{-1}) 3468, 3055, 2987, 1710, 1667, 1627, 1466, 1422, 1369, 1265, 1155, 1112, 1084, 987, 855; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{20}H_{28}N_2O_8Na$: 447.1738, found 447.1737.

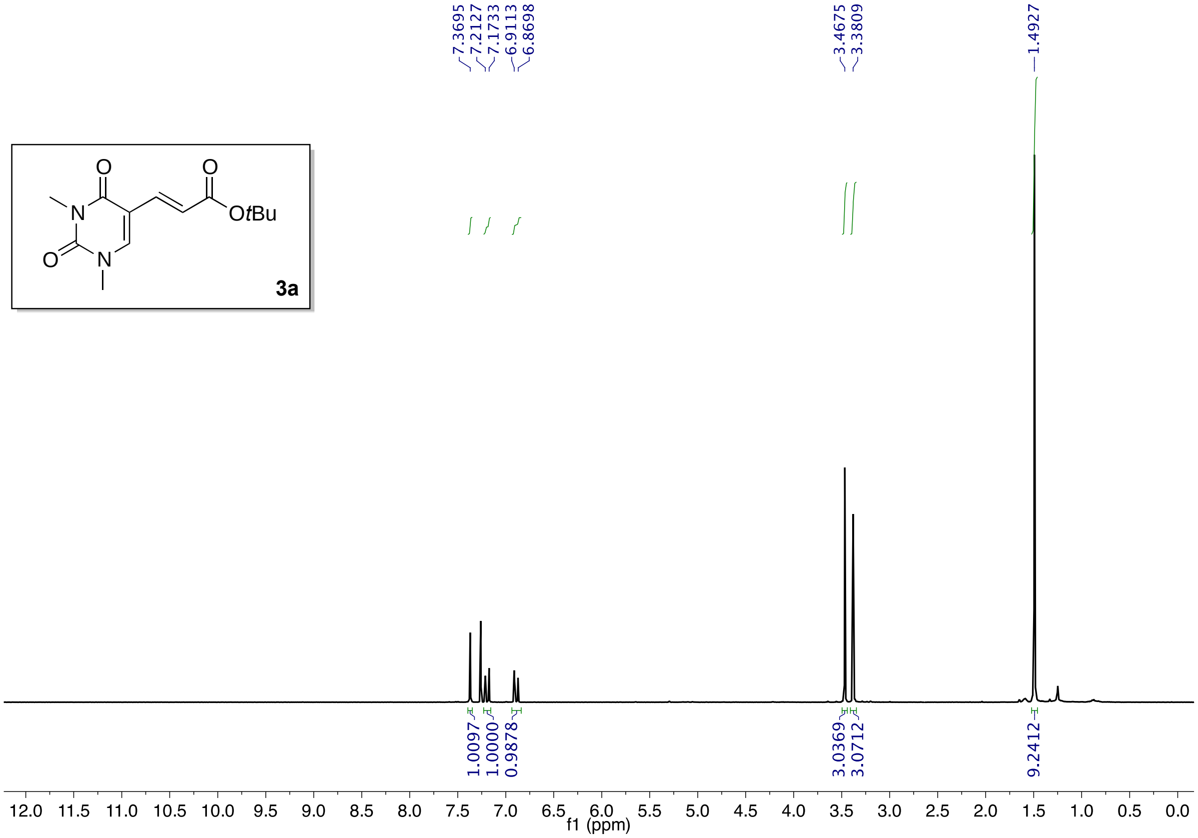


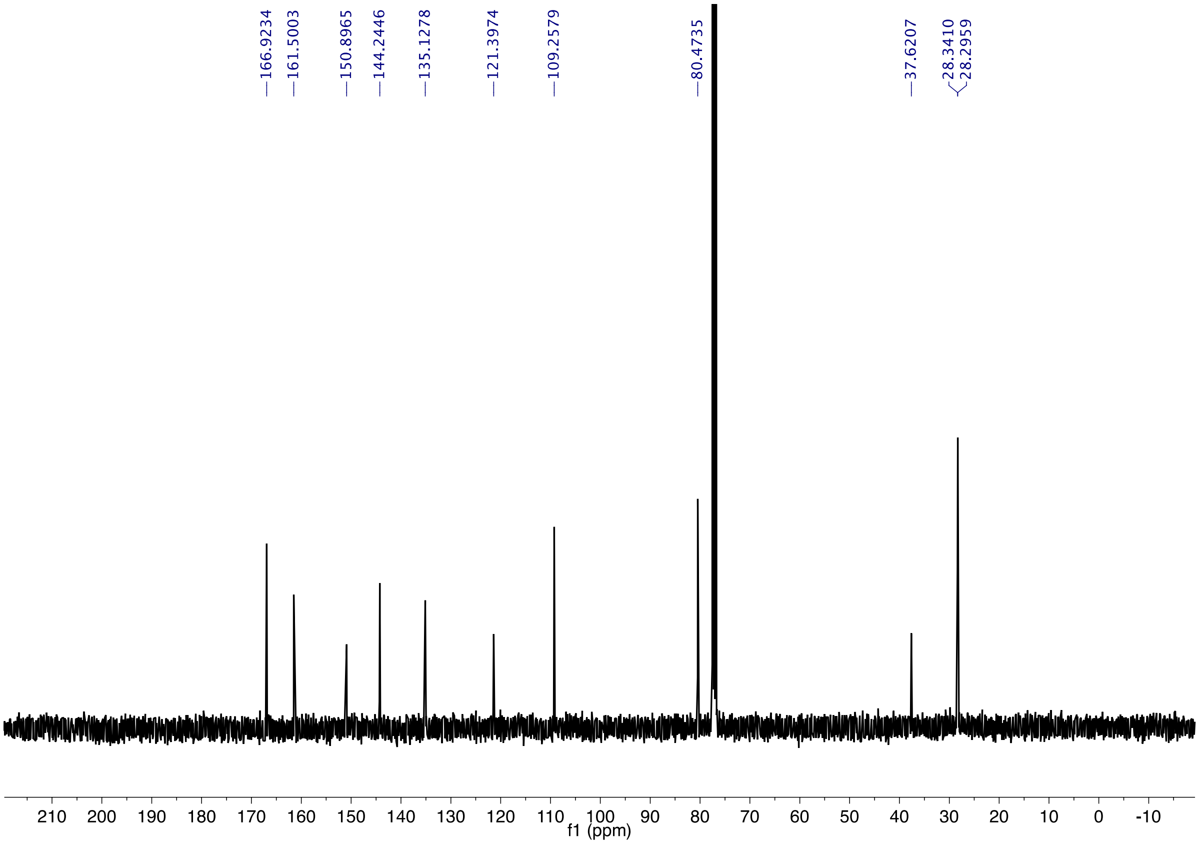
3t

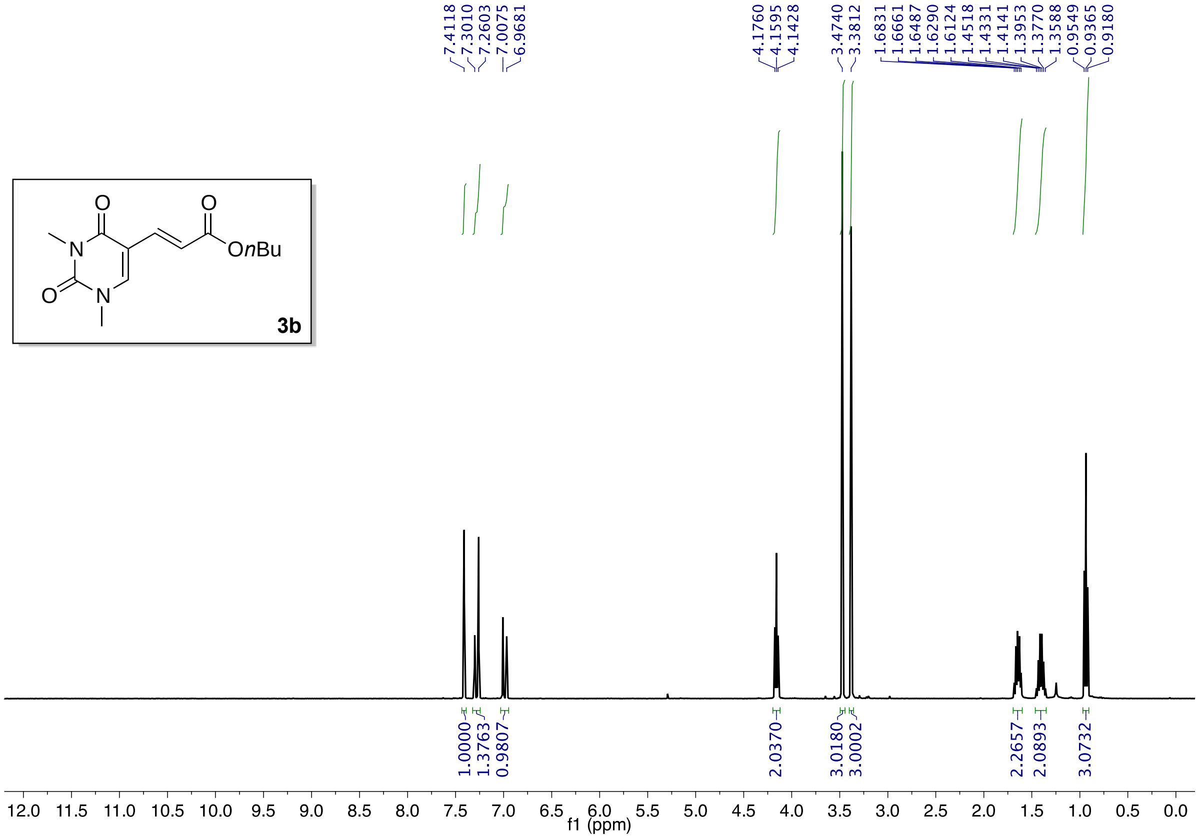
(*E*)-2’-Deoxy-3′,5′-*O*-(1’,1’,3’,3’-tetraisopropyldisiloxy)-3-methyl-5-(2’-*t*-butoxycarbonylvinyl)uridine (3t). **3t** was prepared by the general procedure described above and purified by flash chromatography (10–20% EtOAc in hexanes) on silica gel to provide 44.6 mg (75%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.26 (d, *J* = 15.8 Hz, 1H), 6.84 (d, *J* = 15.9 Hz, 1H), 6.02 (d, *J* = 6.6 Hz, 1H), 4.44 (q, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 13.1 Hz, 1H), 4.03 (dd, *J* = 13.2, 2.5 Hz, 1H), 3.81 (d, *J* = 8.2 Hz, 1H), 3.35 (s, 3H), 2.54 (ddd, *J* = 13.4, 10.2, 7.2 Hz, 1H), 2.29 (dd, *J* = 13.4, 7.2 Hz, 1H), 1.48 (s, 9H), 1.11–0.98 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 161.2, 149.9, 138.6, 135.7, 121.1, 108.8, 85.5, 80.2, 67.1, 60.1, 40.2, 28.3, 27.9, 17.5, 17.1, 13.6, 13.1, 12.8, 12.6; FTIR (NaCl, cm^{-1}) 3156, 2079, 2948, 2869, 1704, 1660, 1466, 1368, 1320, 1297, 1153, 1116, 1041, 993, 908, 885; HRMS (ESI+) *m/e* calculated for $[M+Na]^+$ $C_{29}H_{50}N_2O_8Si_2Na$: 633.3003, found 633.2995.

