Supporting Information

Photooxygenation of 2-Propargylfurans: a Path to Structurally Diverse Nitrogen-Containing 5-Membered Rings

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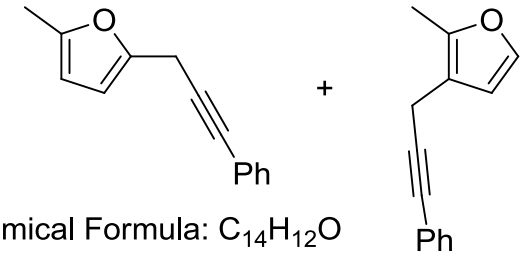
General Information

Analytical thin layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF234) using UV light as the visualizing agent and a solution of phosphomolybdic acid in ethanol as the developing agent. Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 mm). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. NMR spectra were recorded at 298 K on AM250, AV300 or AV360 MHz Bruker spectrometer. Mass spectra were recorded on MicrOTOFq Bruker spectrometer by electrospray ionization. Melting points were determined using a Stuart melting point apparatus SMP30. Infrared spectra were recorded on a FTIR spectrometer (Perkin-Elmer spectrum one, NaCl pellets or Bruker Vertex 70 ATR Pike Germanium) and are reported in cm^{-1}. The gas bag used for collecting oxygen and performing the photooxygenation reactions was purchased from Sigma-Aldrich (Merck) (reference Z186740). Precursors **1a**,[1] **1e**,[2] **1f**,[3] **1i**,[4] **1j**,[5] **1k**[6] and **1l**[7] were prepared according to known procedures. Precursors **1b**, **1c** and **1d** were synthesized according to the procedure reported in reference 1.

[1] C. Li, J. Wang, *J. Org. Chem.* **2007**, *72*, 7431-7434.
[2] F. Ye, X. Ma, Q. Xiao, H. Li, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 5742-5745.
[3] Y. Masuyama, M. Hayashi, N. Suzuki, *Eur. J. Org. Chem.* **2013**, 2914-2921.
[4] Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai, S. Uemura, *J. Am. Chem. Soc.* **2012**, *124*, 11846-11847.
[5] J. S. Yadav, B. V. Subba Reddy, K. V. Raghavendra Rao, G. G. K. S. Kumar, *Synthesis* **2007**, 3205-3210.
[6] M. Lin, L. Hao, X.-tao Liu, Q.-z. Chen, F. Wu, P. Yan, S.-x. Xu, X.-l. Che, J.-j. Wen, Z.-p. Zhan, *Synlett* 2011, 665-670.
[7] C. C. Silveira, S. R. Mendes, G. M. Martins, *Tetrahedron Lett.* **2012**, *53*, 1567-1570.

Characterizations of Compounds

2-methyl-5-(3-phenylprop-2-yn-1-yl)furan (1b)



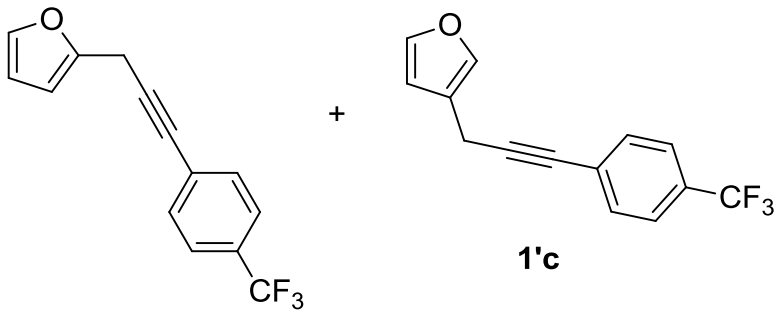
Chemical Formula: $C_{14}H_{12}O$
Exact Mass: 196.0888

1'b

To 2-methylfuran (28.4 mL) were added 3-phenylprop-2-yn-1-yl 2,2,2-trichloroethanecarboximidate (1 g, 3.61 mmol, 1 equiv) and $BF_3{\cdot}OEt_2$ (0.13 mL, 1.08 mmol, 0.3 equiv). The reaction mixture was stirred for 5 min at room temperature and, then, the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography using petroleum ether as eluent to provide compound **1b** (along with **1'b**, ratio 2.8:1) as a yellow oil (210 mg, 30% yield).

1b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.43 (m, 2H), 7.35–7.25 (m, 3H), 6.17 (d, *J* = 2.4 Hz, 1H), 5.95 (d, *J* = 2.1 Hz, 1H), 3.81 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 151.4, 148.4, 140.1, 131.8, 128.3, 128.0, 107.0, 106.4, 85.1, 81.8, 19.5, 13.6; IR (neat) 3055, 2921, 2885, 2242, 1766, 1664, 1598, 1568, 1513, 1490, 1442, 1422, 1384, 1313, 1218, 1175, 1138, 1070, 1020 cm^{-1}.

2-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)furan (1c)



Chemical Formula: $C_{14}H_9F_3O$
Exact Mass: 250.0605

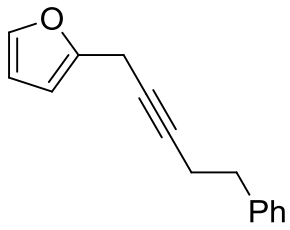
1'c

To furan (18.4 mL) were added 3-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl 2,2,2-trichloroethanecarboximidate (1 g, 2.90 mmol, 1 equiv) and $BF_3{\cdot}OEt_2$ (0.11 mL, 0.87 mmol, 0.3 equiv). The reaction mixture was stirred for 5 min at room temperature and, then, the solvent was removed

by rotary evaporation. The crude product was purified by flash column chromatography using petroleum ether as eluent to provide compound **1c** (along with **1'c**, ratio 10:1) as a yellow oil (225 mg, 31% yield).

1c: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.67–7.47 (m, 4H), 7.38 (d, *J* = 1.2 Hz, 1H), 6.36 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.31–6.21 (m, 1H), 3.85 (s, 2H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 149.8, 142.1, 132.1, 129.9 (q, *J* = 32.7 Hz), 125.3 (q, *J* = 3.7 Hz), 124.1 (q, J = 272.2 Hz), 110.7, 106.6, 87.4, 80.8, 19.6; IR (neat) 2941, 2898, 2885, 2874, 1616, 1506, 1405, 1322, 1166, 1125, 1105, 1067, 1018 cm^{-1}.

2-(5-phenylpent-2-yn-1-yl)furan (1d)

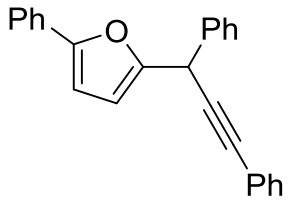


Chemical Formula: $C_{15}H_{14}O$
Exact Mass: 210.1045

To furan (29.2 mL) were added 5-phenylpent-2-yn-1-yl 2,2,2-trichloroethanecarboximidate (1.4 g, 4.6 mmol, 1 equiv) and $BF_3{\cdot}OEt_2$ (0.17 mL, 1.38 mmol, 0.3 equiv). The reaction mixture was stirred for 5 min at room temperature and, then, the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography using petroleum ether as eluent to provide compound **1d** as a yellow oil (290 mg, 30% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.43–7.11 (m, 6H), 6.36 (s, 1H), 6.18 (d, *J* = 0.9 Hz, 1H), 3.61 (s, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.56 (dd, *J* = 10.2, 4.5 Hz, 2H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 151.2, 141.6, 140.9, 128.6, 128.4, 126.3, 110.5, 106.0, 81.3, 75.7, 35.3, 21.0, 18.8; IR (neat) 3062, 3027, 2928, 2857, 1602, 1505, 1496, 1454, 1429, 1383, 1340, 1313, 1255, 1178, 1144, 1073, 1030, 1007 cm^{-1}.

2-(1,3-diphenylprop-2-yn-1-yl)-5-phenylfuran (1g)



Chemical Formula: $C_{25}H_{18}O$
Exact Mass: 334,1358

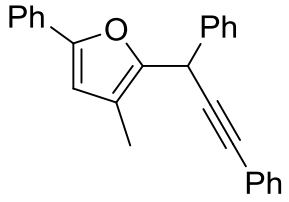
To a solution of 2-phenylfuran (200 mg, 1.38 mmol, 3 equiv) in acetonitrile (0.5 M, 1 mL) were added 1,3-diphenylprop-2-yn-1-ol (96 mg, 0.046 mmol, 1 equiv) and bismuth trichloride (15 mg, 0.0046 mmol, 10 mol%). The reaction mixture was stirred for 16 h at room temperature and, then, the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography using pentane as eluent to provide compound **1g** as an orange oil (130 mg, 84% yield).

^{13}C NMR (91 MHz, $CDCl_3$) δ 153.7, 153.5, 139.0, 131.9, 131.0, 128.8, 128.7, 128.4, 128.3, 128.0, 127.5, 127.3, 123.7, 123.3, 108.9, 105.9, 87.5, 84.2, 38.2; IR (neat) 2985, 2907, 1818, 1794, 1644, 1608, 1471, 1382, 1265, 1163, 1097 cm^{-1}.

Additional substrates tested:

The following substrates were also tested in the photooxygenation reaction to study the influence of the substitution at C3 and C4 of the furan, however, we observed only the decomposition of the precursors.

2-(1,3-diphenylprop-2-yn-1-yl)-3-methyl-5-phenylfuran (1m)

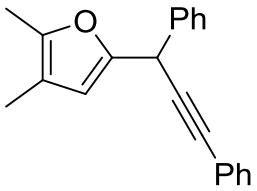


Chemical Formula: $C_{26}H_{20}O$
Exact Mass: 348.1514

To a solution of 4-methyl-2-phenylfuran[8] (161 mg, 1.02 mmol, 1 equiv) in DCM (0.1 M, 12 mL) were added 1,3-diphenylprop-2-yn-1-ol (212 mg, 1.02 mmol, 1 equiv), calcium(II) bis(trifluoromethanesulfonimide) (31 mg, 0.05 mmol, 5 mol%) and tetrabutylammonium hexafluorophosphate (20 mg, 0.05 mmol, 5 mol%). The solution was stirred at room temperature for 10 hours. The solvent was evaporated and the crude product was purified by flash column chromatography (Pentane) to provide compound **1m** as a yellow oil (199 mg, 56% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.54–7.37 (m, 6H), 7.29–7.08 (m, 9H), 6.39 (s, 1H), 5.31 (s, 1H), 2.03 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 152.0, 147.5, 140.4, 131.9, 131.1, 128.7 (2C), 128.4, 128.2, 127.6, 127.2, 127.1, 123.7, 123.5, 117.7, 109.2, 87.5, 84.1, 36.3, 10.3.

5-(1,3-diphenylprop-2-yn-1-yl)-2,3-dimethylfuran (1n)



Chemical Formula: $C_{21}H_{18}O$
Exact Mass: 286.1358

1n was prepared according a known procedure: Y. Nishibayashi, Y. Inada, M. Yoshikawa, M. Hidai, S. Uemura, *Angew. Chem. Int. Ed.* **2003**, *42*, 1495-1498.

General Procedure for the Photooxygenation of 2-Propargylfurans 1

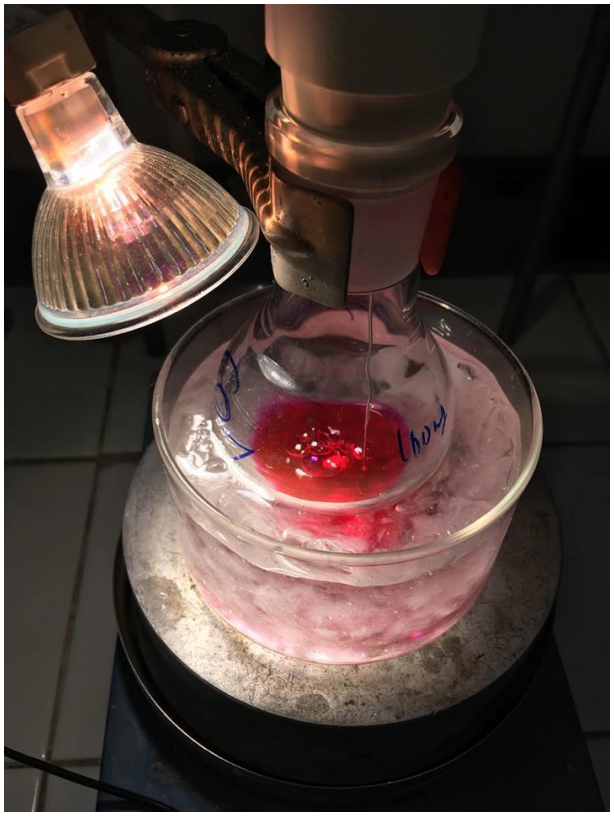
To a round-bottom flask was added 2-propargylfuran **1** (1 equiv), rose Bengal (10 mol%) and methanol (5.10^{-3} M) to give a pink red solution. The solution was cooled with an ice bath. Then, the reaction medium was gently bubbled with dioxygen, while being irradiated with a Xenon lamp (12 V, 35 W). After completion of the reaction (15 min) (step 1), the ice bath was removed and Me_2S (4 equiv) was added to the reaction mixture. After completion of the reduction (1 h) (step 2), amine **2** (2 equiv) was added and the reaction mixture was stirred at room temperature until TLC showed full conversion (step 3). The solvent was removed by rotary evaporation. Then, the crude product was

[8] L. Pauli, R. Tanner, R. Scheil, A. Pfaltz, *Chem. Eur. J.* **2015**, *21*, 1482-1487.

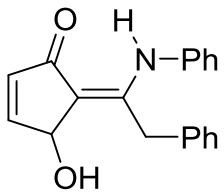
purified by flash column chromatography using gradients of pentane/ethyl acetate to give the desired products.

Caution: In the case of compounds **3**, in order to prevent any decomposition of the products, the solvents must be removed without heating the bath of the rotary evaporator (kept at 20 °C). Regarding their storage, the compounds **3** were kept at −20 °C for several months without observing any decomposition.

Experimental Set-up:



(*Z*)-4-hydroxy-5-(2-phenyl-1-(phenylamino)ethylidene)cyclopent-2-en-1-one (3aa)



Chemical Formula: $C_{19}H_{17}NO_2$
Exact Mass: 291,1259

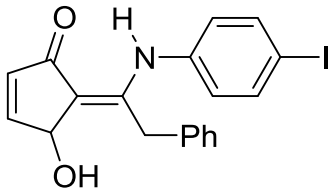
Prepared following general procedure using furan **1a** (30 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2a** (30.7 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3aa** as a yellow solid (39.8 mg, 83% yield).

Mp = 78-82 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 11.53 (s, 1H), 7.34–6.95 (m, 11H), 6.27 (dd, *J* = 5.8, 0.7 Hz, 1H), 5.01 (s, 1H), 4.17 (d, *J* = 15.6 Hz, 1H), 3.94 (d, *J* = 15.6 Hz, 1H), 1.98 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 157.2, 152.5, 138.3, 136.9, 136.2, 129.2, 128.8, 128.3, 126.7, 126.0, 125.4, 108.5, 73.0, 34.2; IR (neat) 3363, 3087, 3064, 3030, 2926, 2895, 2853, 1710, 1643, 1588, 1495, 1447, 1431, 1371, 1328, 1254, 1232, 1194, 1074, 1024 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{19}H_{17}NNaO_2$ $[M+Na]^+$: 314.1151, found: 314.1140.

Scale-up

Prepared following general procedure using furan **1a** (400 mg, 2.2 mmol, 1 equiv), rose Bengal (223.9 mg, 0.022 mmol, 10 mol%), Me_2S (0.65 mL, 8.8 mmol, 4 equiv) and amine **2a** (409 mg, 4.4 mmol, 2 equiv) in methanol (44 mL). After 16 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3aa** as a yellow solid (461 mg, 72% yield).

(*Z*)-4-hydroxy-5-(1-((4-iodophenyl)amino)-2-phenylethylidene)cyclopent-2-en-1-one (3ab)

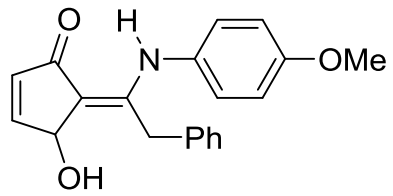


Chemical Formula: $C_{19}H_{16}INO_2$
Exact Mass: 417,0226

Prepared following general procedure using furan **1a** (30 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2b** (72 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 4 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3ab** as a yellow oil (48.8 mg, 71% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 11.47 (s, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.30–7.00 (m, 6H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.31 (d, *J* = 5.8 Hz, 1H), 5.03 (d, *J* = 9.6 Hz, 1H), 4.15 (d, *J* = 15.7 Hz, 1H), 3.90 (d, *J* = 15.8 Hz, 1H), 1.40 (d, *J* = 9.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 156.3, 152.9, 138.3, 138.2, 136.5, 136.2, 128.9, 128.1, 126.9, 109.1, 90.0, 72.8, 34.2, one carbon hidden; IR (neat) 3360, 3087, 3061, 3026, 2955, 2923, 2871, 2853, 1710, 1690, 1630, 1597, 1562, 1535, 1492, 1452, 1375, 1329, 1246, 1197, 1132, 1059, 1030 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{19}H_{16}INNaO_2$ $[M+Na]^+$: 440.0117, found: 444.0106.

(*Z*)-4-hydroxy-5-(1-((4-methoxyphenyl)amino)-2-phenylethylidene)cyclopent-2-en-1-one (3ac)

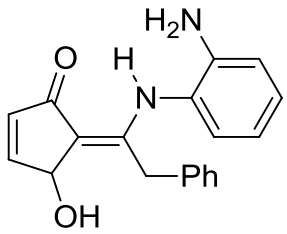


Chemical Formula: $C_{20}H_{19}NO_3$
Exact Mass: 321,1365

Prepared following general procedure using furan **1a** (30 mg, 0.16 mmol, 1 equiv), rose Bengal (16.75 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2c** (40.6 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3ac** as an orange oil (41.3 mg, 78% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 11.35 (s, 1H), 7.26–7.15 (m, 3H), 7.07 (d, *J* = 6.7 Hz, 2H), 7.02 (dd, *J* = 5.8, 2.3 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.29 (dd, *J* = 5.8, 0.8 Hz, 1H), 5.02 (d, *J* = 7.8 Hz, 1H), 4.07 (d, *J* = 15.4 Hz, 1H), 3.84 (d, *J* = 15.4 Hz, 1H), 3.77 (s, 3H), 1.38 (d, *J* = 9.7 Hz, 1H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 194.5, 158.1, 152.2, 136.9, 136.2, 131.0, 128.7, 128.3, 127.4, 126.6, 114.3, 107.8, 73.1, 55.6, 34.2, one carbon hidden; IR (neat) 3271, 3072, 3030, 2955, 2924, 2854, 1710, 1638, 1611, 1577, 1516, 1494, 1463, 1453, 1368, 1328, 1248, 1200, 1172, 1129, 1107, 1077, 1031 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{20}H_{19}NNaO_3$ $[M+Na]^+$: 344.1257, found: 344.1246.

(*Z*)-5-(1-((2-aminophenyl)amino)-2-phenylethylidene)-4-hydroxycyclopent-2-enone (3ad)

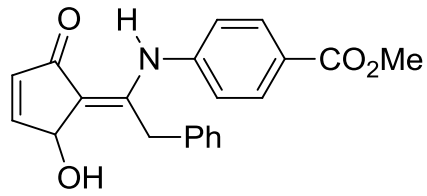


Chemical Formula: $C_{19}H_{18}N_2O_2$
Exact Mass: 306.1368

Prepared following general procedure using furan **1a** (31.5 mg, 0.17 mmol, 1 equiv), rose Bengal (17.6 mg, 0.017 mmol, 10 mol%), Me_2S (51 µL, 0.66 mmol, 4 equiv) and amine **2d** (37.4 mg, 0.35 mmol, 2 equiv) in methanol (3.5 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 2:8) to provide compound **3ad** as a yellow oil (26 mg, 49% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.84 (s, 1H), 7.22–6.91 (m, 7H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.69–6.50 (m, 2H), 6.29 (dd, *J* = 5.9, 0.8 Hz, 1H), 5.14 (dd, *J* = 2.3, 0.8 Hz, 1H), 3.99 (d, *J* = 15.0 Hz, 1H), 3.76 (d, *J* = 15.0 Hz, 1H), 3.54 (bs, 2H), 1.72 (s, 1H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 194.9, 159.7, 152.4, 143.7, 136.7, 136.3, 129.2, 128.9, 128.6, 128.5, 126.6, 123.9, 118.4, 115.9, 108.3, 73.1, 34.9; HRMS-ESI: *m/z* calculated for $C_{19}H_{18}N_2NaO_2$ $[M+Na]^+$: 329.1260, found: 329.1259.

(*Z*)-methyl 4-((1-(2-hydroxy-5-oxocyclopent-3-en-1-ylidene)-2-phenylethyl)amino)benzoate (3ae)

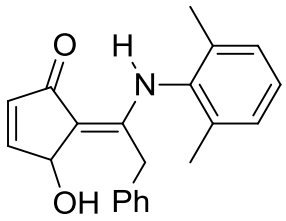


Chemical Formula: $C_{21}H_{19}NO_4$
Exact Mass: 349.1314

Prepared following general procedure using furan **1a** (30 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2e** (49.8 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 20 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 5:5) to provide compound **3ae** as an orange oil (52.9 mg, 92% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.68 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.37–6.94 (m, 8H), 6.29 (dd, *J* = 5.9, 0.9 Hz, 1H), 5.05 (s, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 4.02 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 2.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 166.6, 155.2, 153.4, 142.9, 136.4, 136.1, 130.9, 129.0, 128.1, 126.9, 126.5, 123.1, 110.3, 72.7, 52.2, 34.4; IR (neat) 3350, 3062, 3026, 2952, 2924, 2852, 1712, 1631, 1599, 1566, 1513, 1494, 1434, 1378, 1278, 1246, 1177, 1110, 1016 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{21}H_{19}NNaO_4$ [*M*+Na]$^+$: 372.1206, found: 372.1203.

(*Z*)-5-(1-((2,6-dimethylphenyl)amino)-2-phenylethylidene)-4-hydroxycyclopent-2-enone (3af)

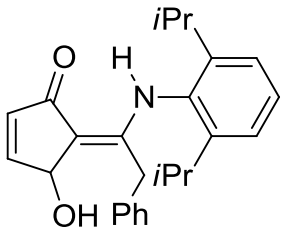


Chemical Formula: $C_{21}H_{21}NO_2$
Exact Mass: 319.1572

Prepared following general procedure using furan **1a** (30 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2f** (40.6 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 24 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3af** as a yellow oil (38 mg, 72% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 10.92 (s, 1H), 7.15–6.91 (m, 7H), 6.80 (dd, *J* = 7.5, 1.6 Hz, 2H), 6.29 (dd, *J* = 5.9, 0.6 Hz, 1H), 5.24 (d, *J* = 1.5 Hz, 1H), 3.86 (d, *J* = 14.5 Hz, 1H), 3.46 (d, *J* = 14.5 Hz, 1H), 2.04 (s, 3H), 1.86 (s, 3H), one H unobserved (OH); ^{13}C NMR (91 MHz, $CDCl_3$) δ 194.8, 159.9, 152.1, 136.8, 136.6, 136.1, 136.0, 135.9, 129.1, 128.3, 127.6, 126.7, 107.4, 73.3, 35.4, 18.3, 18.1; IR (neat) 3362, 3063, 3027, 2954, 2939, 2923, 1710, 1631, 1565, 1470, 1452, 1425, 1375, 1328, 1261, 1233, 1203, 1184, 1136, 1093, 1037 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{21}H_{21}NNaO_2$ [*M*+Na]$^+$: 342.1464, found: 342.1458.

(*Z*)-5-(1-((2,6-diisopropylphenyl)amino)-2-phenylethylidene)-4-hydroxycyclopent-2-enone (3ag)

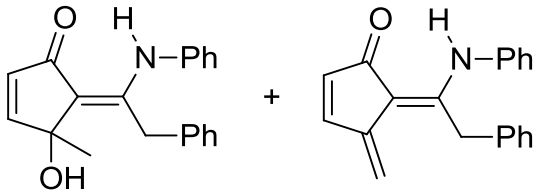


Chemical Formula: $C_{25}H_{29}NO_2$
Exact Mass: 375.2198

Prepared following general procedure using furan **1a** (30 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2g** (58.4 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 24 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 5:5) to provide compound **3ag** as a yellow oil (42 mg, 68% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.16 (s, 1H), 7.30–7.01 (m, 7H), 6.96–6.75 (m, 2H), 6.32 (dd, *J* = 5.8, 0.8 Hz, 1H), 5.20 (s, 1H), 3.90 (d, *J* = 14.6 Hz, 1H), 3.50 (d, *J* = 14.6 Hz, 1H), 2.95 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.82 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.62–1.55 (m, 1H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 159.7, 151.9, 146.7, 146.5, 136.3, 135.8, 132.9, 128.8, 128.4, 126.7, 123.4, 123.3, 107.2, 73.4, 35.0, 28.8, 28.7, 25.6, 25.5, 21.8, 21.4; IR (neat) 3312, 3063, 3027, 2963, 2926, 2869, 1711, 1629, 1595, 1572, 1494, 1466, 1435, 1385, 1364, 1324, 1254, 1195, 1110, 1031 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{25}H_{29}NNaO_2$ $[M+Na]^+$: 398.2090, found: 398.2086.

(*Z*)-4-hydroxy-4-methyl-5-(2-phenyl-1-(phenylamino)ethylidene)cyclopent-2-enone (3ba) and (*Z*)-4-methylene-5-(2-phenyl-1-(phenylamino)ethylidene)cyclopent-2-enone (3'ba)



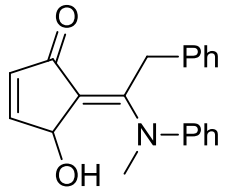
Chemical Formula: $C_{20}H_{19}NO_2$
Exact Mass: 305.1416

Prepared following general procedure using furan **1b** (30 mg, 0.15 mmol, 1 equiv), rose Bengal (15.6 mg, 0.015 mmol, 10 mol%), Me_2S (45 µL, 0.61 mmol, 4 equiv) and amine **2a** (28.5 mg, 0.30 mmol, 2 equiv) in methanol (3.1 mL). After 4 h for step (3), the crude product was purified by flash column

chromatography (Pentane/EtOAc 6:4) to provide compounds **3ba** and **3'ba** as an orange oil (37 mg, 72% and 8% yields, 9:1).

3ba: ^{1}H NMR (250 MHz, $CDCl_3$) δ 11.75 (s, 1H), 7.40–6.80 (m, 11H), 6.17 (d, *J* = 5.8 Hz, 1H), 4.35 (d, *J* = 16.2 Hz, 1H), 3.98 (d, *J* = 16.2 Hz, 1H), 2.21 (s, 1H), 1.49 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 194.9, 158.6, 156.2, 138.6, 137.0, 132.8, 129.0, 128.6, 128.2, 126.4, 125.7, 125.5, 112.3, 79.3, 33.9, 25.7; IR (neat) 3337, 3061, 3028, 2928, 1632, 1593, 1578, 1495, 1453, 1434, 1367, 1327, 1252, 1229, 1205, 1156, 1141, 1076, 1062, 1029, 1003 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{20}H_{19}NNaO_2$ $[M+Na]^+$: 328.1308, found: 328.1298.

(*E*)-4-hydroxy-5-(1-(methyl(phenyl)amino)-2-phenylethylidene)cyclopent-2-enone (3ah)

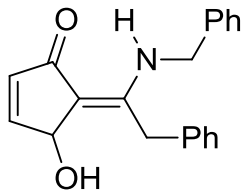


Chemical Formula: $C_{20}H_{19}NO_2$
Exact Mass: 305.1416

Prepared following general procedure using furan **1a** (31.5 mg, 0.17 mmol, 1 equiv), rose Bengal (17.6 mg, 0.017 mmol, 10 mol%), Me_2S (51 µL, 0.66 mmol, 4 equiv) and amine **2h** (37 mg, 0.35 mmol, 2 equiv) in methanol (3.5 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3ah** as an orange oil (33 mg, 63% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.42–6.84 (m, 11H), 6.22 (dd, *J* = 5.9, 0.9 Hz, 1H), 5.07 (d, *J* = 15.0 Hz, 1H), 4.49 (s, 1H), 3.99 (d, *J* = 15.2 Hz, 1H), 3.31 (s, 3H).1.75 (s, 1H); ^{13}C NMR (91 MHz, C_6D_6) δ 194.5, 156.2, 152.6, 147.7, 139.2, 137.2, 129.5, 129.2, 128.7, 126.5, 124.2, 124.1, 120.1, 71.9, 40.4, 34.3; IR (neat) 3359, 3061, 3040, 3026, 2954, 2925, 1657, 1640, 1597, 1536, 1492, 1452, 1425, 1382, 1327, 1213, 1152, 1133, 1106, 1075, 1028 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{20}H_{19}NNaO_2$ $[M+Na]^+$: 328.1308, found: 328.1312.

(*Z*)-5-(1-(benzylamino)-2-phenylethylidene)-4-hydroxycyclopent-2-enone (3ai)

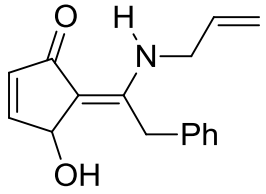


Chemical Formula: $C_{20}H_{19}NO_2$
Exact Mass: 305.1416

Prepared following general procedure using furan **1a** (31.5 mg, 0.17 mmol, 1 equiv), rose Bengal (17.6 mg, 0.017 mmol, 10 mol%), Me_2S (51 µL, 0.66 mmol, 4 equiv) and amine **2i** (37 mg, 0.35 mmol, 2 equiv) in methanol (3.5 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3ai** as a yellow oil (26.4 mg, 50% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.39–7.21 (m, 8H), 7.19–7.13 (m, 2H), 6.99 (dd, *J* = 5.8, 2.2 Hz, 1H), 6.25 (dd, *J* = 5.8, 0.8 Hz, 1H), 5.12 (s, 1H), 4.39–4.22 (m, 2H), 4.07 (d, *J* = 15.9 Hz, 1H), 3.81 (d, *J* = 15.9 Hz, 1H), 1.54 (s, 1H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 194.0, 159.1, 151.5, 138.1, 136.4, 136.1, 129.1, 128.9, 128.0, 127.7, 127.0, 126.9, 107.3, 73.6, 46.7, 34.7; IR (neat) 3305, 3158, 3084, 3064, 3026, 3004, 2929, 2893, 1642, 1597, 1578, 1485, 1451, 1428, 1369, 1346, 1328, 1293, 1238, 1203, 1150, 1096, 1075, 1047, 1025 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{20}H_{19}NNaO_2$ [*M*+Na]$^+$: 328.1308, found: 328.1303.

(*Z*)-5-(1-(allylamino)-2-phenylethylidene)-4-hydroxycyclopent-2-enone (3aj)



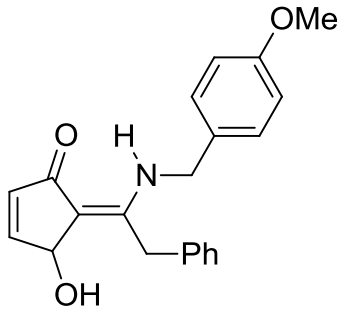
Chemical Formula: $C_{16}H_{17}NO_2$
Exact Mass: 255.1259

Prepared following general procedure using furan **1a** (30 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2j** (18.8 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3aj** as a yellow oil (18.5 mg, 44% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 9.88 (s, 1 H), 7.33–7.20 (m, 6H), 6.98 (dd, *J* = 5.8, 2.2 Hz, 1H), 5.78–5.70 (m, 1H), 5.21–5.09 (m, 3H), 4.08 (d, *J* = 15.9 Hz, 1H), 3.82 (d, *J* = 15.9 Hz, 1H), 3.76–3.70 (m, 2H), 1.70

(s, 1H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 193.3, 159.2, 151.4, 136.4, 136.2, 134.2, 129.1, 128.0, 126.9, 116.6, 107.0, 73.6, 45.2, 34.5; IR (neat) 3314, 3061, 3028, 2926, 2854, 1710, 1631, 1598, 1565, 1491, 1452, 1378, 1330, 1246, 1108, 1072, 1030, 1010 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{16}H_{17}NNaO_2$ [*M*+Na]$^+$: 278.1157, found: 278.1151.

(*Z*)-4-hydroxy-5-(1-((4-methoxybenzyl)amino)-2-phenylethylidene)cyclopent-2-enone (3ak)

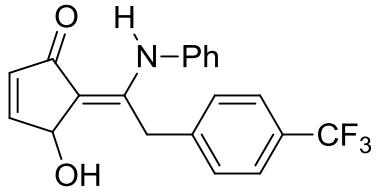


Chemical Formula: $C_{21}H_{21}NO_3$
Exact Mass: 335.1521

Prepared following general procedure using furan **1a** (30 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2k** (45.3 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3ak** as a orange oil (31 mg, 56% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.38–7.19 (m, 5H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.98 (dd, *J* = 5.8, 2.2 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.25 (d, *J* = 5.8 Hz, 1H), 5.11 (s, 1H), 4.32–4.15 (m, 2H), 4.08 (d, *J* = 15.9 Hz, 1H), 3.82 (d, *J* = 16.1 Hz, 1H), 3.78 (s, 3H), 1.35 (s, 1H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 193.9, 159.2, 159.0, 151.4, 136.4, 136.2, 130.0, 129.1, 128.3, 128.0, 127.0, 114.3, 107.2, 73.6, 55.4, 46.3, 34.8; IR (neat) 3287, 3064, 3019, 2933, 2869, 1710, 1632, 1596, 1513, 1494, 1454, 1328, 1302, 1248, 1176, 1145, 1032 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{21}H_{21}NNaO_3$ [*M*+Na]$^+$: 358.1413, found: 358.1406.

(*Z*)-4-hydroxy-5-(1-(phenylamino)-2-(4-(trifluoromethyl)phenyl)ethylidene)cyclopent-2-enone (3ca)

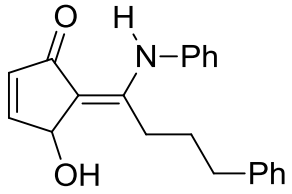


Chemical Formula: $C_{20}H_{16}F_3NO_2$
Exact Mass: 359.1133

Prepared following general procedure using furan **1c** (30 mg, 0.12 mmol, 1 equiv), rose Bengal (12.2 mg, 0.012 mmol, 10 mol%), Me_2S (35 µL, 0.47 mmol, 4 equiv) and amine **2a** (22.1 mg, 0.24 mmol, 2 equiv) in methanol (3.1 mL). After 5 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 5:5) to provide compound **3ca** as a yellow oil (26 mg, 61% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.43 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.32–7.14 (m, 5H), 7.07 (dd, *J* = 5.9, 2.3 Hz, 1H), 7.00–6.91 (m, 2H), 6.29 (dd, *J* = 5.8, 0.9 Hz, 1H), 5.01 (s, 1H), 4.20 (d, *J* = 15.8 Hz, 1H), 3.98 (d, *J* = 15.8 Hz, 1H), 1.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.8, 156.2, 152.6, 141.0, 138.1, 136.3, 129.4, 129.0 (q, *J* = 33.0 Hz), 128.7, 126.4, 125.7, 125.6 (q, *J* = 4.0 Hz), 124.2 (q, *J* = 271.7 Hz), 108.6, 73.0, 34.2; IR (neat) 3343, 3025, 2926, 2899, 2870, 2850, 1632, 1592, 1569, 1500, 1419, 1380, 1328, 1262, 1240, 1189, 1147, 1112, 1068, 1019 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{20}H_{16}F_3NNaO_2$ [*M*+Na]$^+$: 382.1025, found: 382.1016.

(*Z*)-4-hydroxy-5-(4-phenyl-1-(phenylamino)butylidene)cyclopent-2-enone (3da)

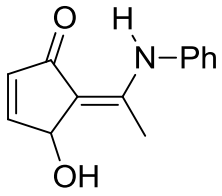


Chemical Formula: $C_{21}H_{21}NO_2$
Exact Mass: 319.1572

Prepared following general procedure using furan **1d** (60 mg, 0.29 mmol, 1 equiv), rose Bengal (29.0 mg, 0.029 mmol, 10 mol%), Me_2S (84 µL, 1.14 mmol, 4 equiv) and amine **2a** (53.2 mg, 0.57 mmol, 2 equiv) in methanol (5.7 mL). After 3 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3da** as an orange oil (52.9 mg, 58% yield).

^{1}H NMR (250 MHz, $CDCl_3$) δ 11.37 (s, 1H), 7.41–7.14 (m, 7H), 7.11–6.95 (m, 5H), 6.23 (dd, *J* = 5.9, 0.8 Hz, 1H), 5.13 (d, *J* = 1.5 Hz, 1H), 2.80–2.67 (m, 1H), 2.64–2.49 (m, 3H), 1.93–1.64 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 194.5, 160.0, 152.0, 141.2, 138.6, 136.1, 129.4, 128.5, 128.4, 126.1, 126.0, 125.3, 107.7, 73.3, 35.7, 29.1, 28.4; IR (neat) 3354, 3061, 3026, 2976, 2928, 2866, 1710, 1632, 1593, 1498, 1453, 1374, 1330, 1254, 1152, 1130, 1073, 1028 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{21}H_{21}NNaO$ [*M*+Na]$^{+}$: 342.1464, found: 342.1448.

(*Z*)-4-hydroxy-5-(1-(phenylamino)ethylidene)cyclopent-2-enone (3ea)

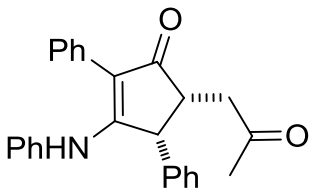


Chemical Formula: $C_{13}H_{13}NO_2$
Exact Mass: 215.0946

Prepared following general procedure using furan **1e** (29.5 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2a** (30.7 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3ea** as a yellow oil (24 mg, 68% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.40 (s, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.12–7.00 (m, 3H), 6.23 (dd, *J* = 5.8, 0.5 Hz, 1H), 5.17 (s, 1H), 2.23 (s, 3H), 1.97 (s, 1H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 193.9, 155.9, 152.2, 138.5, 136.0, 129.3, 125.6, 124.7, 108.1, 73.5, 16.7; IR (neat) 3320, 3071, 3042, 3006, 2987, 2956, 2925, 2852, 1711, 1633, 1595, 1578, 1501, 1439, 1382, 1353, 1329, 1254, 1143, 1078, 1034 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{13}H_{13}NNaO_2$ [*M*+Na]$^{+}$: 238.0838, found: 238.0835.

5-(2-oxopropyl)-2,4-diphenyl-3-(phenylamino)cyclopent-2-enone (3fa)

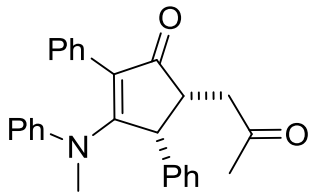


Chemical Formula: $C_{26}H_{23}NO_2$
Exact Mass: 381.1729

Prepared following general procedure using furan **1f** (45 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2a** (40.6 mg, 0.33 mmol, 2 equiv) in methanol (3.3 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 4:6) to provide compound **3fa** as a brown solid (47.2 mg, 75% yield).

Mp = 180-184 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34–6.90 (m, 9H), 6.77 (d, *J* = 6.6 Hz, 2H), 6.58 (s, 1H), 4.53 (d, *J* = 7.4 Hz, 1H), 3.50 (dd, *J* = 13.2, 5.4 Hz, 1H), 2.88 (d, *J* = 18.6 Hz, 1H), 1.99 (dd, *J* = 18.7, 11.3 Hz, 1H), 1.65 (s, 3H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 208.1, 201.4, 170.0, 137.7, 137.2, 131.8, 129.0, 128.7 (2C), 128.3, 127.3, 127.2, 126.2, 125.4, 115.3, 47.0, 45.8, 41.0, 29.9, one carbon hidden; IR (neat) 3257, 3057, 3025, 2926, 2890, 1711, 1665, 1579, 1495, 1443, 1398, 1365, 1308, 1158, 1074, 1028 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{26}H_{23}NNaO_2$ $[M+Na]^+$: 404.1621, found: 404.1626.

3-(methyl(phenyl)amino)-5-(2-oxopropyl)-2,4-diphenylcyclopent-2-enone (3fh)

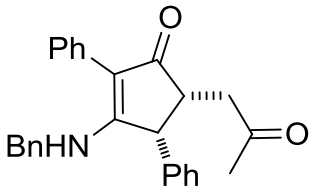


Chemical Formula: $C_{27}H_{25}NO_2$
Exact Mass: 395,1885

Prepared following general procedure using furan **1f** (35 mg, 0.13 mmol, 1 equiv), rose Bengal (13.2 mg, 0.013 mmol, 10 mol%), Me_2S (38 µL, 0.51 mmol, 4 equiv) and amine **2h** (27.7 mg, 0.26 mmol, 2 equiv) in methanol (2.6 mL). After 4 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 4:6) to provide compound **3gh** as a yellow oil (25.9 mg, 51% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.43–7.07 (m, 9H), 7.06–6.93 (m, 3H), 6.80–6.70 (m, 2H), 6.57 (s, 1H), 4.43 (d, *J* = 7.6 Hz, 1H), 3.51 (ddd, *J* = 10.9, 7.6, 3.1 Hz, 1H), 3.08 (s, 3H), 2.89 (dd, *J* = 18.8, 3.1 Hz, 1H), 1.91 (dd, *J* = 18.7, 11.1 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.3, 202.6, 170.7, 145.3, 138.6, 133.9, 131.2, 130.2, 128.7, 128.6, 127.6, 127.4, 126.5, 126.4, 116.4, 49.6, 46.2, 43.7, 41.2, 30.0, one C hidden; IR (neat) 3056, 2918, 2851, 1713, 1664, 1605, 1566, 1493, 1454, 1388, 1305, 1266, 1161, 1094, 1076, 1024 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{27}H_{26}NO_2$ $[M+H]^+$: 396.1958, found: 396.1965.