5. ^{1}H NMR and ^{13}C NMR spectra for compounds **3a**–**3t**

3a



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6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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1.0
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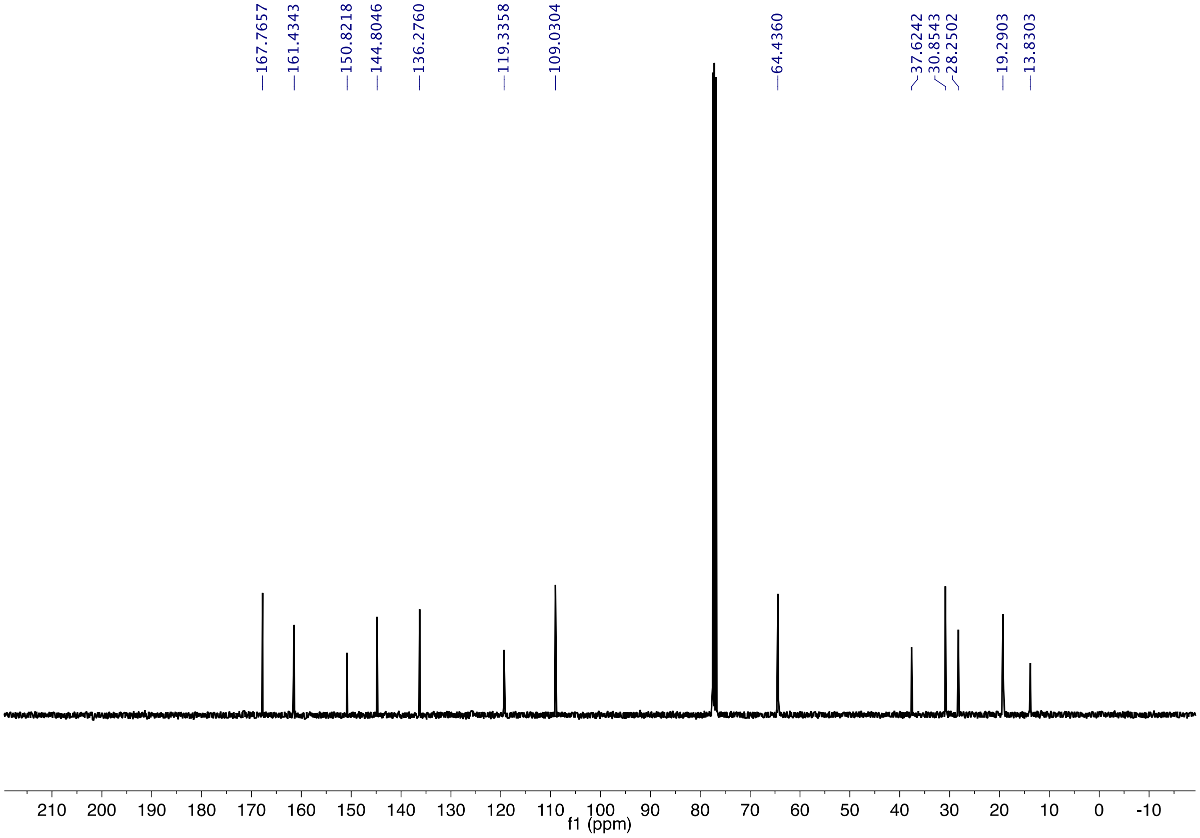
0.0
f1 (ppm)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150.8218
144.8046
136.2760
119.3358
109.0304
64.4360
37.6242
30.8543
28.2502
19.2903
13.8303
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
40
30
20
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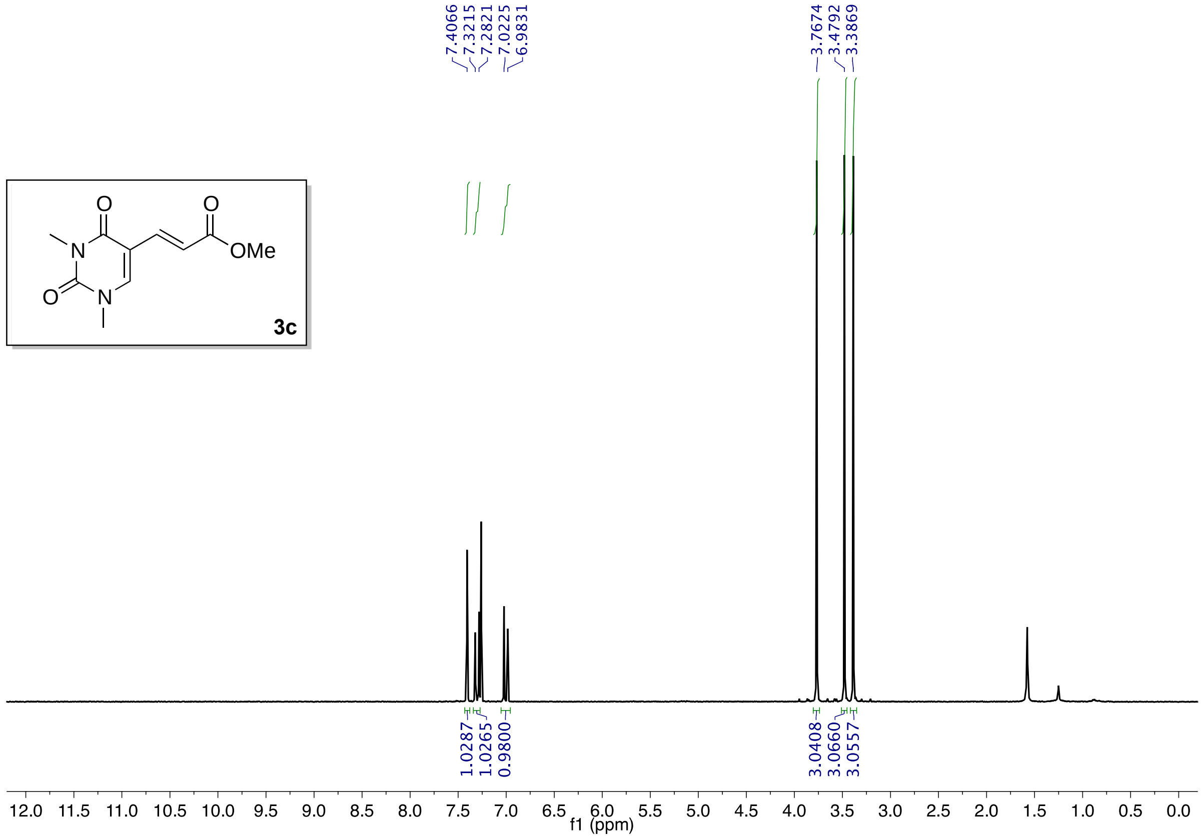
0
-10
f1 (ppm)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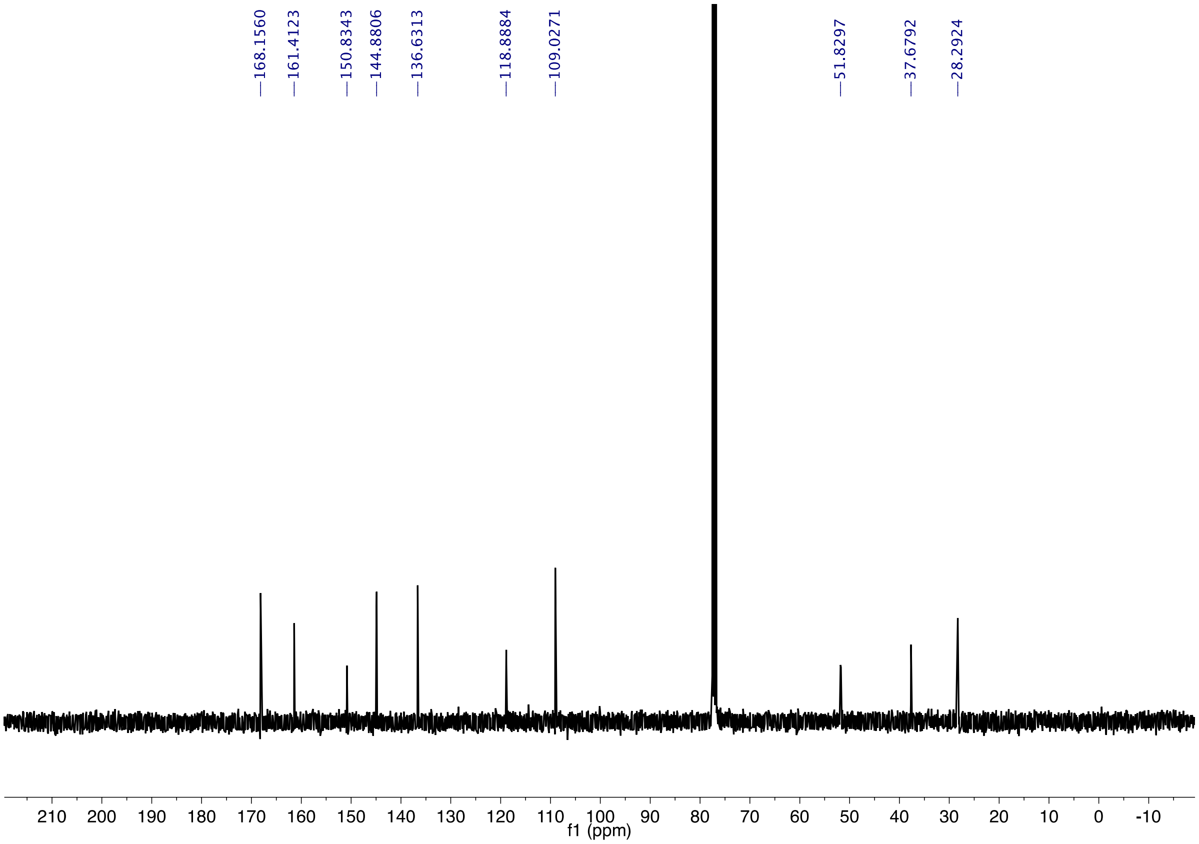
7.3215
7.2821
7.0225
6.9831
3.7674
3.4792
3.3869
1.0287
1.0265
0.9800
3.0408
3.0660
3.0557
O
O
N
OMe
O
N
3c
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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136.6313
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109.0271
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37.6792
28.2924
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200
190
180
170
160
150
140
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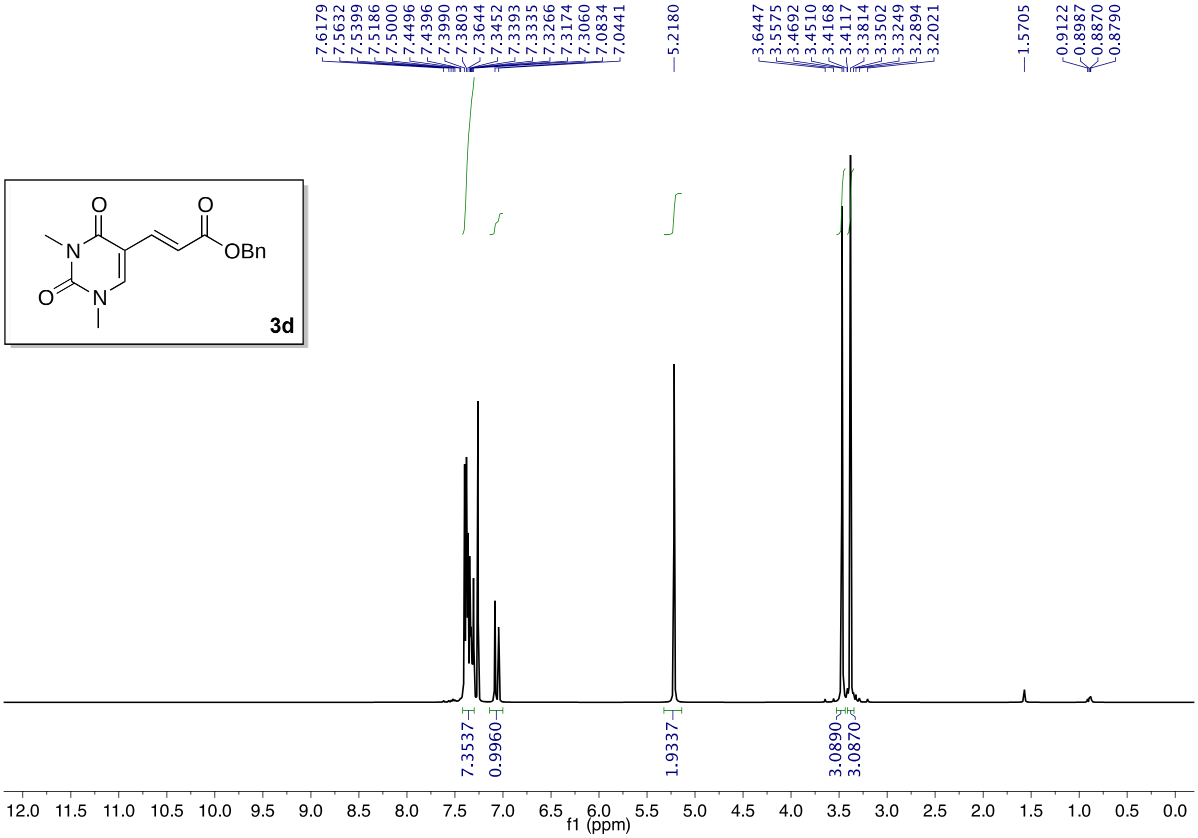
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.5399
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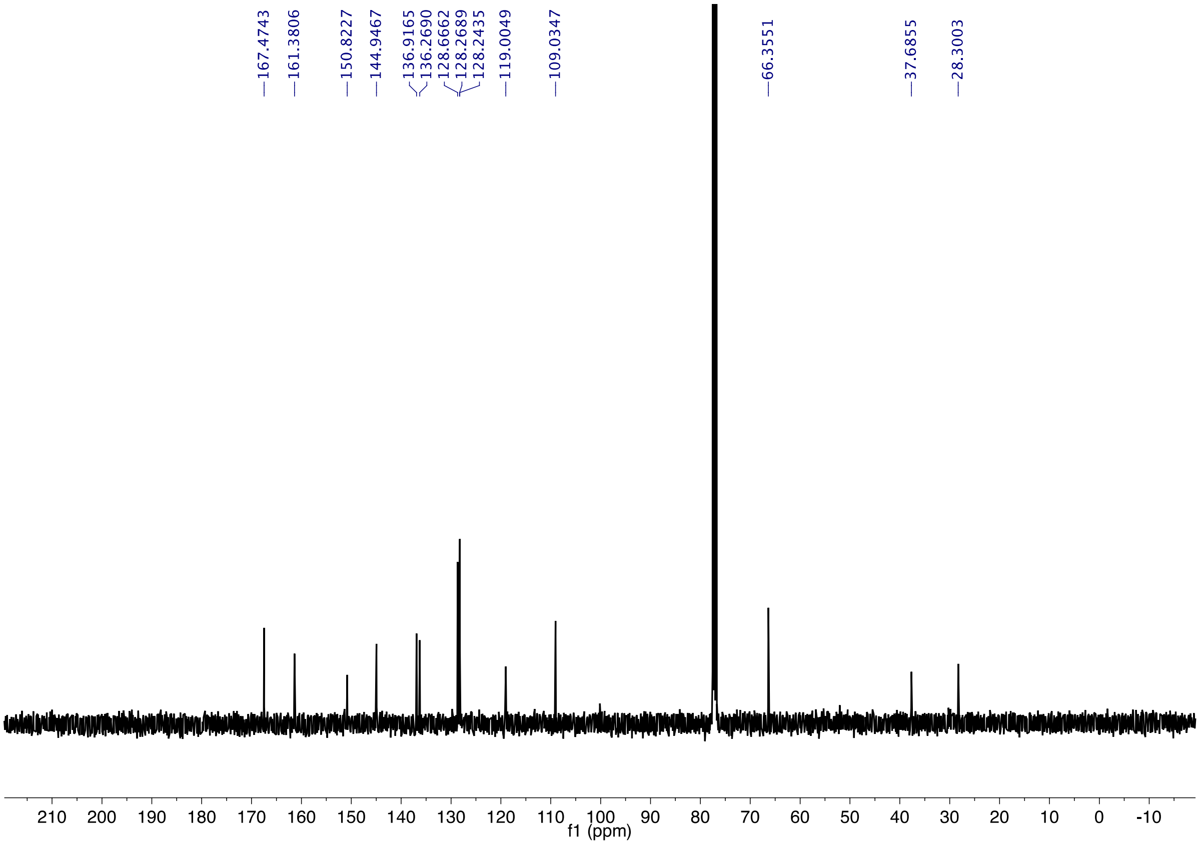
7.5000
7.4496
7.4396
7.3990
7.3803
7.3644
7.3452
7.3393
7.3335
7.3266
7.3174
7.3060
7.0834
7.0441
5.2180
3.6447
3.5575
3.4692
3.4510
3.4168
3.4117
3.3814
3.3502
3.3249
3.2894
3.2021
1.5705
0.9122
0.8987
0.8870
0.8790
O
O
N
OBn
O
N
3d
7.3537
0.9960
1.9337
3.0890
3.0870
12.0 11.5 11.0 10.5 10.0 9.5 9.0 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)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136.9165
136.2690
128.6662
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128.2435
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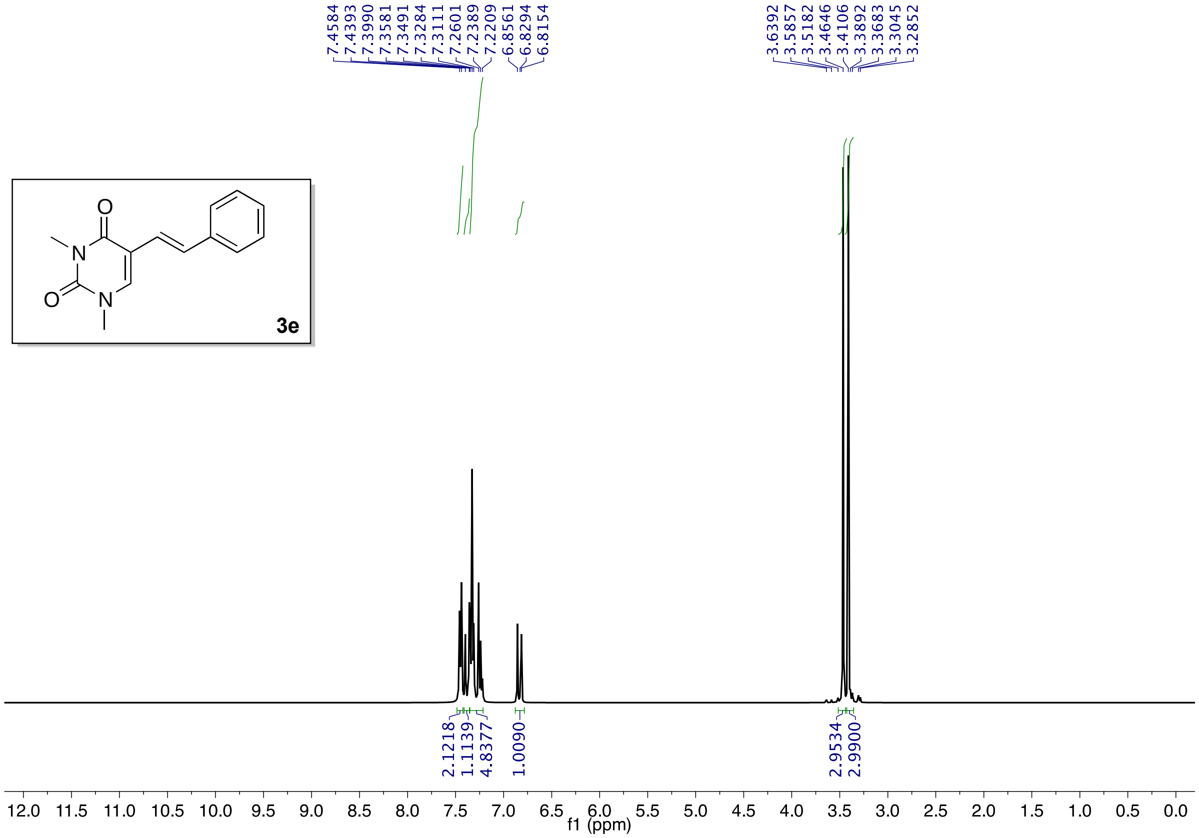
109.0347
66.3551
37.6855
28.3003
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3284
7.3111
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7.2389
7.2209
6.8561
6.8294
6.8154
3.6392
3.5857
3.5182
3.4646
3.4106
3.3892
3.3683
3.3045
3.2852
O
N
O
N
3e
2.1218
1.1139
4.8377
1.0090
2.9534
2.9900
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
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3.0
2.5
2.0
1.5
1.0
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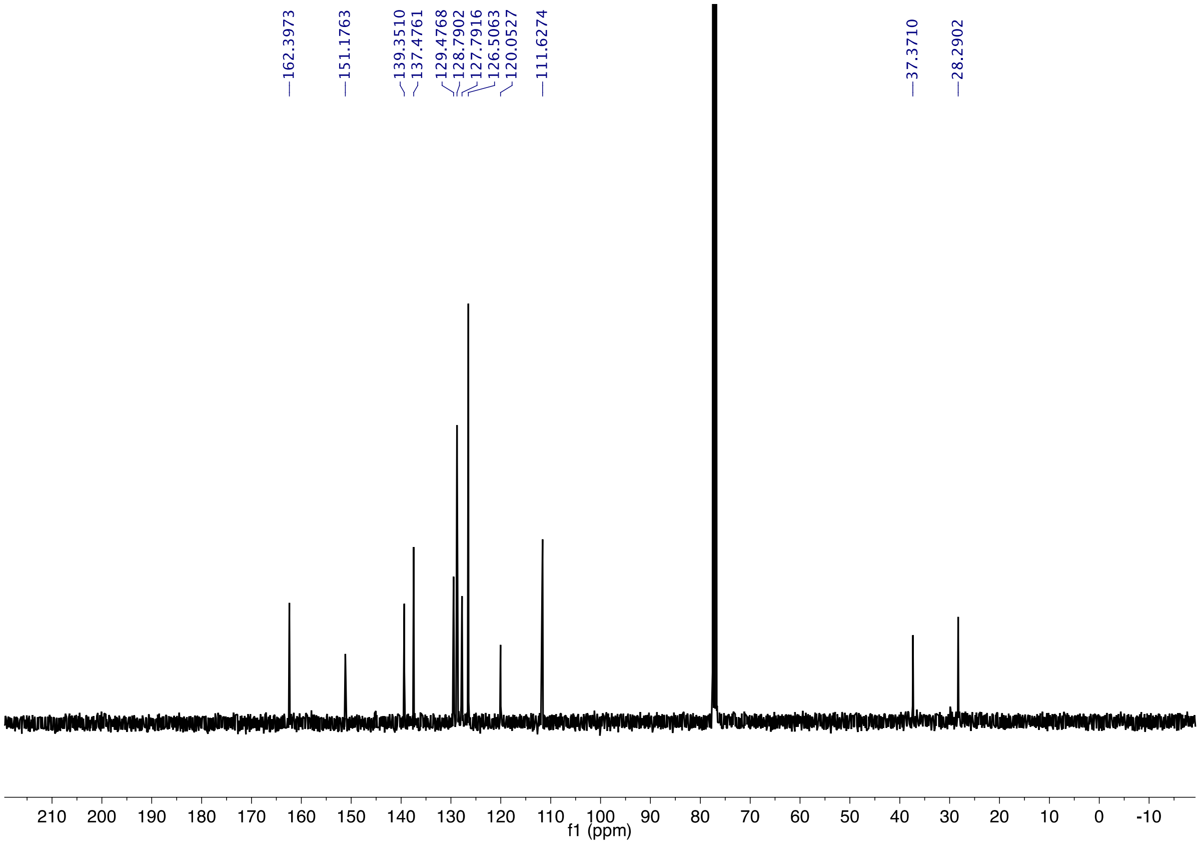
0.0
f1 (ppm)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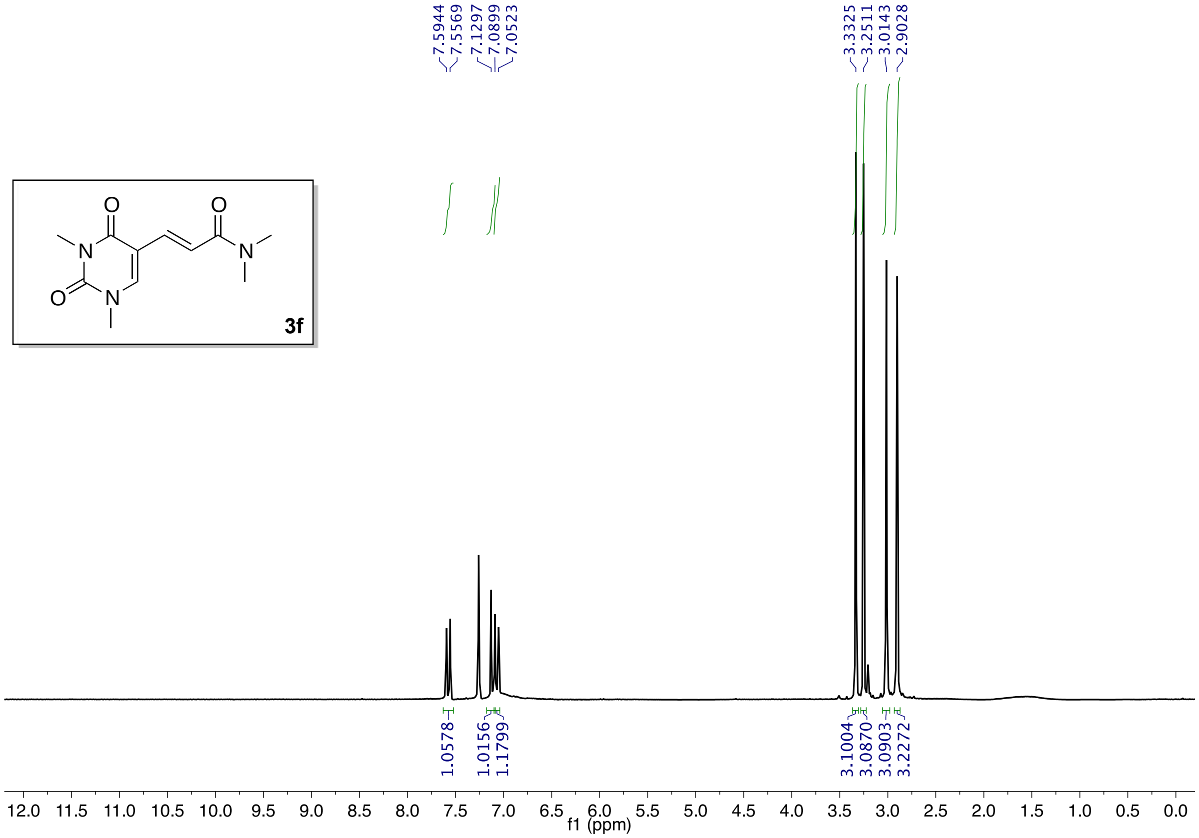
139.3510
137.4761
129.4768
128.7902
127.7916
126.5063
120.0527
111.6274
37.3710
28.2902
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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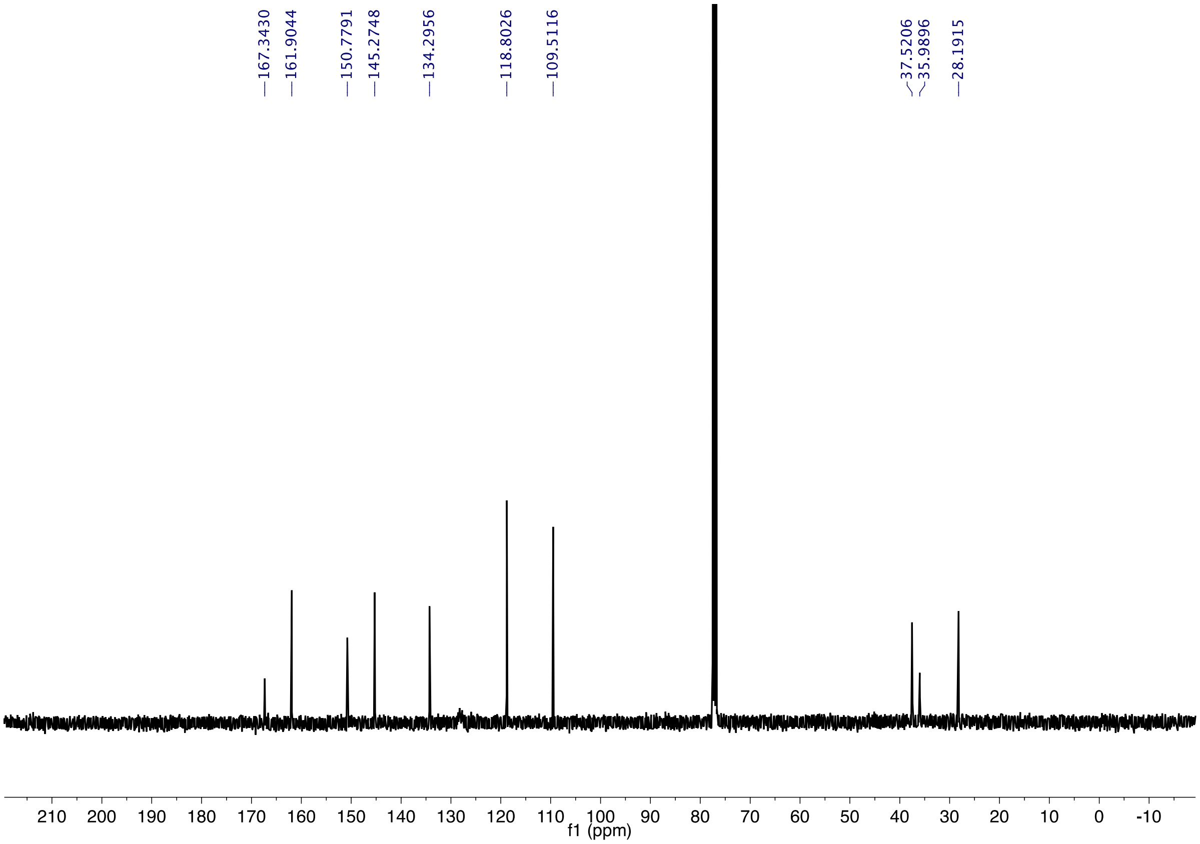
7.5569
7.1297
7.0899
7.0523
3.3325
3.2511
3.0143
2.9028
3f
1.0578
1.0156
1.1799
3.1004
3.0870
3.0903
3.2272
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.2956
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109.5116
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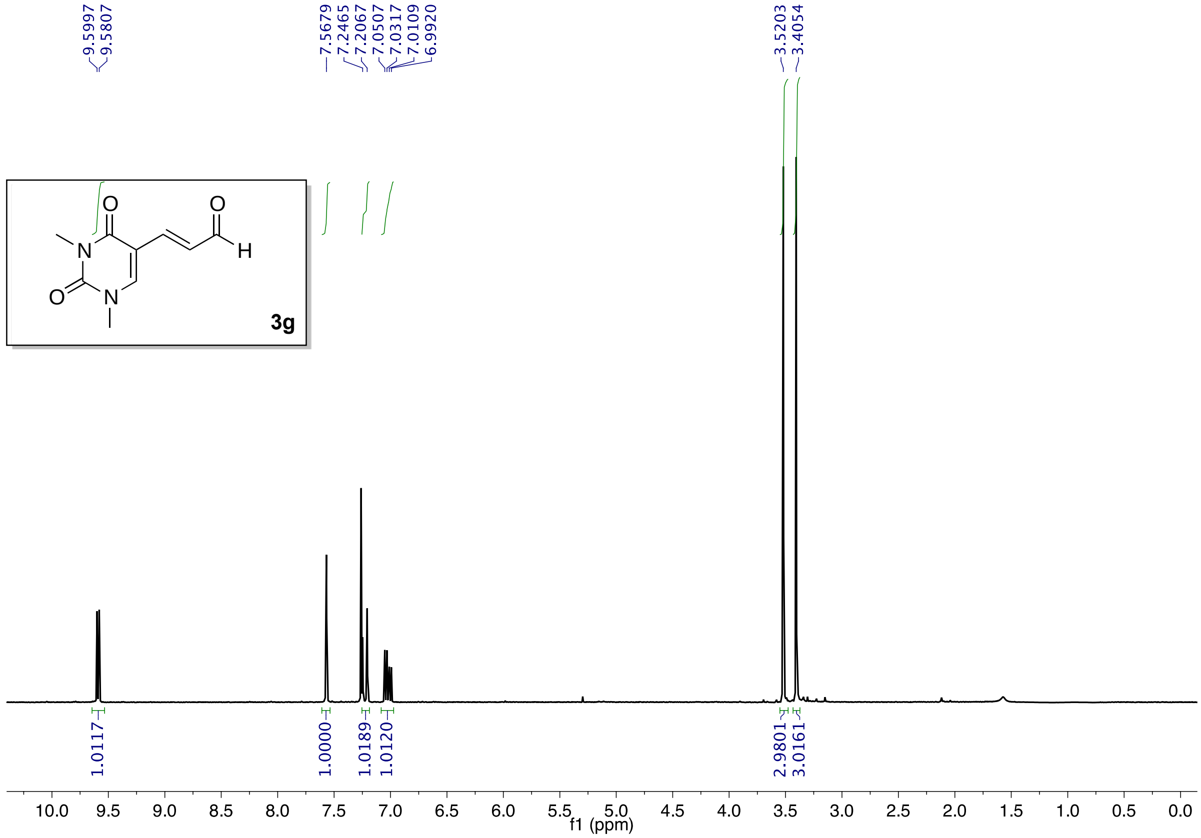
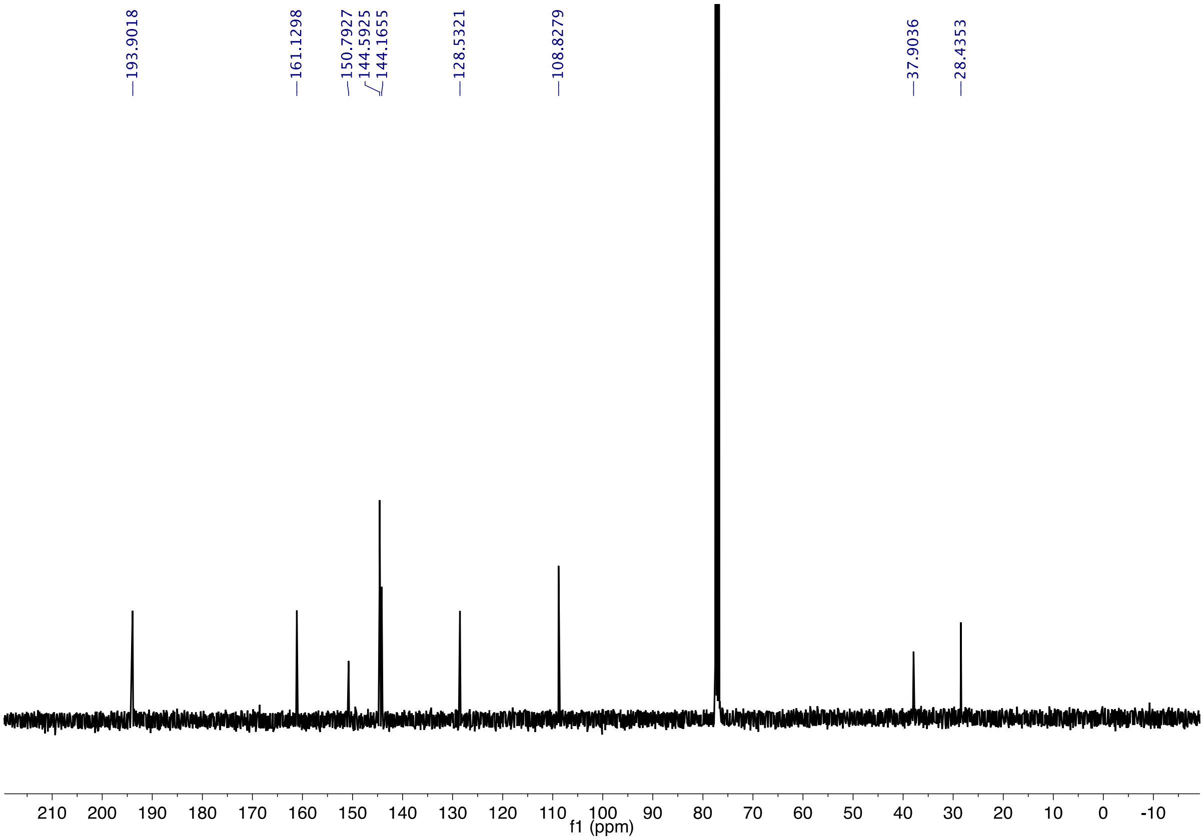
35.9896
28.1915
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.5997
9.5807
7.5679
7.2465
7.2067
7.0507
7.0317
7.0109
6.9920
3.5203
3.4054
O
O
N
H
O
N
3g
1.0117
1.0000
1.0189
1.0120
2.9801
3.0161
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)