3-(benzylamino)-5-(2-oxopropyl)-2,4-diphenylcyclopent-2-enone (3fi)

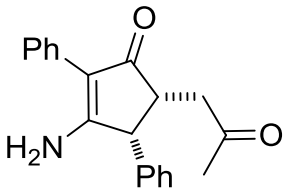


Chemical Formula: $C_{27}H_{25}NO_2$
Exact Mass: 395.1885

Prepared following general procedure using furan **1f** (38 mg, 0.14 mmol, 1 equiv), rose Bengal (14.2 mg, 0.014 mmol, 10 mol%), Me_2S (41 µL, 0.56 mmol, 4 equiv) and amine **2i** (30 mg, 0.28 mmol, 2 equiv) in methanol (2.8 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 4:6) to provide compound **3fi** as a yellow solid (39.1 mg, 70% yield).

Mp = 139-143 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.53–7.24 (m, 10H), 7.18–7.10 (m, 2H), 7.01–6.91 (m, 2H), 5.90 (s, 1H), 4.44 (d, *J* = 7.4 Hz, 1H), 4.23 (dd, *J* = 14.9, 6.0 Hz, 1H), 4.06 (dd, *J* = 14.9, 6.1 Hz, 1H), 3.48 (ddd, *J* = 10.8, 7.4, 3.0 Hz, 1H), 2.90 (dd, *J* = 18.8, 3.0 Hz, 1H), 1.93 (dd, *J* = 18.8, 11.3 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 200.3, 171.7, 137.8, 137.3, 132.2, 131.1, 129.2, 129.1, 129.0, 128.7, 128.1, 127.9, 127.2, 127.0, 113.8, 47.9, 47.0, 46.2, 41.1, 29.9; IR (neat) 3279, 3064, 3030, 2926, 2897, 1710, 1665, 1641, 1604, 1580, 1535, 1501, 1453, 1411, 1351, 1327, 1305, 1163, 1094, 1075, 1029 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{27}H_{25}NNaO_2$ $[M+Na]^+$: 418.1777, found: 418.1761.

3-amino-5-(2-oxopropyl)-2,4-diphenylcyclopent-2-enone (3fl)

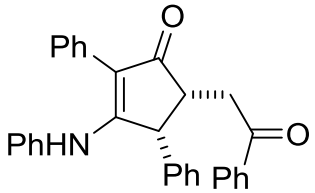


Chemical Formula: $C_{20}H_{19}NO_2$
Exact Mass: 305.1416

Prepared following general procedure using furan **1f** (15.7 mg, 0.057 mmol, 1 equiv), rose Bengal (5.8 mg, 0.0057 mmol, 10 mol%), Me_2S (17 µL, 0.23 mmol, 4 equiv) and ammonia **2l** (24 µL, 7 M in methanol, 0.17 mmol, 2 equiv,) in methanol (1.2 mL). After 4 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 4:6) to provide compound **3fl** as a light brown solid (12.8 mg, 74% yield).

Mp = 188-192 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.55–7.39 (m, 4H), 7.38–7.22 (m, 4H), 7.10 (s, 2H), 5.07 (s, 2H), 4.30 (d, *J* = 7.6 Hz, 1H), 3.57–3.42 (m, 1H), 2.87 (dd, *J* = 18.6, 2.7 Hz, 1H), 2.06 (dd, *J* = 18.6, 11.3 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 201.6, 171.0, 137.4, 132.0, 129.1, 128.9, 128.3, 128.0, 127.1, 114.7, 48.9, 45.8, 41.1, 29.9, one carbon hidden; IR (neat) 3342,3195, 3056, 2928, 2891, 1708, 1622, 1558, 1495, 1455, 1415, 1352, 1308, 1259, 1157, 1104, 1052, 1003, 907 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1494, found: 306.1503.

5-(2-oxo-2-phenylethyl)-2,4-diphenyl-3-(phenylamino)cyclopent-2-enone (3ga)



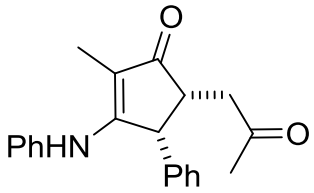
Chemical Formula: $C_{31}H_{25}NO_2$
Exact Mass: 443.1885

Prepared following general procedure using furan **1g** (57 mg, 0.17 mmol, 1 equiv), rose Bengal (17.4 mg, 0.017 mmol, 10 mol%), Me_2S (50 µL, 0.68 mmol, 4 equiv) and amine **2a** (28.9 mg, 0.31 mmol, 2 equiv) in methanol (3.4 mL). After 4 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 4:6) to provide compound **3ga** as a yellow oil (62 mg, 83% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 25.8, 11.3, 7.1 Hz, 7H), 7.37–7.19 (m, 5H), 7.17–6.91 (m, 5H), 6.81 (d, *J* = 6.5 Hz, 3H), 6.55 (s, 1H), 4.69 (d, *J* = 7.3 Hz, 1H), 3.87–3.69 (m, 1H), 3.45 (dd, *J* = 18.7,

2.4 Hz, 1H), 2.59 (dd, *J* = 18.7, 11.4 Hz, 1H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 201.6, 199.8, 170.1, 137.7, 137.1, 136.9, 132.8, 132.0, 131.3, 129.1, 128.8, 128.4, 128.3, 127.7, 127.2, 126.2, 125.5, 115.4, 47.3, 46.3, 36.4, two C hidden; IR (neat) 3377, 3054, 2986, 2905, 1680, 1610, 1587, 1498, 1421, 1396, 1364, 1263, 1222, 1178, 1152, 1074, 1027, 1002 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{31}H_{26}NO_2$ $[M+H]^+$: 444.1958, found: 444.1951.

2-methyl-5-(2-oxopropyl)-4-phenyl-3-(phenylamino)cyclopent-2-enone (3ha)



Chemical Formula: $C_{21}H_{21}NO_2$
Exact Mass: 319.1572

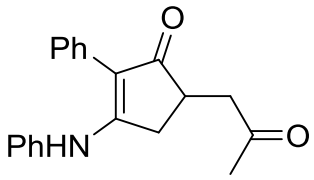
Prepared following general procedure using furan **1h** (25 mg, 0.12 mmol, 1 equiv), rose Bengal (12.1 mg, 0.012 mmol, 10 mol%), Me_2S (35 µL, 0.48 mmol, 4 equiv) and amine **2a** (22.2 mg, 0.24 mmol, 2 equiv) in methanol (2.3 mL). After 3 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 4:6) to provide compound **3ha** as a yellow oil (33.1 mg, 87% yield, dr 12:1).

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.25–7.01 (m, 6H), 6.96–6.61 (m, 4H), 6.45 (s, 1H), 4.39 (d, *J* = 7.3 Hz, 1H), 3.46–3.28 (m, 1H), 2.79 (dd, *J* = 18.6, 3.0 Hz, 1H), 1.93 (dd, *J* = 18.6, 11.4 Hz, 1H), 1.69 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 208.0, 204.2, 169.1, 138.5, 137.5, 131.4, 128.9, 128.4, 127.4, 125.9, 125.0, 111.5, 48.1, 45.5, 41.1, 29.8, 8.0; IR (neat) 3251, 3059, 2919, 1715, 1667, 1582, 1496, 1454, 1407, 1352, 1293, 1262, 1216, 1160, 1130, 1099, 1075, 1032 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{21}H_{22}NO_2$ $[M+H]^+$: 320.1645, found: 320.1650.

5-(2-oxo-2-phenylethyl)-2-phenyl-3-(phenylamino)cyclopent-2-enone (3ia) and 5-methyl-2-(2-oxopropyl)-1,4-diphenyl-1,2-dihydro-3H-pyrrol-3-one (3'ia)

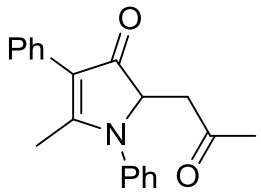
Prepared following general procedure using furan **1i** (18 mg, 0.092 mmol, 1 equiv), rose Bengal (10.0 mg, 0.009 mmol, 10 mol%), Me_2S (27 µL, 0.37 mmol, 4 equiv) and amine **2a** (17.1 mg, 0.18 mmol, 2 equiv) in methanol (1.8 mL). After 4 h for step (3), the crude product was purified by flash column

chromatography (Pentane/EtOAc 4:6) to provide compounds **3ia** as a yellow oil (9 mg, 32% yield) and compound **3'ia** as a yellow oil (14.6 mg, 52% yield).



Chemical Formula: $C_{20}H_{19}NO_2$
Exact Mass: 305,1416

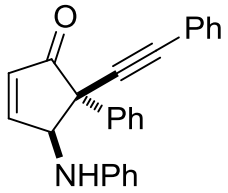
^{1}H NMR (360 MHz, $CDCl_3$) δ 7.52–7.42 (m, 3H), 7.42–7.31 (m, 4H), 7.26–7.19 (m, 1H), 7.14 (dd, *J* = 8.1, 0.6 Hz, 2H), 3.51 (s, 1H), 3.23 (ddd, *J* = 17.9, 14.2, 5.2 Hz, 2H), 2.98 (ddd, *J* = 7.3, 4.5, 2.4 Hz, 1H), 2.54 (dd, *J* = 18.0, 10.5 Hz, 1H), 2.44 (dd, *J* = 17.8, 2.9 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 207.8, 201.7, 169.1, 138.3, 131.8, 129.7, 129.4, 128.8, 127.4, 126.0, 123.5, 115.0, 45.9, 40.4, 33.5, 30.2; IR (neat) 3054, 2986, 1716, 1667, 1613, 1584, 1499, 1421, 1264, 1157 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1489, found: 306.1476.



Chemical Formula: $C_{20}H_{19}NO_2$
Exact Mass: 305,1416

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.50–7.30 (m, 9H), 7.26–7.20 (m, 1H), 5.21 (s, 1H), 2.89–2.72 (m, 2H), 2.18 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 196.5, 173.2, 136.4, 131.6, 129.7, 129.4, 129.0, 128.6, 128.5, 126.4, 88.3, 46.0, 31.9, 29.8, 15.5.IR (neat) 3331, 3053, 2919, 2840, 1714, 1657, 1597, 1547, 1494, 1420, 1382, 1264, 1222, 1121 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{18}H_{16}NO$ [*M*-COMe]$^+$: 262.1226, found: 262.1222.

5-phenyl-4-(phenylamino)-5-(phenylethynyl)cyclopent-2-enone (3ja)

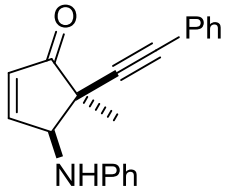


Chemical Formula: $C_{25}H_{19}NO$
Exact Mass: 349.1467

Prepared following general procedure using furan **1j** (36.5 mg, 0.14 mmol, 1 equiv), rose Bengal (14.5 mg, 0.014 mmol, 10 mol%), Me_2S (42 µL, 0.57 mmol, 4 equiv) and amine **2a** (26.5 mg, 0.28 mmol, 2 equiv) in methanol (2.8 mL). After 5 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 6:4) to provide compound **3ja** as an orange oil (38.3 mg, 78% yield, dr 3.5:1).

Major diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 5.8, 2.2 Hz, 1H), 7.50–7.24 (m, 12H), 7.12 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.82–6.70 (m, 1H), 6.62–6.42 (m, 3H), 5.00 (s, 1H), one H unobserved (NH); ^{13}C NMR (91 MHz, $CDCl_3$) δ 202.9, 161.9, 146.2, 139.8, 133.6, 132.1, 129.4, 129.0, 128.7, 128.4, 127.8, 126.6, 122.3, 118.8, 114.2, 88.8, 84.8, 66.8, 59.4; IR (neat) 3384, 3059, 2926, 2855, 1719, 1601, 1493, 1447, 1372, 1311, 1265, 1156, 1071, 1030 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{25}H_{19}NNaO$ $[M+Na]^+$: 372.1358, found: 372.1344.

5-methyl-4-(phenylamino)-5-(phenylethynyl)cyclopent-2-enone (3ka)

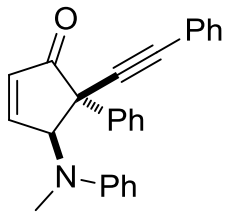


Chemical Formula: $C_{20}H_{17}NO$
Exact Mass: 287.1310

Prepared following general procedure using furan **1k** (30 mg, 0.15 mmol, 1 equiv), rose Bengal (15.6 mg, 0.015 mmol, 10 mol%), Me_2S (45 µL, 0.61 mmol, 4 equiv) and amine **2a** (28.5 mg, 0.31 mmol, 2 equiv) in methanol (3.1 mL). After 24 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 9:1) to provide compound **3ka** as a yellow oil (21 mg, 48% yield, dr 4:1).

Major diastereoisomer: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 5.9, 2.0 Hz, 1H), 7.35–7.18 (m, 7H), 6.85–6.72 (m, 3H), 6.34 (dd, *J* = 5.9, 1.6 Hz, 1H), 4.60 (t, *J* = 1.8 Hz, 1H), 4.36 (s, 1H), 1.63 (s, 3H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 204.0, 160.6, 146.7, 132.5, 132.0, 129.7, 128.6, 128.4, 122.5, 118.8, 114.1, 87.1, 85.7, 63.6, 49.9, 23.5; IR (neat) 3383, 3055, 2926, 2855, 1719, 1601, 1497, 1442, 1372, 1340, 1310, 1250, 1190, 1145, 1110, 1062, 1030 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{20}H_{17}NNaO$ [*M*+Na]$^{+}$: 310.1202, found: 310.1190.

4-(methyl(phenyl)amino)-5-phenyl-5-(phenylethynyl)cyclopent-2-enone (3jh)

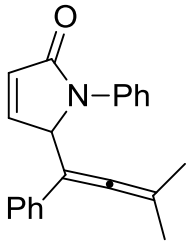


Chemical Formula: $C_{26}H_{21}NO$
Exact Mass: 363.1623

Prepared following general procedure using furan **1j** (18 mg, 0.070 mmol, 1 equiv), rose Bengal (7.1 mg, 0.0070 mmol, 10 mol%), Me_2S (21 µL, 0.28 mmol, 4 equiv) and amine **2h** (14.9 mg, 0.14 mmol, 2 equiv) in methanol (1.5 mL). After 3 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 9:1) to provide compound **3jh** as an orange oil (18.5 mg, 73% yield, dr 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.9, 2.6 Hz, 1H), 7.53–7.33 (m, 6H), 7.29–7.19 (m, 5H), 7.16–7.08 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.64 (dd, *J* = 5.9, 2.1 Hz, 1H), 6.48 (d, *J* = 8.3 Hz, 2H), 5.29 (s, 1H), 3.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 162.8, 149.2, 140.2, 134.3, 131.9, 129.2 (2C), 128.4, 128.3, 127.8, 126.4, 122.9, 117.5, 113.1, 88.4, 84.9, 74.1, 58.3, 35.2; IR (neat) 3060, 2932, 1721, 1599, 1504, 1446, 1377, 1317, 1228, 1158, 1112, 1069, 1032, 991 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{26}H_{22}NO$ [*M*+H]$^{+}$: 364.1701, found: 364.1713.

5-(3-methyl-1-phenylbuta-1,2-dien-1-yl)-1-phenyl-1H-pyrrol-2(5H)-one (3la)

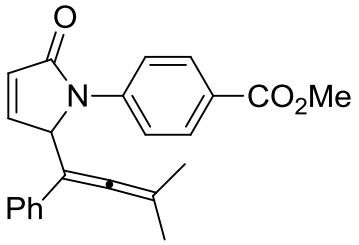


Chemical Formula: $C_{21}H_{19}NO$
Exact Mass: 301.1467

Prepared following general procedure using furan **1l** (35 mg, 0.16 mmol, 1 equiv), rose Bengal (16.9 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2a** (30.7 mg, 0.33 mmol, 2 equiv) in methanol (3.5 mL). After 5 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 7:3) to provide compound **3la** as an orange oil (34.7 mg, 70% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.45–7.23 (m, 8H), 7.18–7.04 (m, 1H), 6.25 (dd, *J* = 6.0, 1.7 Hz, 1H), 5.73 (t, *J* = 1.8 Hz, 1H), 1.65 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 170.1, 146.7, 137.7, 135.5, 128.8, 128.7, 127.3, 127.1, 126.2, 124.2, 121.0, 103.0, 100.0, 63.7, 19.7, 19.4; IR (neat) 2955, 2923, 2854, 1699, 1598, 1548, 1500, 1445, 1391, 1365, 1280, 1260, 1204, 1153, 1066, 1031 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{21}H_{19}NNaO$ [*M*+Na]$^+$: 324.1358, found: 324.1357.

Methyl 4-(2-(3-methyl-1-phenylbuta-1,2-dien-1-yl)-5-oxo-2,5-dihydro-1H-pyrrol-1-yl)benzoate (3le)

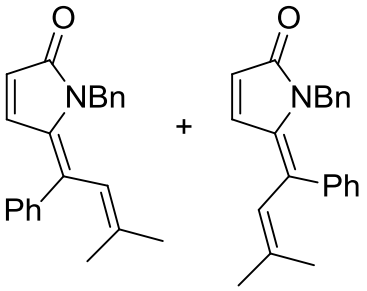


Chemical Formula: $C_{23}H_{21}NO_3$
Exact Mass: 359.1521

Prepared following general procedure using furan **1l** (35 mg, 0.16 mmol, 1 equiv), rose Bengal (16.8 mg, 0.016 mmol, 10 mol%), Me_2S (49 µL, 0.66 mmol, 4 equiv) and amine **2e** (50.3 mg, 0.33 mmol, 2 equiv) in methanol (3.5 mL). After 5 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 8:2) to provide compound **3le** as a yellow solid (47.2 mg, 79% yield).

Mp = 123-127 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.42–7.16 (m, 6H), 6.21 (dd, *J* = 6.0, 1.7 Hz, 1H), 5.70 (s, 1H), 3.87 (s, 3H), 1.62 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 201.5, 170.3, 166.8, 147.4, 142.0, 135.1, 130.4, 128.9, 127.5, 126.8, 126.1, 125.2, 119.5, 103.7, 100.0, 63.4, 52.1, 19.7, 19.3; IR (neat) 3047, 2974, 1947, 1708, 1605, 1514, 1495, 1435, 1361, 1279, 1184, 1112, 1069, 1016 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{23}H_{21}NNaO_3$ [*M*+Na]$^{+}$: 382.1413, found: 382.1400.

(*E*)-1-benzyl-5-(3-methyl-1-phenylbut-2-en-1-ylidene)-1H-pyrrol-2(5H)-one (3li) and (*Z*)-1-benzyl-5-(3-methyl-1-phenylbut-2-en-1-ylidene)-1H-pyrrol-2(5H)-one (3'li)

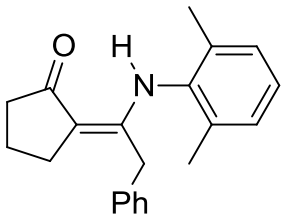


Chemical Formula: $C_{22}H_{21}NO$
Exact Mass: 315.1623

Prepared following general procedure using furan **1l** (25 mg, 0.12 mmol, 1 equiv), rose Bengal (12.2 mg, 0.012 mmol, 10 mol%), Me_2S (35 µL, 0.48 mmol, 4 equiv) and amine **2i** (25.5 mg, 0.24 mmol, 2 equiv) in methanol (2.4 mL). After 2 h for step (3), the crude product was purified by flash column chromatography (Pentane/EtOAc 7:3) to provide compounds **3li** and **3'li** as a yellow oil (32.2 mg, 86% yield, 6.3:1).

3li: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.35–7.25 (m, 5H), 7.24–7.12 (m, 3H), 7.08 (d, *J* = 7.1 Hz, 2H), 6.98 (d, *J* = 5.8 Hz, 1H), 6.21 (d, *J* = 5.8 Hz, 1H), 5.89 (s, 1H), 5.03 (s, 2H), 1.80 (d, *J* = 1.3 Hz, 3H), 1.26 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 173.0, 142.5, 139.7, 139.0, 138.7, 138.3, 130.9, 128.5, 128.2, 128.1, 127.0, 126.5, 123.5, 121.5, 45.0, 26.4, 20.2; IR (neat) 3367, 3062, 3030, 2971, 2929, 2909, 2852, 2245, 1686, 1596, 1545, 1494, 1444, 1374, 1357, 1332, 1290, 1261, 1182, 1129, 1078, 1027 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{22}H_{21}NNaO$ [*M*+Na]$^{+}$: 338.1515, found: 338.1506.

(*Z*)-2-(1-((2,6-dimethylphenyl)amino)-2-phenylethylidene)cyclopentanone (19)

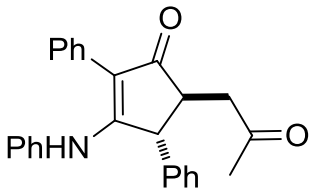


Chemical Formula: $C_{21}H_{23}NO$
Exact Mass: 305.1780

In a vial were placed compound **3af** (38 mg, 0.12 mmol, 1 equiv.), Pd/C (3.8 mg, 10% w/w) and dichloromethane (5mL). The vial was placed in autoclave and the reaction mixture was purged three times with H_2 (10 bar) and the solution was stirred at room temperature for 16 under H_2 (10 bar). Then, the solution was passed through a short pad of Celite and rinsed with ethyl acetate. The solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (Pentane/EtOAc 8:2) to provide compound **19** as a yellow oil (33.1 mg, 91 % yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 11.45 (s, 1H), 7.20–6.94 (m, 6H), 6.79 (d, *J* = 3.3 Hz, 2H), 3.38 (s, 2H), 2.70 (t, *J* = 7.0 Hz, 2H), 2.46 (t, *J* = 7.8 Hz, 2H), 2.03–1.94 (m, 2H), 1.97 (s, 6H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 204.5, 159.0, 136.8, 137.7, 136.1, 128.8, 128.4, 128.3, 127.3, 126.7, 104.4, 39.5, 36.3, 28.5, 20.9, 18.3; IR (neat) 3061, 3029, 2956, 2925, 2849, 1658, 1634, 1572, 1513, 1493, 1479, 1451, 1377, 1292, 1237, 1201, 1182, 1103, 1029 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{21}H_{23}NNaO$ $[M+Na]^+$: 328.1677, found: 328.1663.

5-(2-oxopropyl)-2,4-diphenyl-3-(phenylamino)cyclopent-2-enone (20)



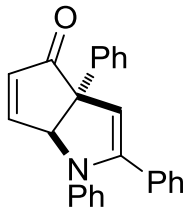
Chemical Formula: $C_{26}H_{23}NO_2$
Exact Mass: 381.1729

To a solution of compound **3fa** (28 mg, 0.073 mmol, 1 equiv) in *tert*-butanol (1 mL) was added *t*BuOK (33 mg, 0.29 mmol, 4 equiv). The reaction mixture was stirred at 80 °C for 2 h. The reaction was then quenched with saturated NH_4Cl aqueous solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed by rotary

evaporation. The crude product was purified by flash column chromatography (Pentane/EtOAc 7:3) to provide compound **20** as an orange solid (23.5 mg, 84% yield).

Mp = 172-176 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.52–7.33 (m, 4H), 7.30–7.23 (m, 1H), 7.20–6.93 (m, 9H), 6.76 (d, *J* = 6.4 Hz, 2H), 4.04 (s, 1H), 3.07 (d, *J* = 12.9 Hz, 1H), 2.88–2.71 (m, 2H), 2.15 (s, 3H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 207.9, 201.2, 169.8, 140.3, 137.7, 131.8, 129.0, 128.9, 128.8 (2C), 127.7, 127.2, 127.1, 126.0, 125.0, 115.7, 52.0, 50.3, 45.1, 30.3. IR (neat) 3230, 3055, 3029, 2915, 2887, 1704, 1652, 1611, 1572, 1513, 1492, 1443, 1411, 1364, 1294, 1253, 1197, 1174, 1162, 1100, 1075, 1029, 1003 cm^{-1}. HRMS-ESI: *m/z* calculated for $C_{26}H_{23}NNaO_2$ $[M+Na]^+$: 404.1621, found: 404.1606.

1,2,3a-triphenyl-1,6a-dihydrocyclopenta[*b*]pyrrol-4(3aH)-one (21)

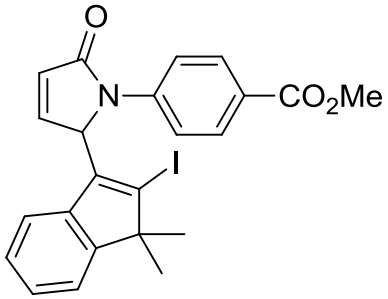


Chemical Formula: $C_{25}H_{19}NO$
Exact Mass: 349.1467

To a solution of compound **3ja** (20 mg, 0.057 mmol, 1 equiv) in HFIP (0.3 mL) was added $Cu(OTf)_2$ (2.1 mg, 0.0057 mmol, 10 mol%). The reaction mixture was stirred at room temperature for 2 h. Then, the crude product was purified by flash column chromatography (Pentane/EtOAc 9:1) to provide compound **21** as an orange oil (19 mg, 95% yield).

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.8, 2.3 Hz, 1H), 7.49–7.40 (m, 2H), 7.34–7.21 (m, 8H), 7.14 (t, *J* = 7.9 Hz, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.86–6.80 (m, 2H), 6.58 (d, *J* = 5.8 Hz, 1H), 5.44 (s, 1H), 4.87 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 206.8, 158.0, 147.3, 146.6, 140.9, 134.9, 132.7, 129.0, 128.9, 128.8, 128.6, 127.4, 127.3, 127.1, 122.6, 121.2, 107.7, 80.2, 65.3; IR (neat) 3364, 3059, 3030, 1767, 1709, 1596, 1494, 1447, 1369, 1289, 1269, 1175, 1124, 1075, 1030, 1003 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{25}H_{19}NNaO$ $[M+Na]^+$: 372.1358, found: 372.1341.

Methyl 4-(2-(2-iodo-1,1-dimethyl-1H-inden-3-yl)-5-oxo-2,5-dihydro-1H-pyrrol-1-yl)benzoate (22)



Chemical Formula: $C_{23}H_{20}INO_3$
Exact Mass: 485.0488

To a solution of compound **3le** (16 mg, 0.045 mmol, 1 equiv) in 1,2-DCE (0.9 mL) was added *N*-iodosuccimide (12 mg, 0.053 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 2 h. Then, the crude product was purified by flash column chromatography (Pentane/EtOAc 8:2) to provide compound **22** as a white solid (19.1 mg, 88% yield).

Mp = 169-173 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 5.3 Hz, 1H), 7.17 (dd, *J* = 5.9, 2.0 Hz, 1H), 7.14–6.92 (m, 3H), 6.49 (dd, *J* = 5.9, 2.0 Hz, 1H), 6.04 (t, *J* = 2.0 Hz, 1H), 3.83 (s, 3H), 1.22 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 170.6, 166.7, 153.0, 145.8, 141.5, 137.9, 136.6, 130.6, 128.9, 126.9, 126.2, 125.9, 123.6, 122.3, 119.9, 119.4, 66.3, 53.3, 52.1, 25.7, 25.3; IR (neat) 3089, 2960, 2920, 2855, 1709, 1602, 1570, 1460, 1431, 1353, 1331, 1314, 1273, 1185, 1159, 1110, 1071, 1060, 1015, 1001 cm^{-1}; HRMS-ESI: *m/z* calculated for $C_{23}H_{20}INNaO_3$ $[M+Na]^+$: 508.0358, found: 508.0386.

X-Ray Crytallography Data

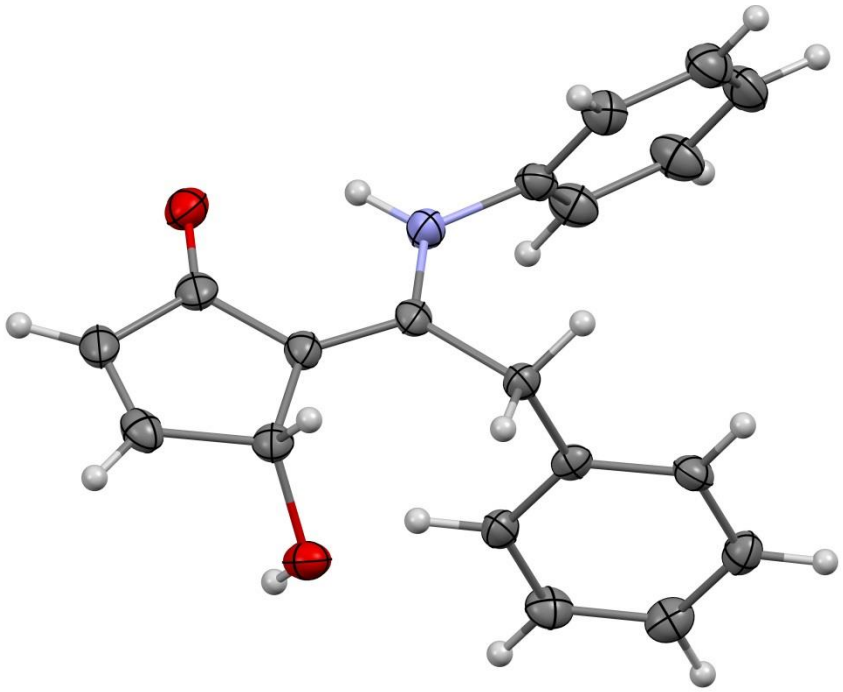


Fig. 1. ORTEP view of the crystal structure of **3aa**. Thermal ellipsoids are shown at the 50% probability level.

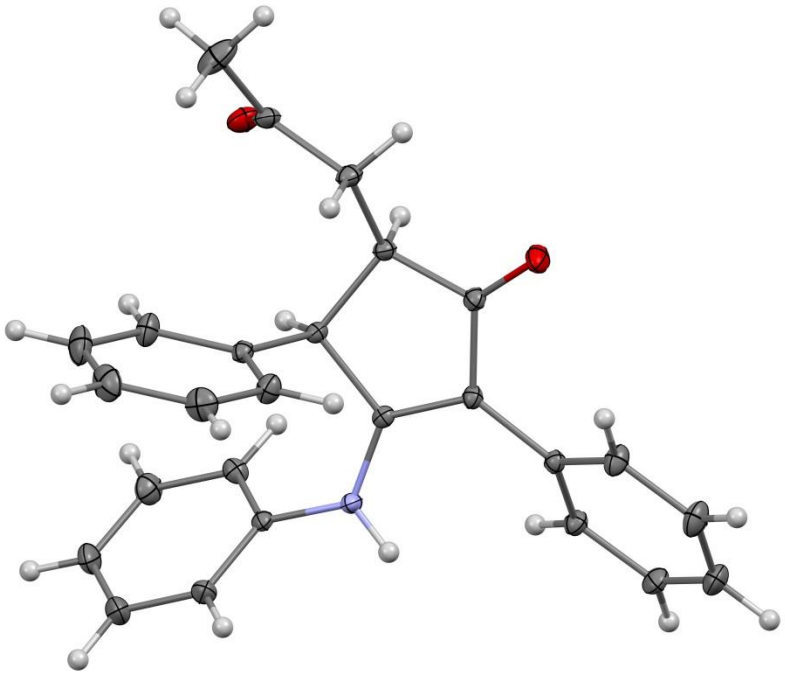


Fig. 2. ORTEP view of the crystal structure of **3fa**. Solvent molecules are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

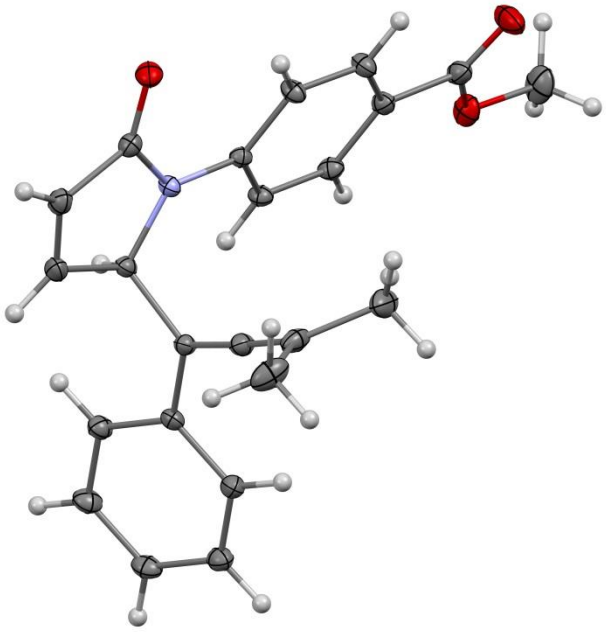


Fig. 3. ORTEP view of the crystal structure of **3le**. Thermal ellipsoids are shown at the 50% probability level.

X-ray diffraction data for compounds **3aa** and **10** were collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IuS source Mo $_{K\alpha}$ radiation (for compound **3fa**) and Cu $_{K\alpha}$ radiation (for compound **3aa**). X-ray diffraction data for compound **3le** were collected by using a X8 APEXII CCD Bruker diffractometer with graphite-monochromated MoKα radiation. All crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. For compounds, the temperature of the crystal was maintained at the selected value by means of a 700 series Cryostream (for X8) or N-Helix (for VENTURE) cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[9] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018[10] with anisotropic displacement parameters for all non-hydrogen atoms. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[11]

The crystal data collection and refinement parameters are given in Table X1.

[7] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, **1997**.

[8] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.

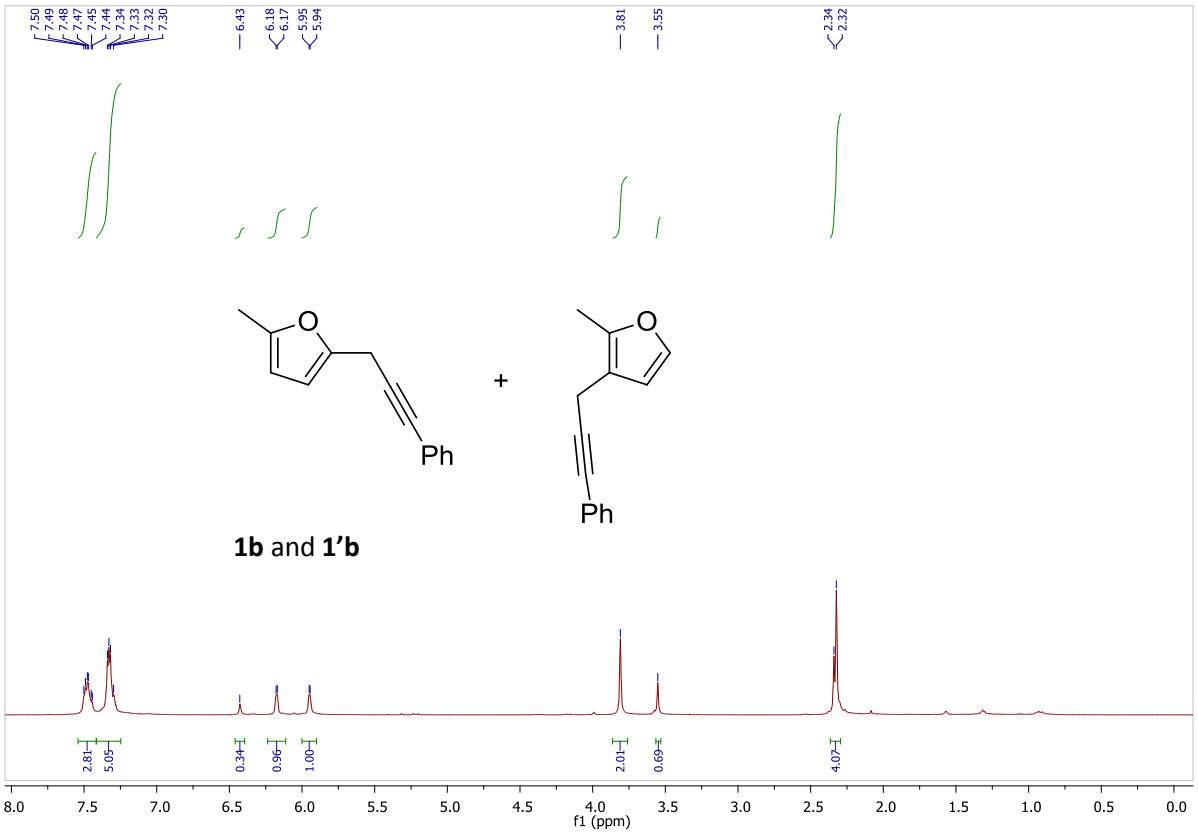
[9] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

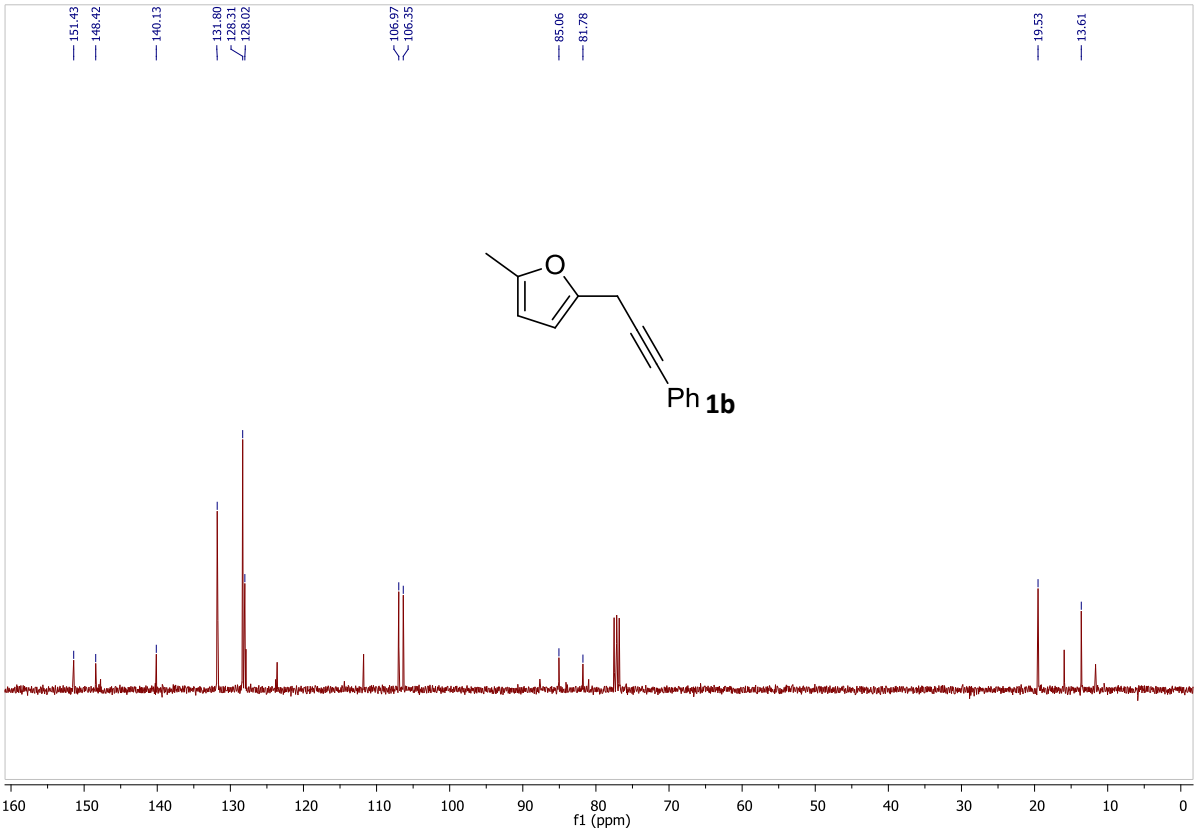
CCDC 1892976-1892978 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

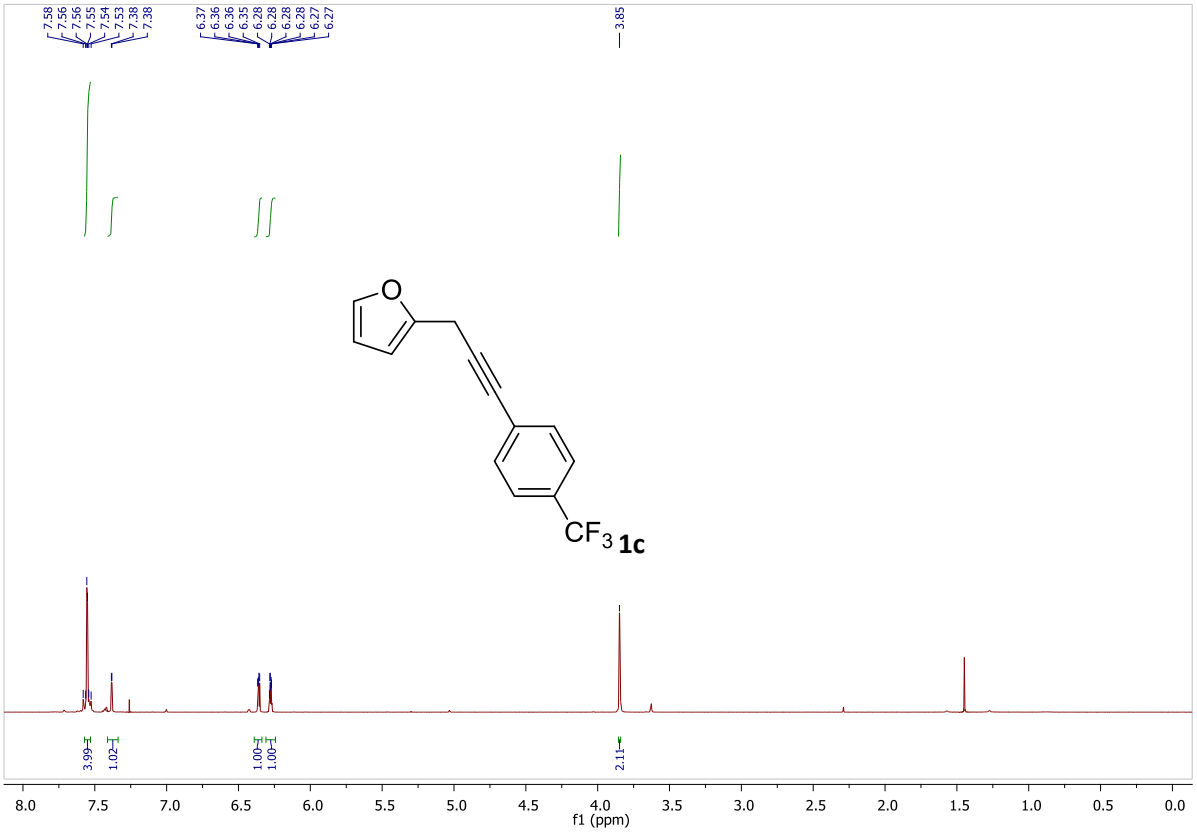
Table X1. Crystallographic data and structure refinement details.