193.9018
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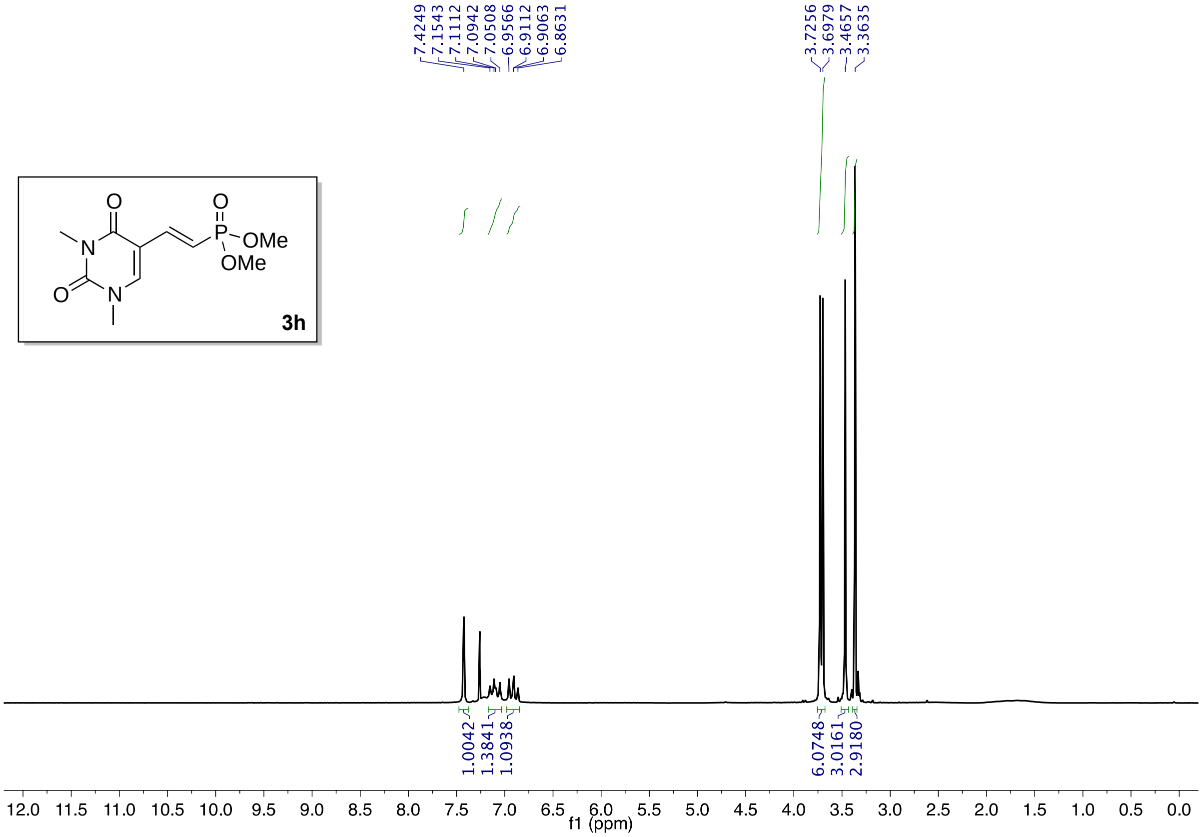
144.1655
128.5321
108.8279
37.9036
28.4353
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.0942
7.0508
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6.9112
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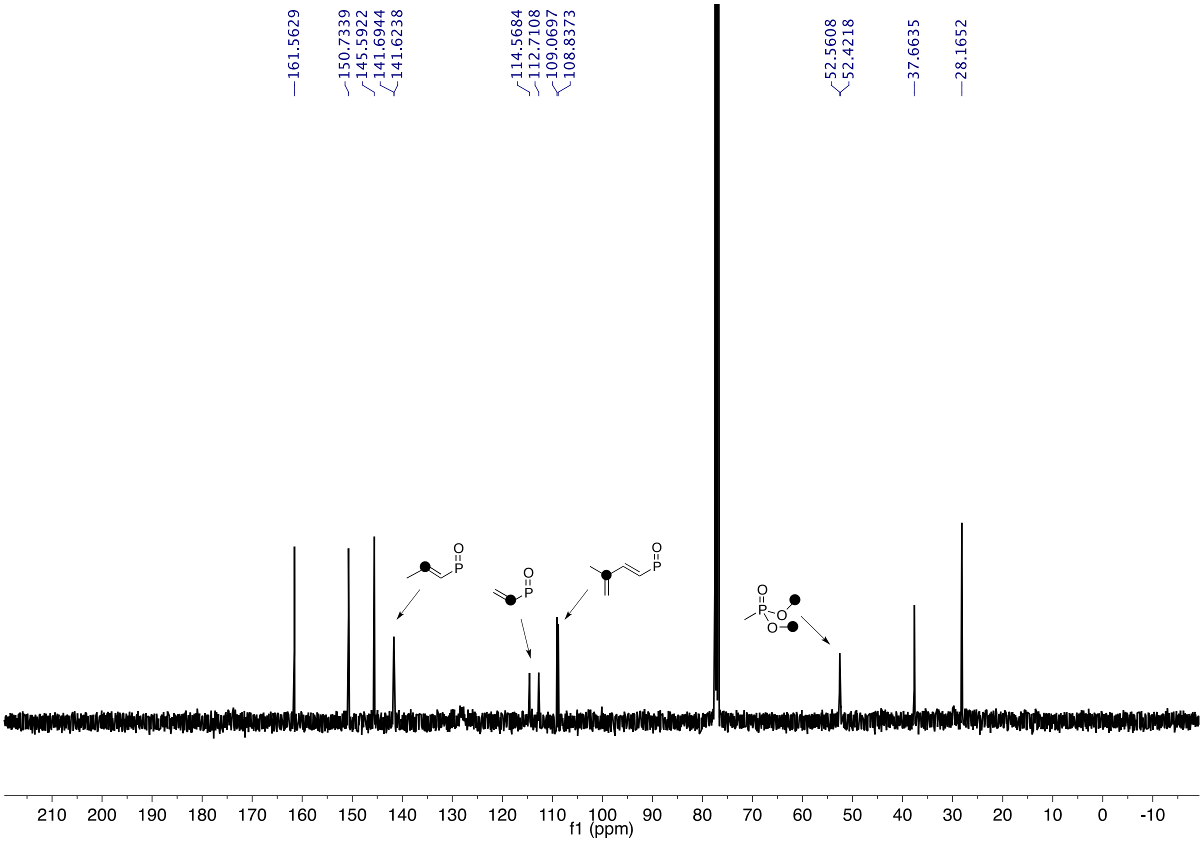
6.8631
3.7256
3.6979
3.4657
3.3635
O
O
N
P
OMe
OMe
O
N
3h
1.0042
1.3841
1.0938
6.0748
3.0161
2.9180
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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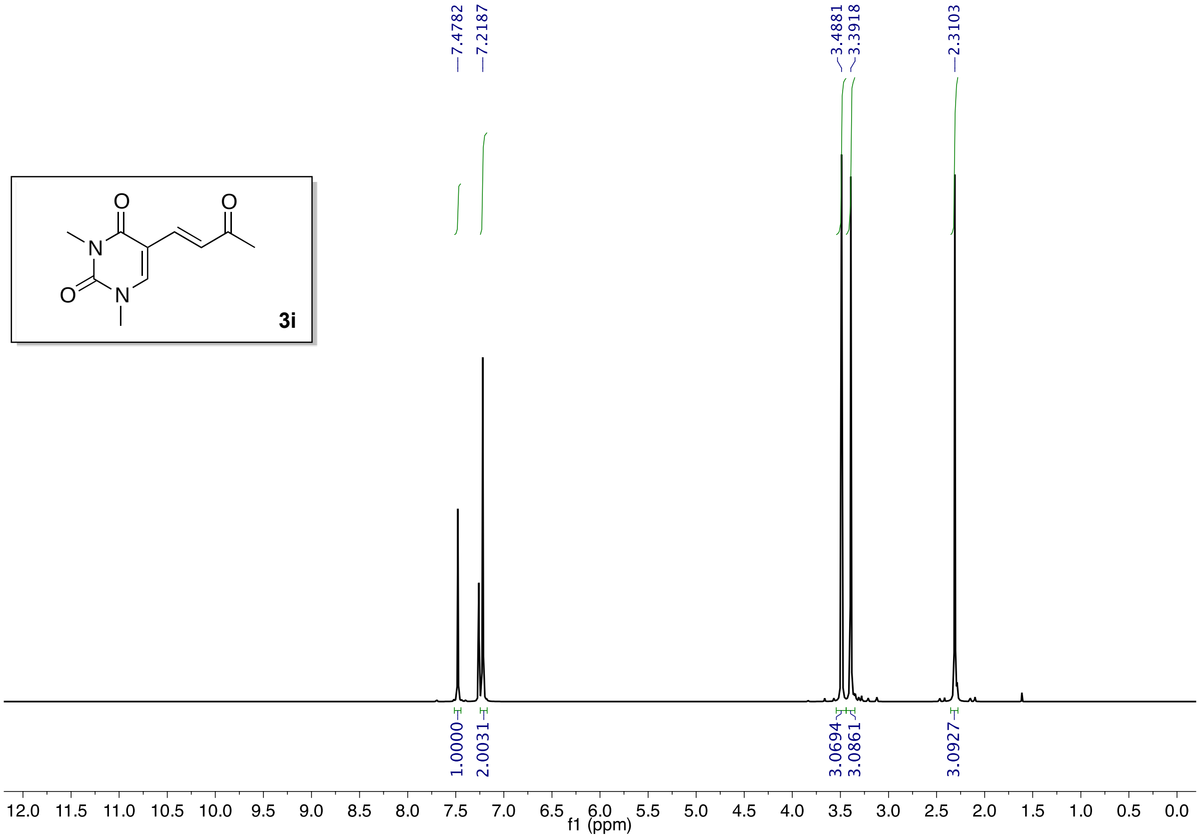
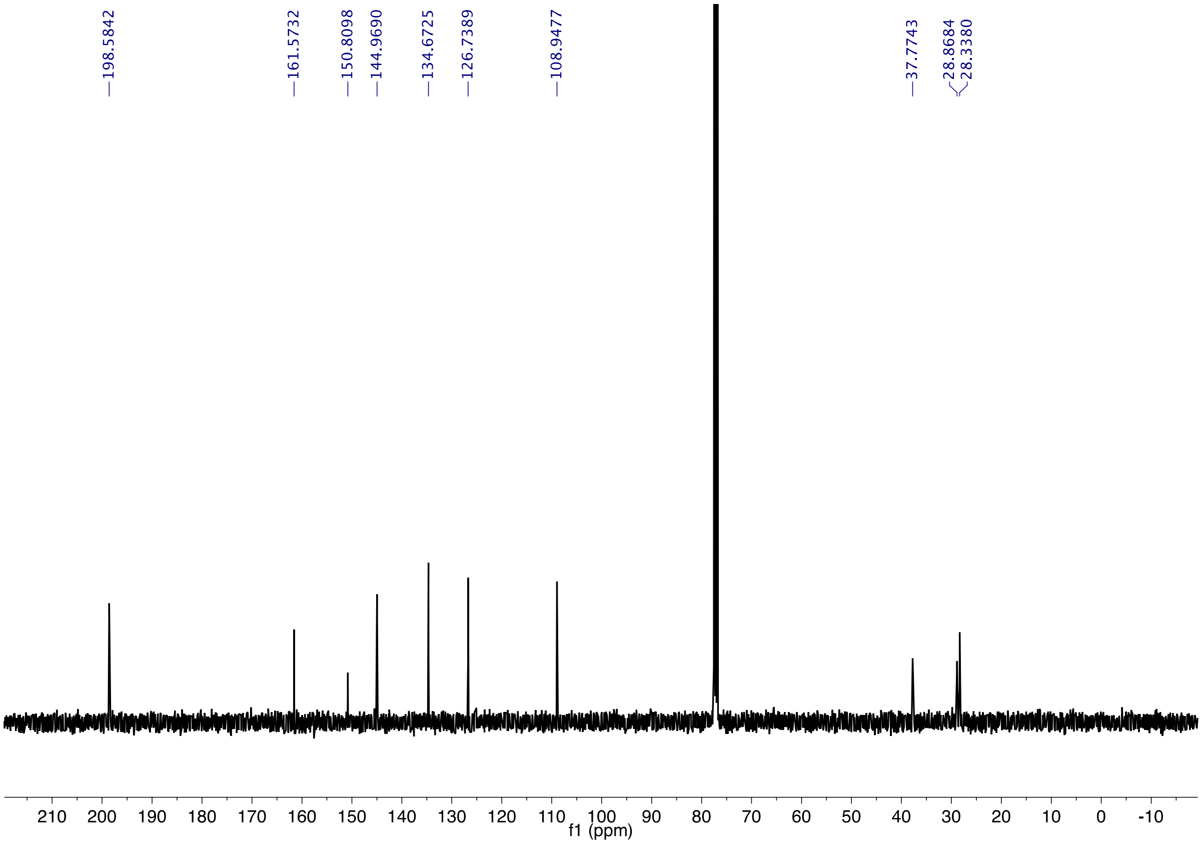
145.5922
141.6944
141.6238
114.5684
112.7108
109.0697
108.8373
52.5608
52.4218
37.6635
28.1652
O
P
O
P
O
P
O
P
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.4782
7.2187
3.4881
3.3918
2.3103
3i
1.0000
2.0031
3.0694
3.0861
3.0927
12.0 11.5 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)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144.9690
134.6725
126.7389
108.9477
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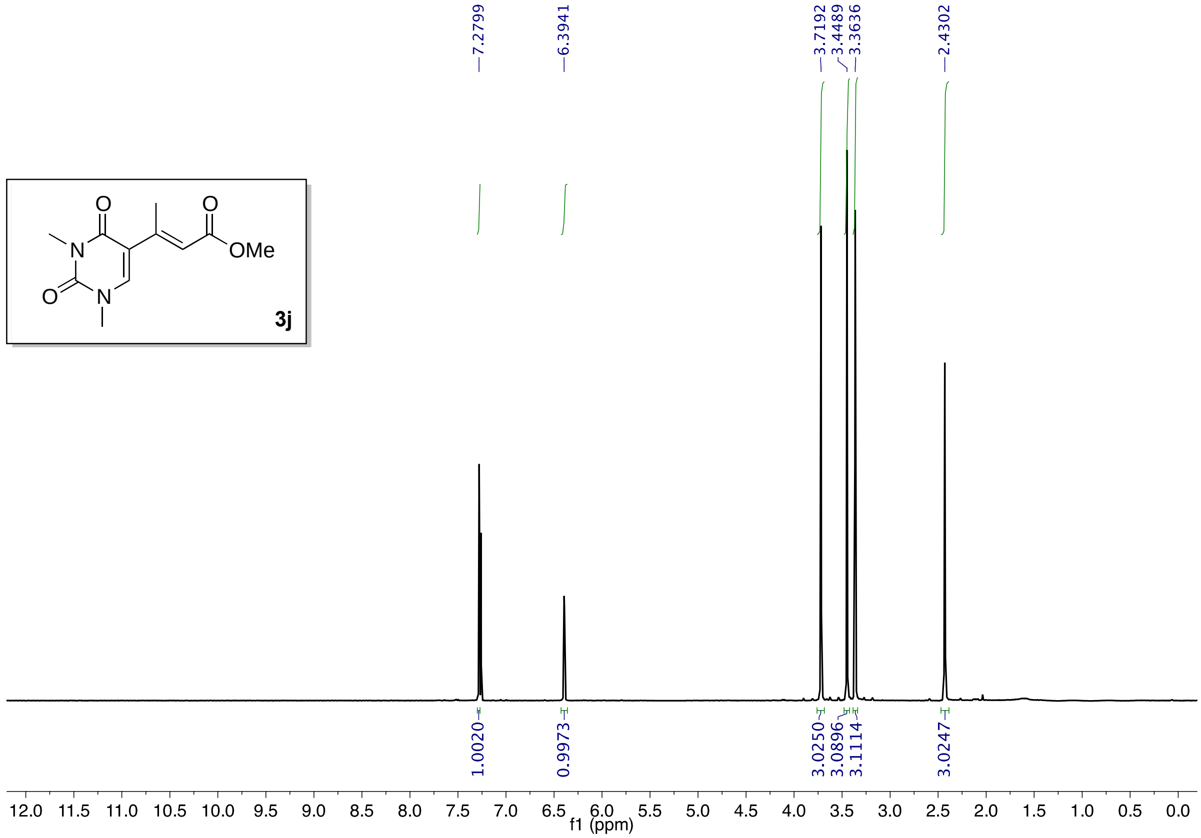
28.8684
28.3380
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.2799
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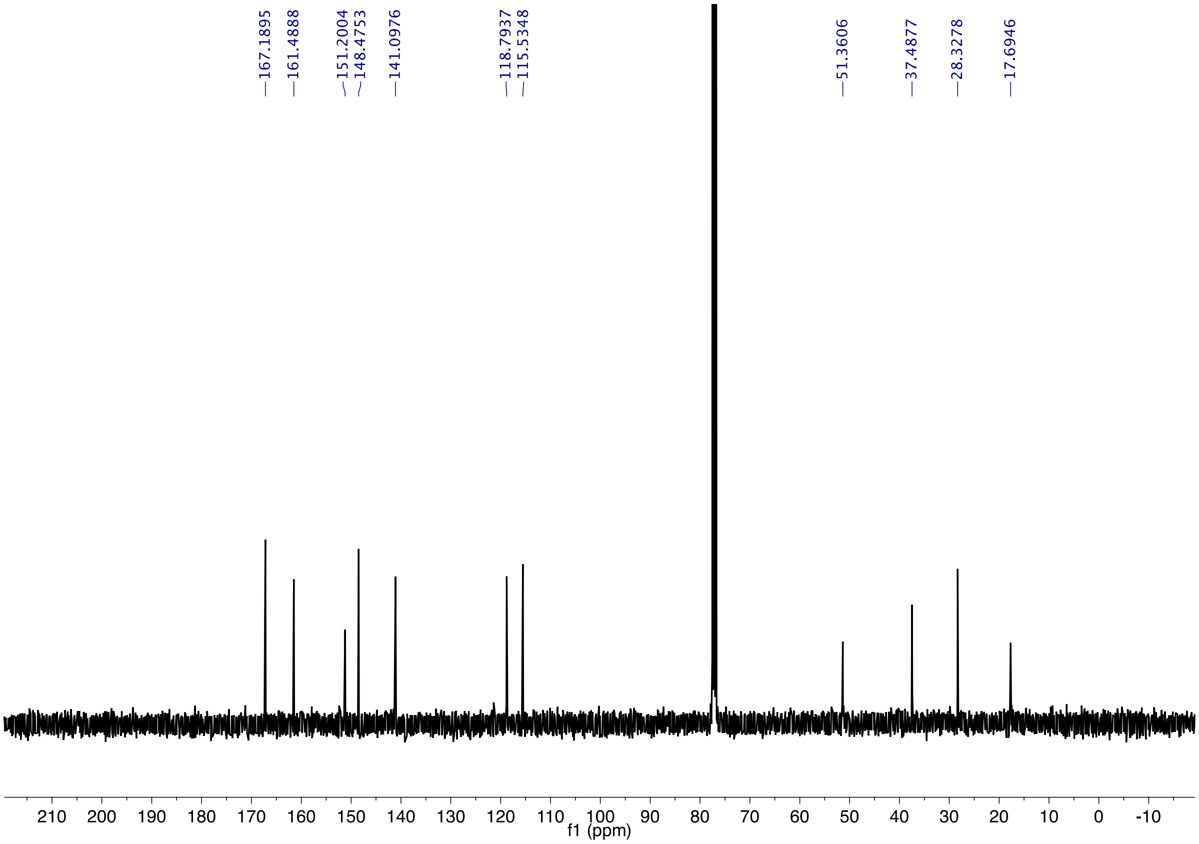
3.7192
3.4489
3.3636
2.4302
O
O
N
OMe
O
N
3j
1.0020
0.9973
3.0250
3.0896
3.1114
3.0247
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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148.4753
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118.7937
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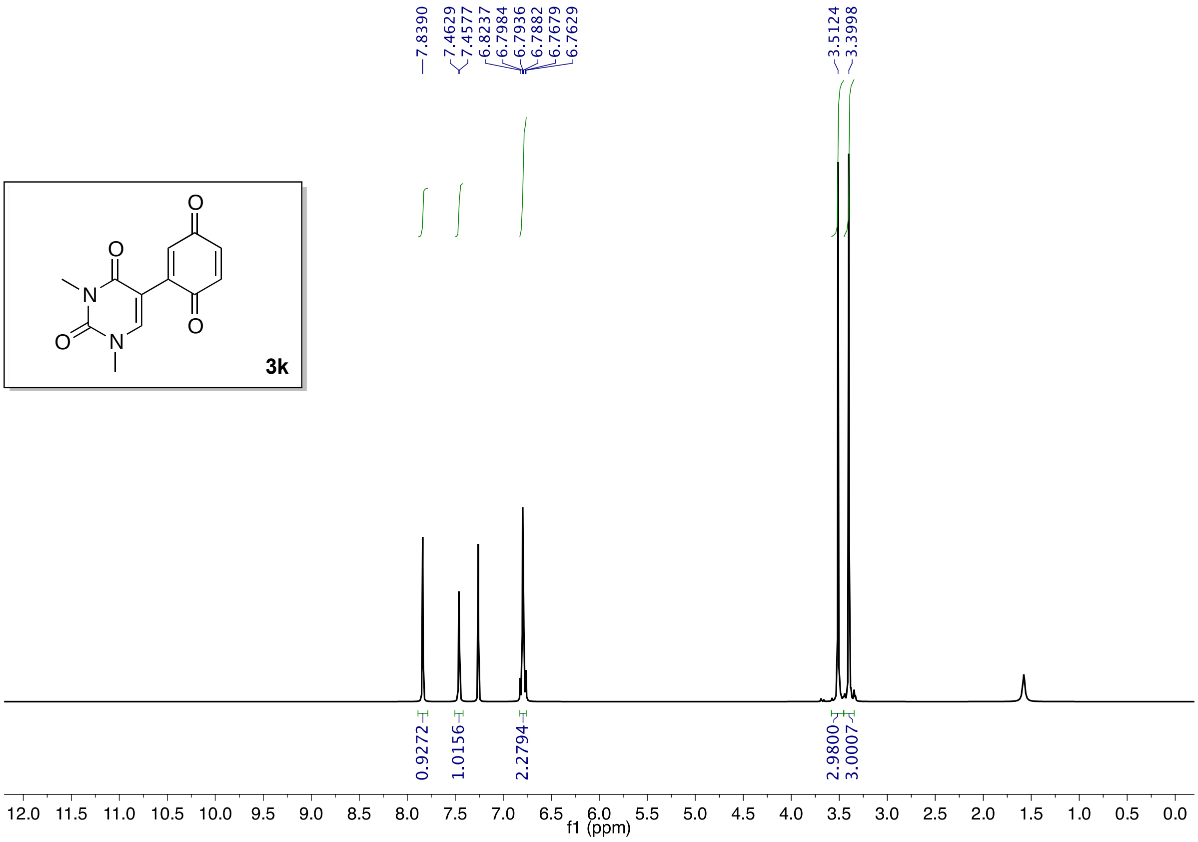
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3k
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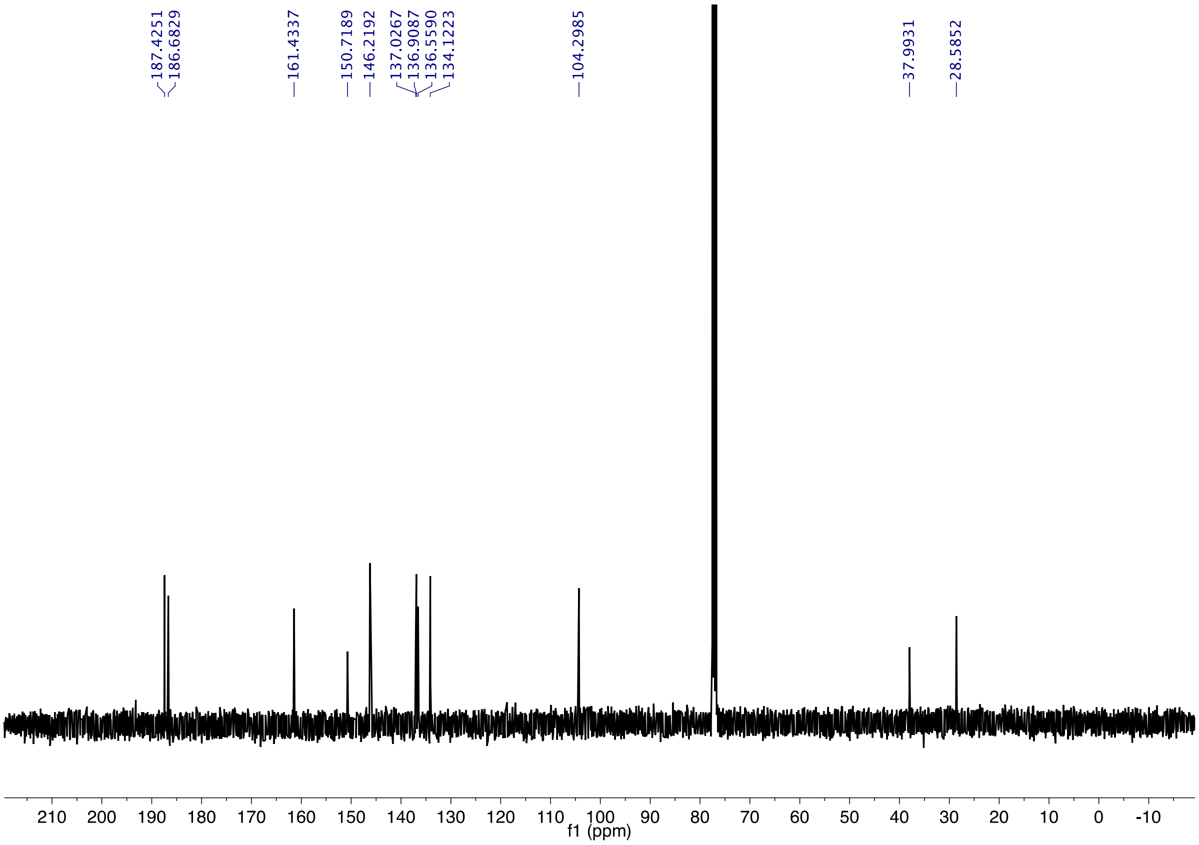
7.4629
7.4577
6.8237
6.7984
6.7936
6.7882
6.7679
6.7629
3.5124
3.3998
0.9272
1.0156
2.2794
2.9800
3.0007
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


187.4251
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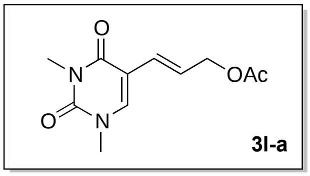
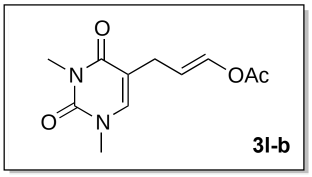
150.7189
146.2192
137.0267
136.9087
136.5590
134.1223
104.2985
37.9931
28.5852
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
N
O
N
OAc

3l-a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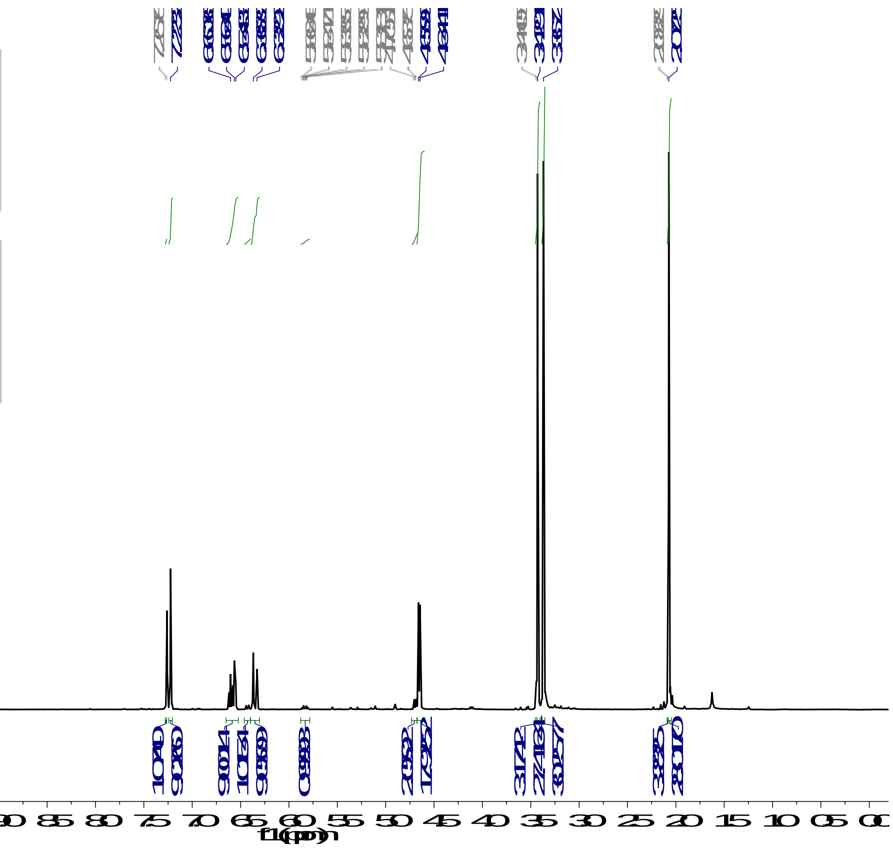
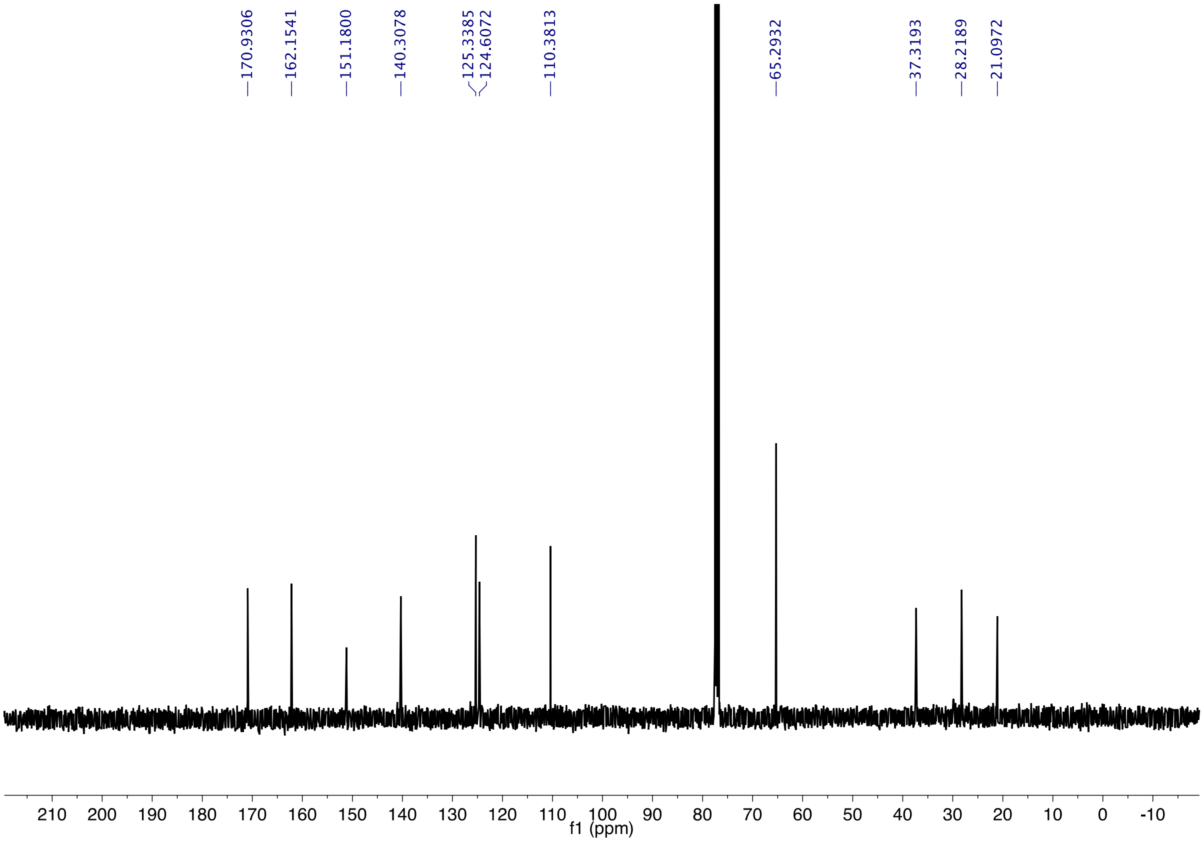
N
O
N
OAc

3l-b


f1 (ppm)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151.1800
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110.3813
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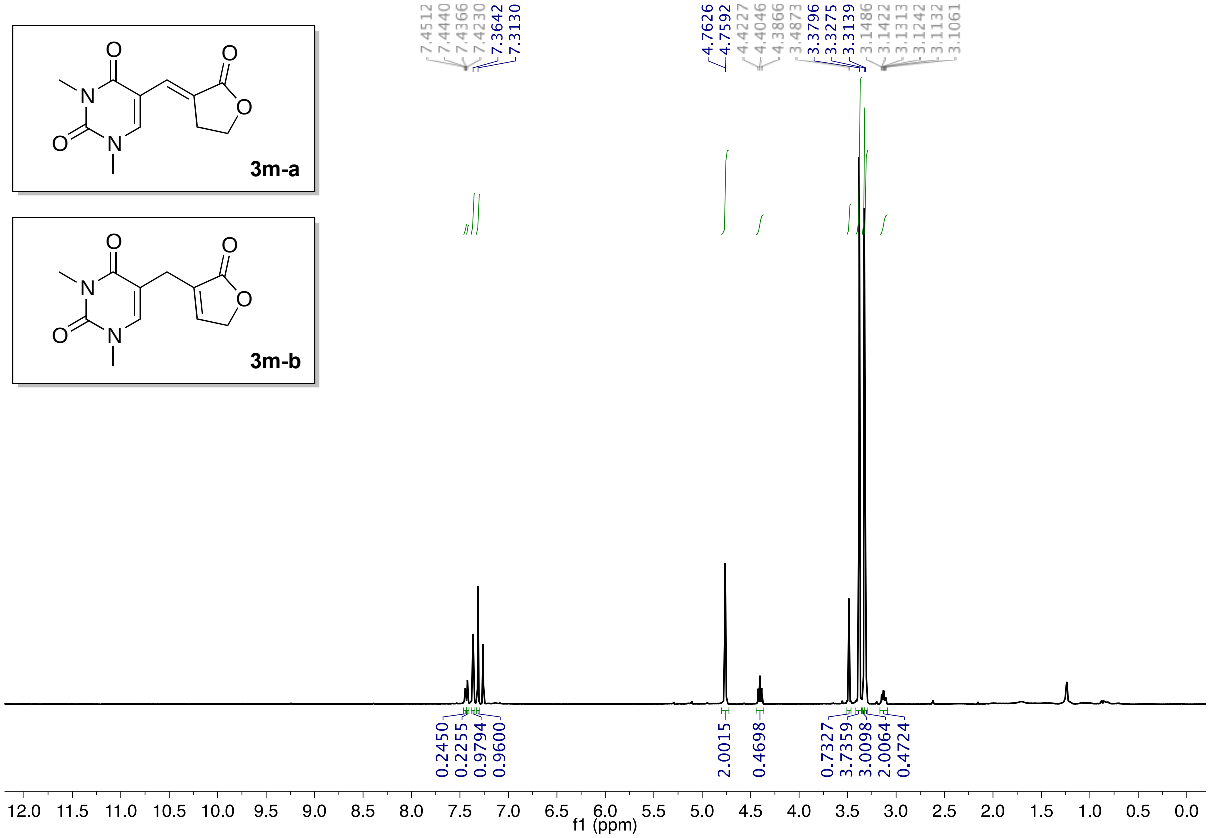
37.3193
28.2189
21.0972
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3m-a