Compounds	**3aa**	**3fa**	**3le**
	CCDC 1892976	CCDC 1892978	CCDC 1892977
Empirical Formula	C_{19} H_{17} N O_2	C_{26} H_{23} N O_2, C H_2 Cl_2	C_{23} H_{21} N O_3
M_r	291.33	466.38	359.41
Crystal size, mm^3	0.23 x 0.04 x 0.01	0.14 x 0.12 x 0.11	0.33 x 0.24 x 0.11
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1$	$P2_1/c$	P -1
a, Å	9.358(2)	8.3898(6)	8.1794(2)
b, Å	5.3966(14)	14.8000(9)	10.7510(2)
c, Å	15.126(3)	18.8914(12)	11.9840(3)
α, °	90	90	74.5430(10)
β, °	107.380(16)	91.871(2)	70.1210(10)
γ, °	90	90	76.3680(10)
Cell volume, $Å^3$	729.0(3)	2344.5(3)	942.88(4)
Z ; Z’	2 ; 1	4 ; 1	2 ; 1
T, K	100(1)	100(1)	100(1)
Radiation type ; wavelength Å	CuKα ; 1.54178	MoKα ; 0.71073	MoKα ; 0.71073
F_{000}	308	976	380
μ, mm^{-1}	0.686	0.301	0.084
θ range, °	3.061 - 66.928	2.429 - 36.436	1.846 - 36.381
Reflection collected	8 823	102 888	24 636
Reflections unique	2 488	11 417	8 644
R_{int}	0.0814	0.0641	0.0218
GOF	1.043	1.032	1.050
Flack parameter	0.2(3)	/	/
Refl. obs. (I>2σ(I))	2 081	8 149	7 160
Parameters	205	290	247
wR_2 (all data)	0.1077	0.1332	0.1246
R value (I>2σ(I))	0.0501	0.0543	0.0409
Largest diff. peak and hole (e-.$Å^{-3}$)	0.185 ; -0.213	0.956 ; -0.933	0.541 ; -0.262

Spectra Compounds



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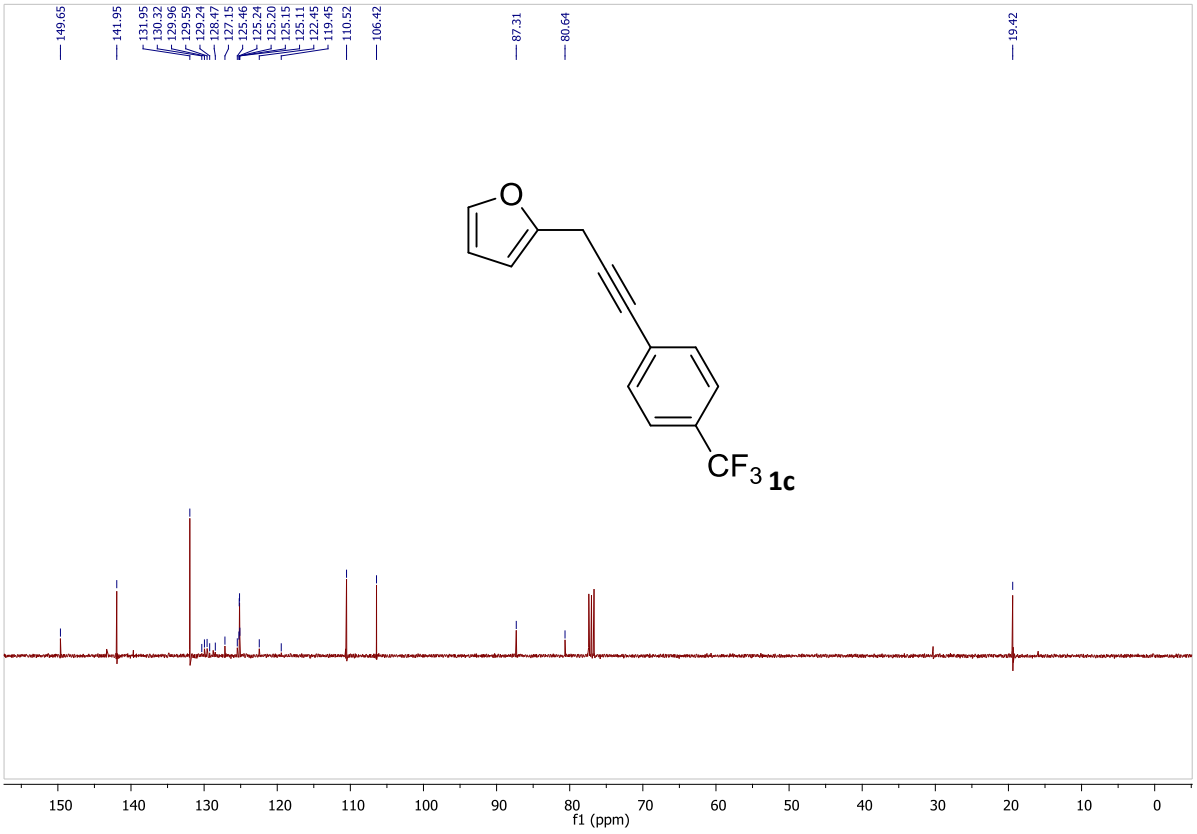
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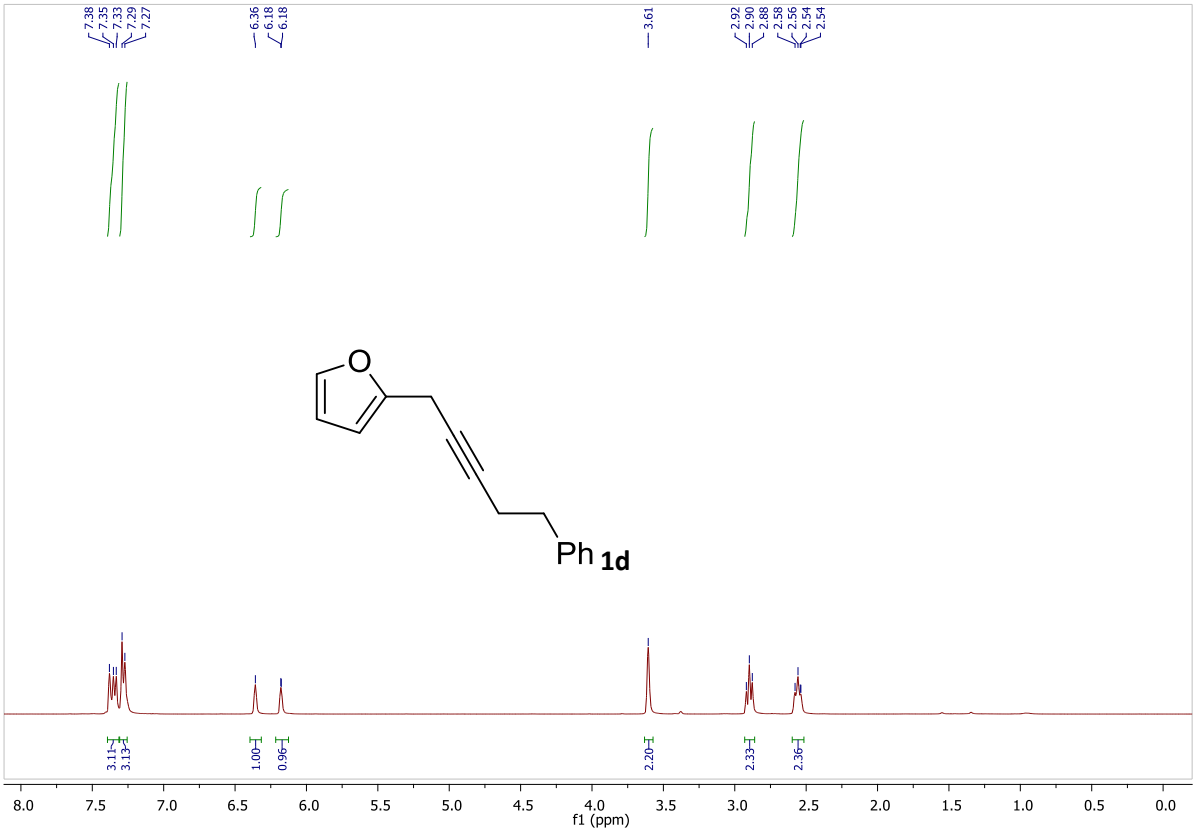
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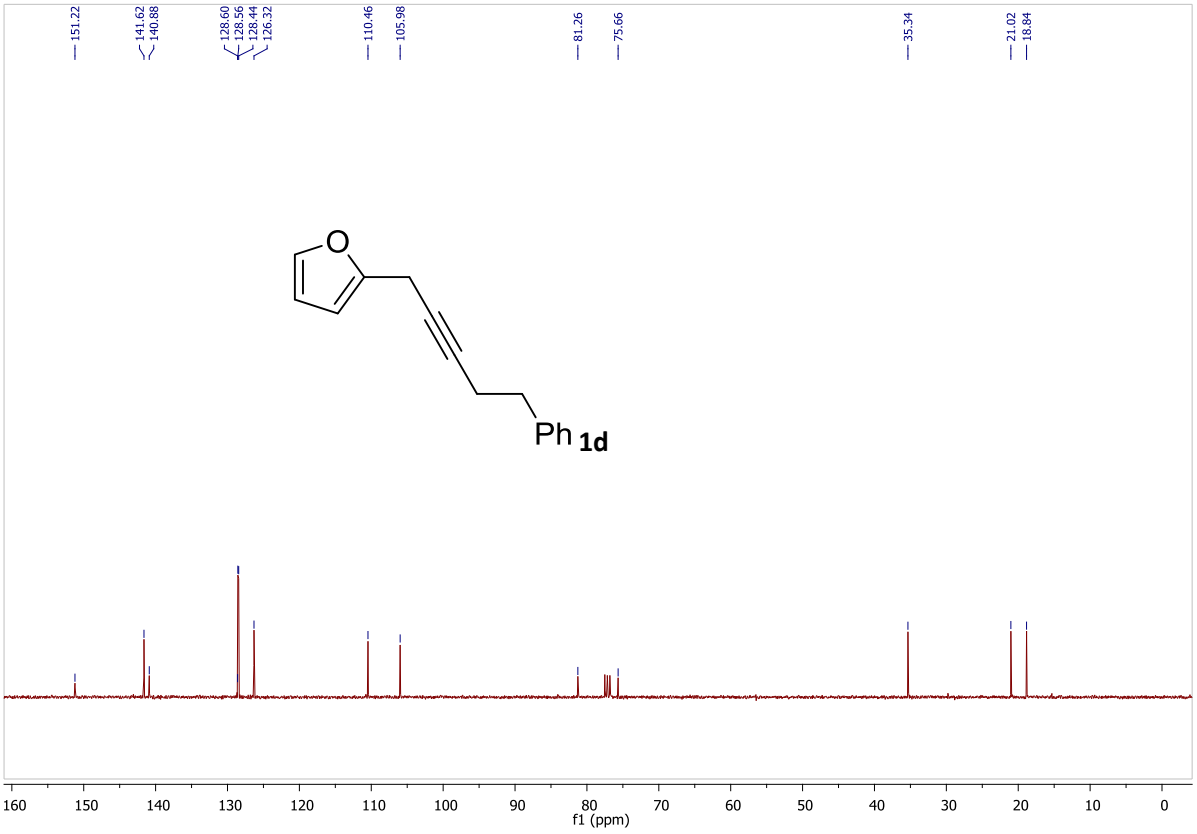
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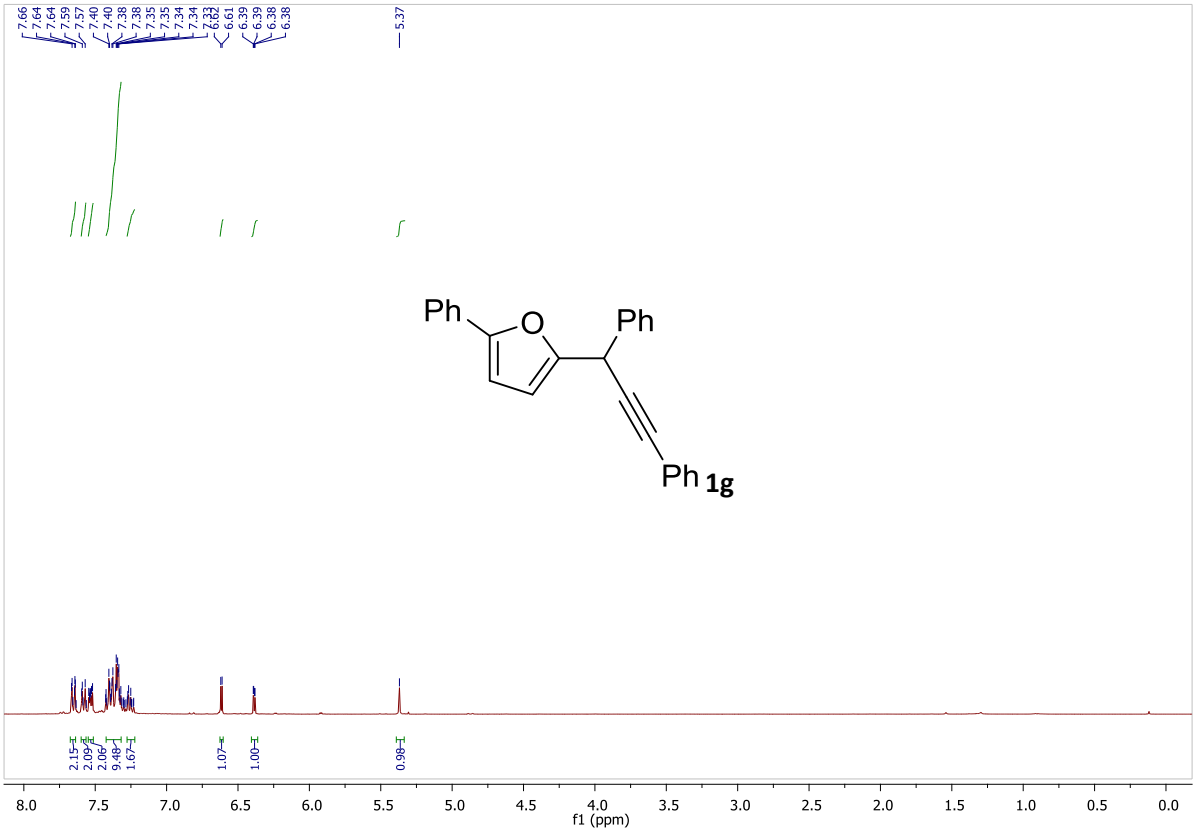
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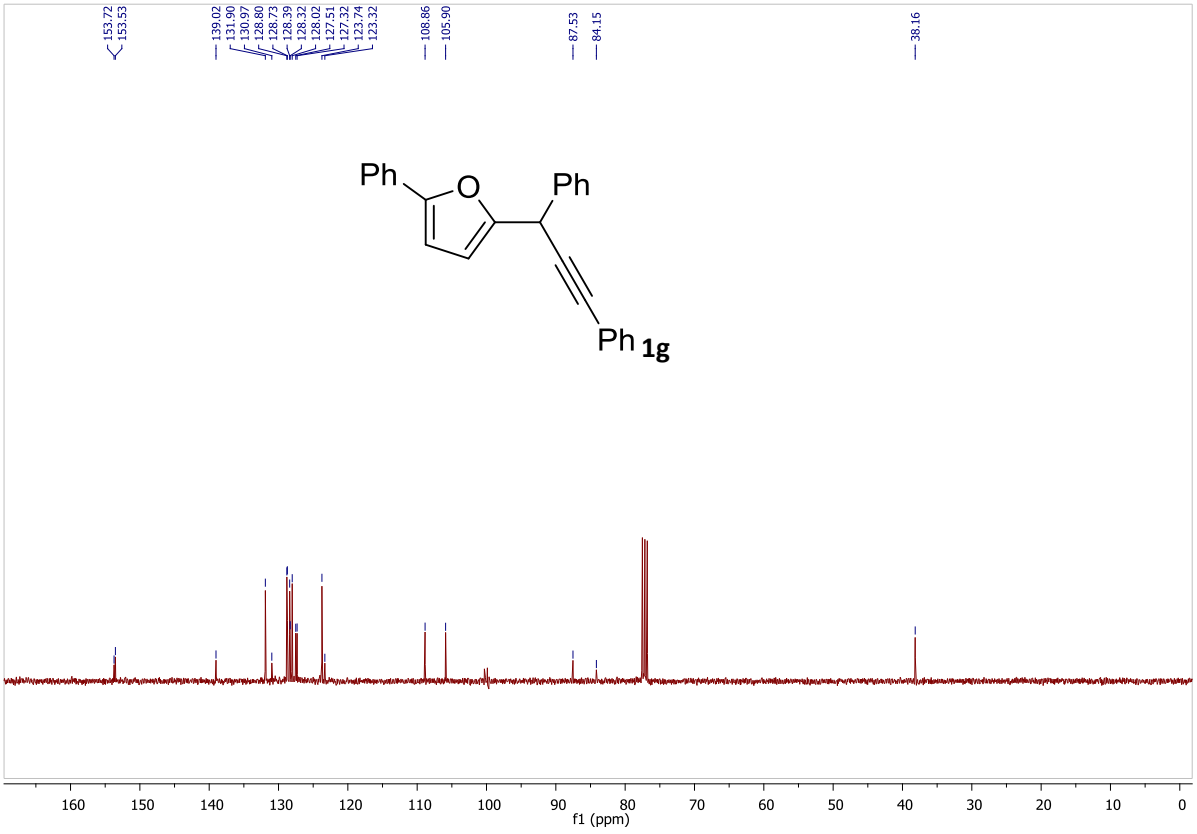
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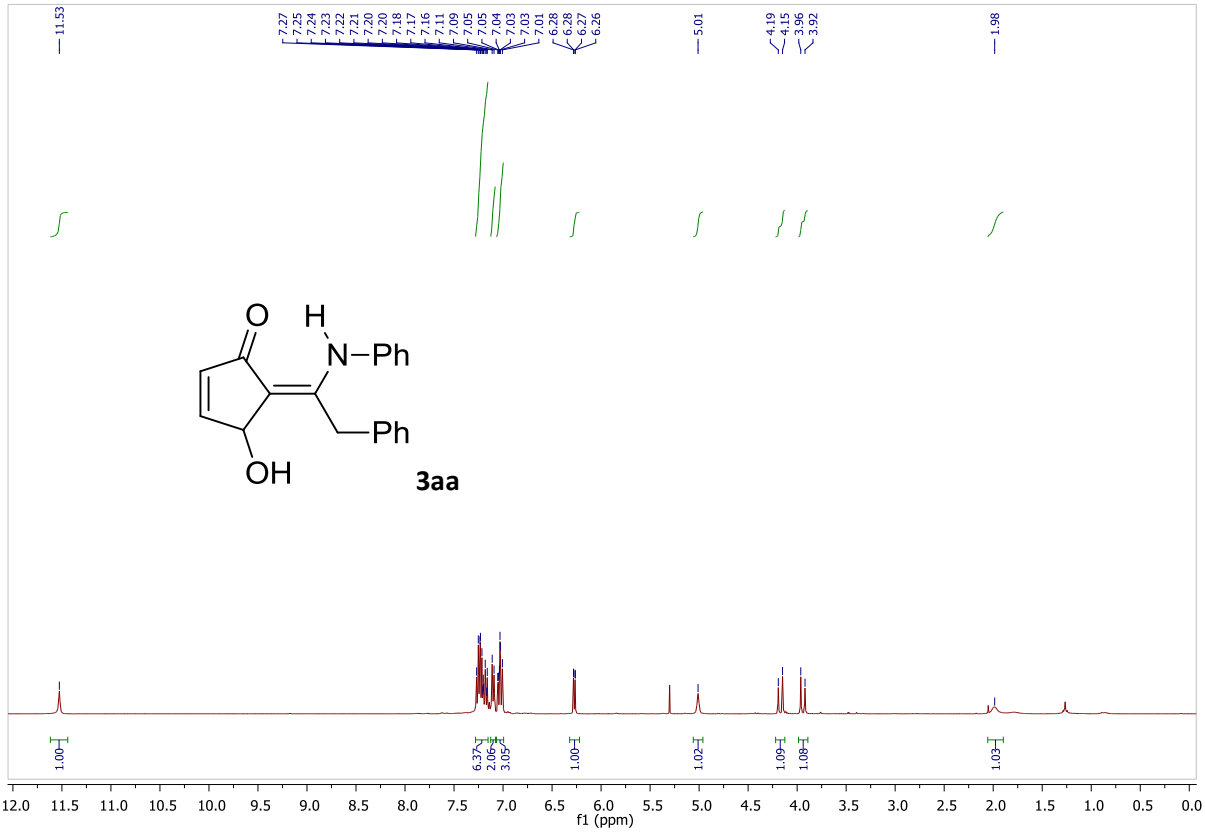
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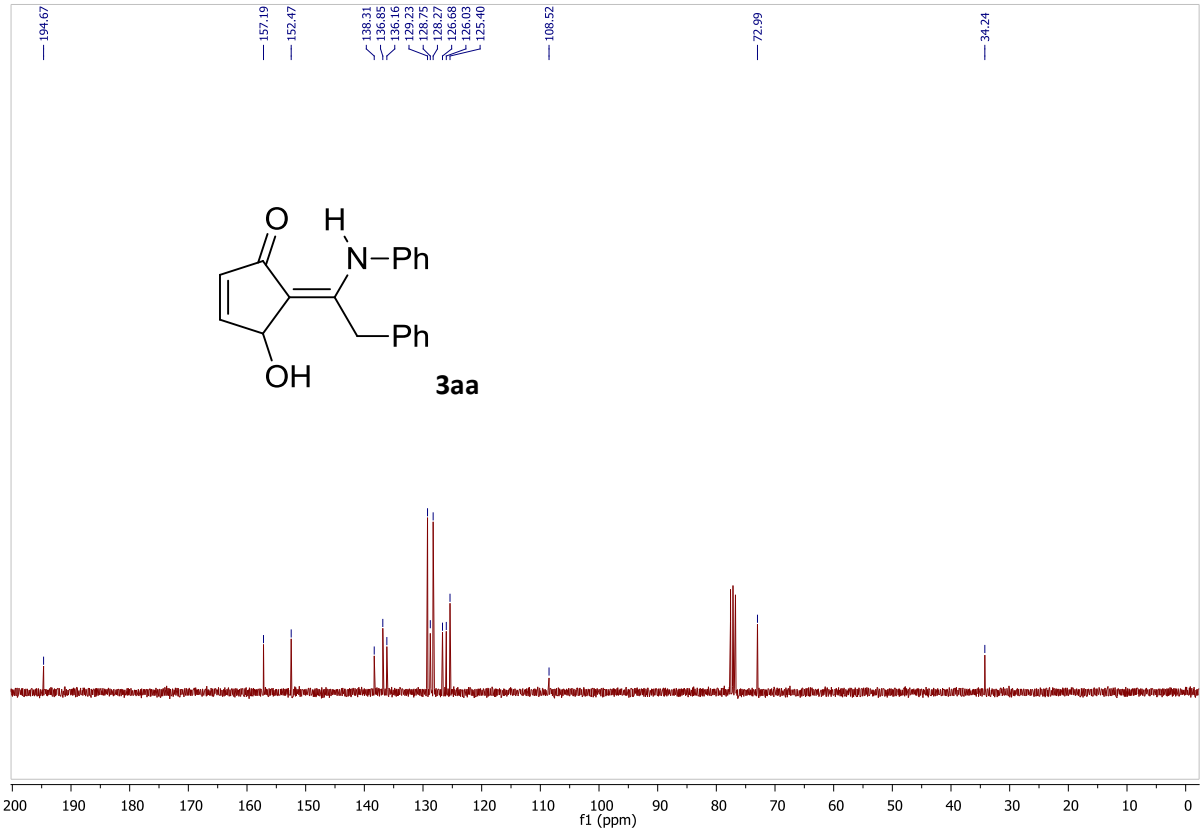
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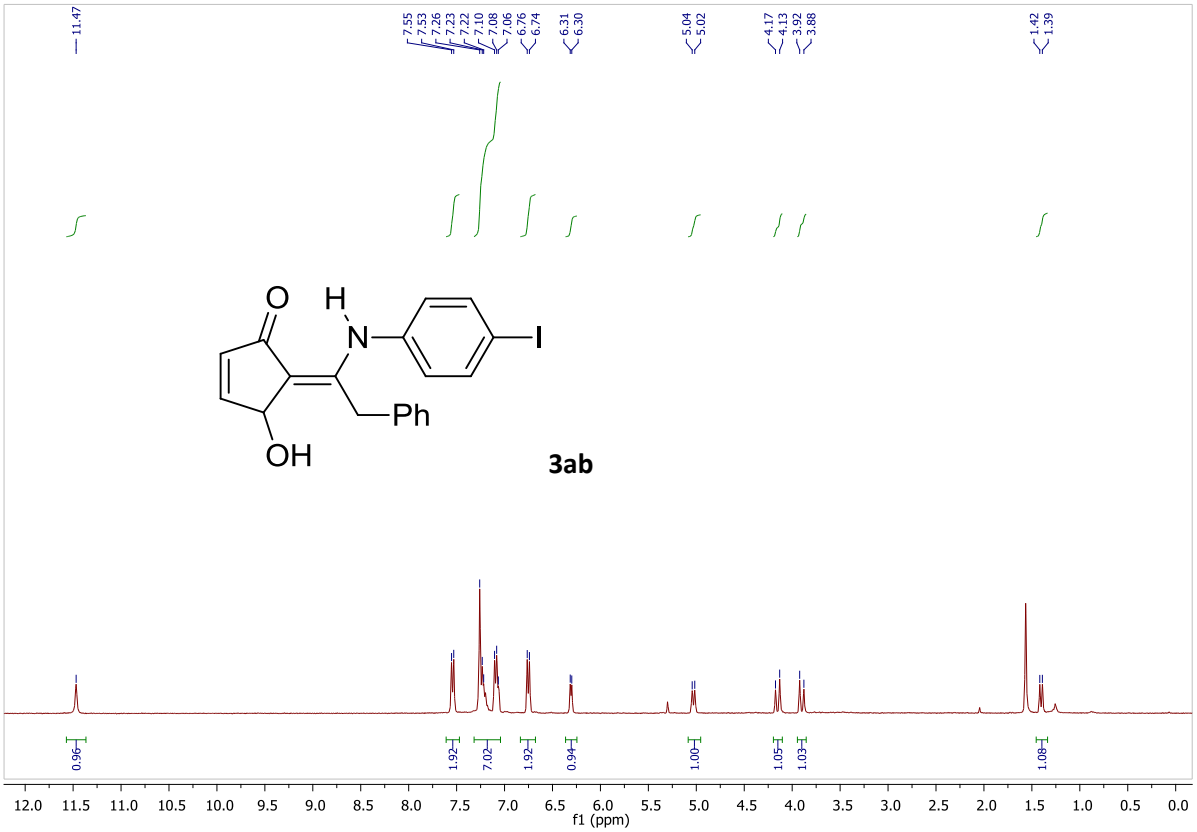
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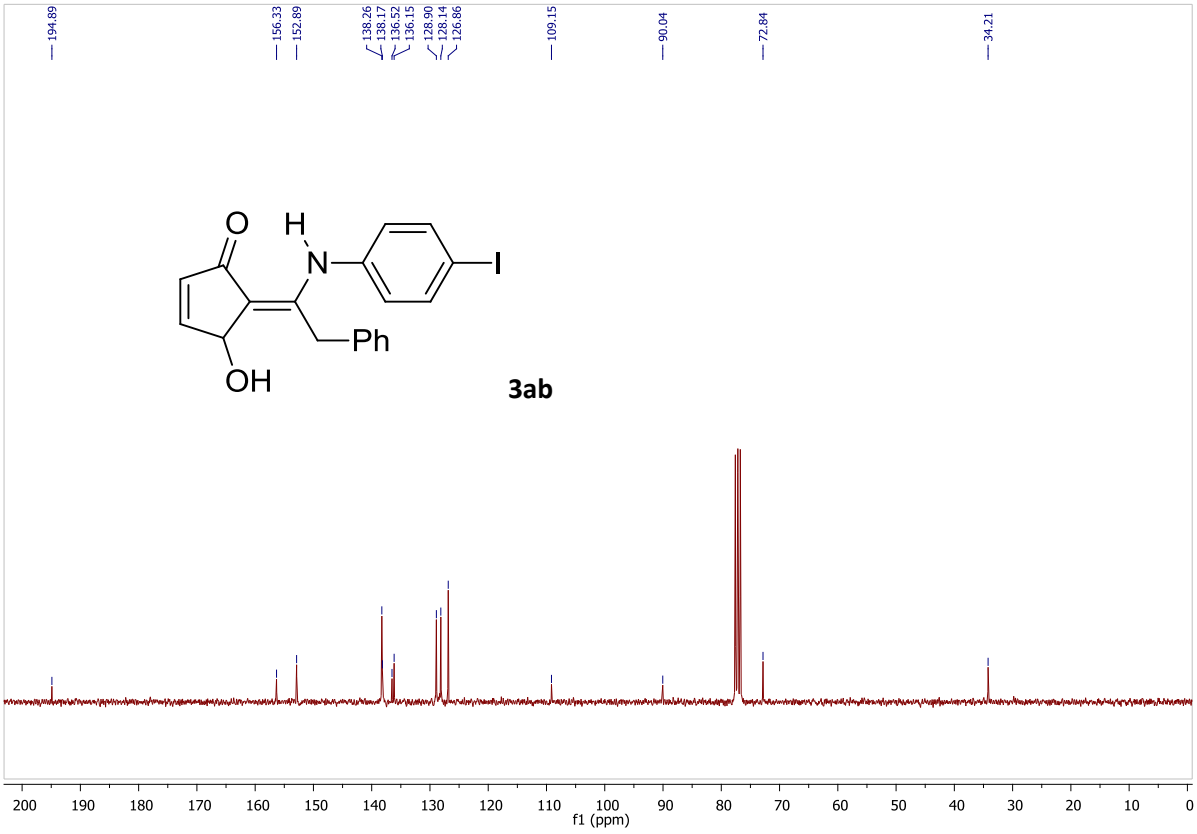
1.03
1.08
f1 (ppm)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156.33
152.89
138.26
138.17
136.52
136.15
128.90
128.14
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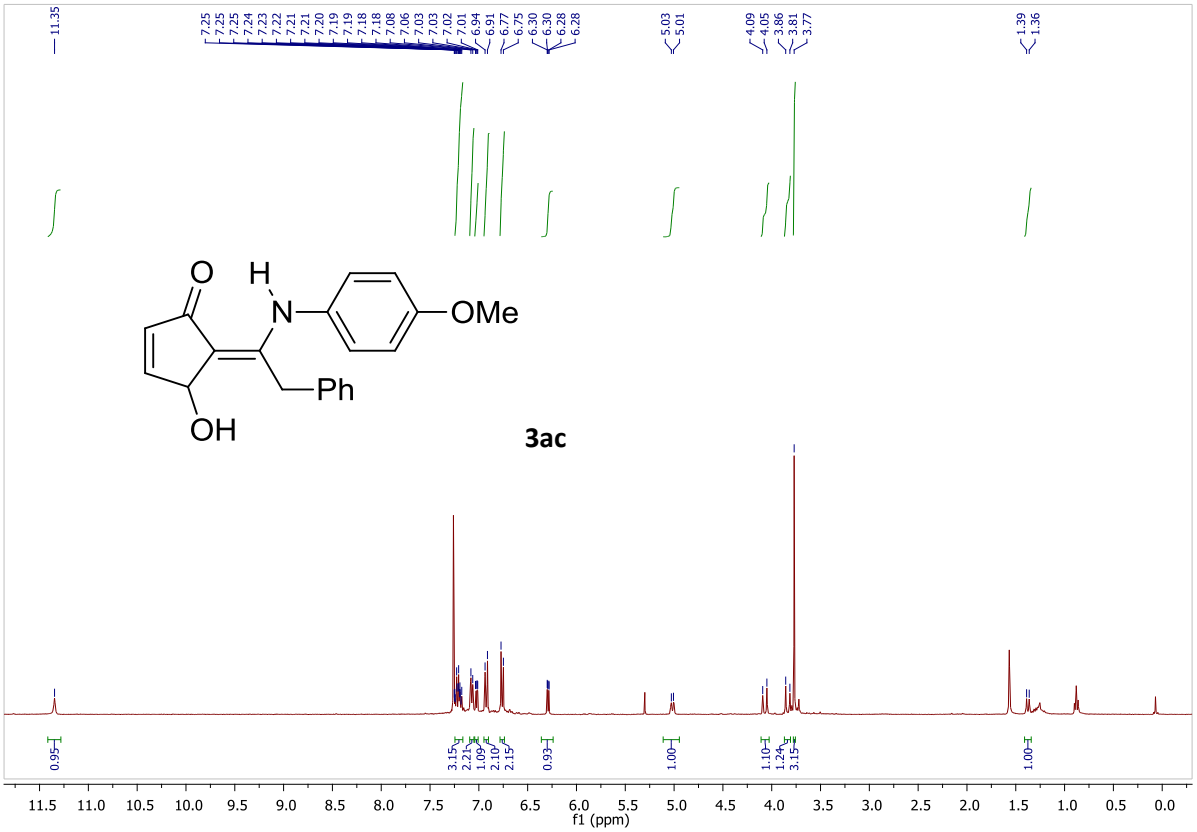
109.15
90.04
72.84
34.21
O
H
N
I
Ph
OH
3ab
f1 (ppm)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7.21
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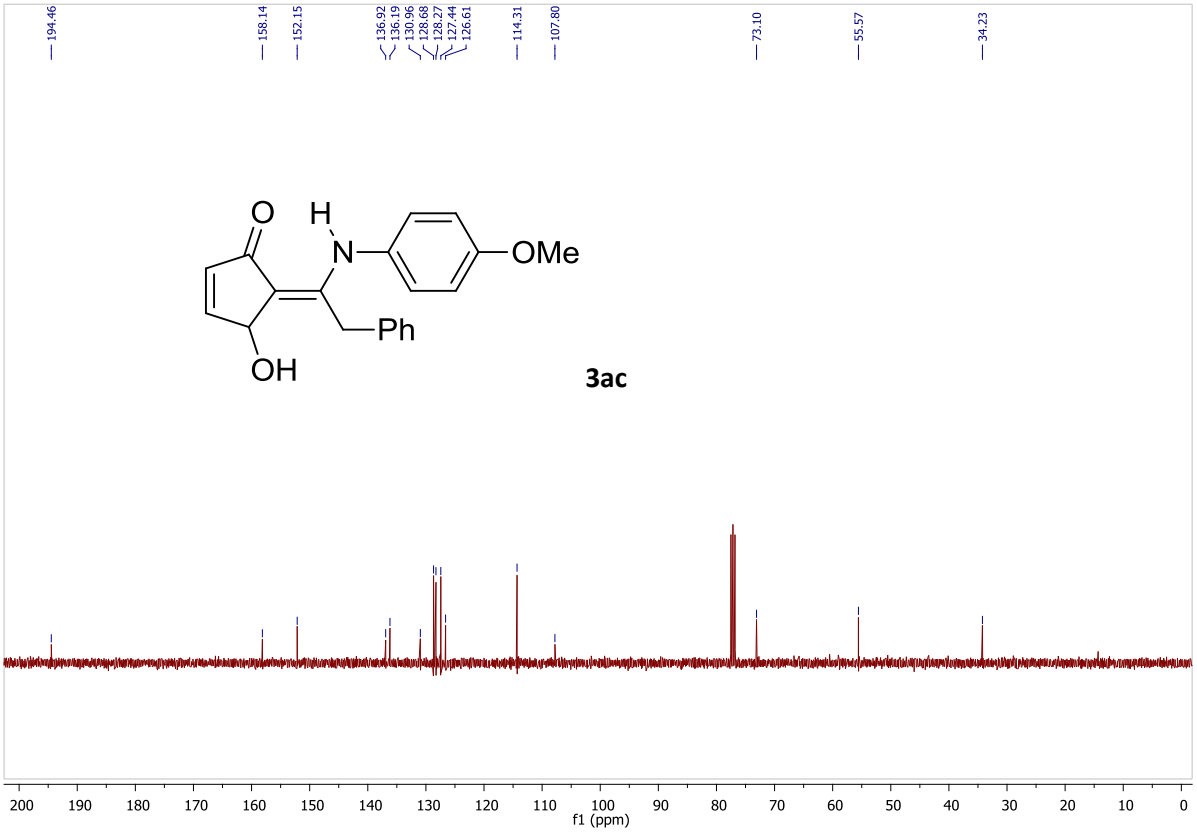
7.20
7.19
7.19
7.18
7.18
7.08
7.06
7.03
7.03
7.02
7.01
6.94
6.91
6.77
6.75
6.30
6.30
6.28
6.28
5.03
5.01
4.09
4.05
3.86
3.81
3.77
1.39
1.36
O
H
N
OMe
Ph
OH
3ac
0.95
3.15
2.21
1.09
2.10
2.15
0.93
1.00
1.10
1.24
3.15
1.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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152.15
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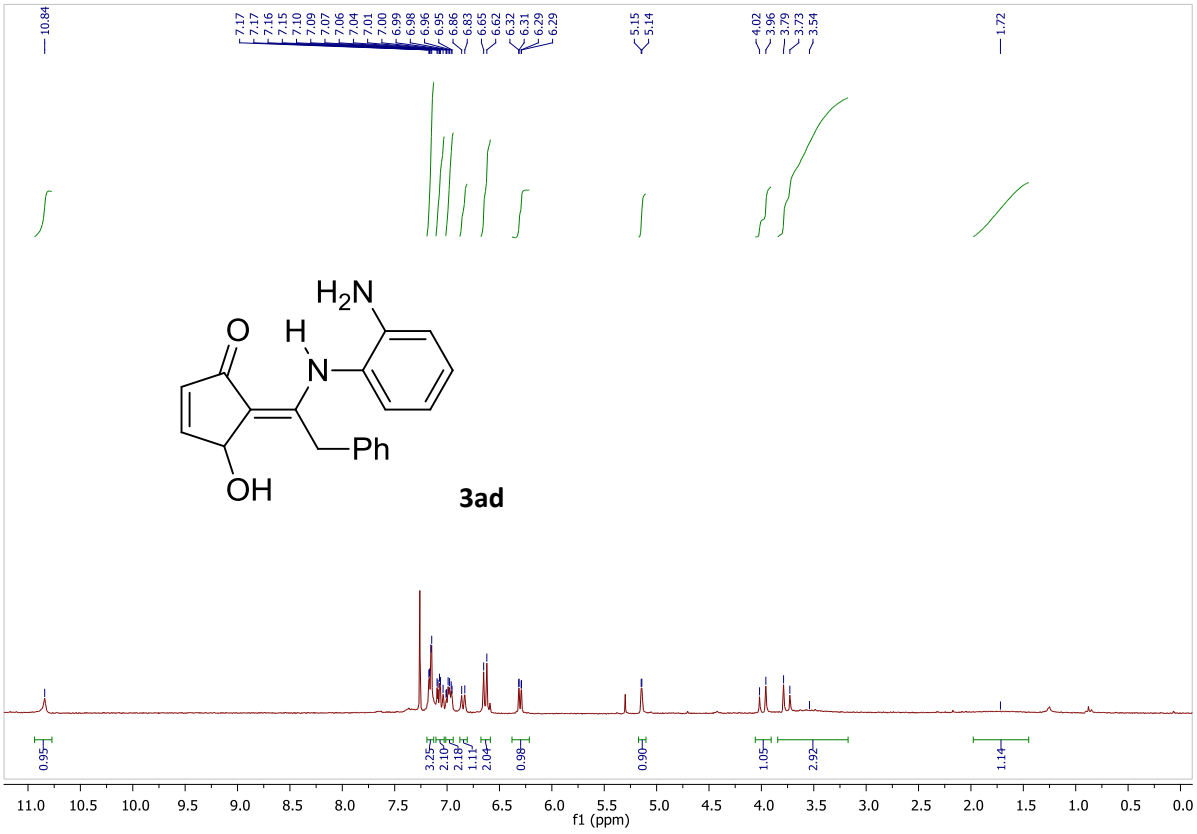
130.96
128.68
128.27
127.44
126.61
114.31
107.80
73.10
55.57
34.23
O
H
N
OMe
Ph
OH
3ac
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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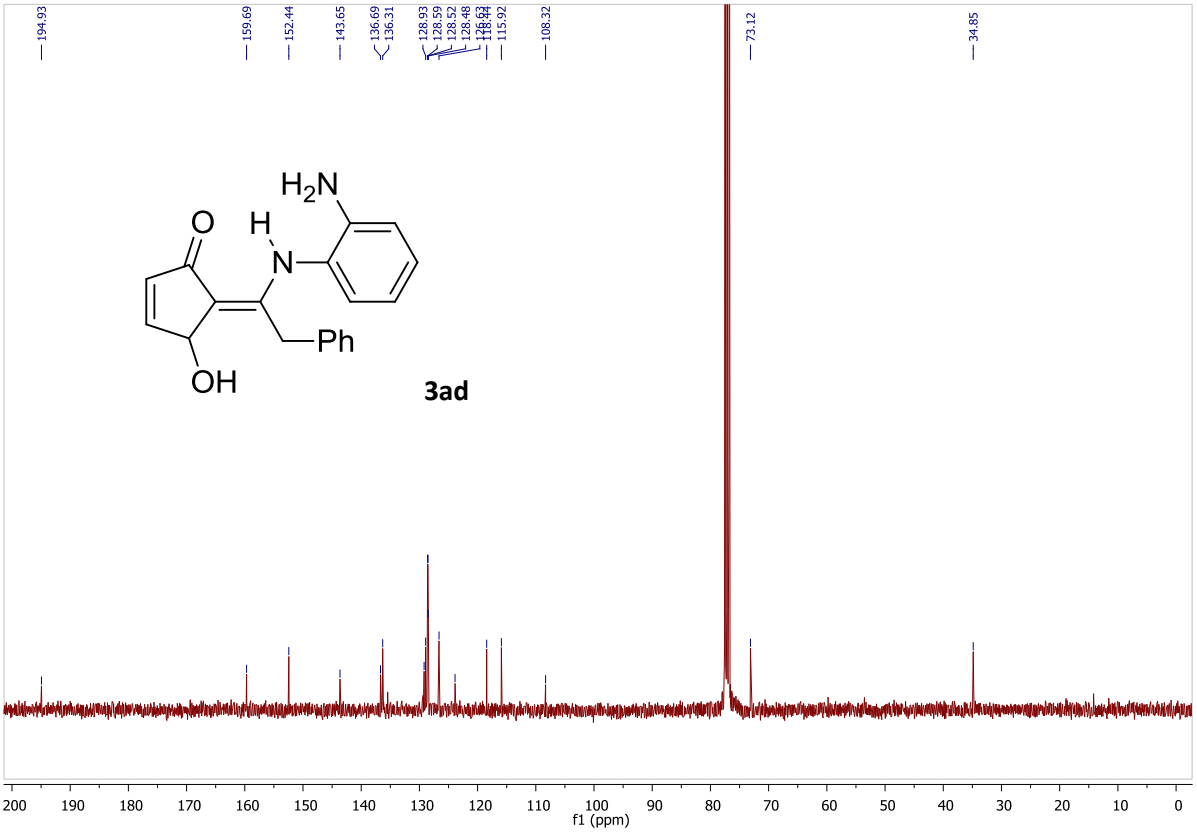
7.17
7.17
7.16
7.15
7.10
7.09
7.07
7.06
7.04
7.01
7.00
6.99
6.98
6.96
6.95
6.86
6.83
6.65
6.62
6.32
6.31
6.29
6.29
5.15
5.14
4.02
3.96
3.79
3.73
3.54
1.72
H2N
O
H
N
Ph
OH
3ad
0.95
3.25
2.10
2.18
1.11
2.04
0.98
0.90
1.05
2.92
1.14
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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159.69
152.44
143.65
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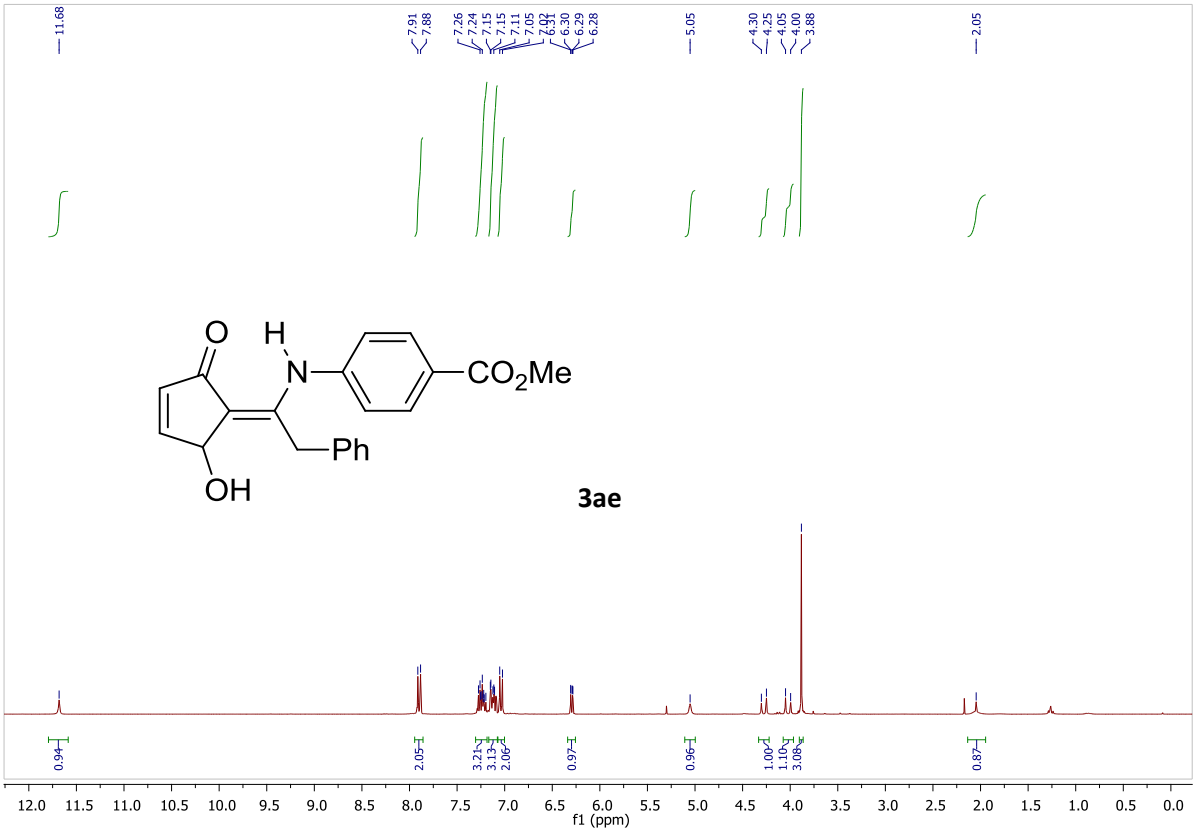
136.31
128.93
128.59
128.52
128.48
115.92
108.32
73.12
34.85
H2N
O
H
N
Ph
OH
3ad
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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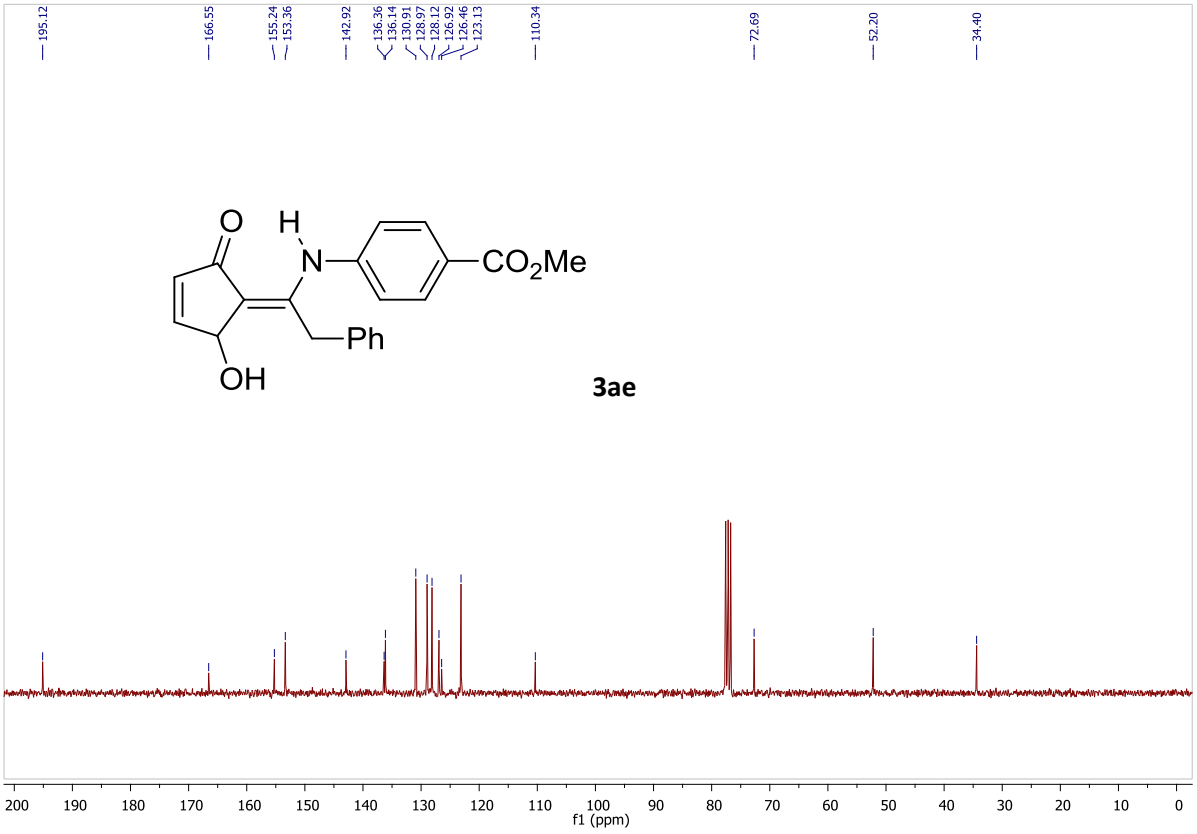
7.91
7.88
7.26
7.24
7.15
7.15
7.11
7.05
7.02
6.31
6.30
6.29
6.28
5.05
4.30
4.25
4.05
4.00
3.88
2.05
O
H
N
CO2Me
Ph
OH
3ae
0.94
2.05
3.21
3.13
2.06
0.97
0.96
1.00
1.10
3.08
0.87
f1 (ppm)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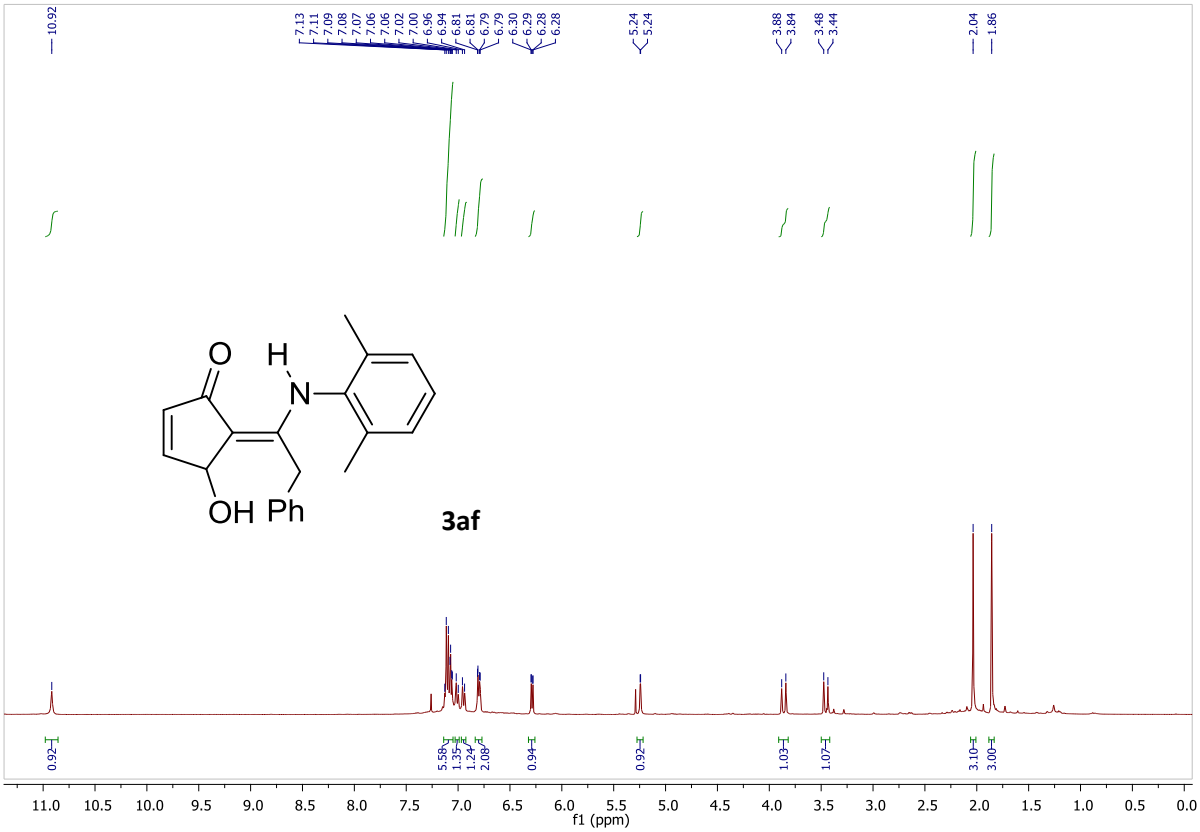
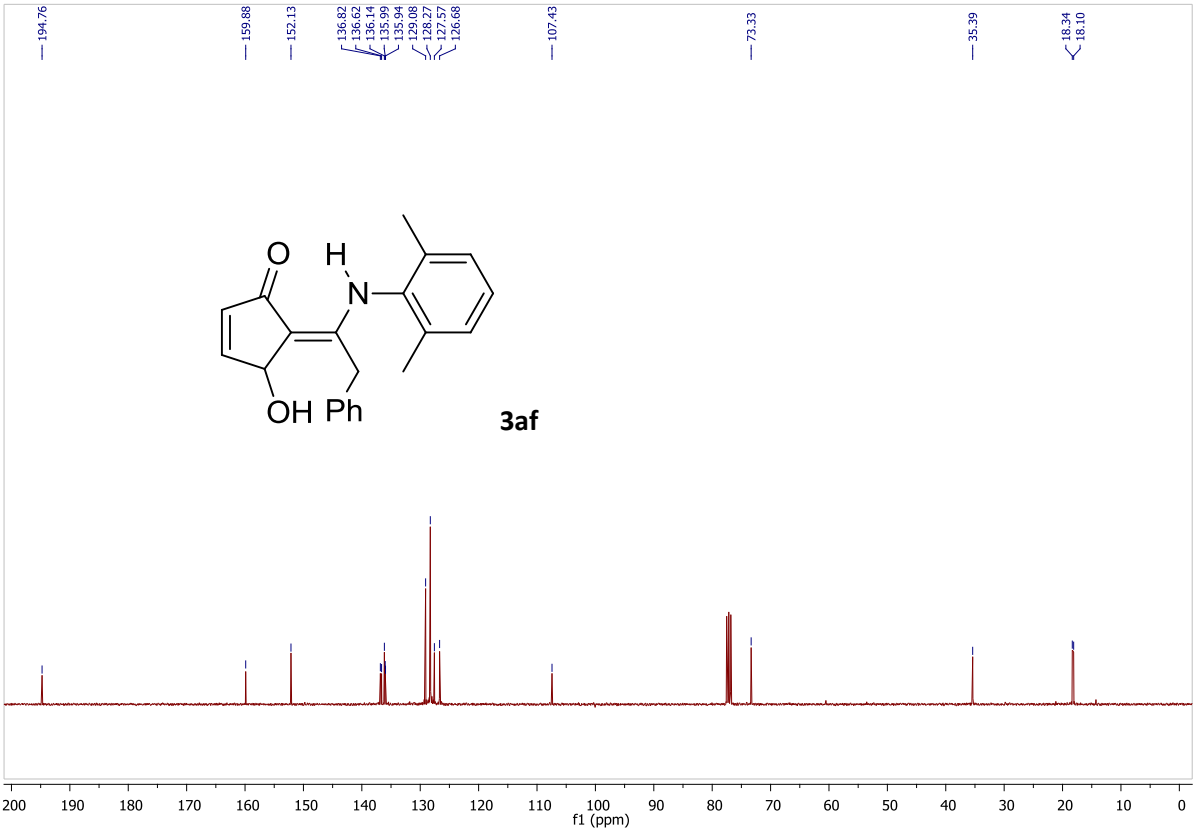
155.24
153.36
142.92
136.36
136.14
130.91
128.97
128.12
126.92
126.46
123.13
110.34
72.69
52.20
34.40
O
H
N
CO2Me
Ph
OH
3ae
f1 (ppm)