3m-b

7.4512
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7.4230
7.3642
7.3130
4.7626
4.7592
4.4227
4.4046
4.3866
3.4873
3.3796
3.3275
3.3139
3.1486
3.1422
3.1313
3.1242
3.1132
3.1061
0.2450
0.2255
0.9794
0.9600
2.0015
0.4698
0.7327
3.7359
3.0098
2.0064
0.4724
12.0
11.5
11.0
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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
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1.0
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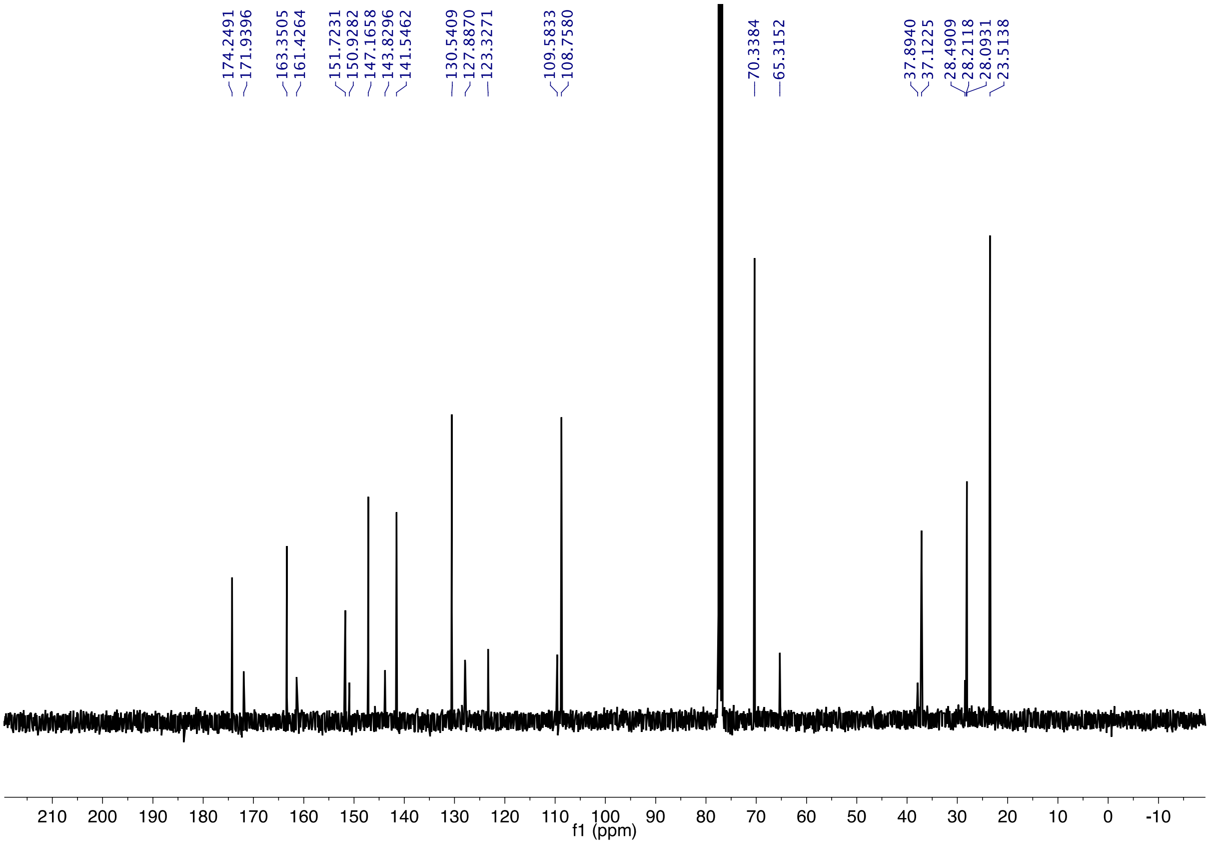
0.0
f1 (ppm)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150.9282
147.1658
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127.8870
123.3271
109.5833
108.7580
70.3384
65.3152
37.8940
37.1225
28.4909
28.2118
28.0931
23.5138
210
200
190
180
170
160
150
140
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120
110
100
90
80
70
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50
40
30
20
10
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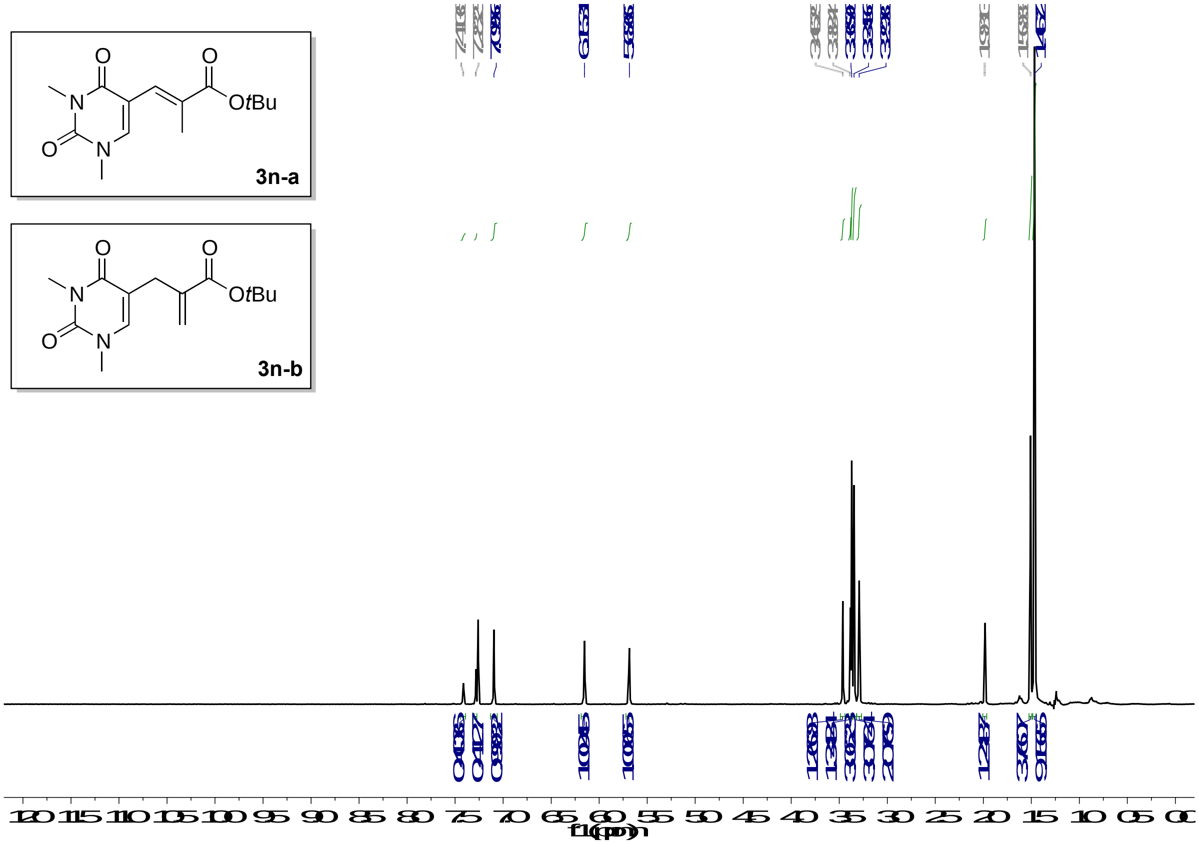
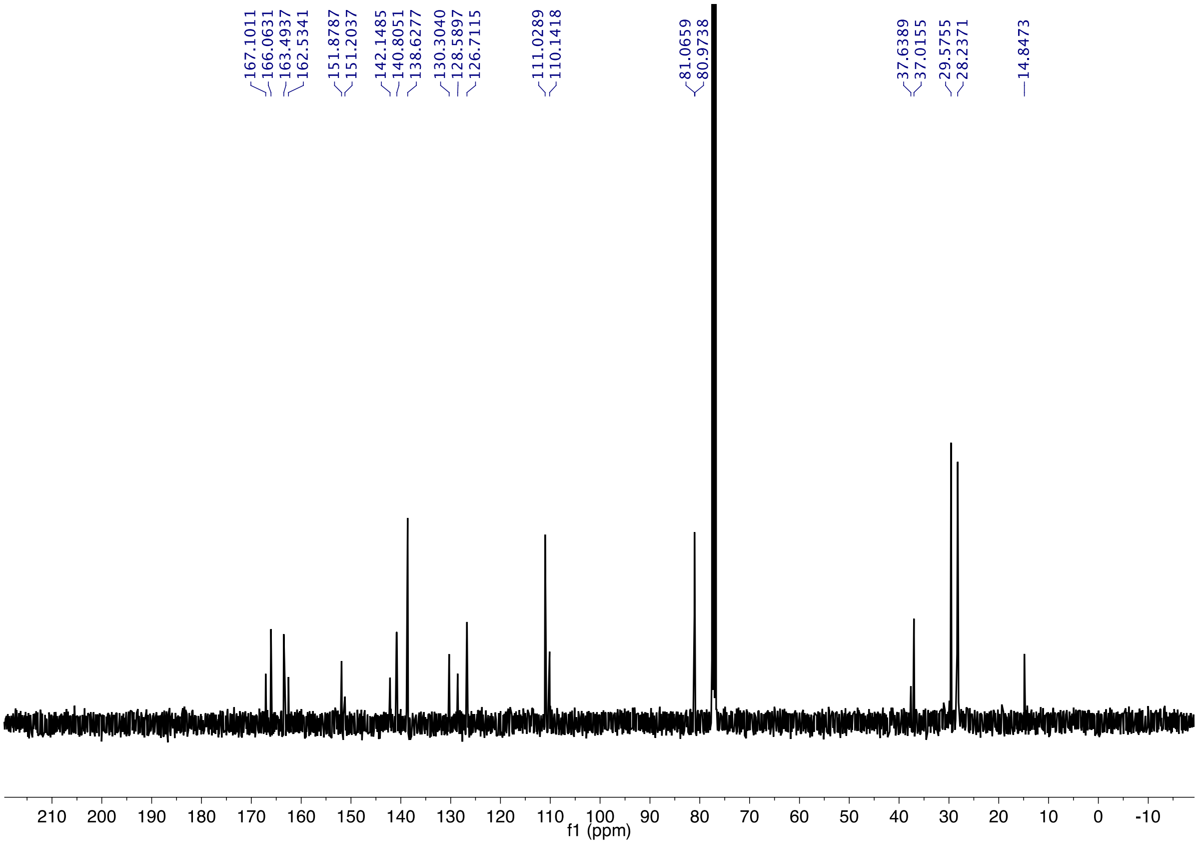
-10
f1 (ppm)



3n-a

3n-b

O
O
N
N
OtBu
O
f1 (ppm)



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162.5341
151.8787
151.2037
142.1485
140.8051
138.6277
130.3040
128.5897
126.7115
111.0289
110.1418
81.0659
80.9738
37.6389
37.0155
29.5755
28.2371
14.8473
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200
190
180
170
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100
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80
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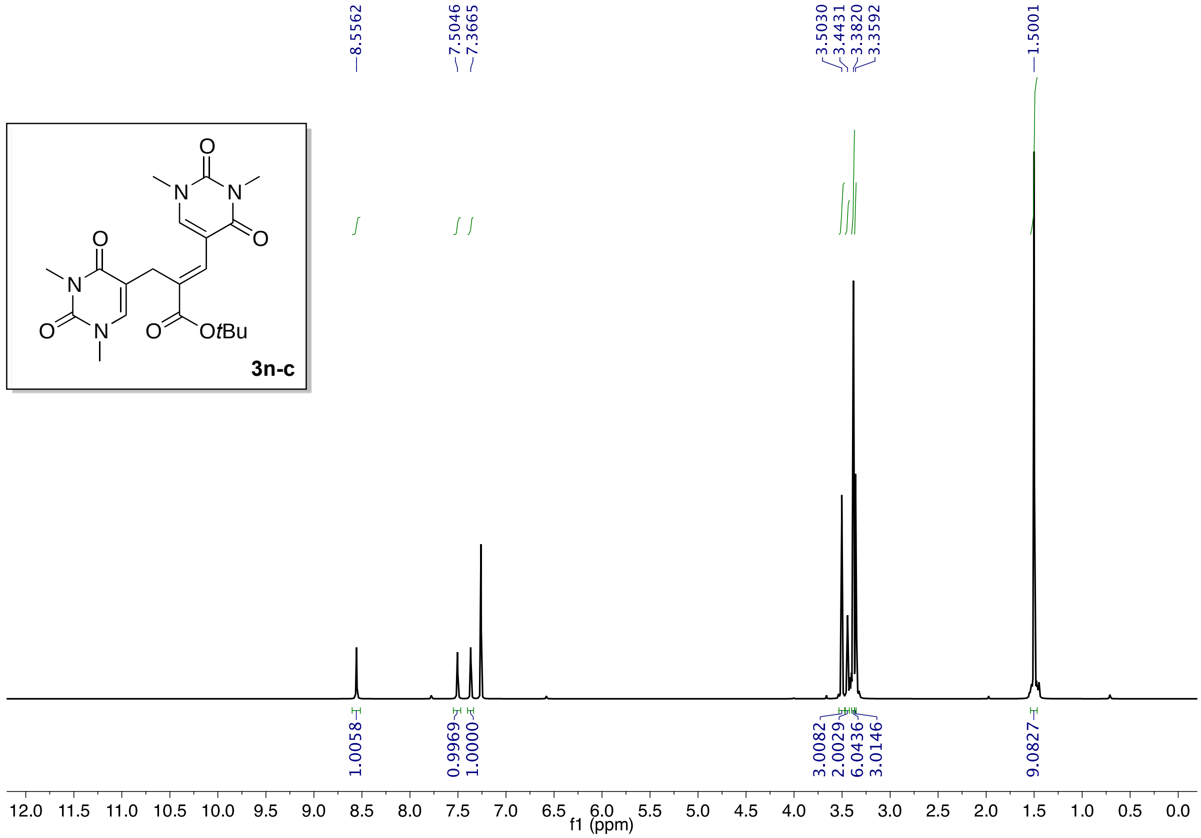
40
30
20
10
0
-10
f1 (ppm)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7.5046
7.3665