10.92
7.13
7.11
7.09
7.08
7.07
7.06
7.06
7.02
7.00
6.96
6.94
6.81
6.81
6.79
6.79
6.30
6.29
6.28
6.28
5.24
5.24
3.88
3.84
3.48
3.44
2.04
1.86
O
H
N
OH Ph
3af
0.92
5.58
1.35
1.24
2.08
0.94
0.92
1.03
1.07
3.10
3.00
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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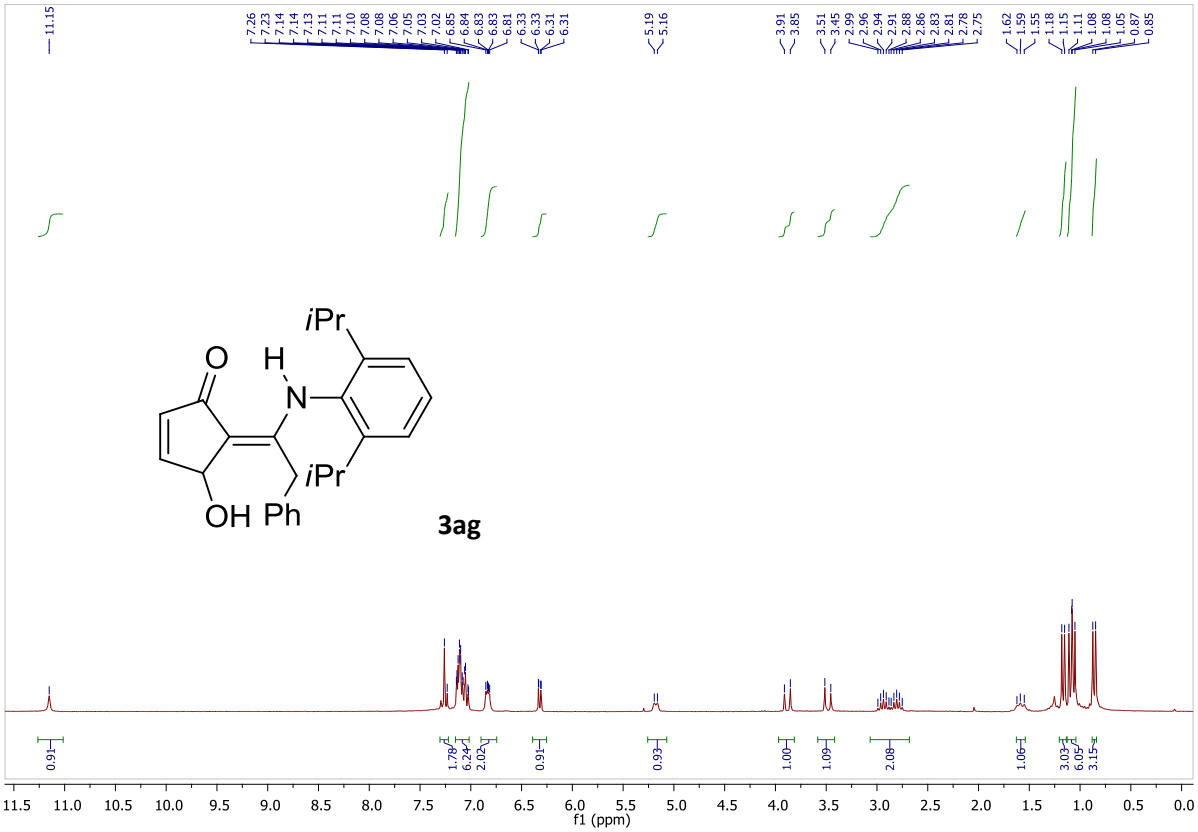
135.99
135.94
129.08
128.27
127.57
126.68
107.43
73.33
35.39
18.34
18.10
O
H
N
OH Ph
3af
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.06
7.05
7.03
7.02
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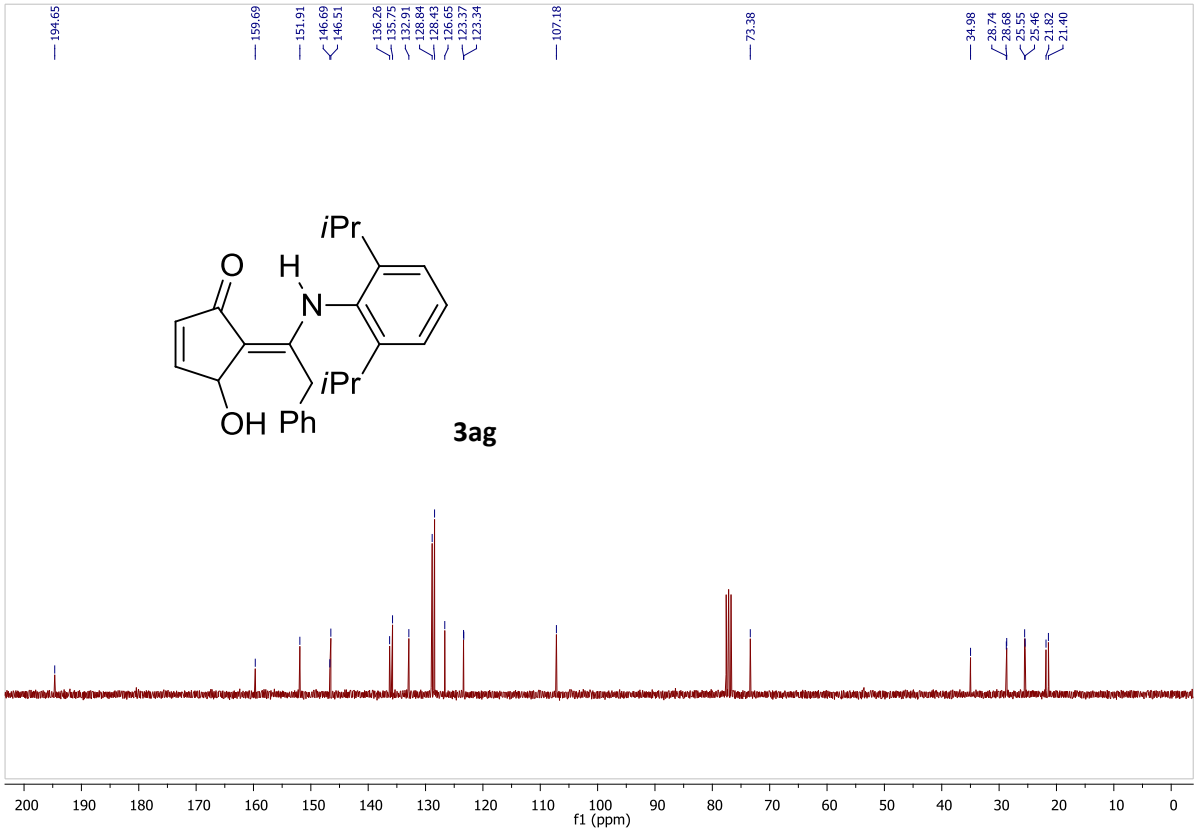
6.84
6.83
6.81
6.33
6.31
6.31
5.19
5.16
3.91
3.85
3.51
3.45
2.99
2.96
2.94
2.91
2.88
2.86
2.83
2.81
2.78
2.75
1.62
1.59
1.55
1.18
1.15
1.11
1.08
1.05
0.87
0.85
iPr
O
H
N
iPr
OH Ph
3ag
0.91
1.79
6.24
2.02
0.91
0.93
1.00
1.09
2.08
1.06
3.03
6.05
3.15
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 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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146.69
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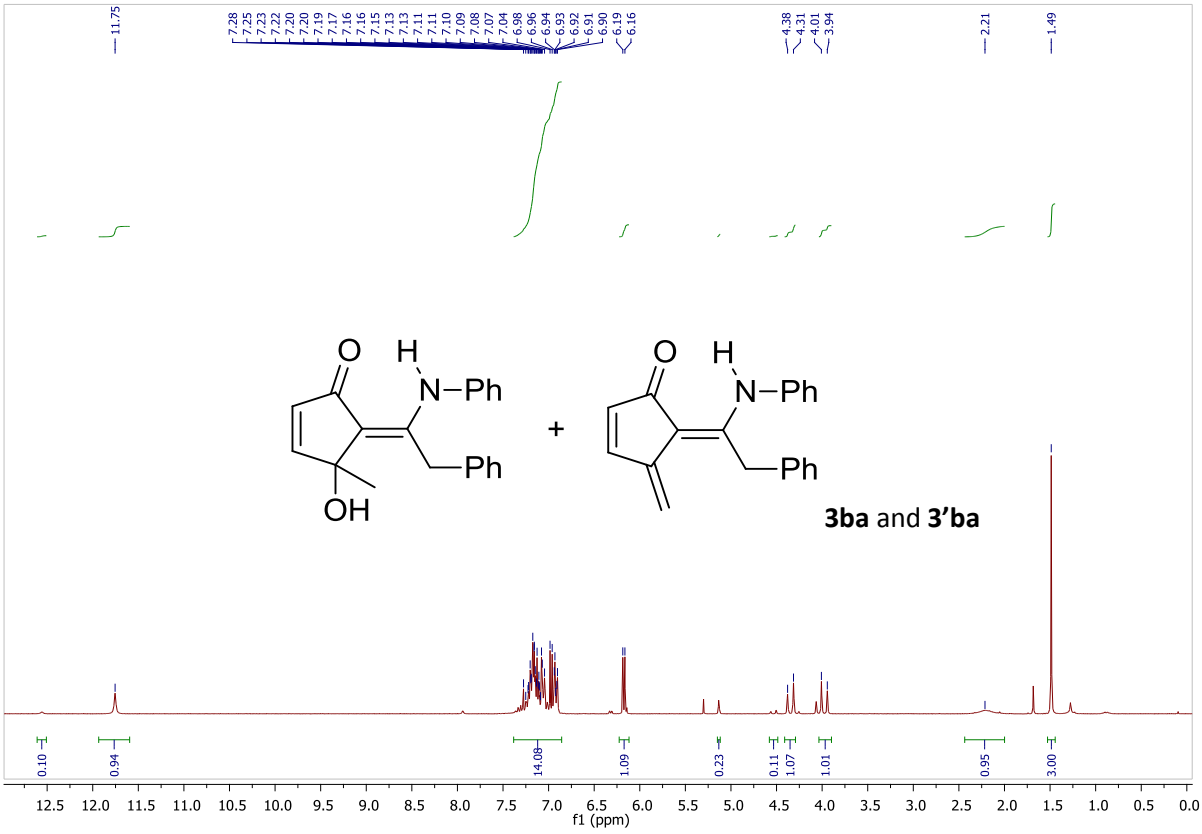
136.26
135.75
132.91
128.84
128.43
126.65
123.37
123.34
107.18
73.38
34.98
28.74
28.68
25.55
25.46
21.82
21.40
iPr
O
H
N
iPr
OH Ph
3ag
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.23
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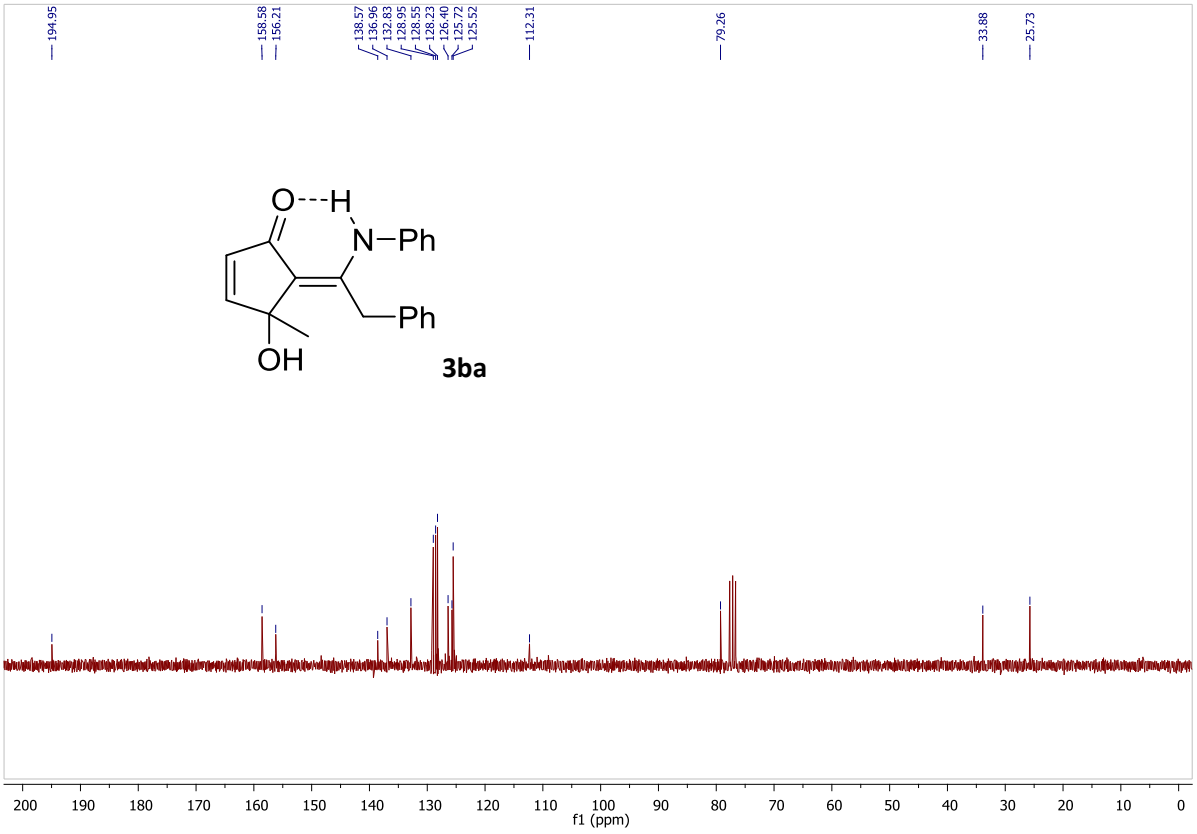
7.20
7.20
7.19
7.17
7.16
7.16
7.15
7.13
7.13
7.11
7.11
7.10
7.09
7.08
7.07
7.04
6.98
6.96
6.94
6.93
6.92
6.91
6.90
6.19
6.16
4.38
4.31
4.01
3.94
2.21
1.49
O
H
N–Ph
Ph
OH
+
O
H
N–Ph
Ph
3ba and 3'ba
0.10
0.94
14.08
1.09
0.23
0.11
1.07
1.01
0.95
3.00
f1 (ppm)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158.58
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132.83
128.95
128.55
128.23
126.40
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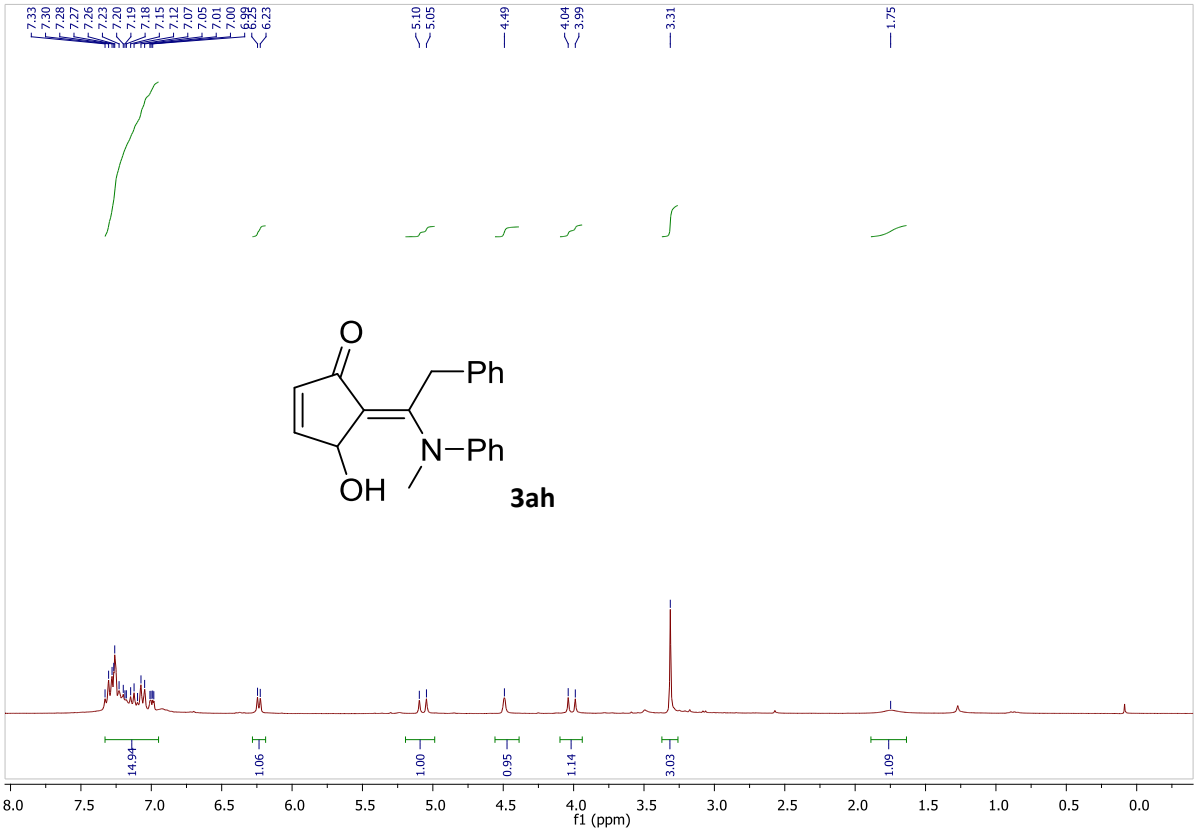
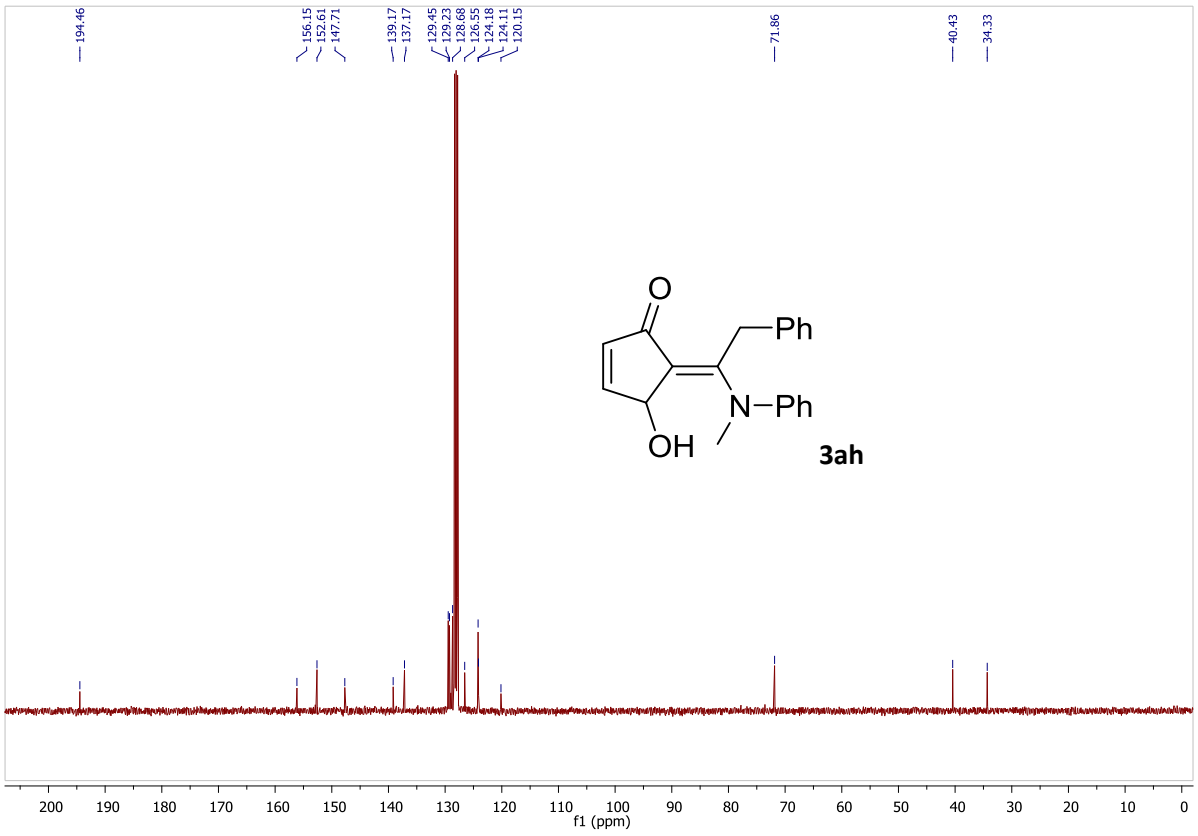
125.52
112.31
79.26
33.88
25.73
O---H
N–Ph
Ph
OH
3ba
f1 (ppm)