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3.4431
3.3820
3.3592
1.5001
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O
O
N
O
N
O
O*t*Bu
3n-c
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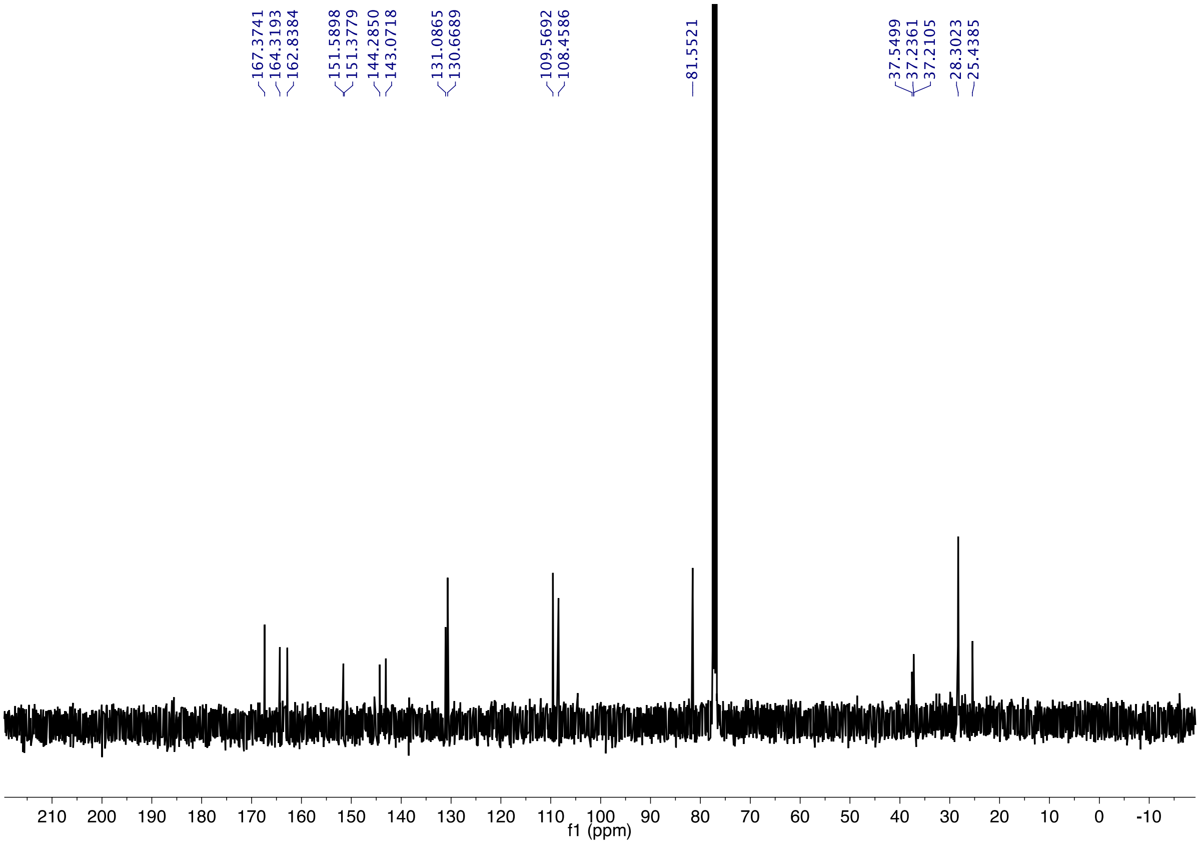
0.9969
1.0000
3.0082
2.0029
6.0436
3.0146
9.0827
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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162.8384
151.5898
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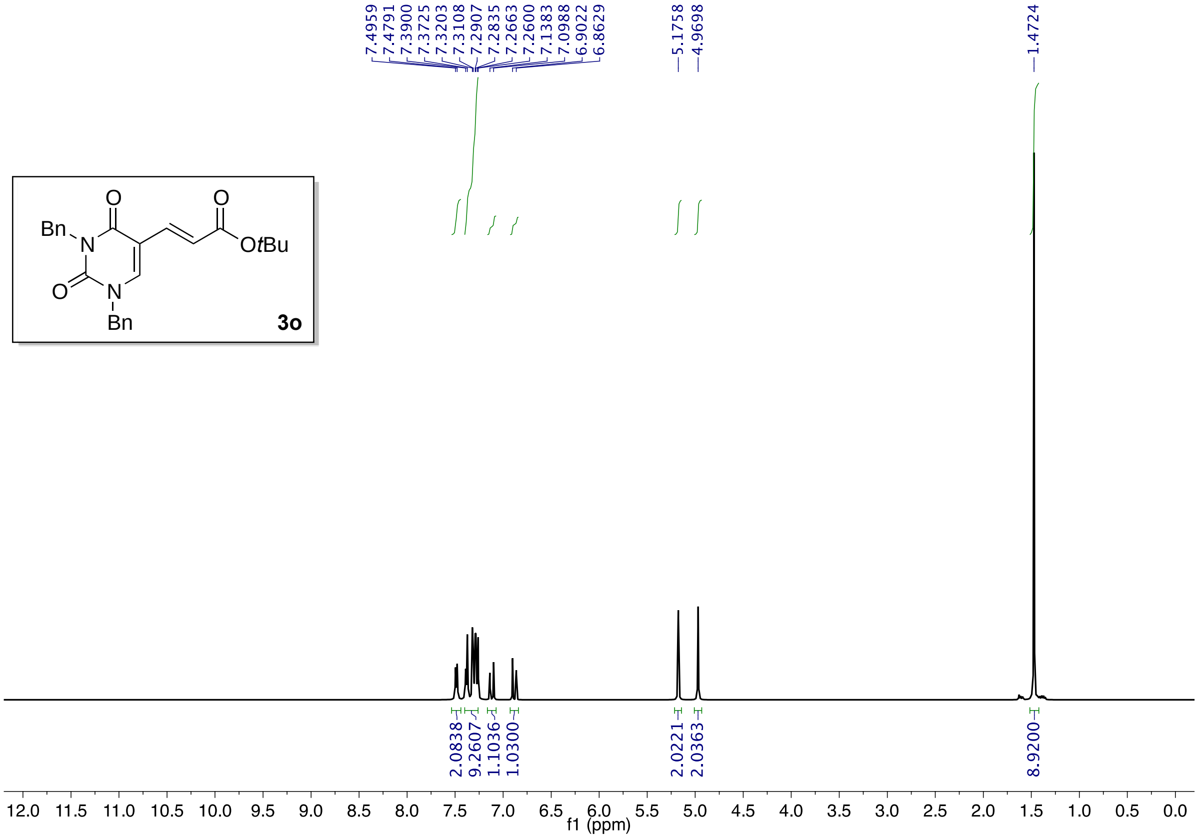
143.0718
131.0865
130.6689
109.5692
108.4586
81.5521
37.5499
37.2361
37.2105
28.3023
25.4385
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.2907
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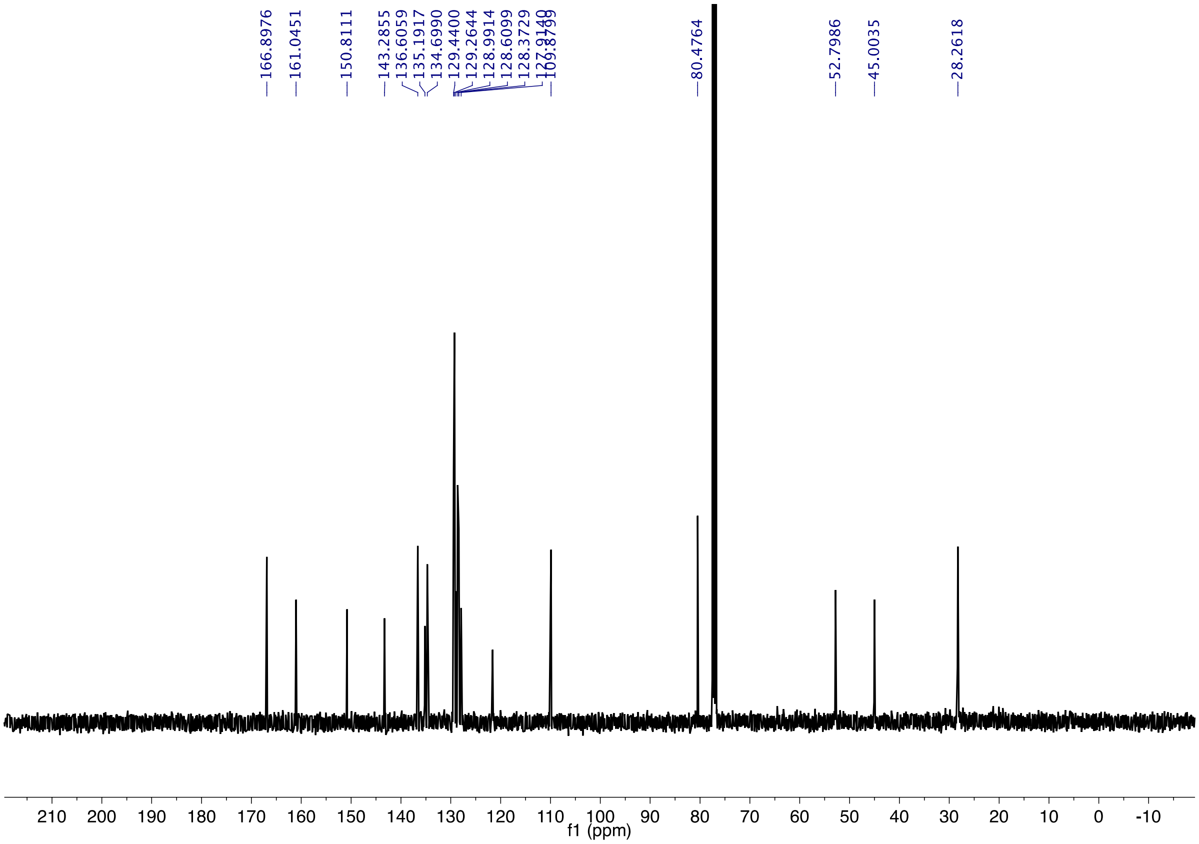
7.2600
7.1383
7.0988
6.9022
6.8629
5.1758
4.9698
1.4724
Bn
N
O
O
OtBu
O
N
Bn
3o
2.0838
9.2607
1.1036
1.0300
2.0221
2.0363
8.9200
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.6990
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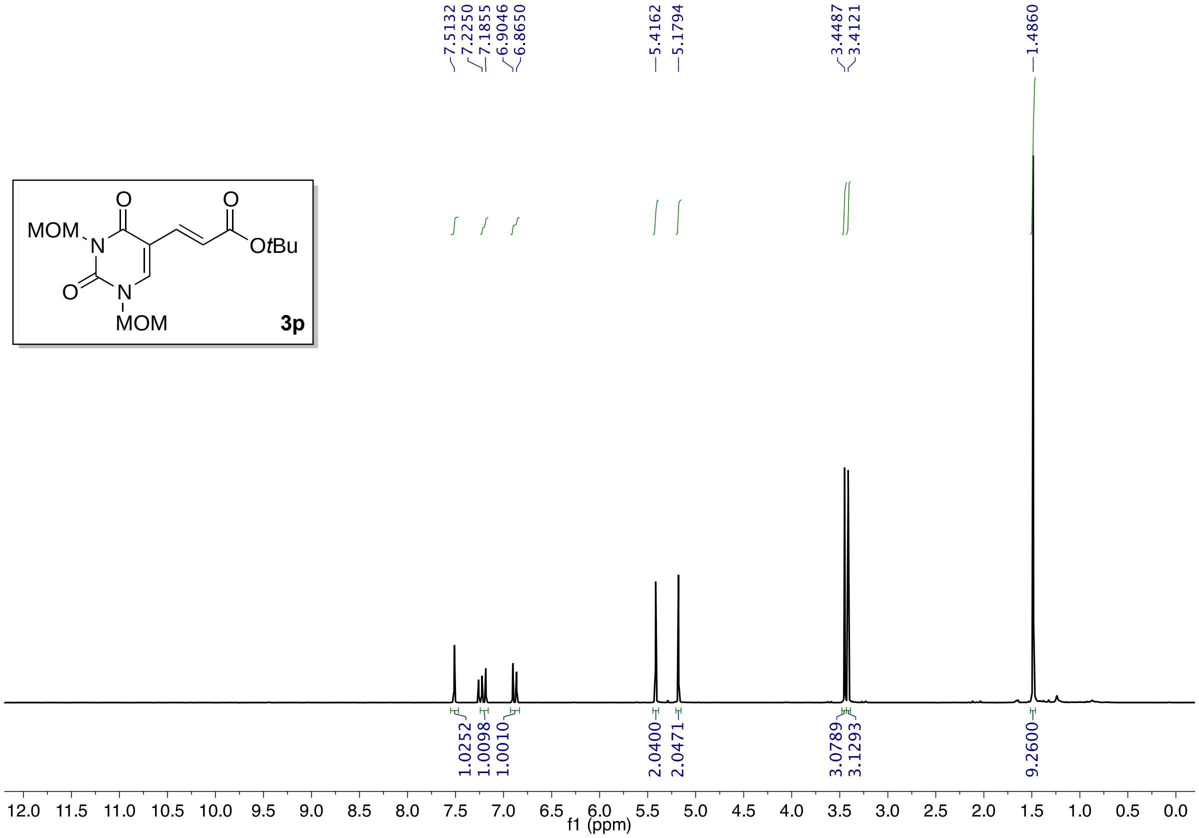
129.2644
128.9914
128.6099
128.3729
127.9140
109.8799
80.4764
52.7986
45.0035
28.2618
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.1855
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6.8650
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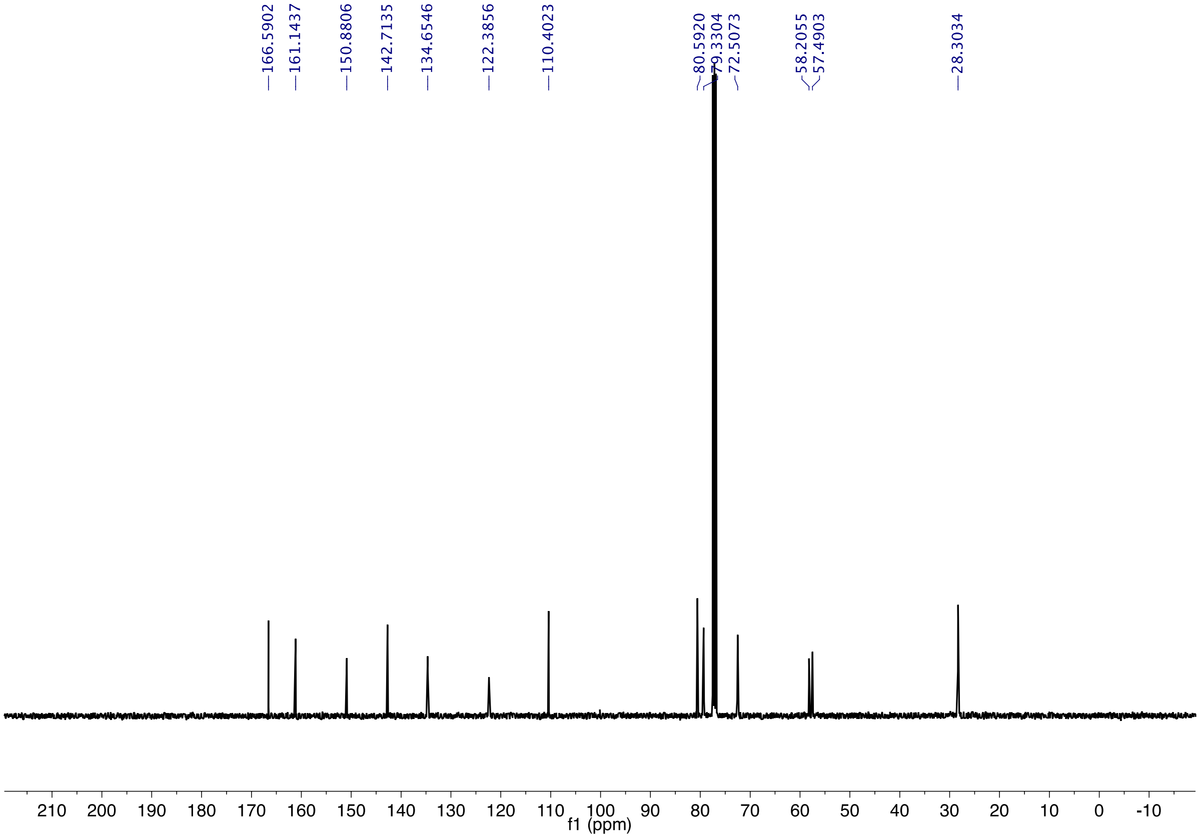
5.1794
3.4487
3.4121
1.4860
MOM
O
O
N
OtBu
O
N
MOM
3p
1.0252
1.0098
1.0010
2.0400
2.0471
3.0789
3.1293
9.2600
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.6546
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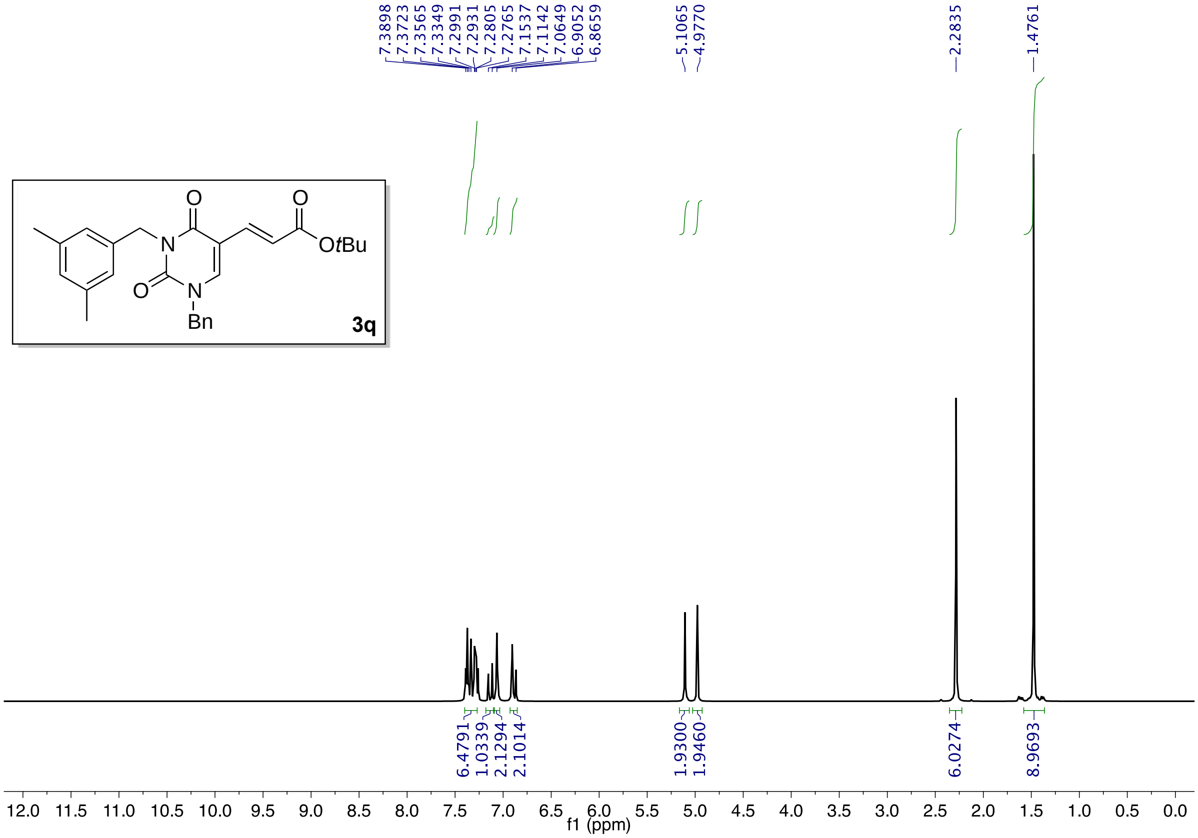
110.4023
80.5920
79.3304
72.5073
58.2055
57.4903
28.3034
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
N
OtBu
O
N
Bn