7.33
7.30
7.28
7.27
7.26
7.23
7.20
7.19
7.18
7.15
7.12
7.07
7.05
7.01
7.00
6.99
6.95
6.23
5.10
5.05
4.49
4.04
3.99
3.31
1.75
O
Ph
N−Ph
OH
3ah
14.94
1.06
1.00
0.95
1.14
3.03
1.09
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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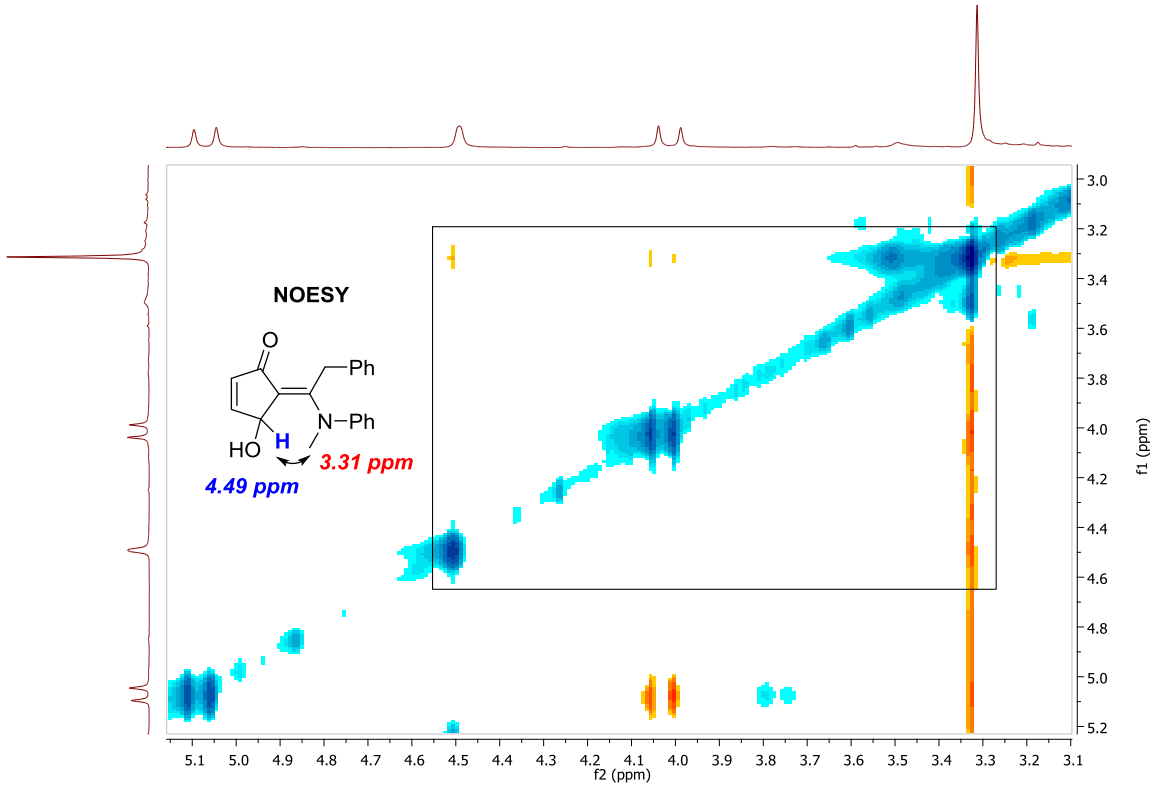
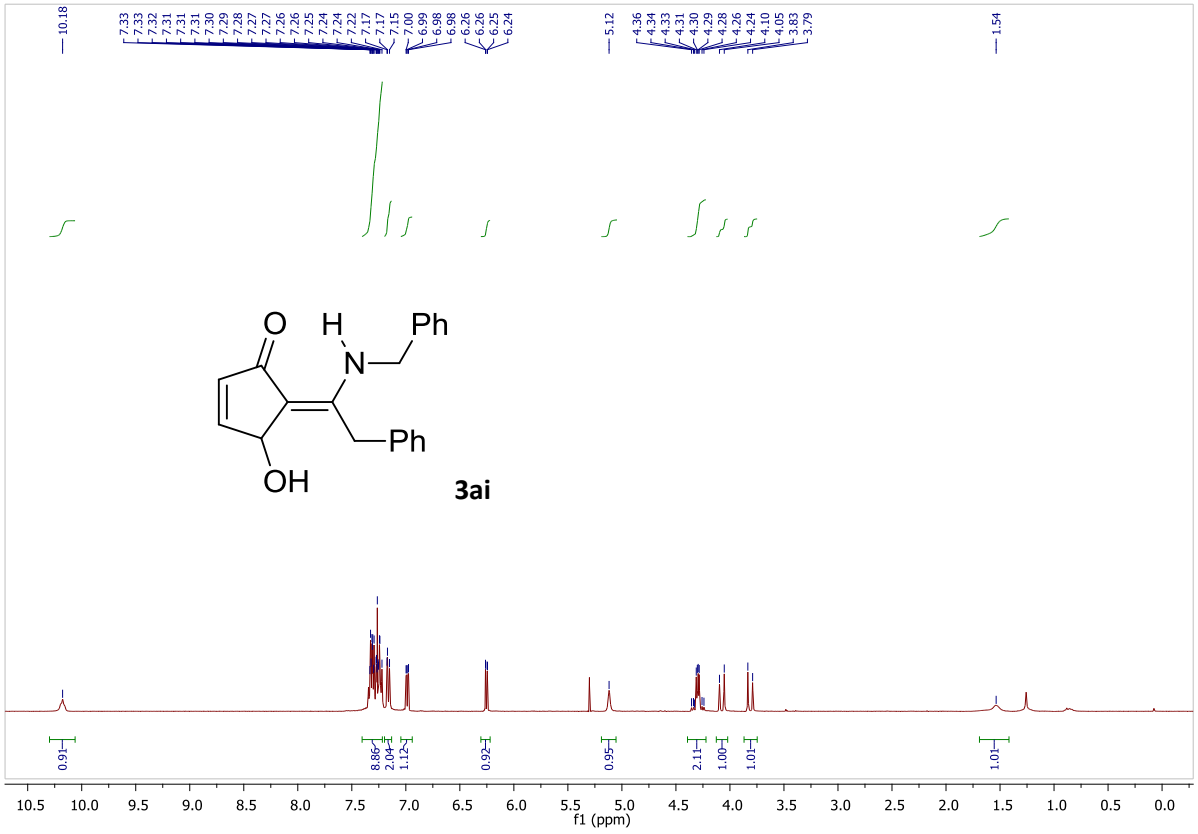
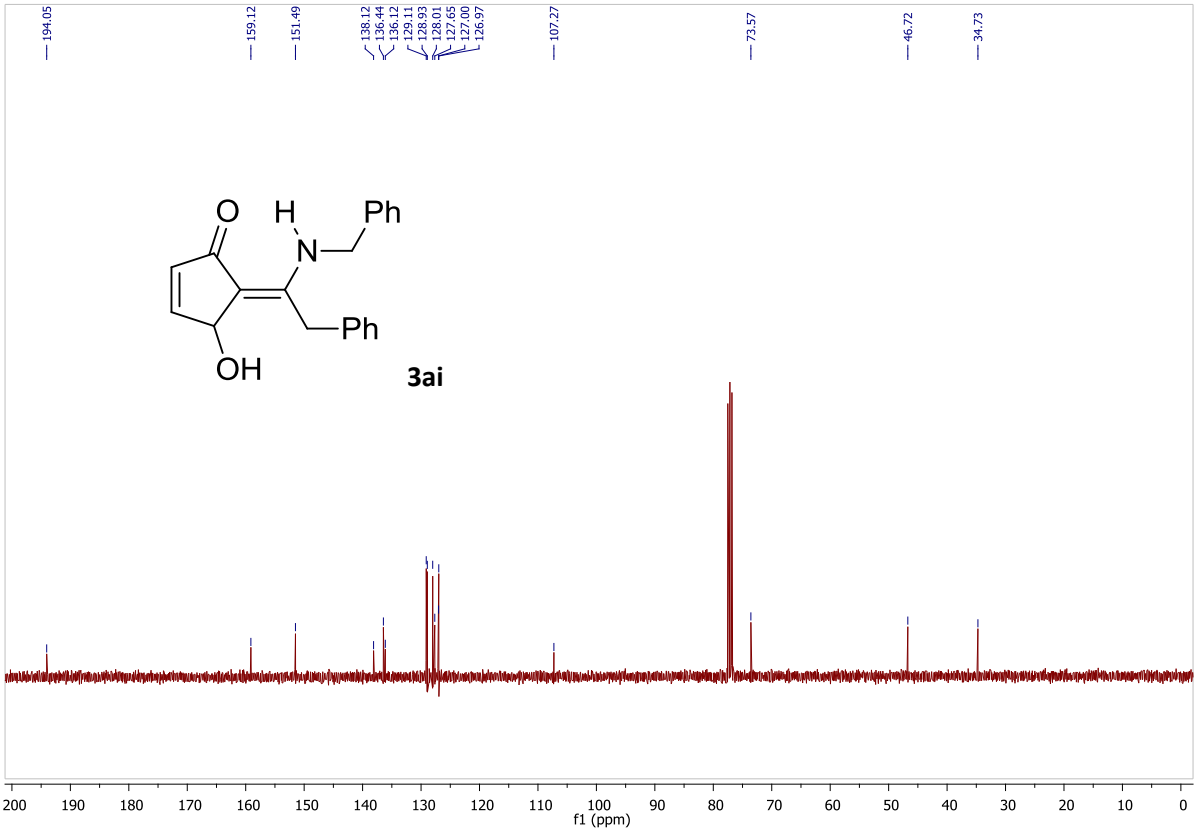
156.15
152.61
147.71
139.17
137.17
129.45
129.23
128.68
126.55
124.18
124.11
120.15
71.86
40.43
34.33
O
Ph
N−Ph
OH
3ah
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NOESY
O
Ph
N–Ph
HO
H
3.31 ppm
4.49 ppm
f2 (ppm)
f1 (ppm)