3q

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7.3565
7.3349
7.2991
7.2931
7.2805
7.2765
7.1537
7.1142
7.0649
6.9052
6.8659
5.1065
4.9770
2.2835
1.4761
6.4791
1.0339
2.1294
2.1014
1.9300
1.9460
6.0274
8.9693
12.0
11.5
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
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1.0
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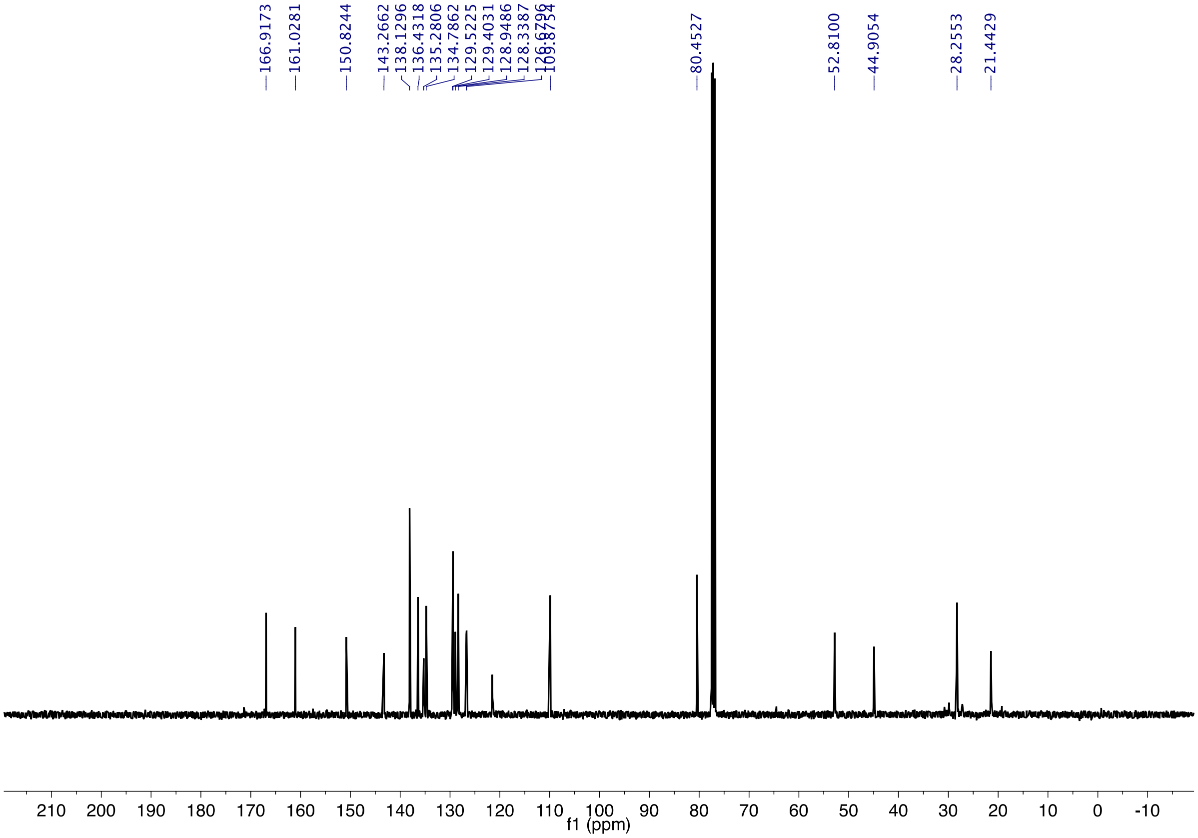
0.0
f1 (ppm)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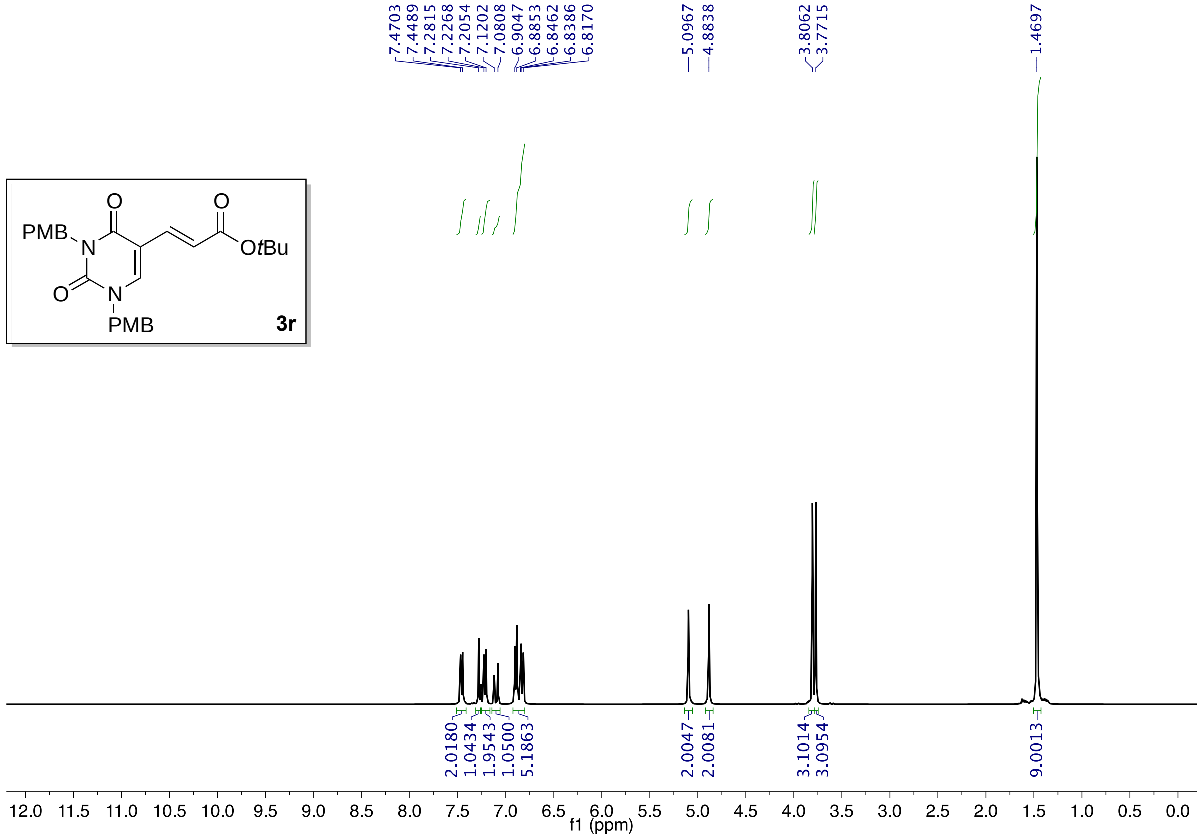
128.3387
126.6796
109.8754
80.4527
52.8100
44.9054
28.2553
21.4429
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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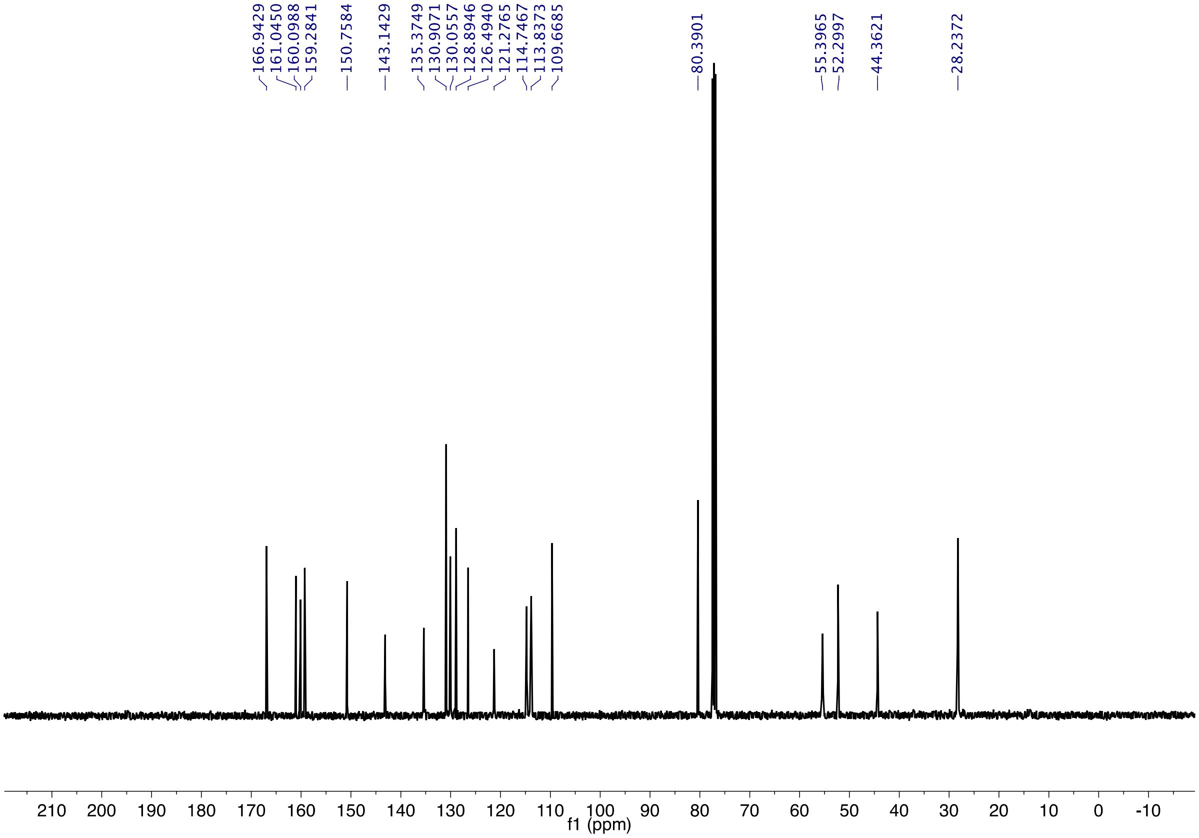
6.8386
6.8170
5.0967
4.8838
3.8062
3.7715
1.4697
PMB
N
O
O
OtBu
O
N
PMB
3r
2.0180
1.0434
1.9543
1.0500
5.1863
2.0047
2.0081
3.1014
3.0954
9.0013
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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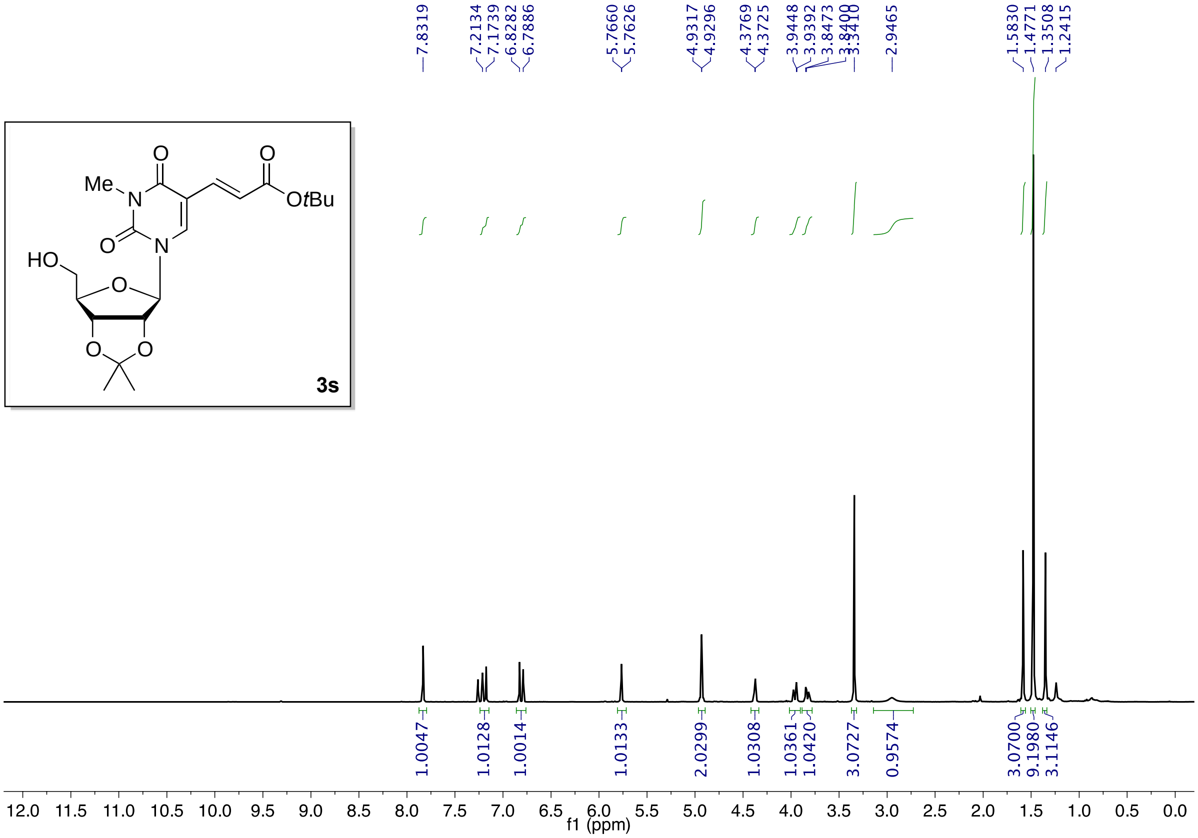
126.4940
121.2765
114.7467
113.8373
109.6685
80.3901
55.3965
52.2997
44.3621
28.2372
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.1739
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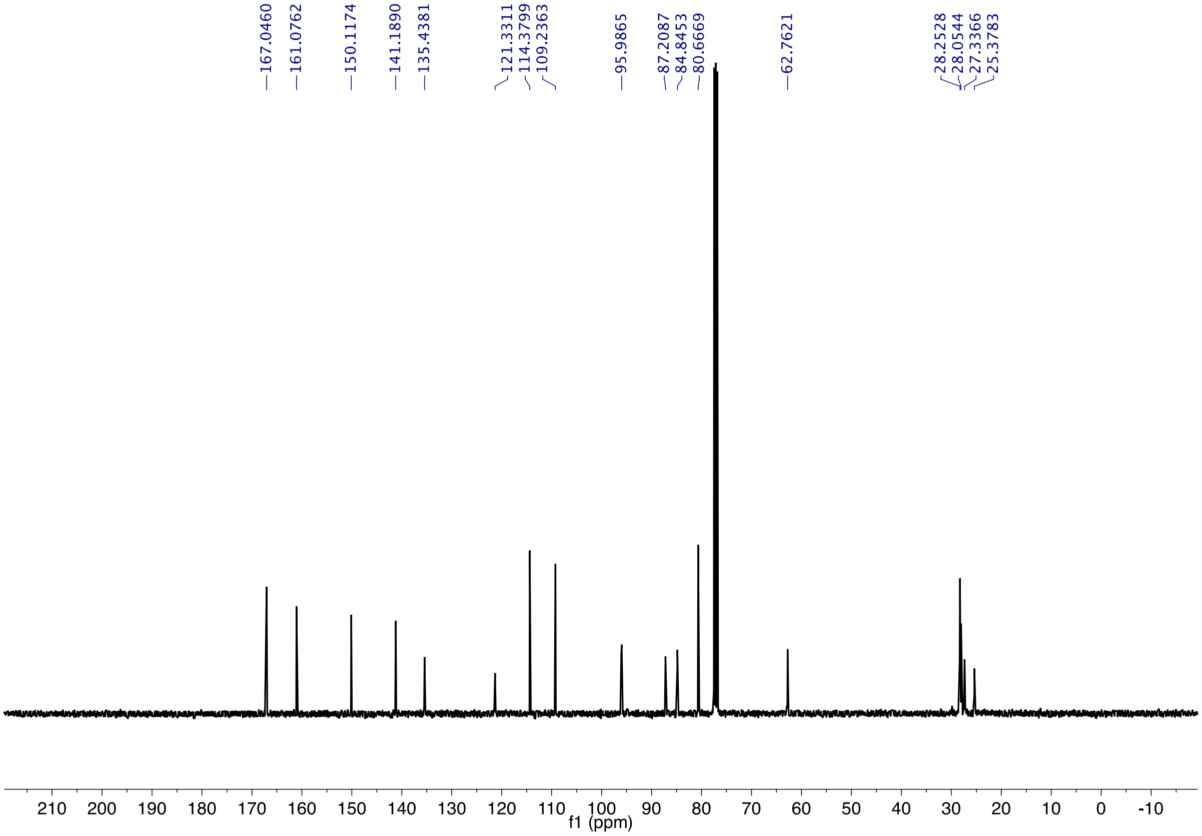
4.9296
4.3769
4.3725
3.9448
3.9392
3.8473
3.8400
3.3410
2.9465
1.5830
1.4771
1.3508
1.2415
O
O
Me
N
O*t*Bu
O
N
HO
O
O
O
1.0047
1.0128
1.0014
1.0133
2.0299
1.0308
1.0361
1.0420
3.0727
0.9574
3.0700
9.1980
3.1146
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3s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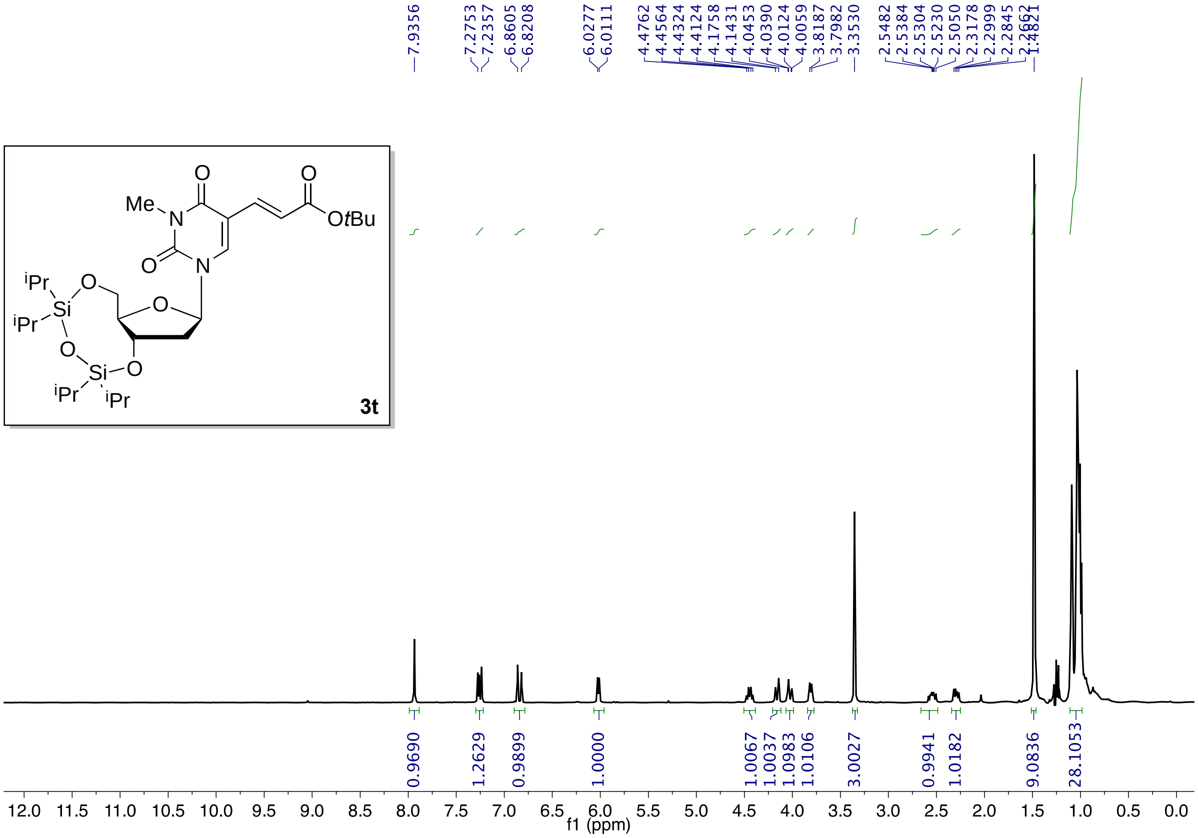
87.2087
84.8453
80.6669
62.7621
28.2528
28.0544
27.3366
25.3783
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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4.4564
4.4324
4.4124
4.1758
4.1431
4.0453
4.0390
4.0124
4.0059
3.8187
3.7982
3.3530
2.5482
2.5384
2.5304
2.5230
2.5050
2.3178
2.2999
2.2845
2.2662
1.4821
Me
N
O
OtBu
N
O
ⁱPr
Si
ⁱPr
O
Si
ⁱPr
ⁱPr
3t
0.9690
1.2629
0.9899
1.0000
1.0067
1.0037
1.0983
1.0106
3.0027
0.9941
1.0182
9.0836
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12.0
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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
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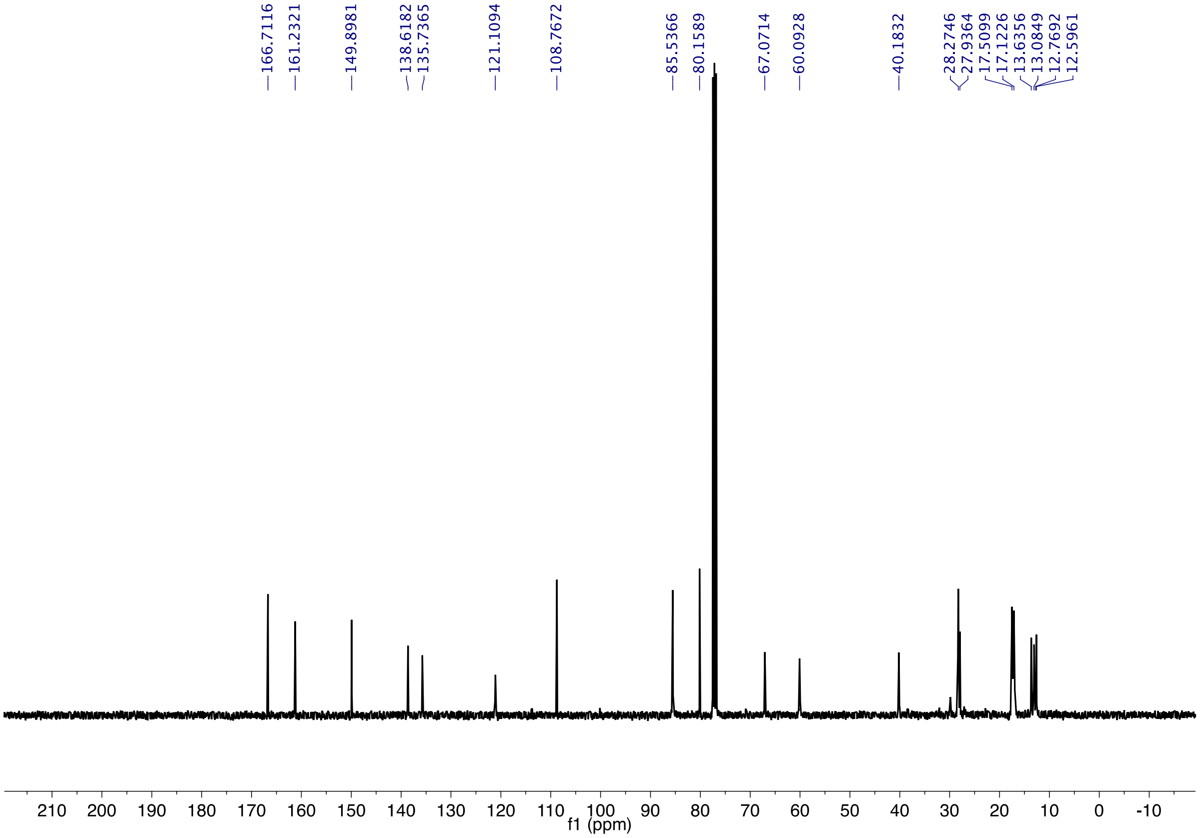
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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60.0928
40.1832
28.2746
27.9364
17.5099
17.1226
13.6356
13.0849
12.7692
12.5961
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)