O
H
Ph
N
Ph
OH
3ai
f1 (ppm)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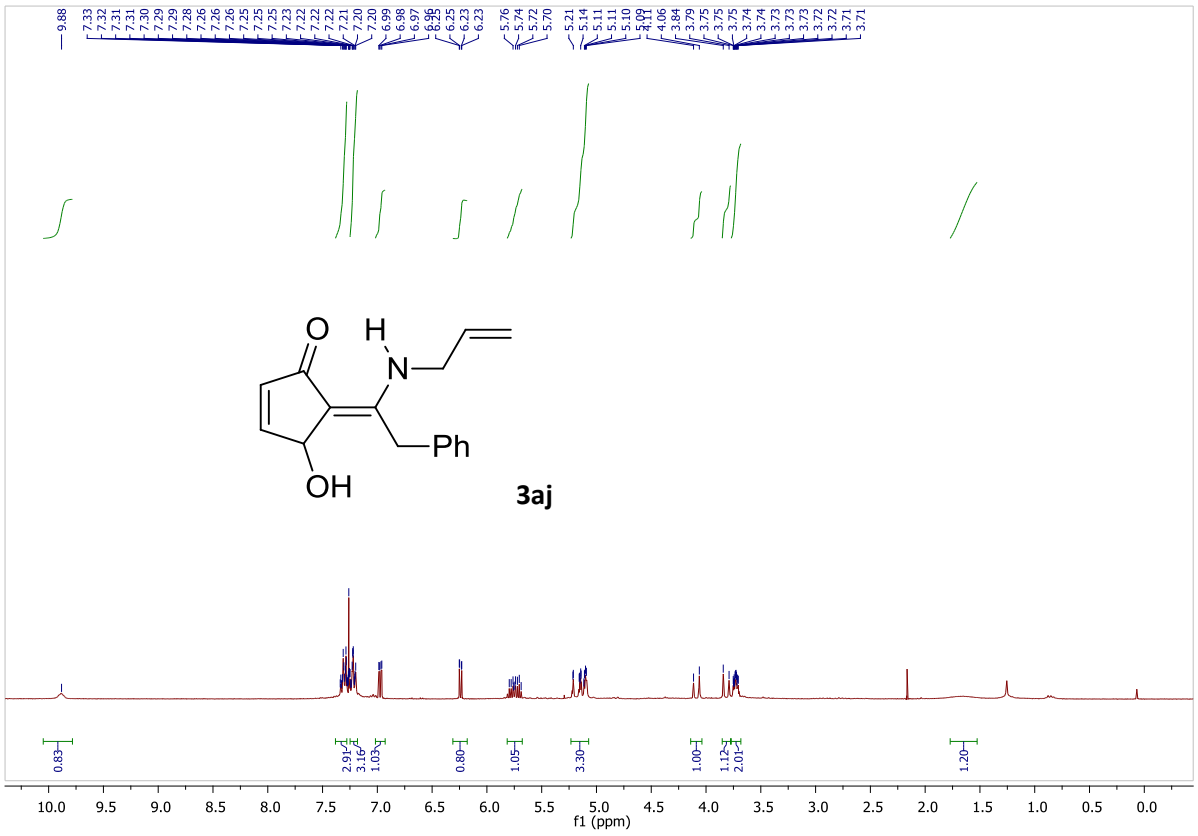
136.12
129.11
128.93
128.01
127.65
127.00
126.97
107.27
73.57
46.72
34.73
O
H
N
Ph
Ph
OH
3ai
f1 (ppm)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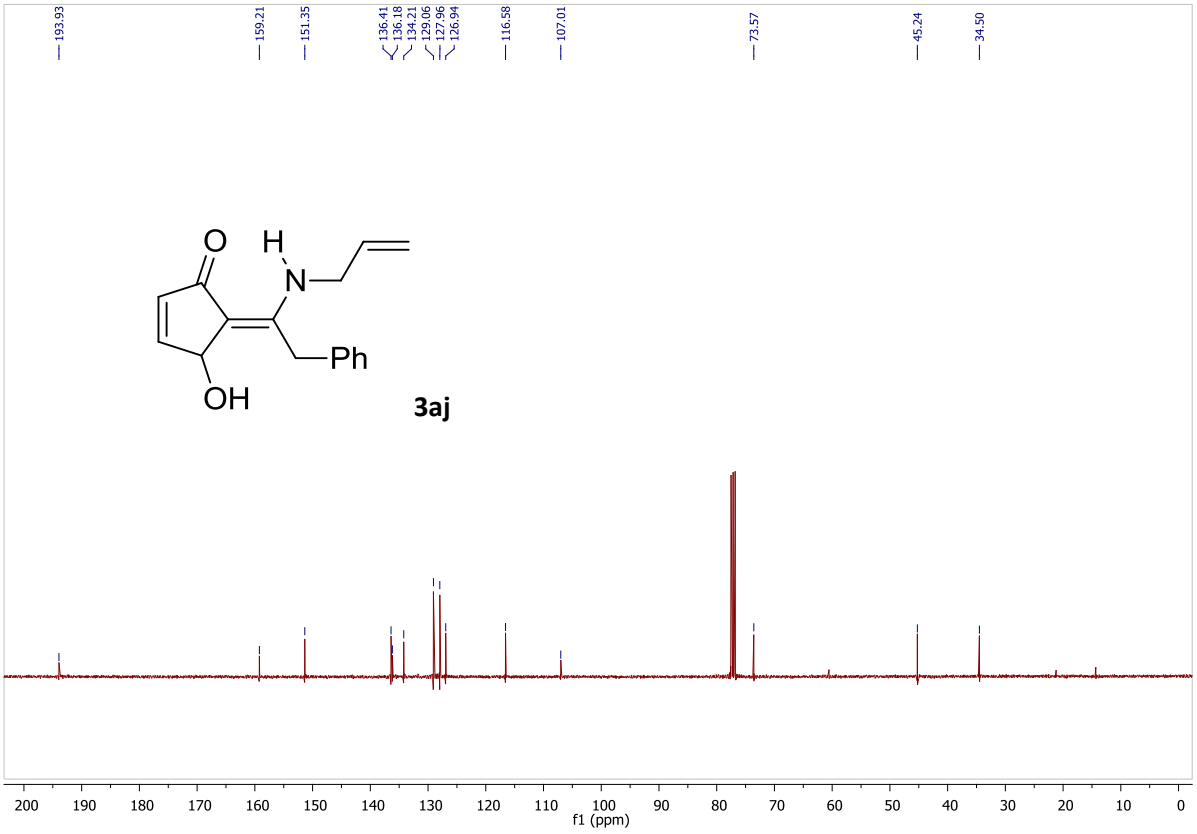
7.26
7.25
7.25
7.25
7.23
7.22
7.22
7.22
7.21
7.20
7.20
6.99
6.98
6.97
6.96
6.25
6.23
6.23
5.76
5.74
5.72
5.70
5.21
5.14
5.11
5.11
5.10
5.09
4.11
4.06
3.84
3.79
3.75
3.75
3.75
3.74
3.74
3.73
3.73
3.73
3.72
3.72
3.71
3.71
O
H
N
Ph
OH
3aj
0.83
2.91
3.16
1.03
0.80
1.05
3.30
1.00
1.12
2.01
1.20
f1 (ppm)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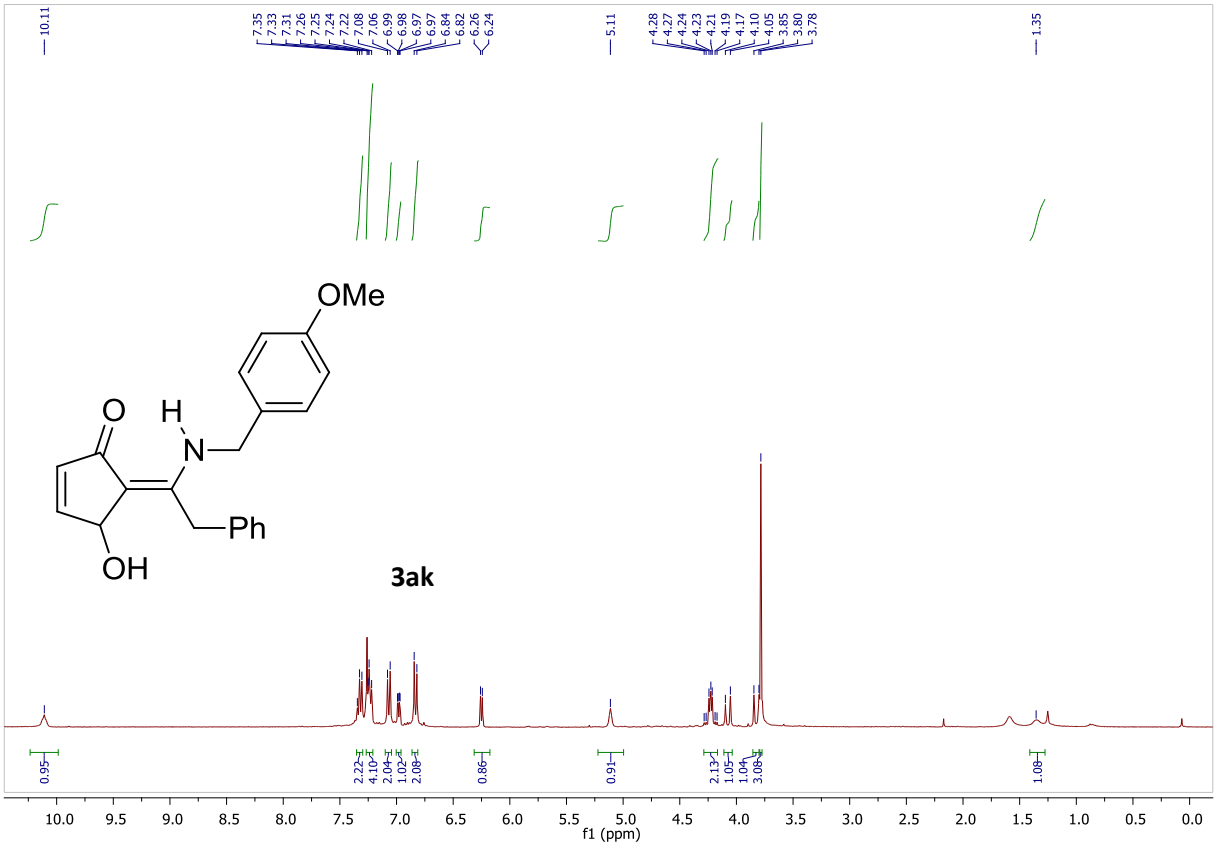
136.41
136.18
134.21
129.06
127.96
126.94
116.58
107.01
73.57
45.24
34.50
O
H
N
Ph
OH
3aj
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.33
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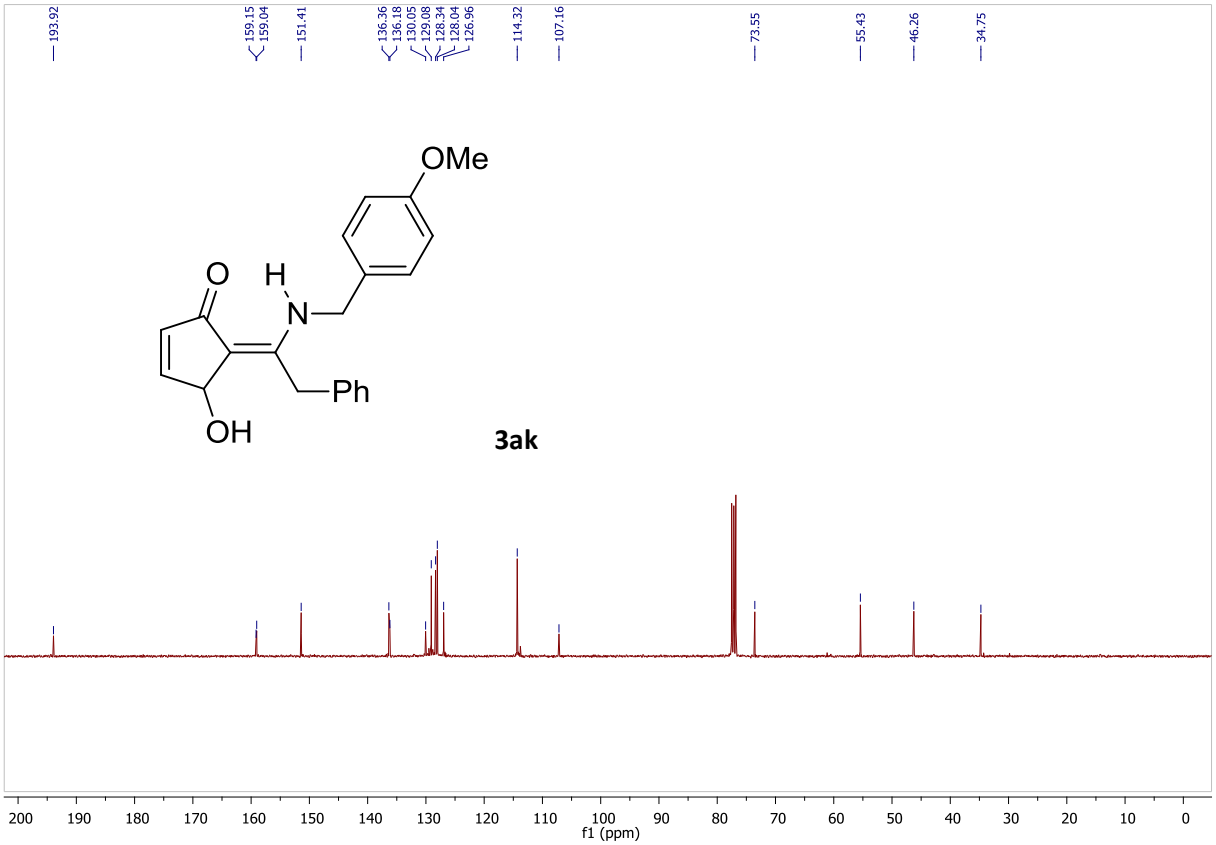
7.26
7.25
7.24
7.22
7.08
7.06
6.99
6.98
6.97
6.97
6.84
6.82
6.26
6.24
5.11
4.28
4.27
4.24
4.23
4.21
4.19
4.17
4.10
4.05
3.85
3.80
3.78
1.35
OMe
O
H
N
Ph
OH
3ak
0.95
2.22
4.10
2.04
1.02
2.08
0.86
0.91
2.13
1.05
1.04
3.08
1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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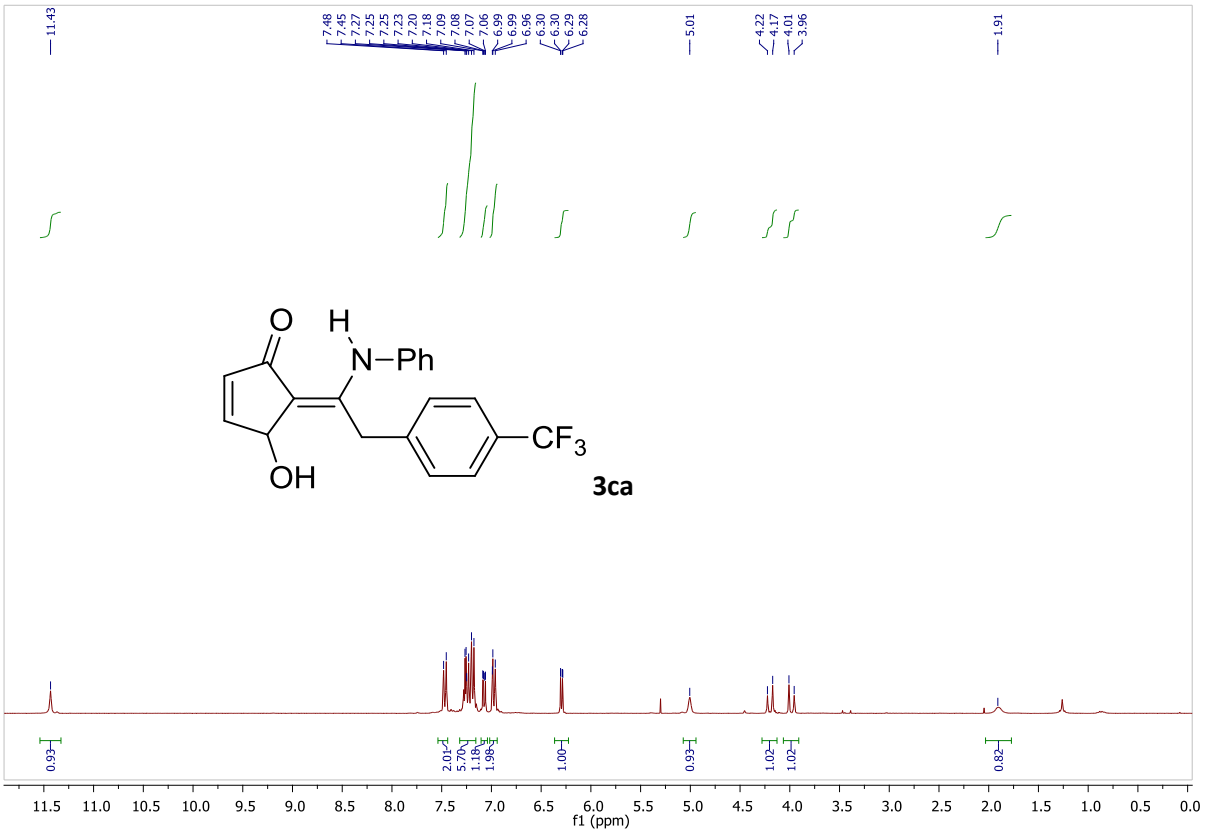
159.15
159.04
151.41
136.36
136.18
130.05
129.08
128.34
128.04
126.96
114.32
107.16
73.55
55.43
46.26
34.75
OMe
O
H
N
Ph
OH
3ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.43
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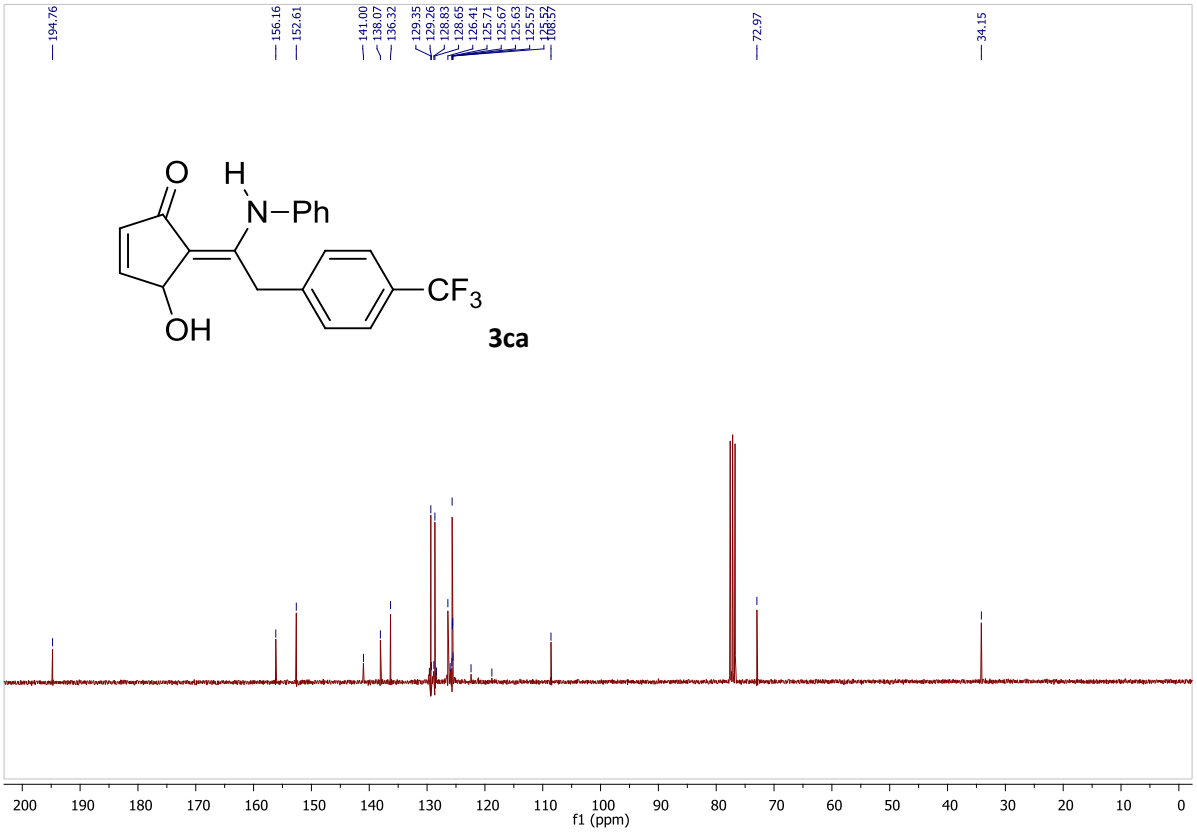
7.27
7.25
7.25
7.23
7.20
7.18
7.09
7.08
7.07
7.06
6.99
6.96
6.30
6.29
6.28
5.01
4.22
4.17
4.01
3.96
1.91
O
H
N–Ph
CF3
OH
3ca
0.93
2.01
5.70
1.16
1.98
1.00
0.93
1.02
1.02
0.82
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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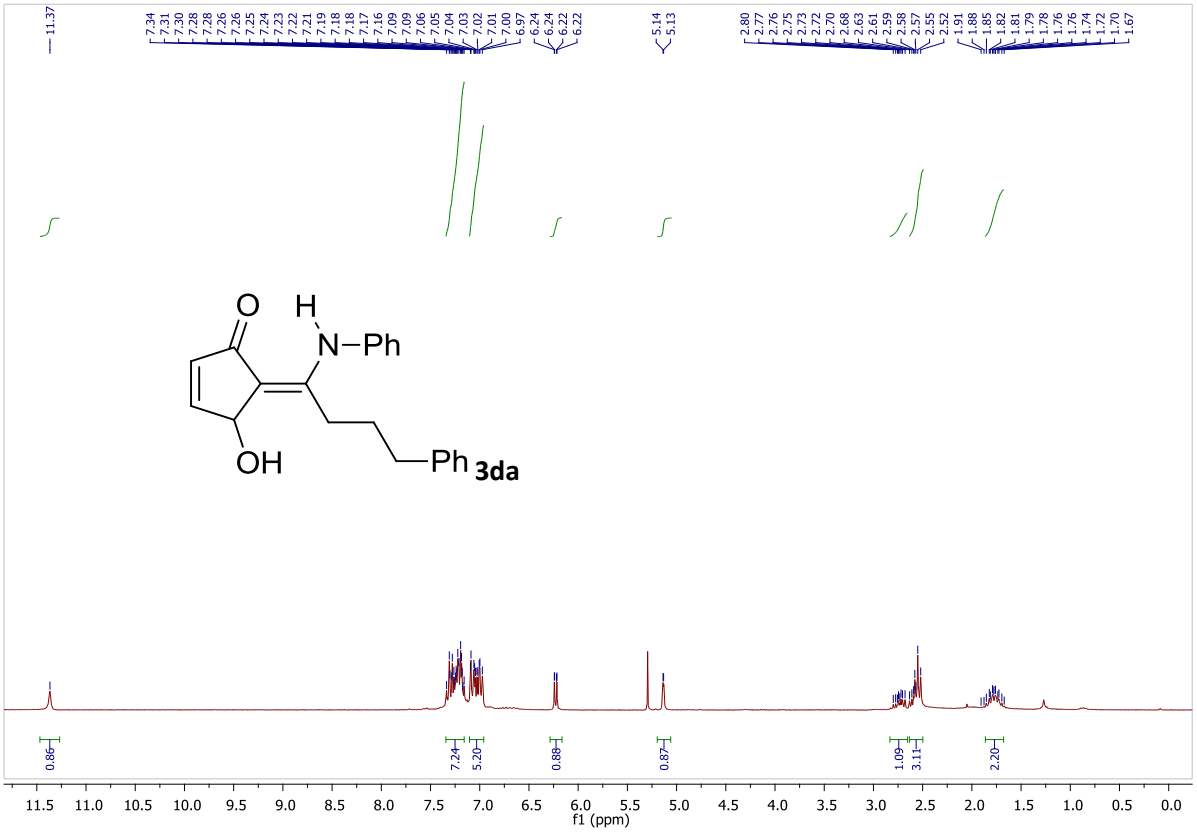
136.32
129.35
129.26
128.83
128.65
126.41
125.71
125.67
125.63
125.57
125.52
108.57
72.97
34.15
O
H
N–Ph
CF3
OH
3ca
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.37
7.34
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7.30
7.28
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.19
7.18
7.18
7.17
7.16
7.09
7.09
7.06
7.05
7.04
7.03
7.02
7.01
7.00
6.97
6.24
6.24
6.22
6.22
5.14
5.13
2.80
2.77
2.76
2.75
2.73
2.72
2.70
2.68
2.63
2.61
2.59
2.58
2.57
2.55
2.52
1.91
1.88
1.85
1.82
1.81
1.79
1.78
1.76
1.76
1.74
1.72
1.70
1.67
O
H
N–Ph
OH
Ph
3da
0.86
7.24
5.20
0.88
0.87
1.09
3.11
2.20
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
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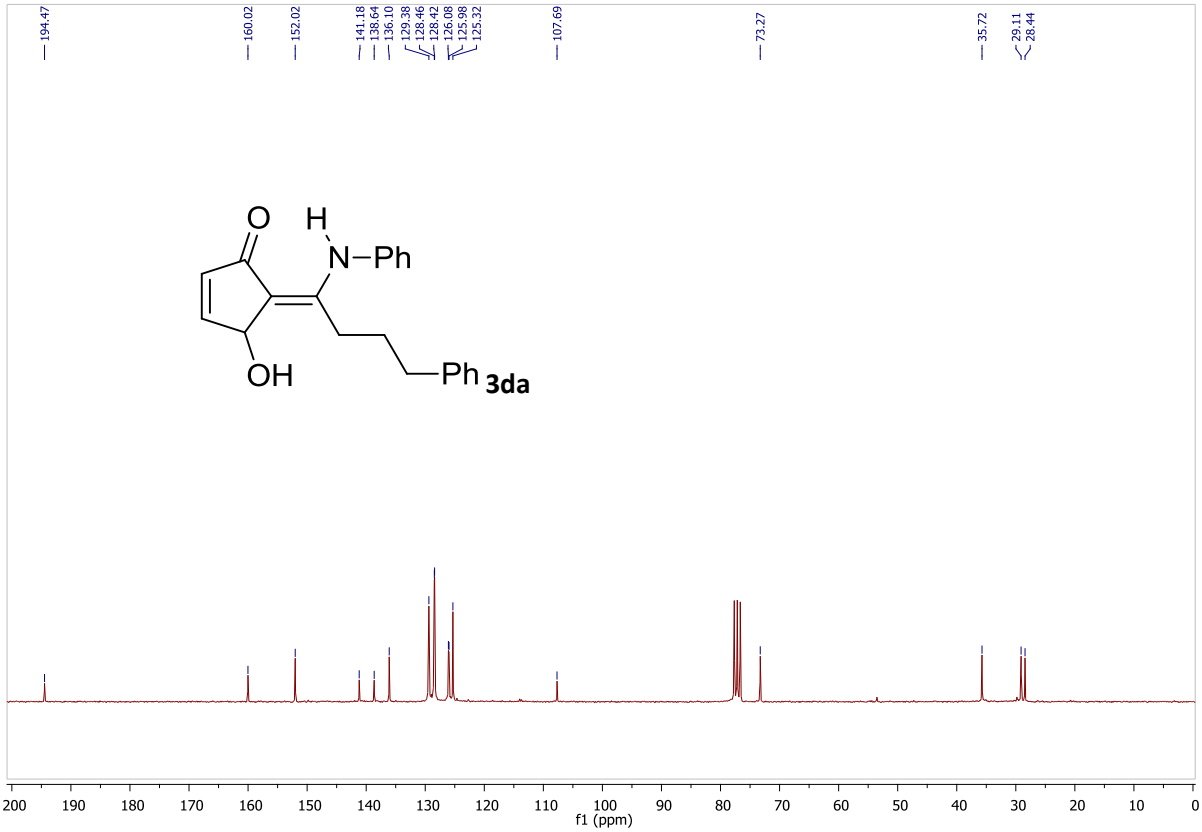
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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152.02
141.18
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136.10
129.38
128.46
128.42
126.08
125.98
125.32
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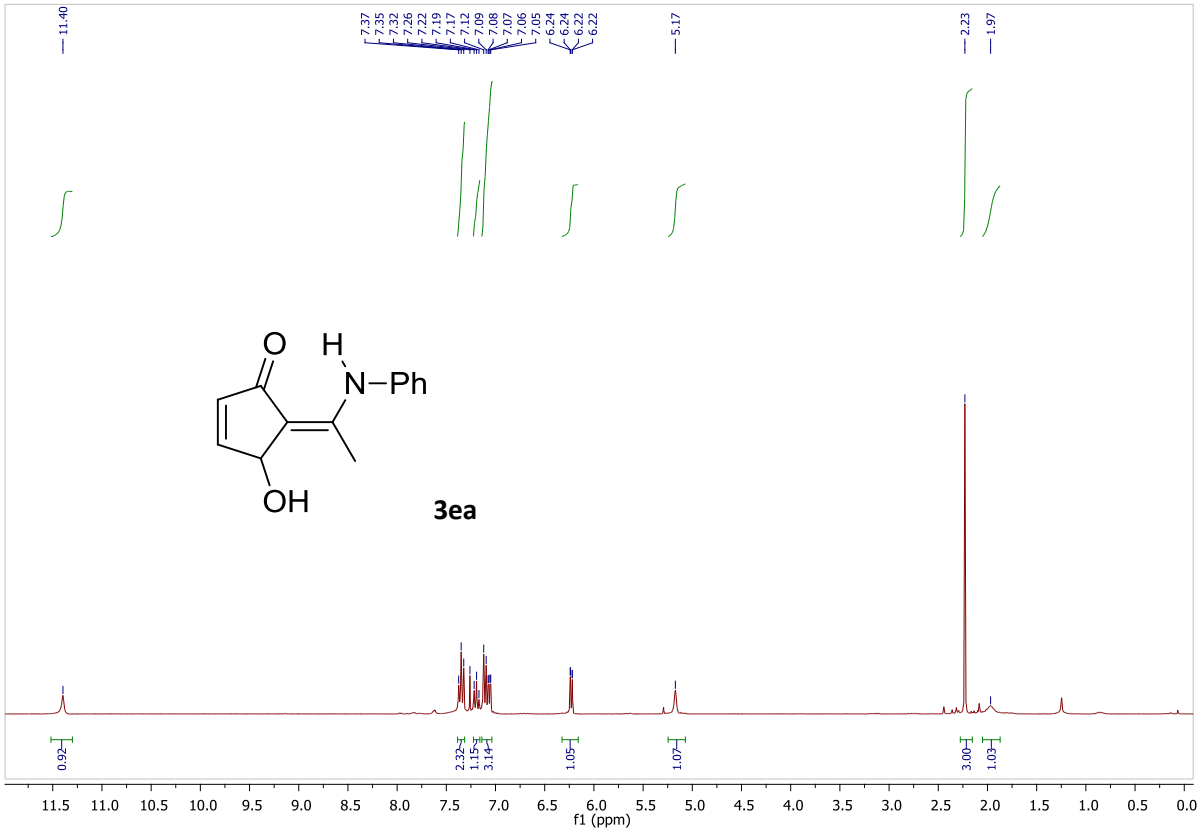
73.27
35.72
29.11
28.44
O
H
N–Ph
OH
Ph
3da
f1 (ppm)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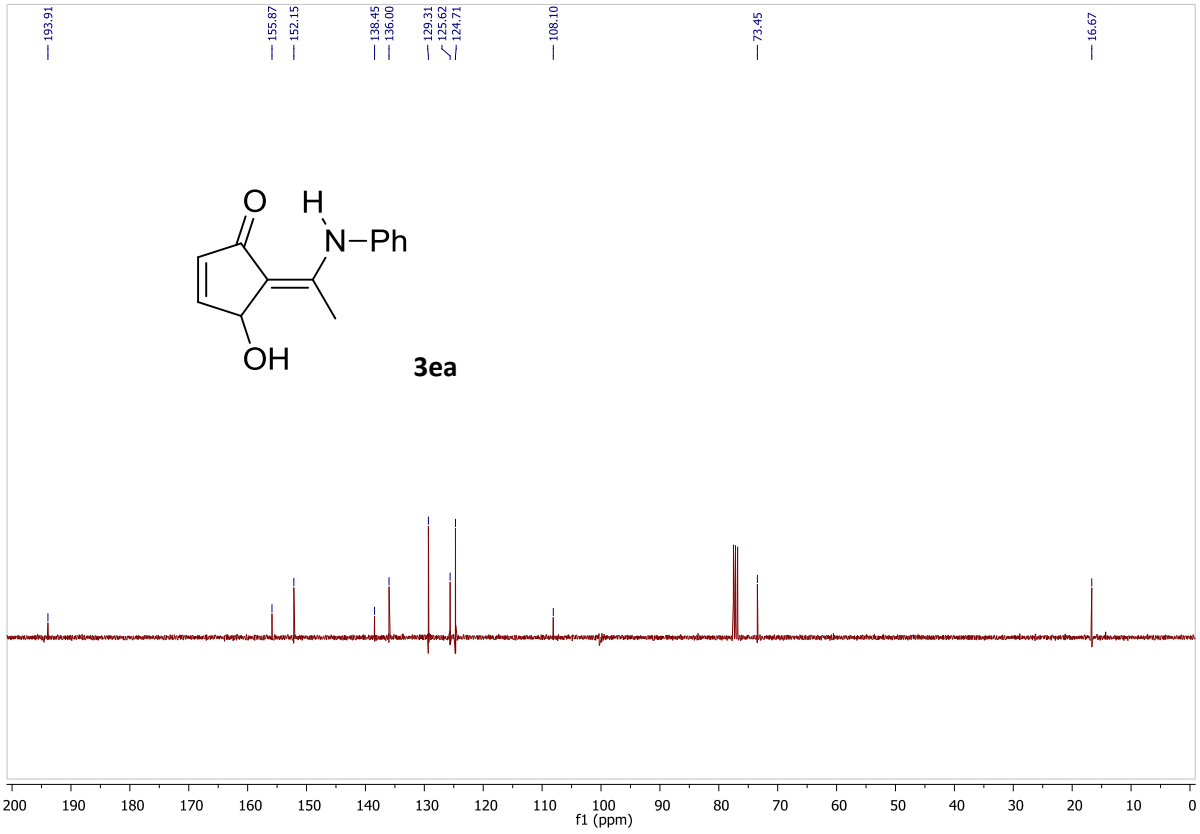
7.19
7.17
7.12
7.09
7.08
7.07
7.06
7.05
6.24
6.22
6.22
5.17
2.23
1.97
O
H
N–Ph
OH
3ea
0.92
2.32
1.15
3.14
1.05
1.07
3.00
1.03
f1 (ppm)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155.87
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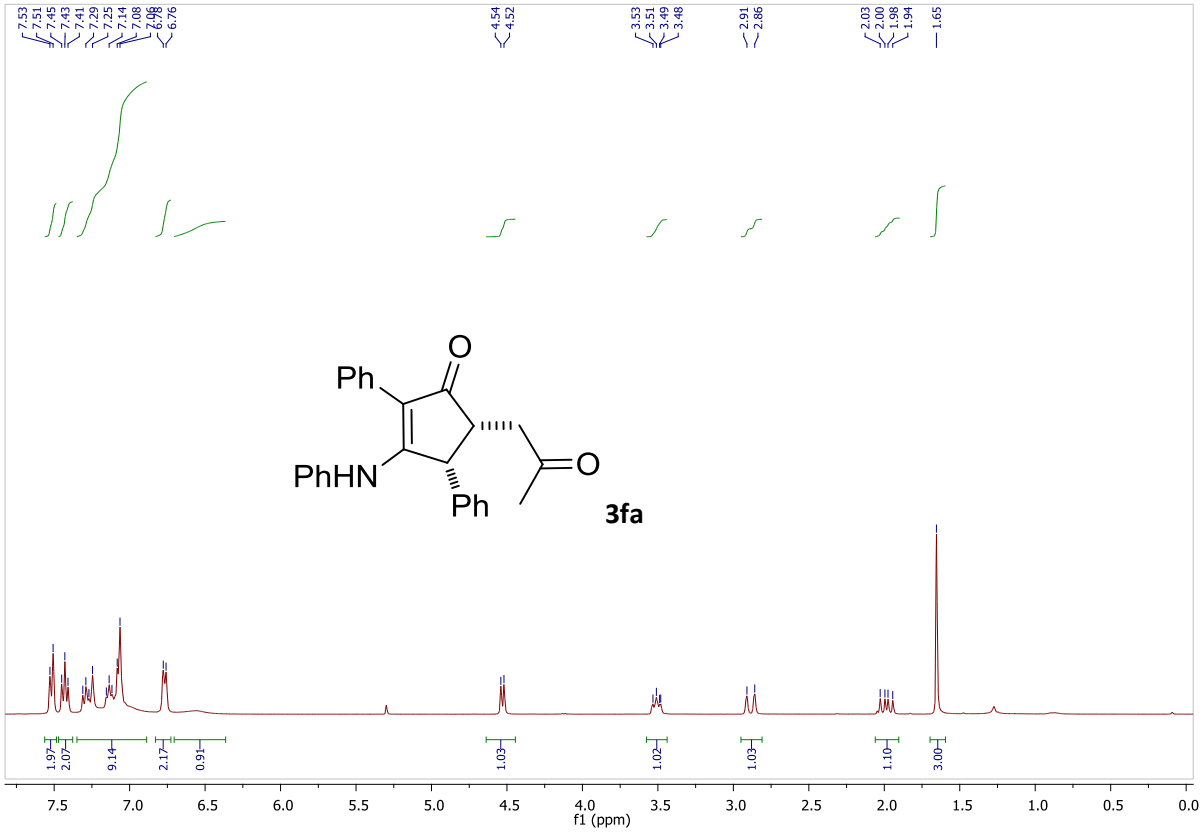
136.00
129.31
125.62
124.71
108.10
73.45
16.67
O
H
N–Ph
OH
3ea
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.45
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7.41
7.29
7.25
7.14
7.08
7.06
6.78
6.76
4.54
4.52
3.53
3.51
3.49
3.48
2.91
2.86
2.03
2.00
1.98
1.94
1.65
O
Ph
PhHN
Ph
O
3fa
1.97
2.07
9.14
2.17
0.91
1.03
1.02
1.03
1.10
3.00
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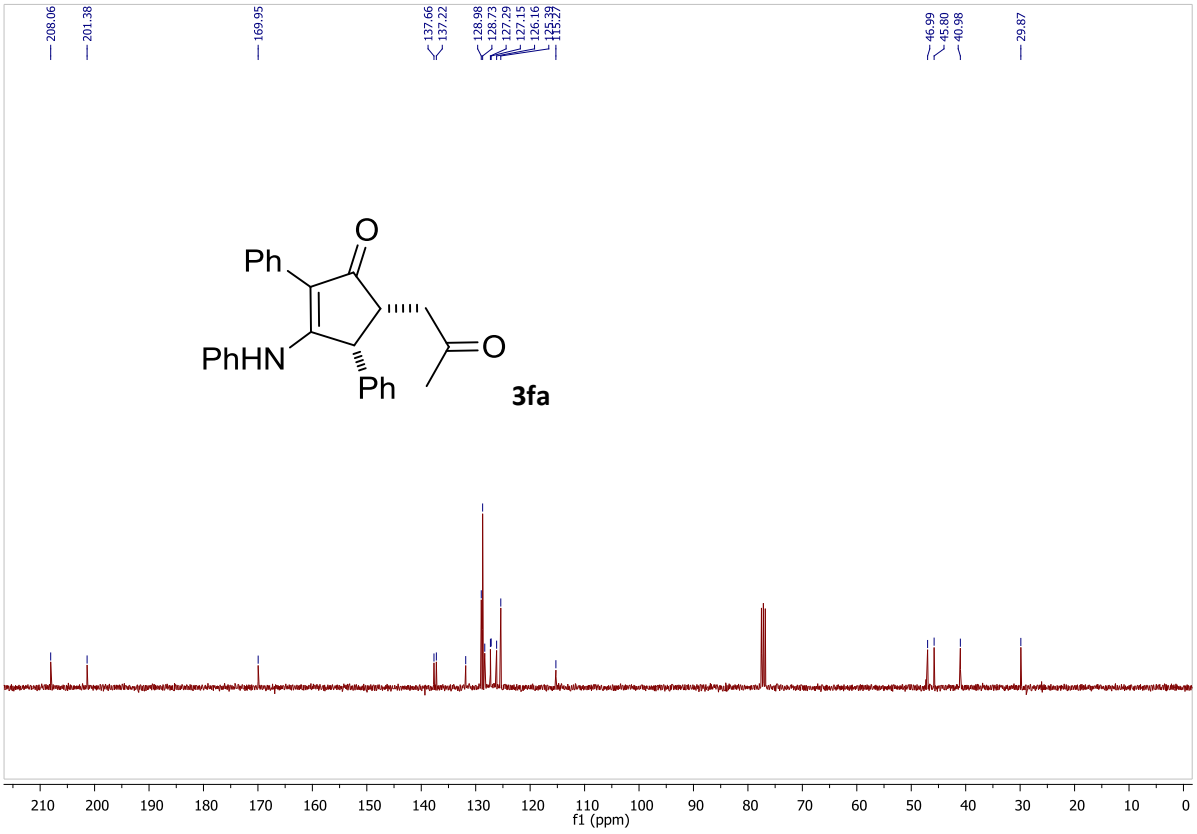
f1 (ppm)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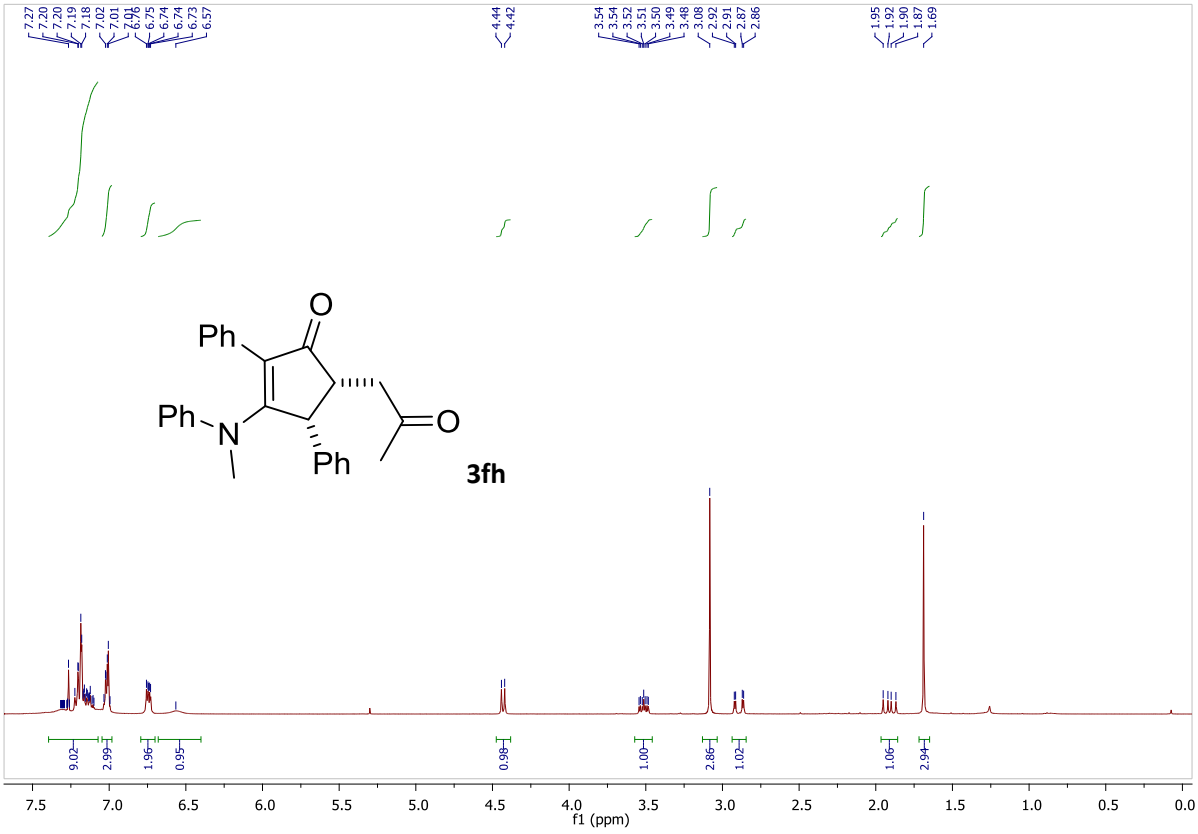
201.38
169.95
137.66
137.22
128.98
128.73
127.29
127.15
126.16
46.99
45.80
40.98
29.87
O
Ph
PhHN
Ph
O
3fa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.01
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6.74
6.73
6.57
4.44
4.42
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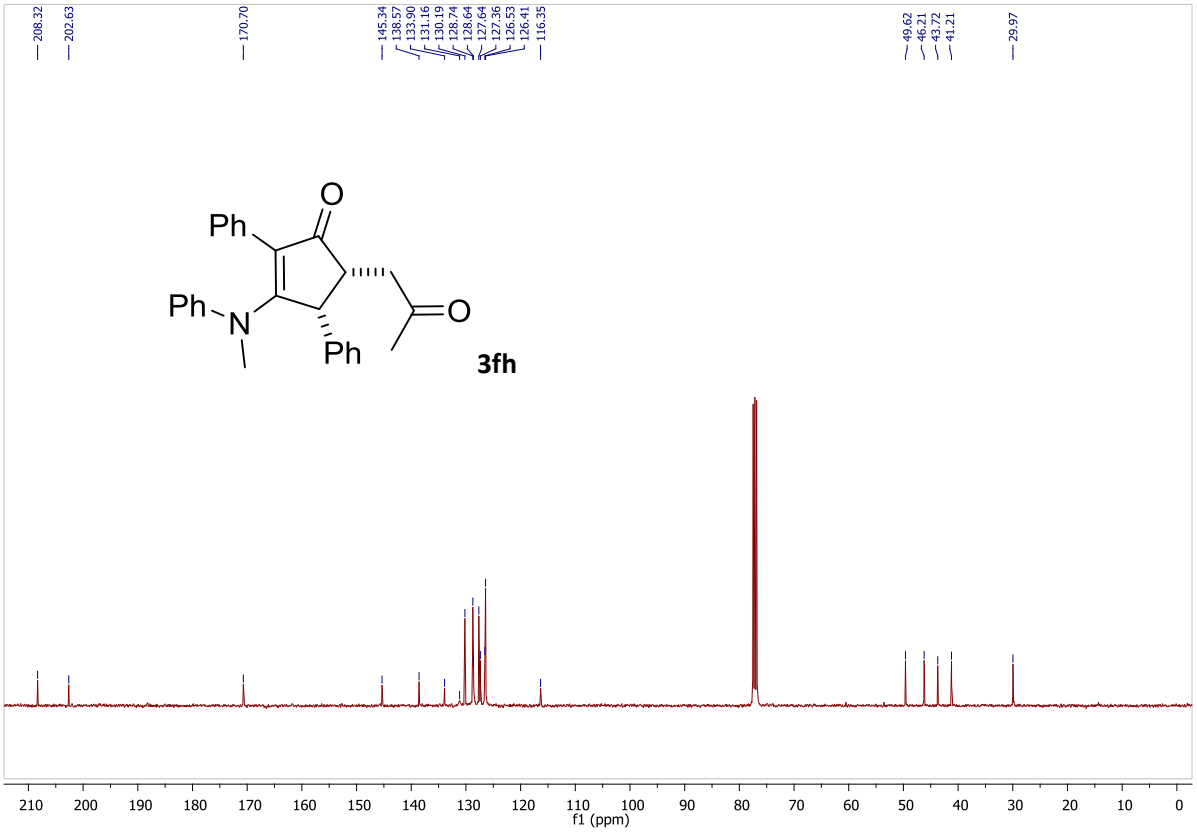
3.52
3.51
3.50
3.49
3.48
3.08
2.92
2.91
2.87
2.86
1.95
1.92
1.90
1.87
1.69
O
Ph
Ph
N
Ph
O
3fh
9.02
2.99
1.96
0.95
0.98
1.00
2.86
1.02
1.06
2.94
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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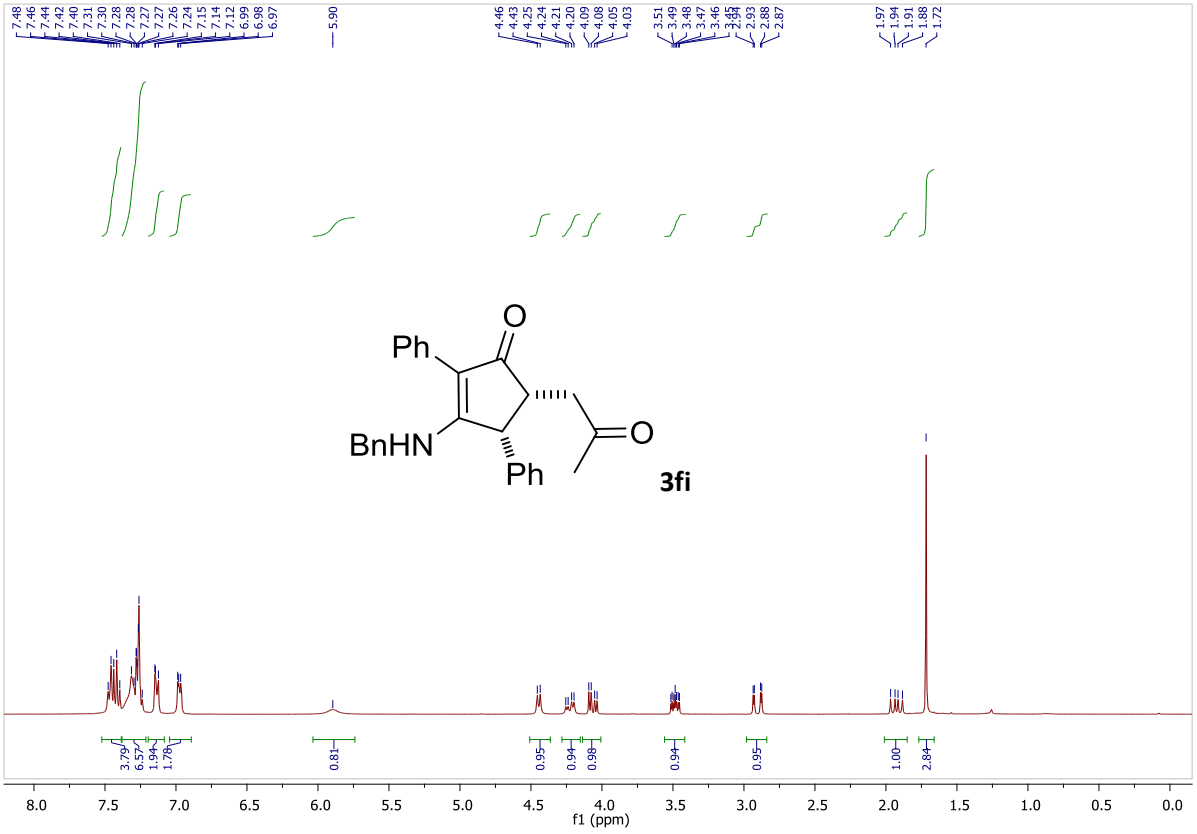
130.19
128.74
128.64
127.64
127.36
126.53
126.41
116.35
49.62
46.21
43.72
41.21
29.97
O
Ph
Ph
N
Ph
O
3fh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.31
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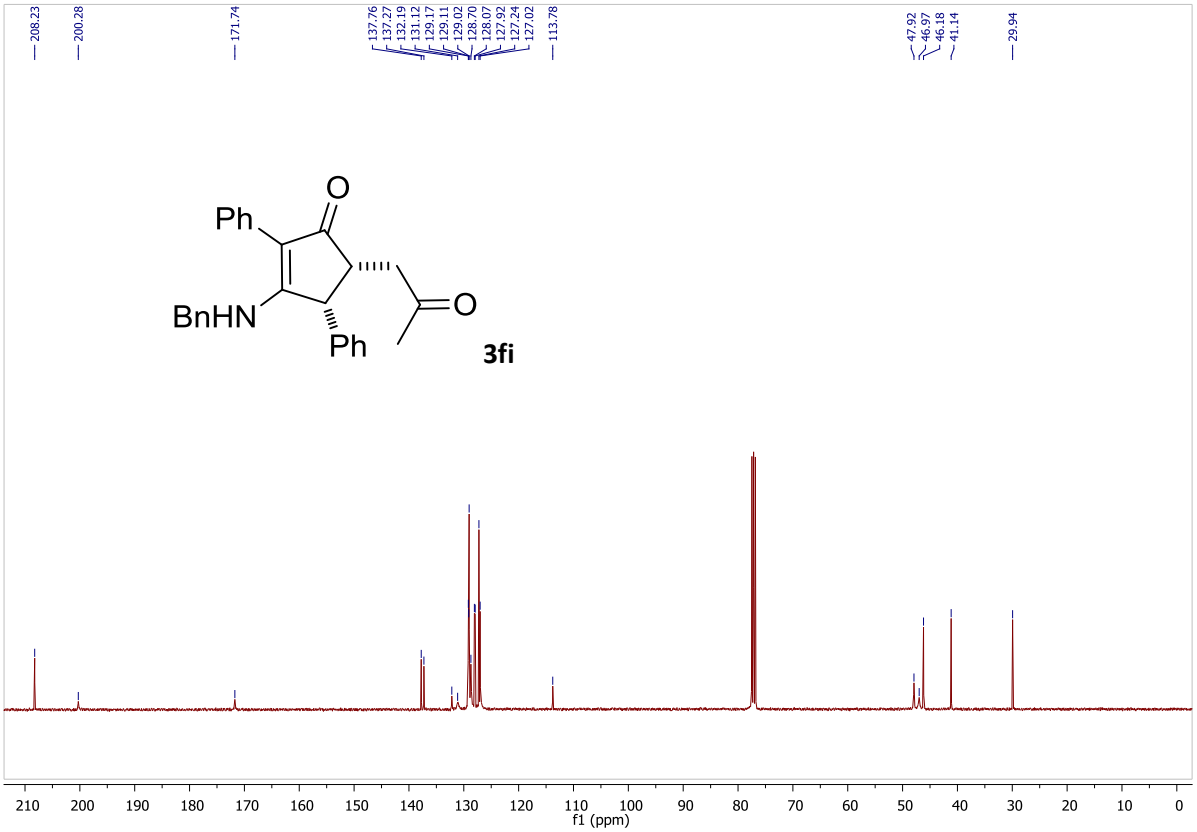
7.28
7.28
7.27
7.27
7.26
7.24
7.15
7.14
7.12
6.99
6.98
6.97
5.90
4.46
4.43
4.25
4.24
4.21
4.20
4.09
4.08
4.05
4.03
3.51
3.49
3.48
3.47
3.46
2.93
2.88
2.87
1.97
1.94
1.91
1.88
1.72
O
Ph
BnHN
Ph
O
3fi
3.79
6.57
1.94
1.78
0.81
0.95
0.94
0.98
0.94
0.95
1.00
2.84
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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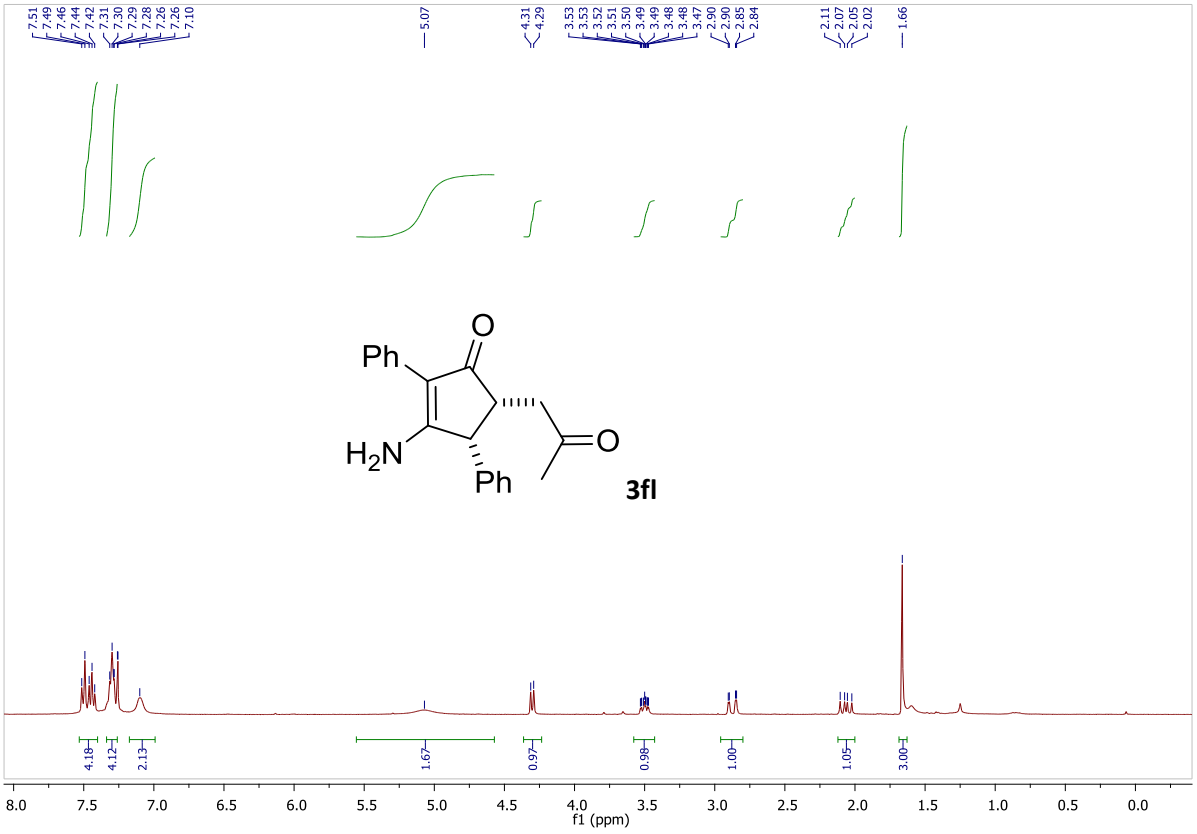
200.28
171.74
137.76
137.27
132.19
131.12
129.17
129.11
129.02
128.70
128.07
127.92
127.24
127.02
113.78
47.92
46.97
46.18
41.14
29.94
O
Ph
BnHN
Ph
O
3fi
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.49
7.46
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7.28
7.26
7.26
7.10
5.07
4.31
4.29
3.53
3.53
3.52
3.51
3.50
3.49
3.49
3.48
3.48
3.47
2.90
2.90
2.85
2.84
2.11
2.07
2.05
2.02
1.66
O
Ph
H2N
Ph
O
3fl
4.18
4.12
2.13
1.67
0.97
0.98
1.00
1.05
3.00
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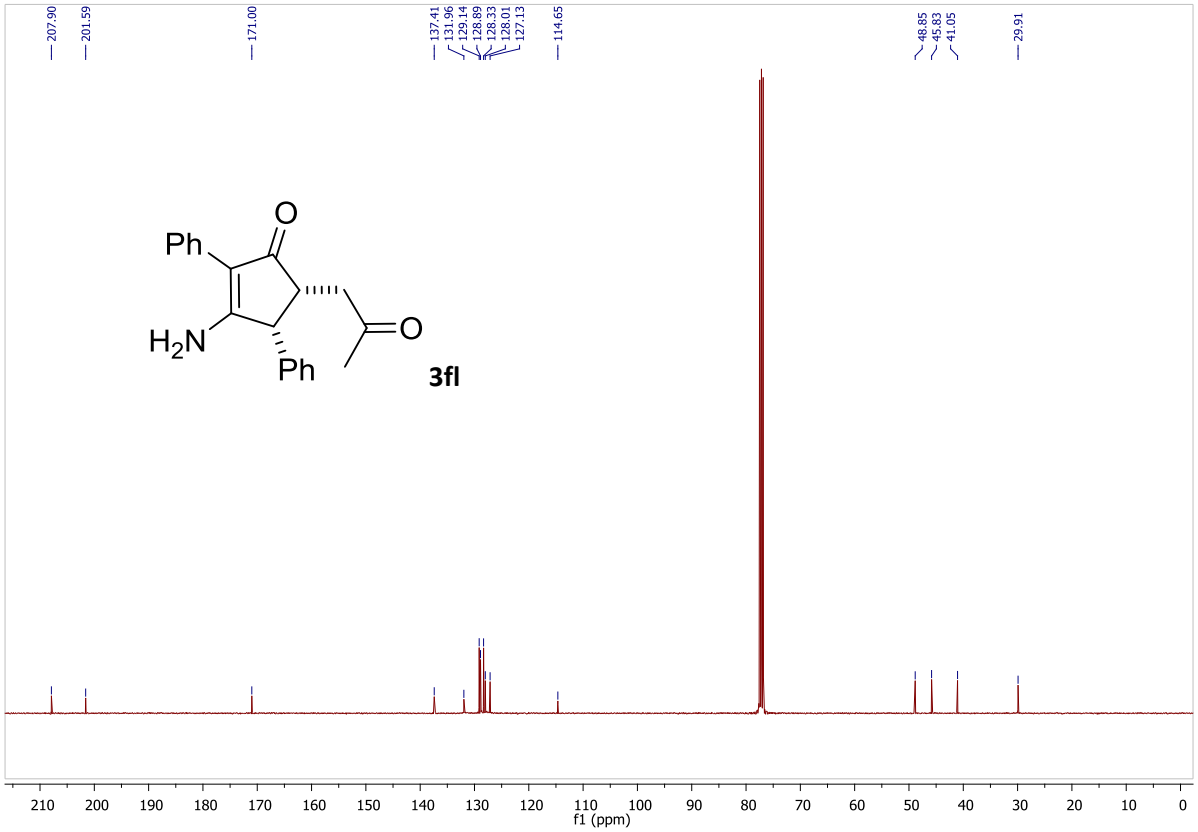
f1 (ppm)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129.14
128.89
128.33
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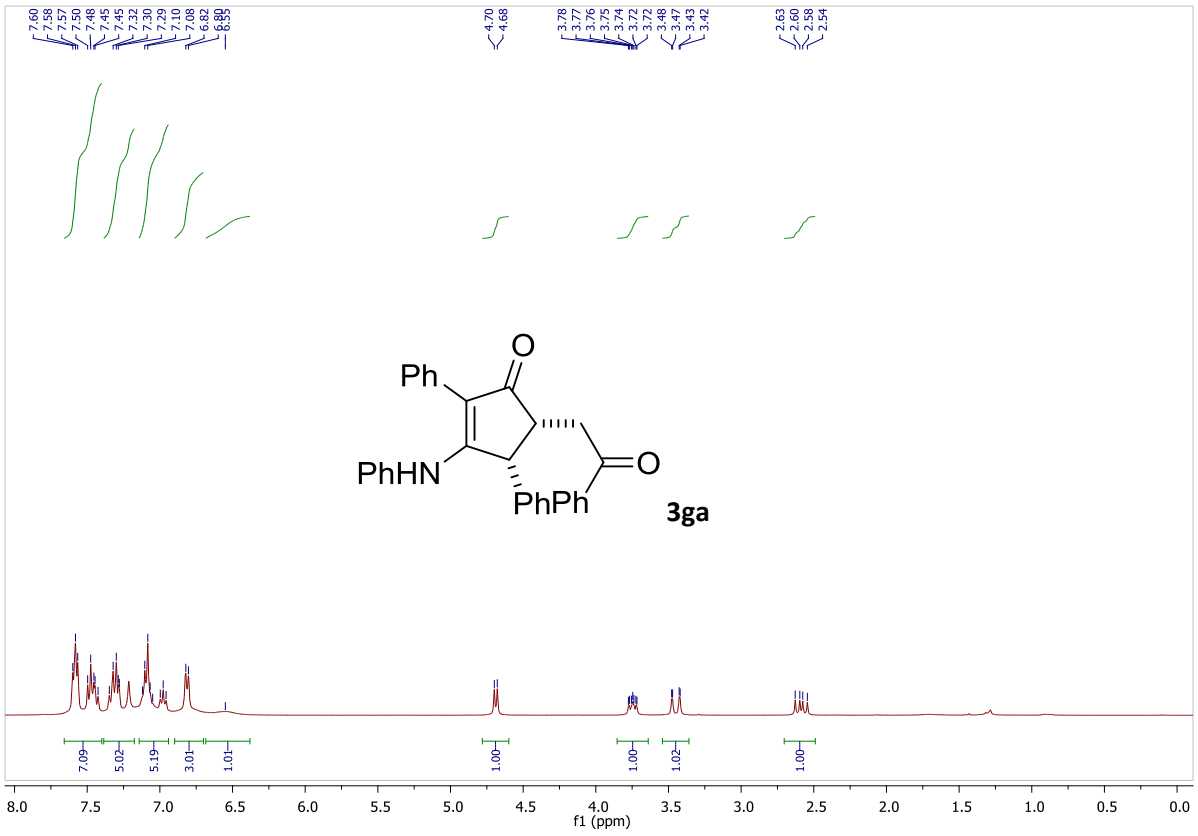
48.85
45.83
41.05
29.91
Ph
O
H2N
Ph
O
3fl
f1 (ppm)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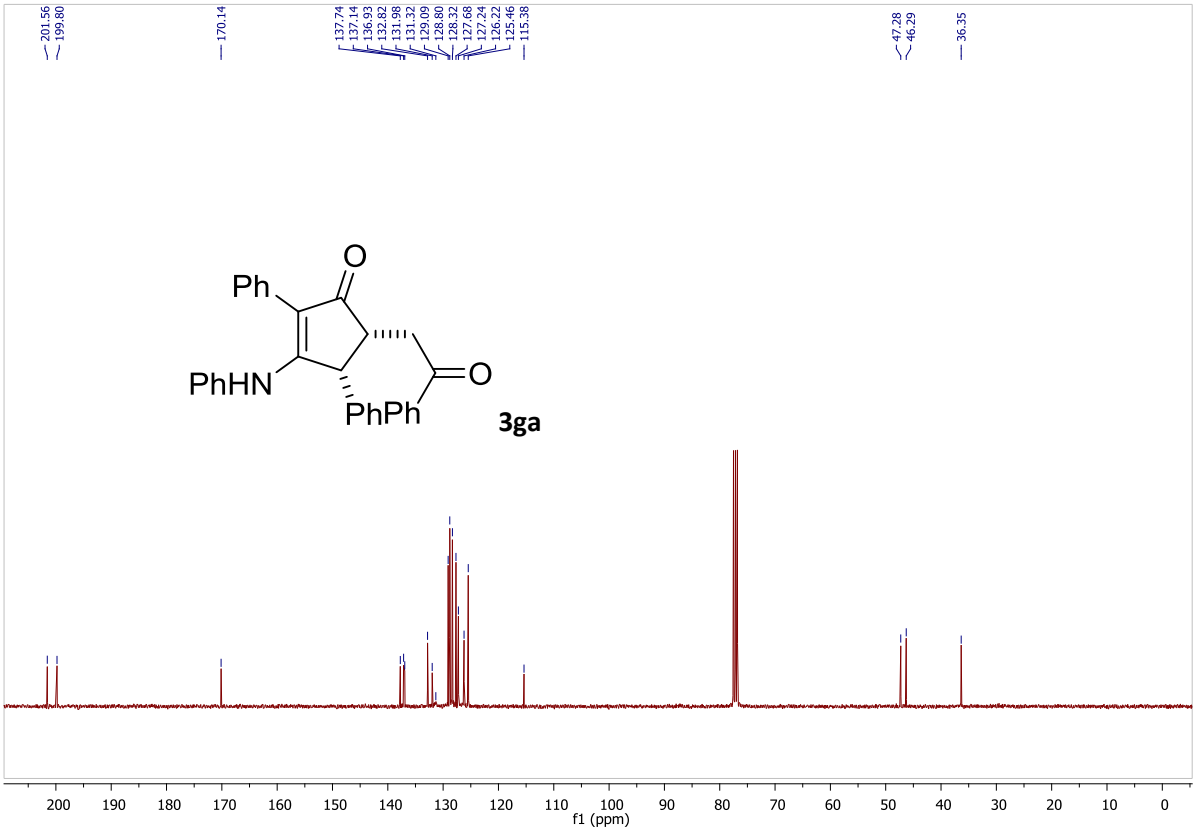
7.45
7.45
7.32
7.30
7.29
7.10
7.08
6.82
6.80
6.55
4.70
4.68
3.78
3.77
3.76
3.75
3.74
3.72
3.72
3.48
3.47
3.43
3.42
2.63
2.60
2.58
2.54
Ph
O
PhHN
O
PhPh
3ga
7.09
5.02
5.19
3.01
1.01
1.00
1.00
1.02
1.00
f1 (ppm)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131.98
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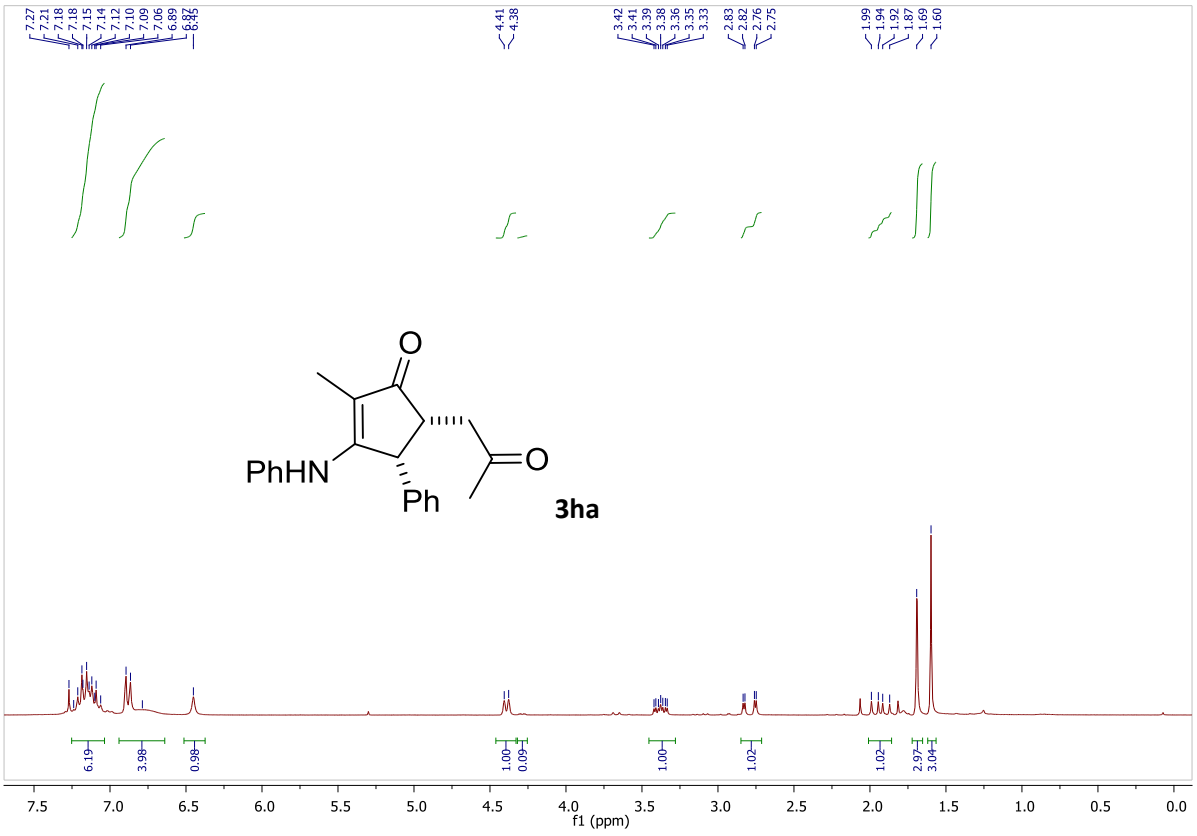
129.09
128.80
128.32
127.68
127.24
126.22
125.46
115.38
47.28
46.29
36.35
O
Ph
PhHN
O
PhPh
3ga
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.09
7.06
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6.85
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4.38
3.42
3.41
3.39
3.38
3.36
3.35
3.33
2.83
2.82
2.76
2.75
1.99
1.94
1.92
1.87
1.69
1.60
O
PhHN
Ph
O
3ha
6.19
3.98
0.98
1.00
0.09
1.00
1.02
1.02
2.97
3.04
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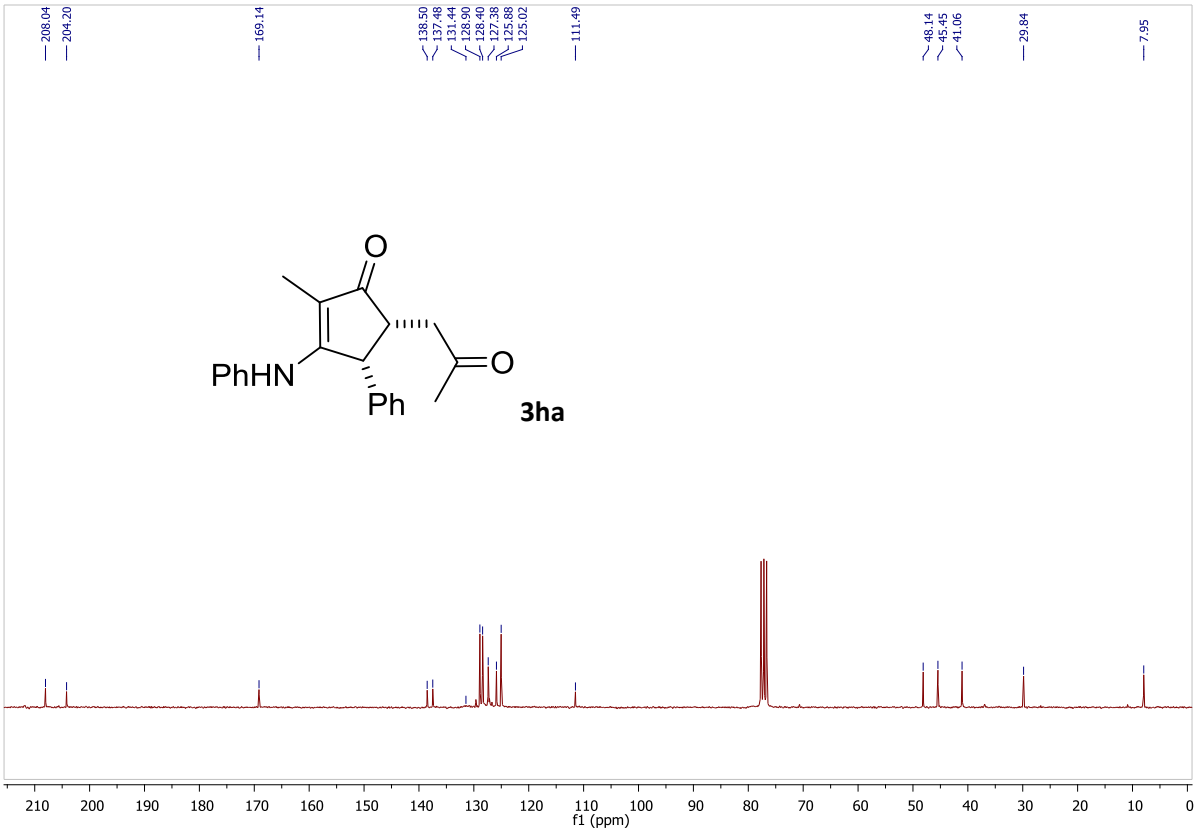
f1 (ppm)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128.40
127.38
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125.02
111.49
48.14
45.45
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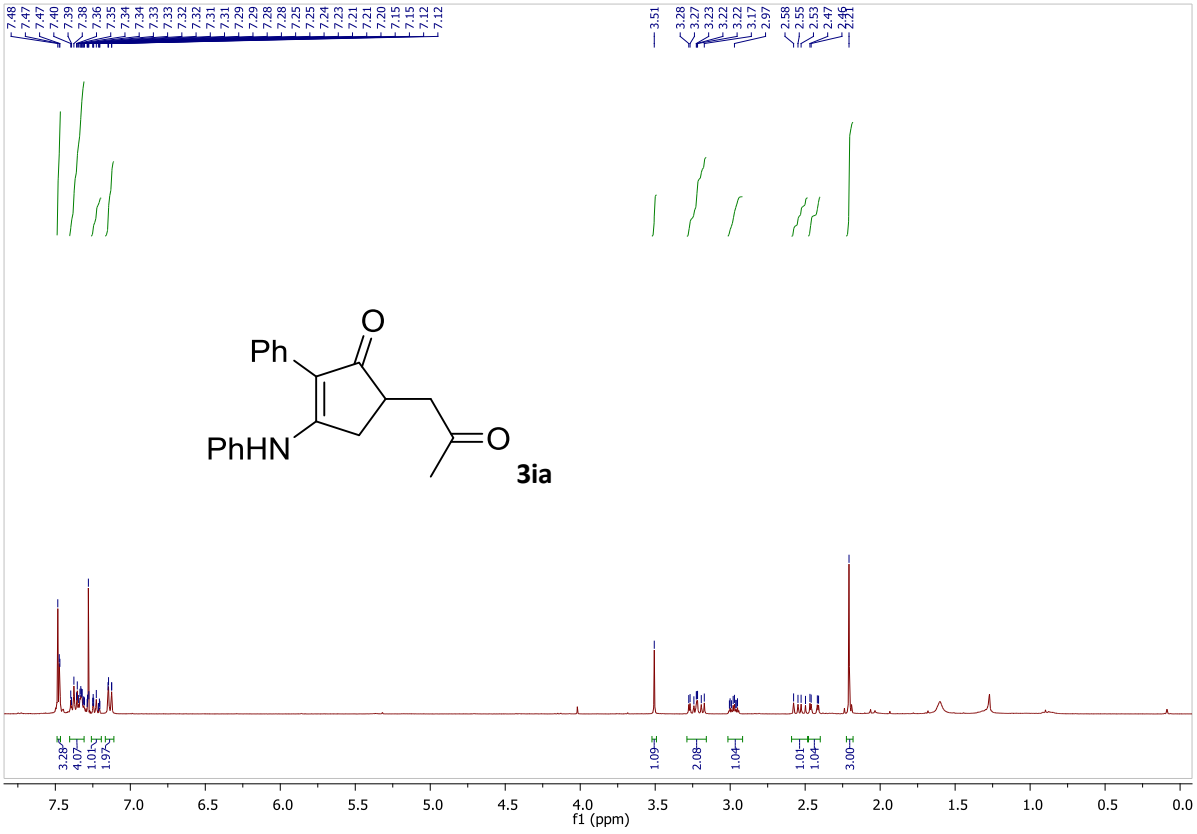
7.95
O
PhHN
Ph
O
3ha
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.32
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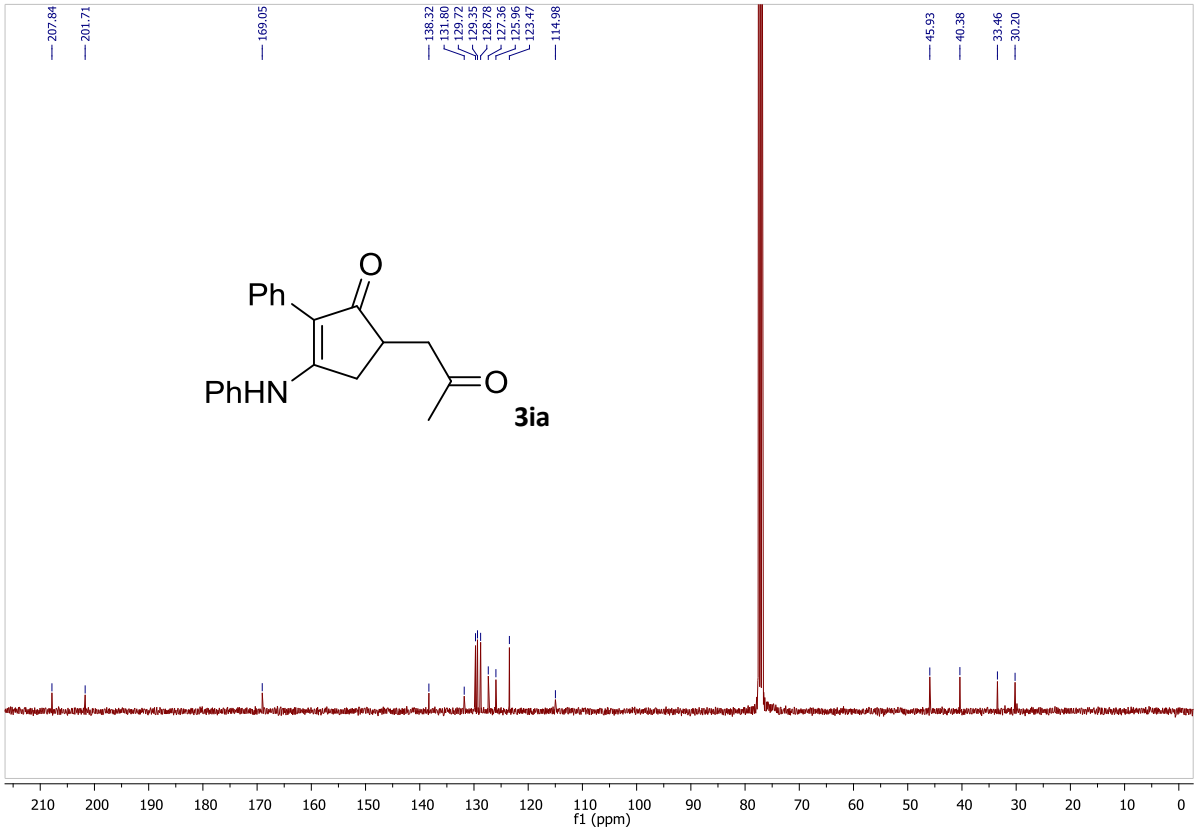
7.31
7.31
7.29
7.29
7.28
7.28
7.25
7.25
7.24
7.23
7.21
7.21
7.20
7.15
7.15
7.12
7.12
3.51
3.28
3.27
3.23
3.22
3.22
3.17
2.97
2.58
2.55
2.53
2.47
2.46
2.44
O
Ph
PhHN
O
3ia
3.28
4.07
1.01
1.97
1.09
2.08
1.04
1.01
1.04
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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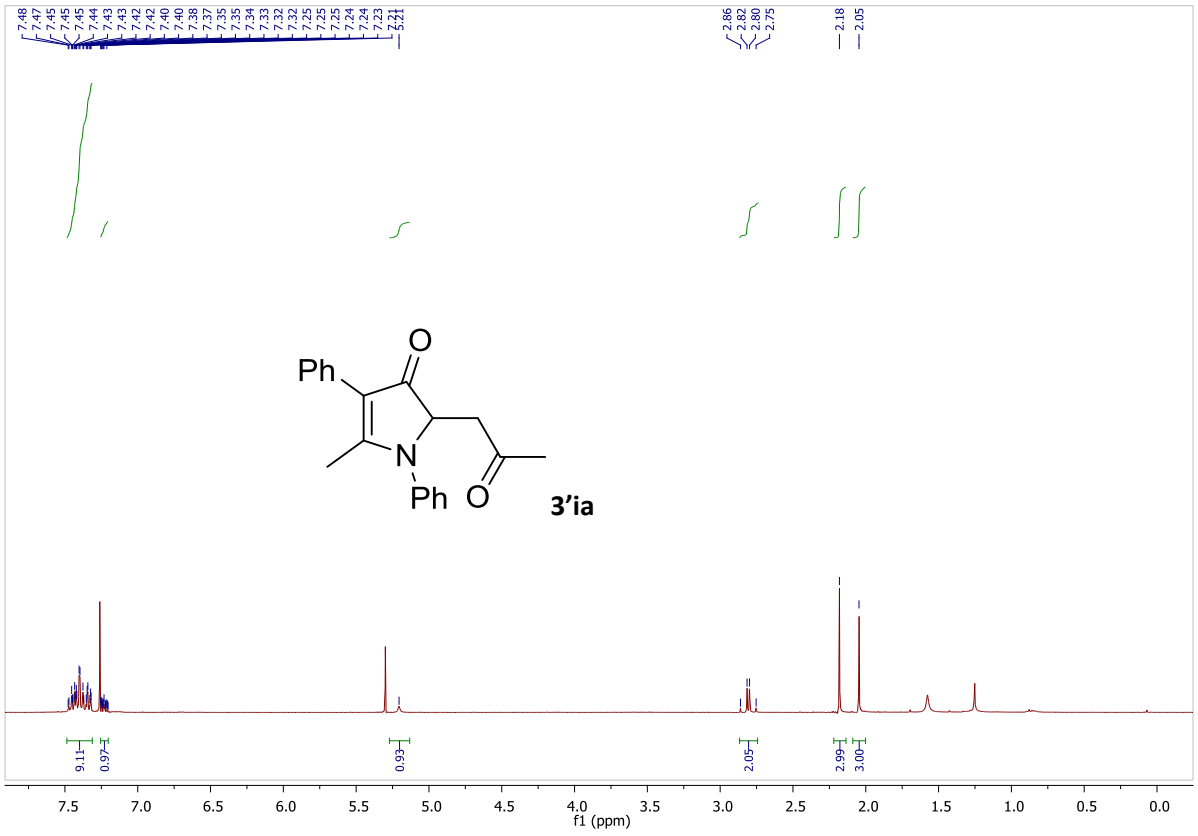
128.78
127.36
125.96
123.47
114.98
45.93
40.38
33.46
30.20
O
Ph
PhHN
O
3ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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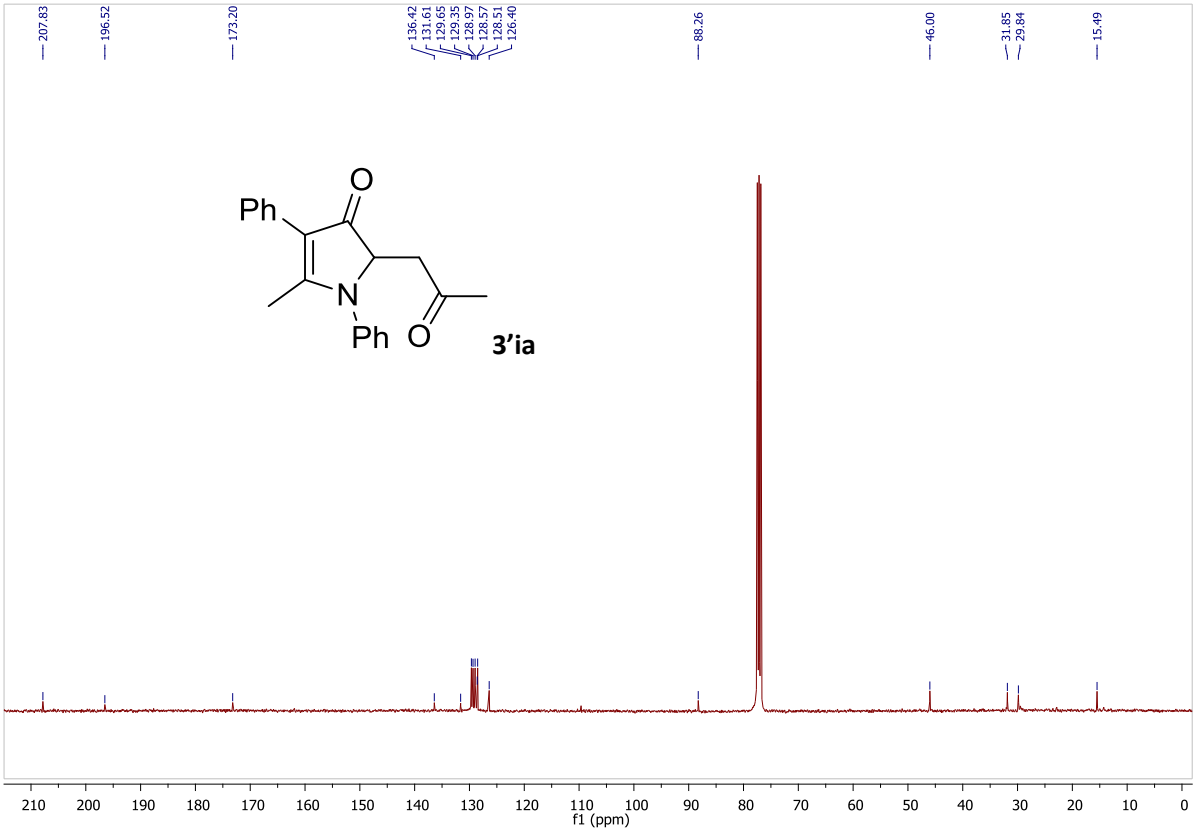
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.40
7.40
7.38
7.37
7.35
7.35
7.34
7.33
7.32
7.25
7.25
7.25
7.24
7.24
7.23
7.21
5.21
2.86
2.82
2.80
2.75
2.18
2.05
O
Ph
N
Ph
O
3'ia
9.11
0.97
0.93
2.05
2.99
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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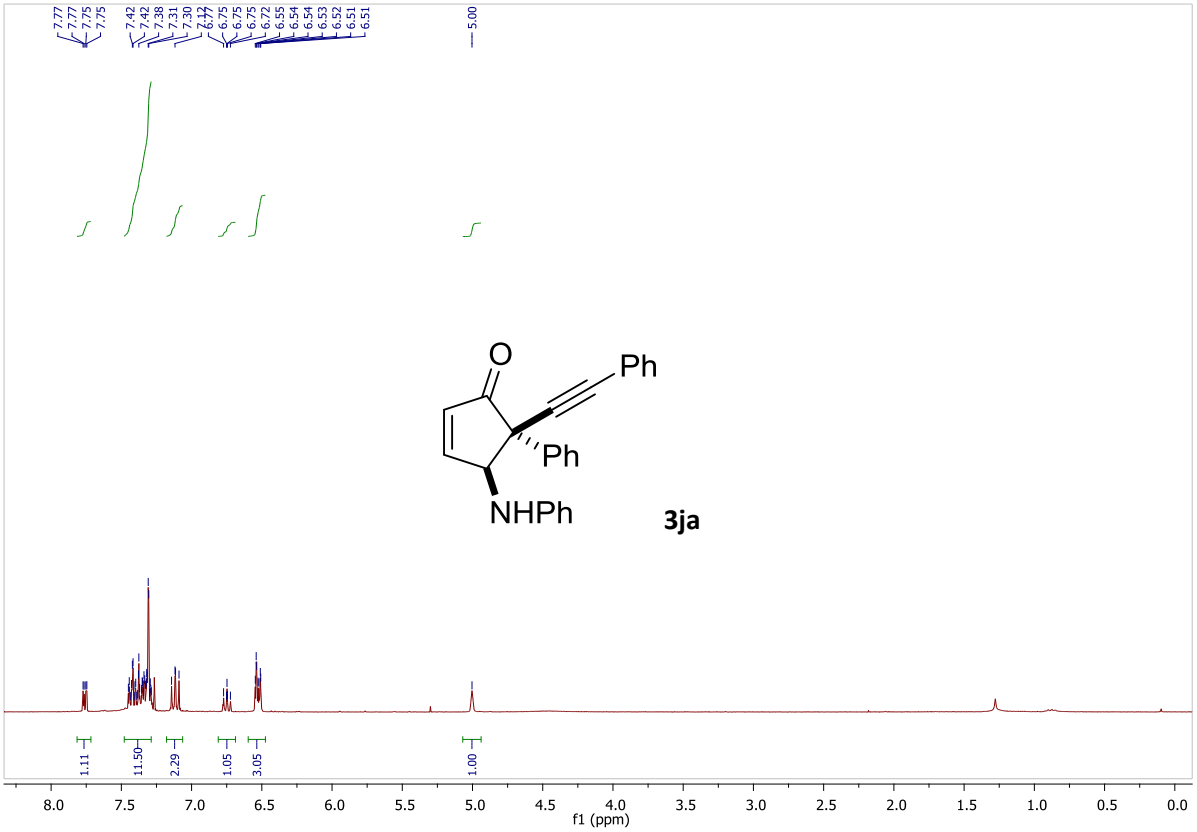
129.65
129.35
128.97
128.57
128.51
126.40
88.26
46.00
31.85
29.84
15.49
O
Ph
N
Ph
O
3'ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.42
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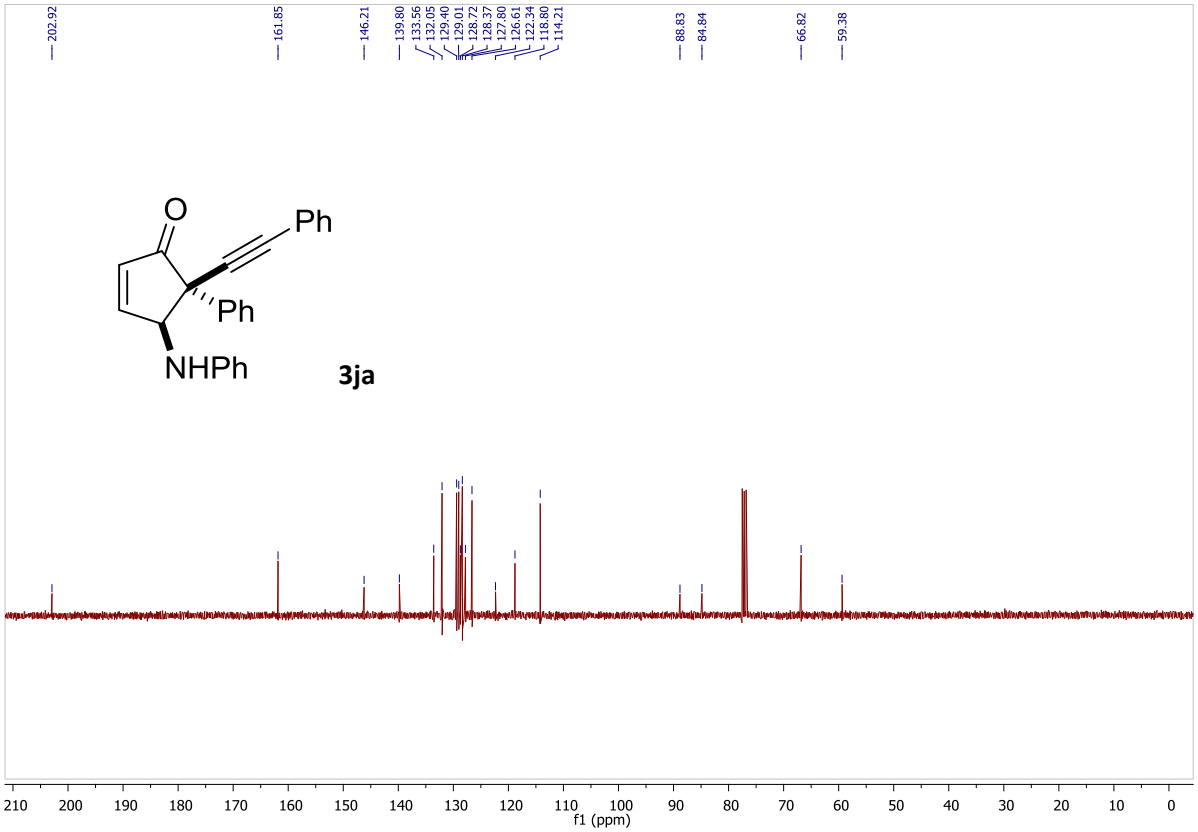
7.31
7.30
6.75
6.75
6.75
6.72
6.55
6.54
6.54
6.53
6.52
6.51
6.51
5.00
O
Ph
Ph
NHPh
3ja
1.11
11.50
2.29
1.05
3.05
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.01
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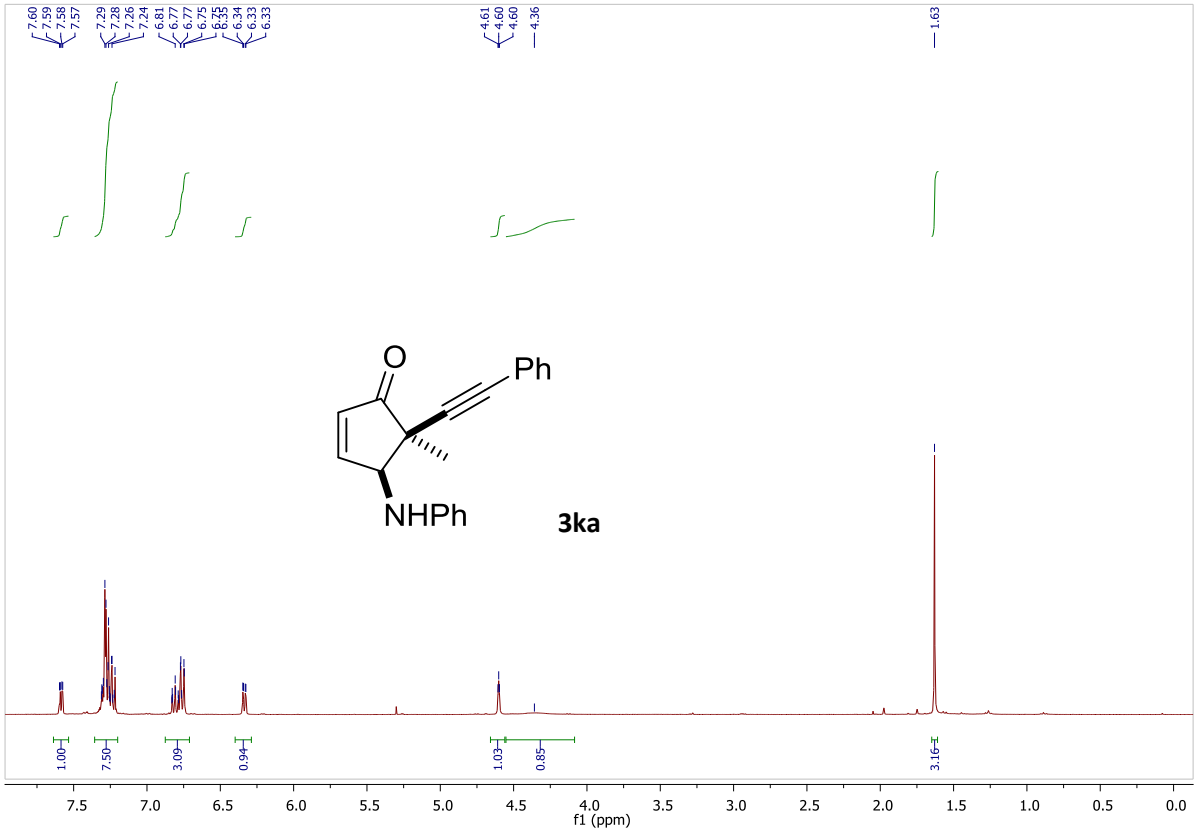
127.80
126.61
122.34
118.80
114.21
88.83
84.84
66.82
59.38
O
Ph
Ph
NHPh
3ja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.75
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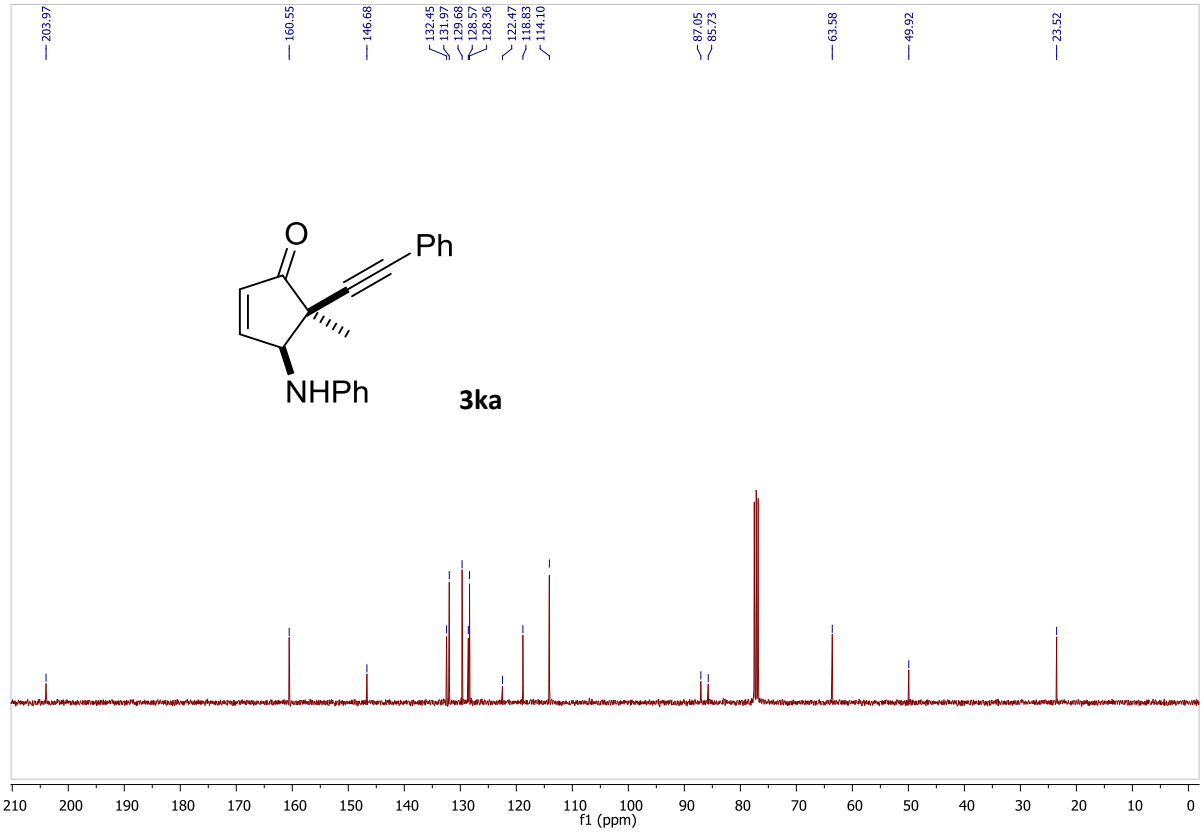
6.34
6.33
6.33
4.61
4.60
4.60
4.36
1.63
O
Ph
NHPh
3ka
1.00
7.50
3.09
0.94
1.03
0.85
3.16
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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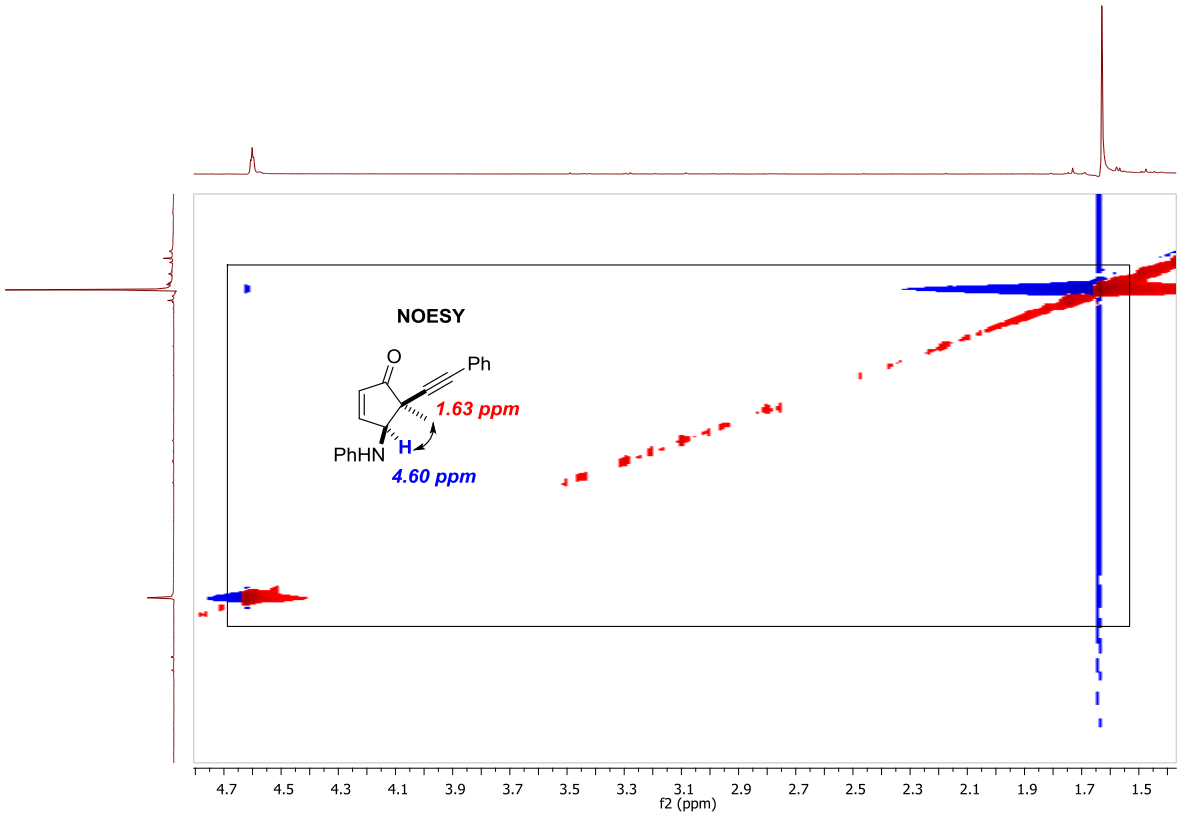
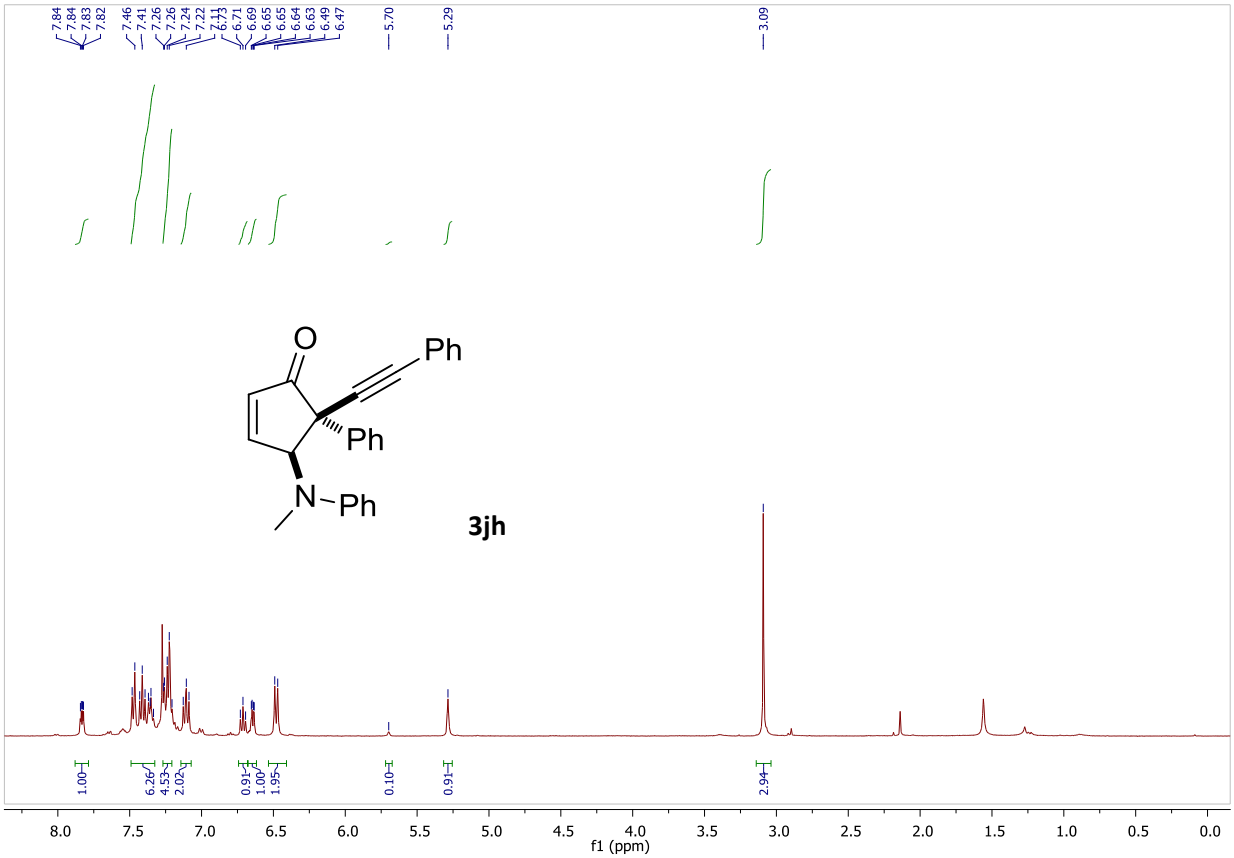
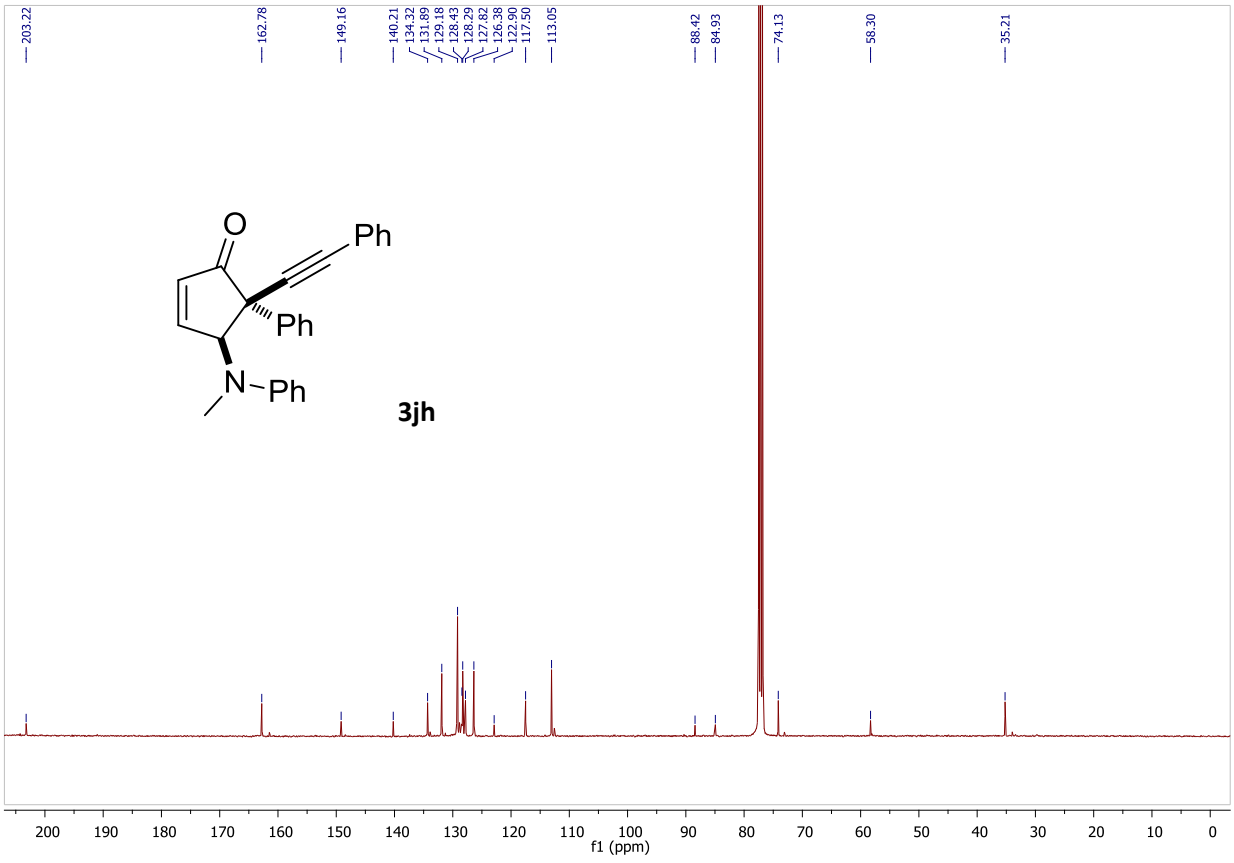
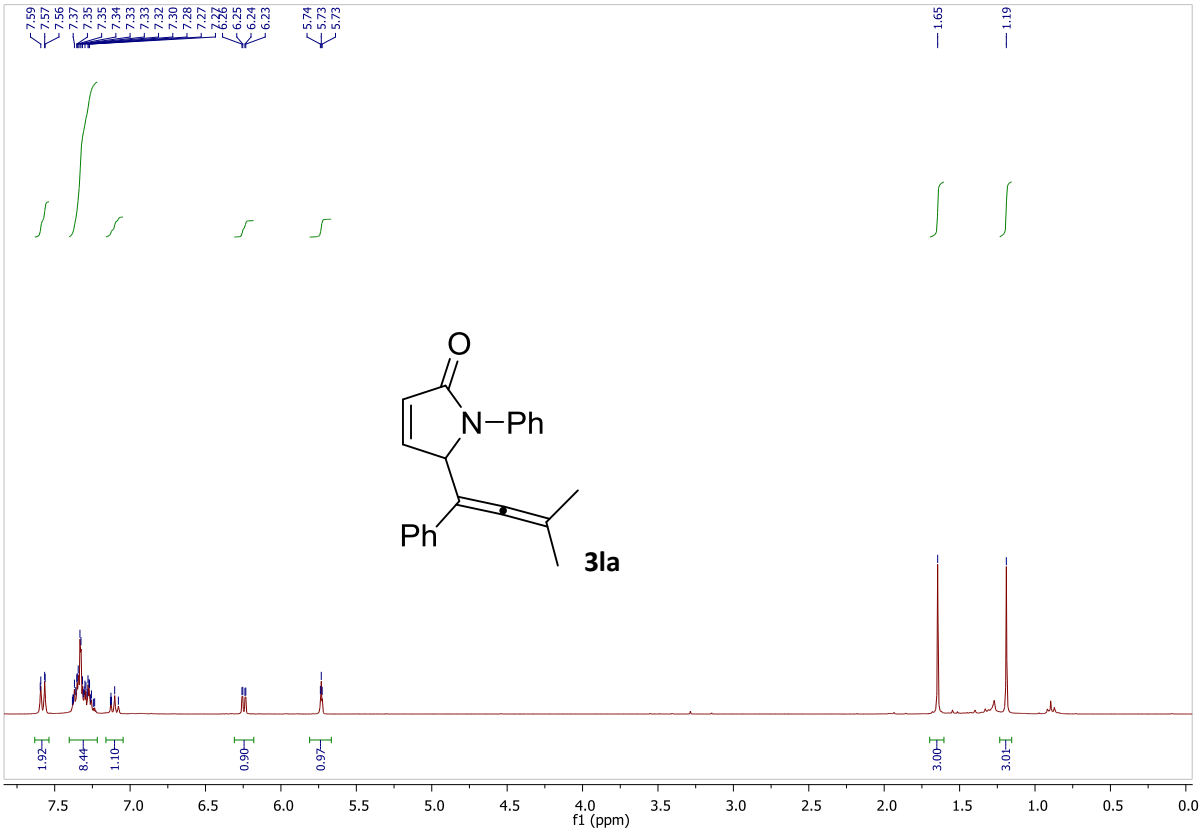
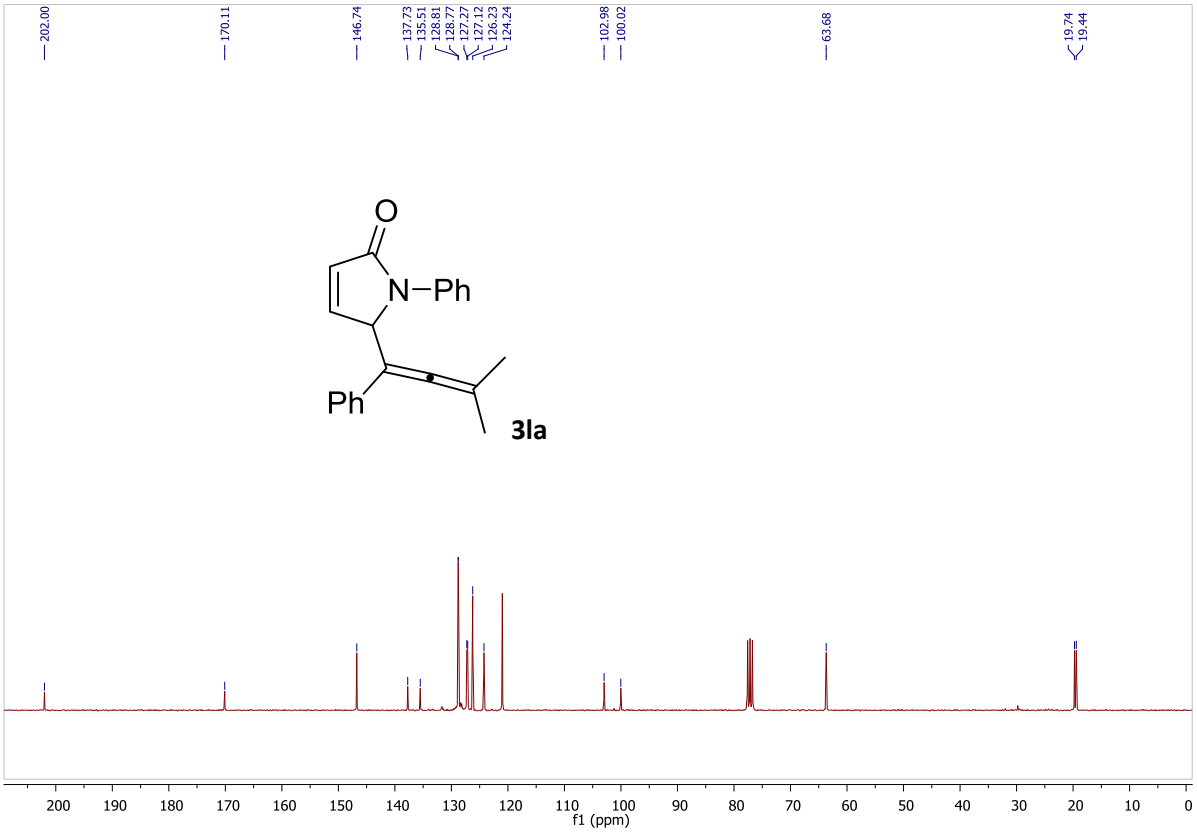
131.97
129.68
128.57
128.36
122.47
118.83
114.10
87.05
85.73
63.58
49.92
23.52
O
Ph
NHPh
3ka
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

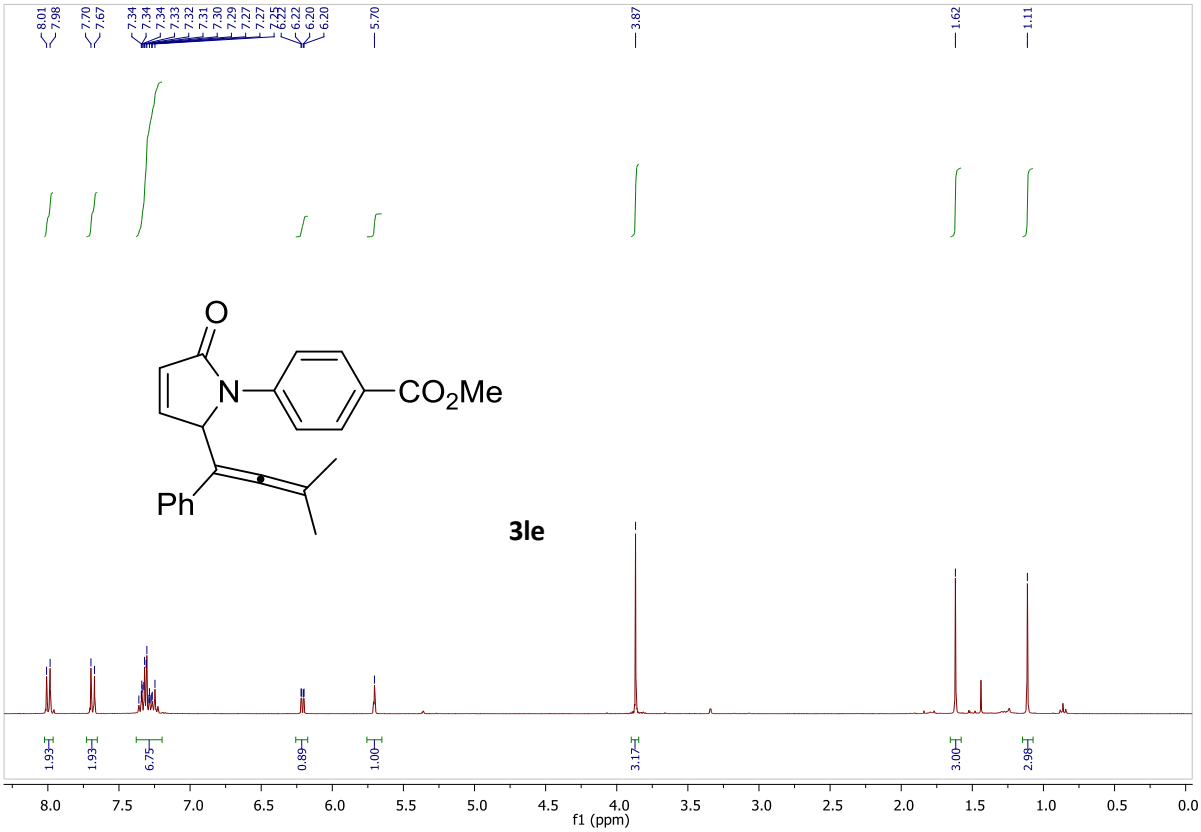

NOESY
O
Ph
1.63 ppm
PhHN
H
4.60 ppm
4.7 4.5 4.3 4.1 3.9 3.7 3.5 3.3 3.1 2.9 2.7 2.5 2.3 2.1 1.9 1.7 1.5
f2 (ppm)

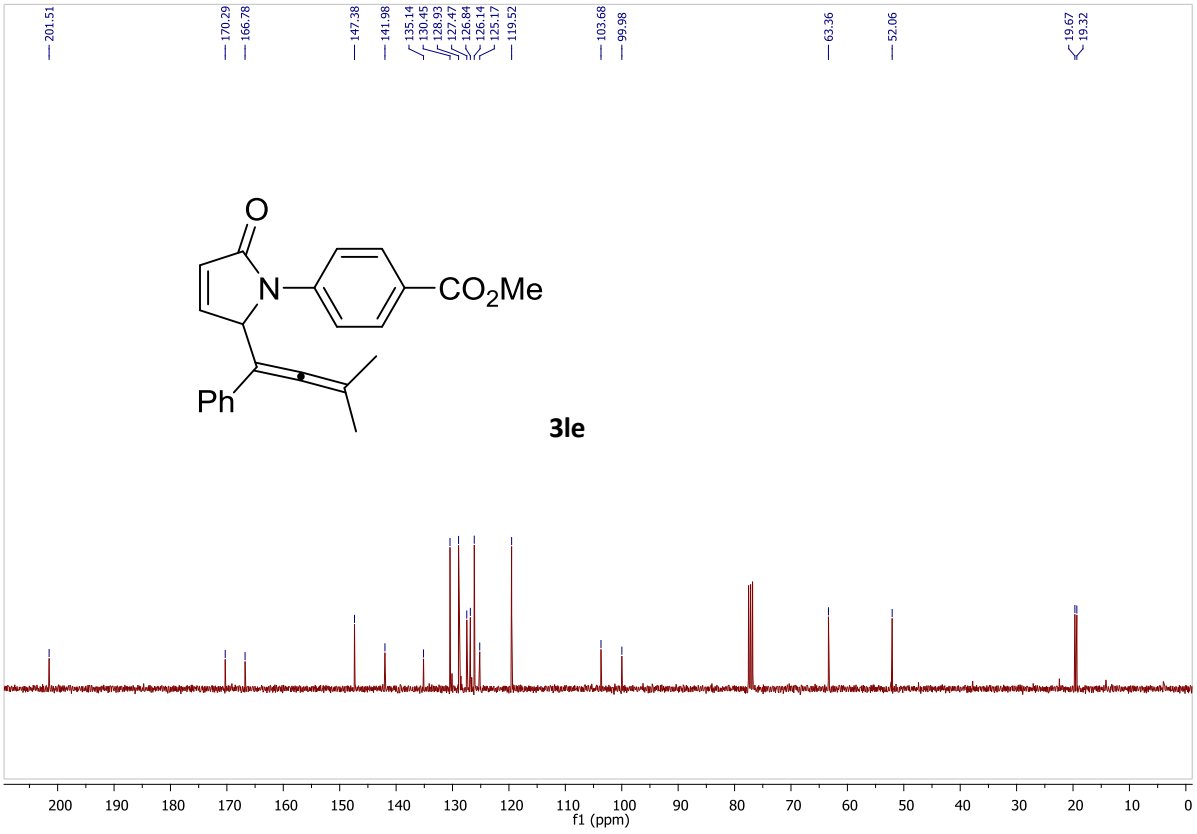

7.84
7.84
7.83
7.82
7.46
7.41
7.26
7.26
7.24
7.22
7.11
7.10
6.71
6.69
6.65
6.65
6.64
6.63
6.49
6.47
5.70
5.29
3.09
O
Ph
Ph
N
Ph
3jh
1.00
6.26
4.53
2.02
0.91
1.00
1.95
0.10
0.91
2.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


203.22
162.78
149.16
140.21
134.32
131.89
129.18
128.43
128.29
127.82
126.38
122.90
117.50
113.05
88.42
84.93
74.13
58.30
35.21
O
Ph
Ph
N
Ph
3jh
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.59
7.57
7.56
7.37
7.35
7.35
7.34
7.33
7.33
7.32
7.30
7.28
7.27
6.26
6.25
6.24
6.23
5.74
5.73
5.73
1.65
1.19
O
N−Ph
Ph
3la
1.92
8.44
1.10
0.90
0.97
3.00
3.01
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)


202.00
170.11
146.74
137.73
135.51
128.81
128.77
127.27
127.12
126.23
124.24
102.98
100.02
63.68
19.74
19.44
O
N−Ph
Ph
3la
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.01
7.98
7.70
7.67
7.34
7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.27
7.27
7.25
6.22
6.20
6.20
5.70
3.87
1.62
1.11
O
N
CO2Me
Ph
3le
1.93
1.93
6.75
0.89
1.00
3.17
3.00
2.98
f1 (ppm)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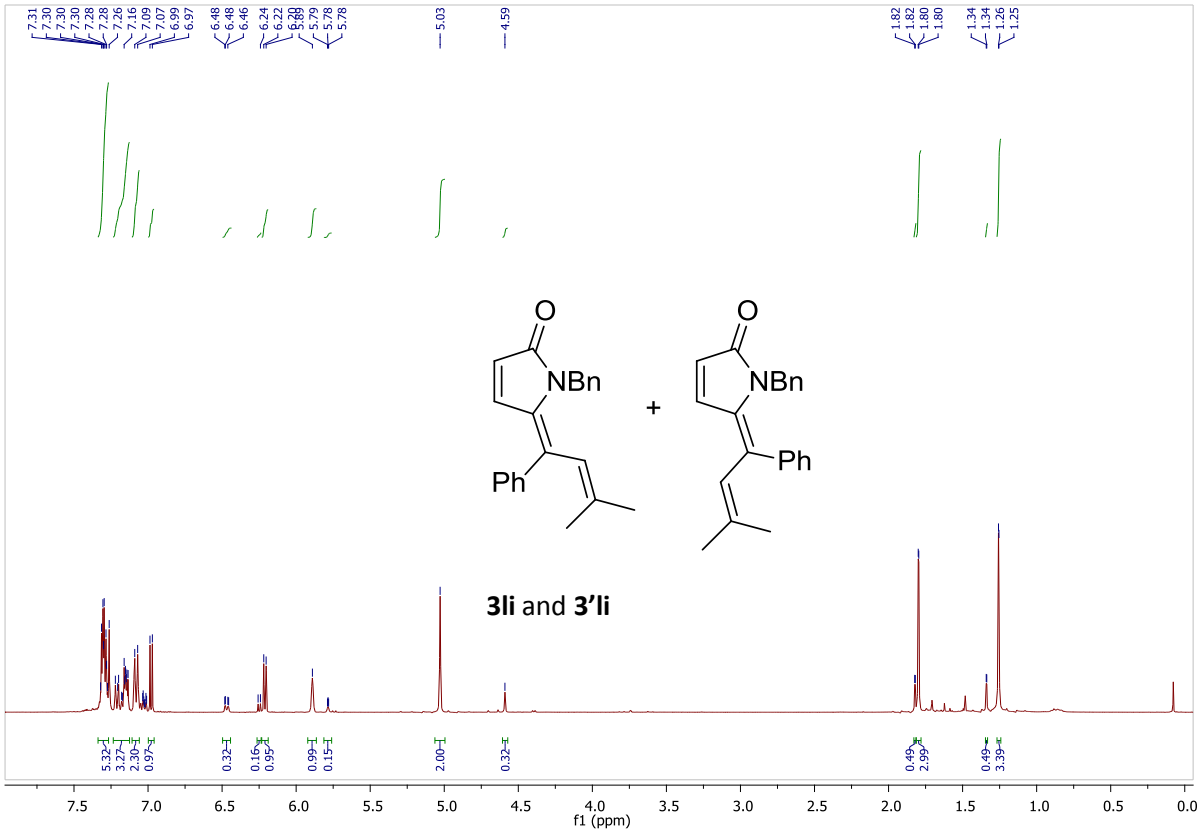
170.29
166.78
147.38
141.98
135.14
130.45
128.93
127.47
126.84
126.14
125.17
119.52
103.68
99.98
63.36
52.06
19.67
19.32
O
N
CO2Me
Ph
3le
f1 (ppm)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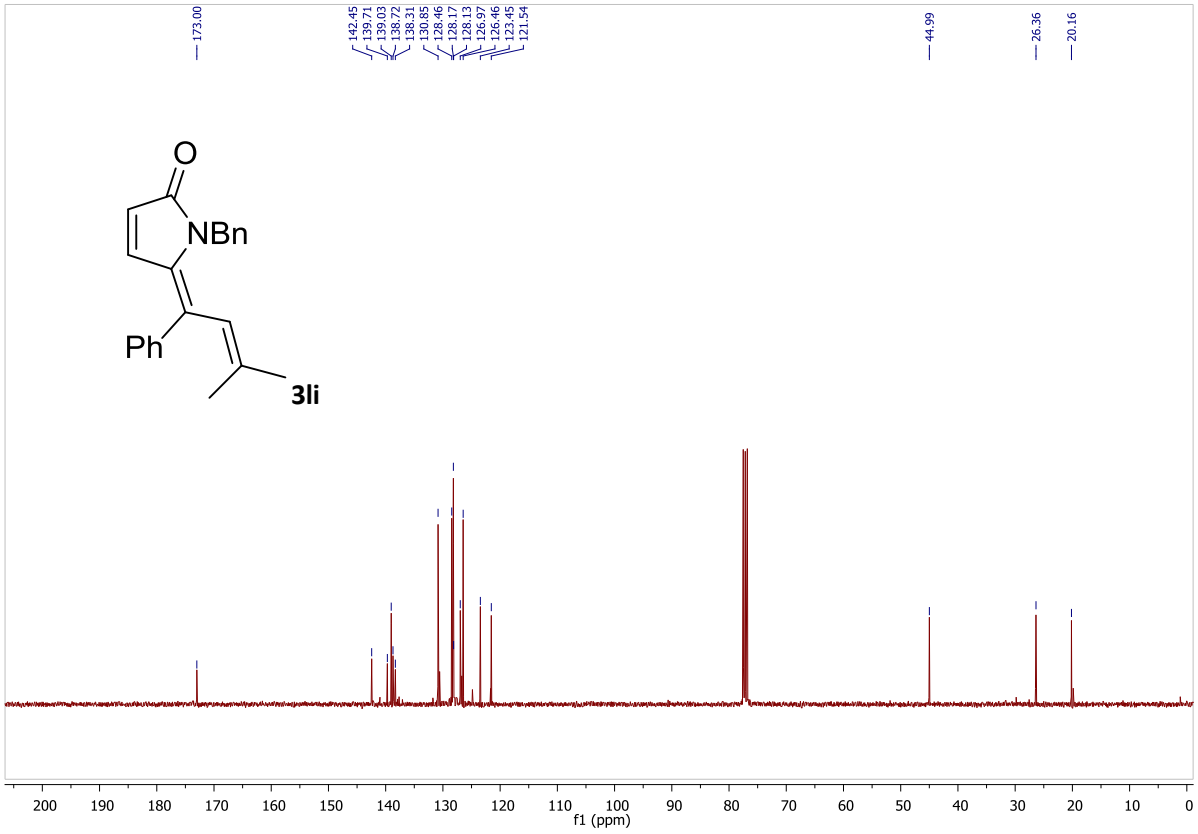
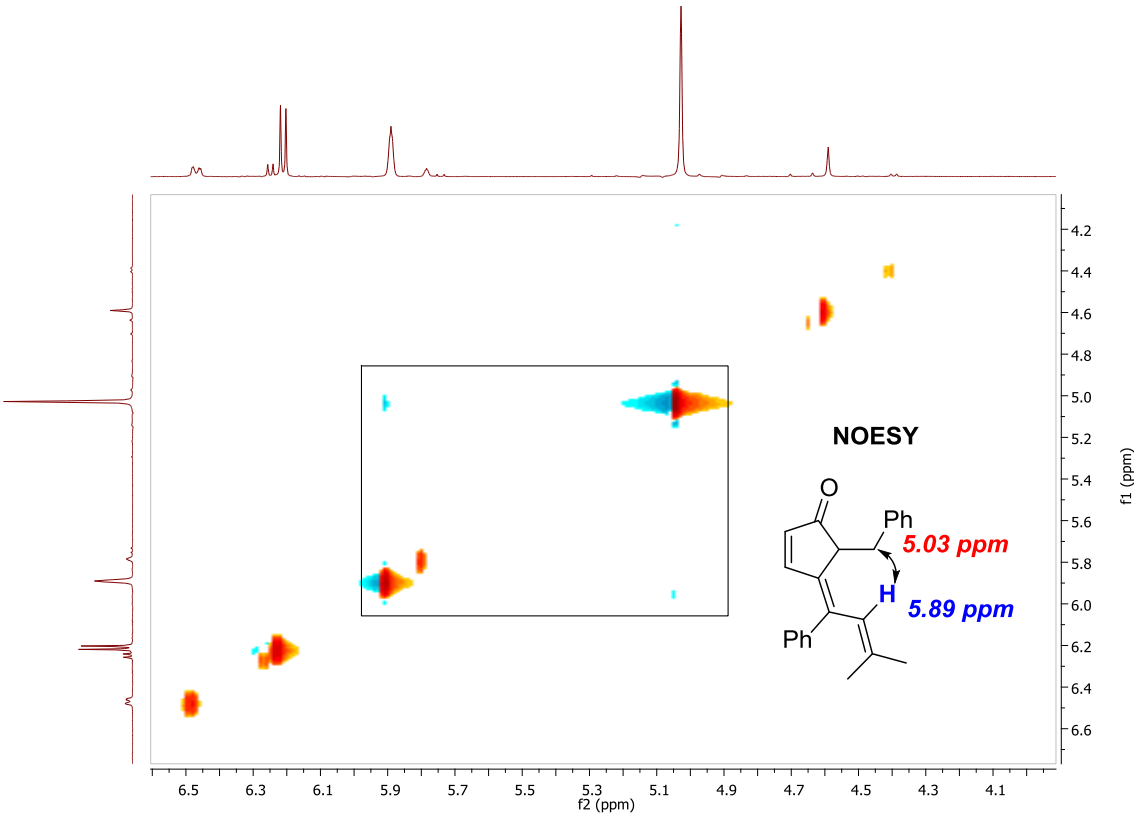
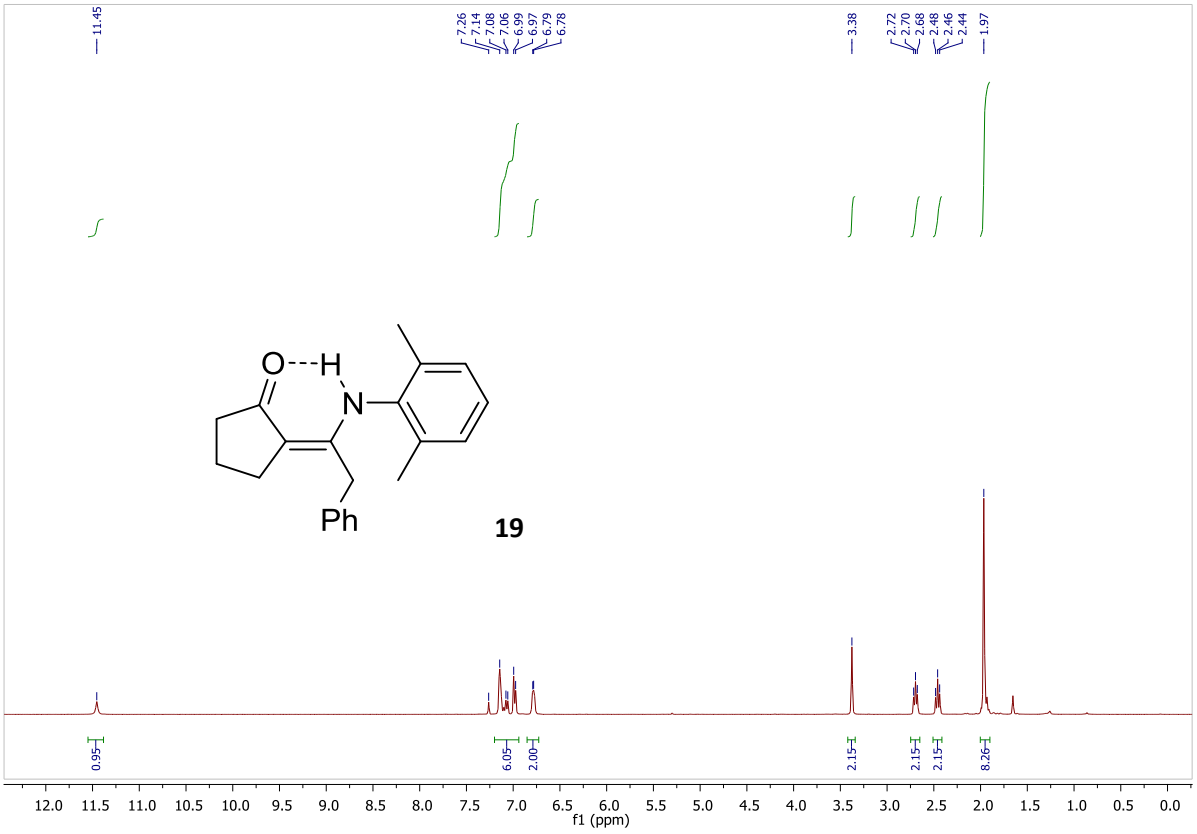
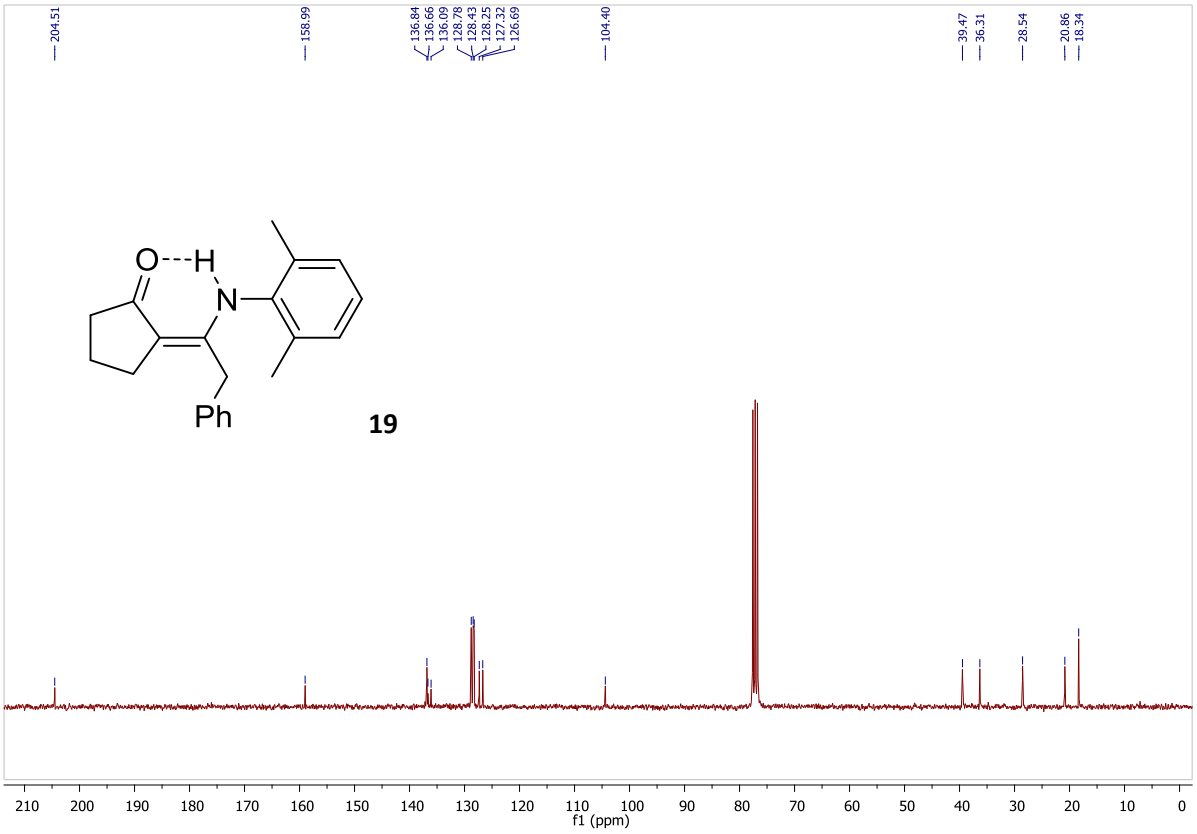
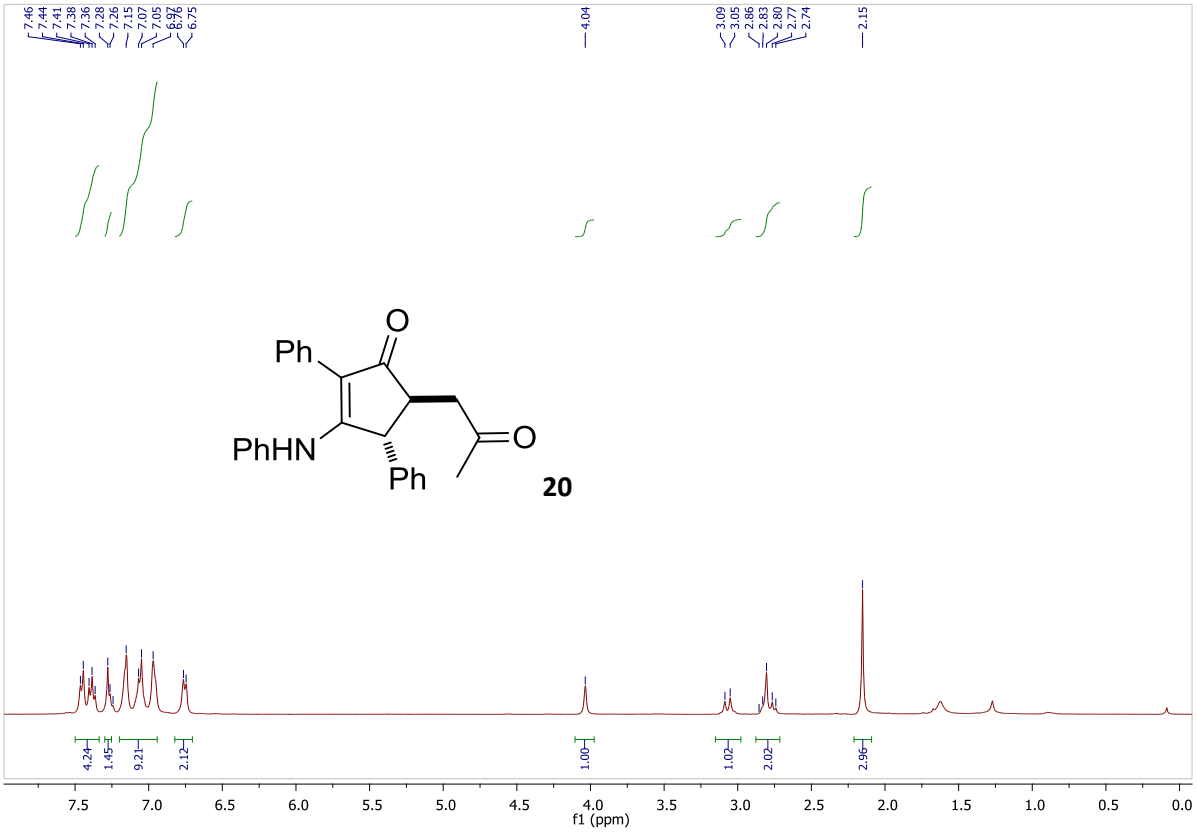
7.30
7.30
7.30
7.28
7.28
7.26
7.16
7.09
7.07
6.99
6.97
6.48
6.48
6.46
6.24
6.22
6.20
5.89
5.79
5.78
5.78
5.03
4.59
1.82
1.82
1.80
1.80
1.34
1.34
1.26
1.25
O
NBn
Ph
+
O
NBn
Ph
3li and 3'li
5.32
3.27
2.30
0.97
0.32
0.16
0.99
0.99
0.15
2.00
0.32
0.49
2.99
0.49
3.39
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

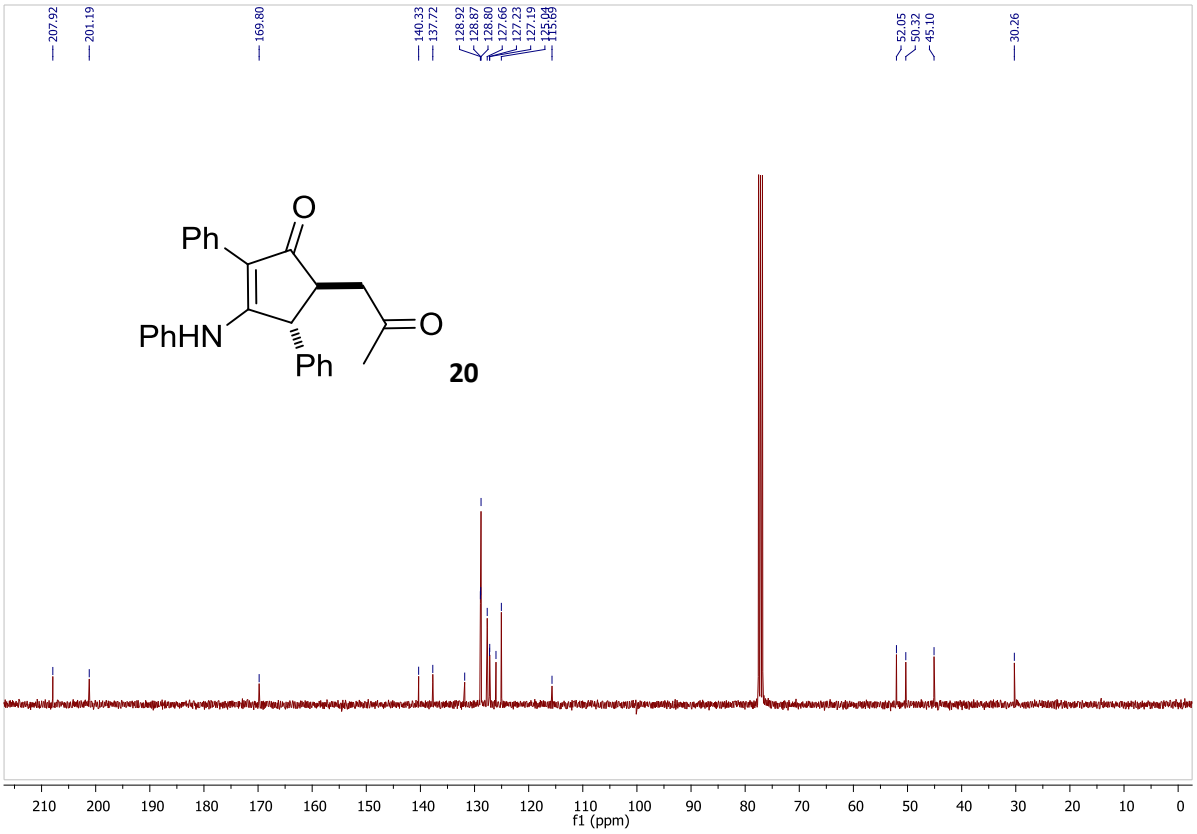

173.00
142.45
139.71
139.03
138.72
138.31
130.85
128.46
128.17
128.13
126.97
126.46
123.45
121.54
44.99
26.36
20.16
O
NBn
Ph
3li
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

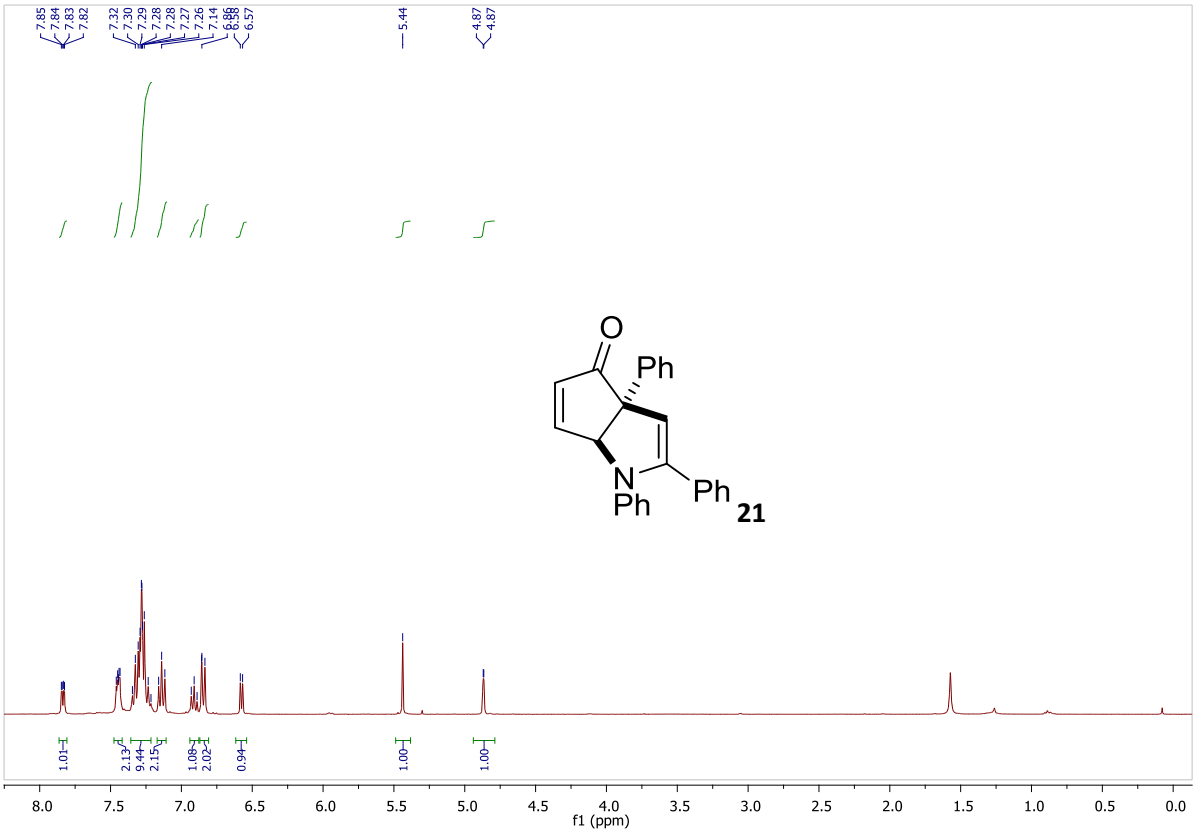

NOESY
O
Ph
5.03 ppm
H
5.89 ppm
Ph
f1 (ppm)
f2 (ppm)

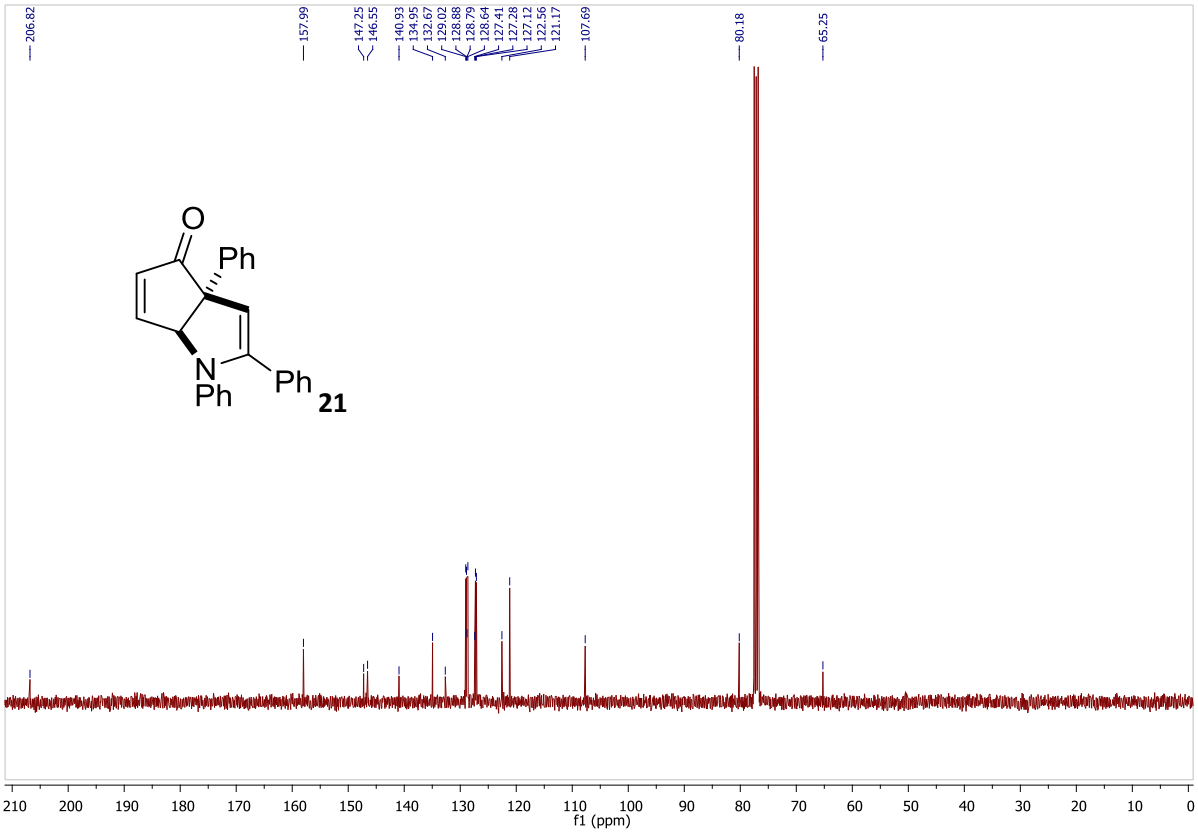

O---H
N
Ph
19
f1 (ppm)

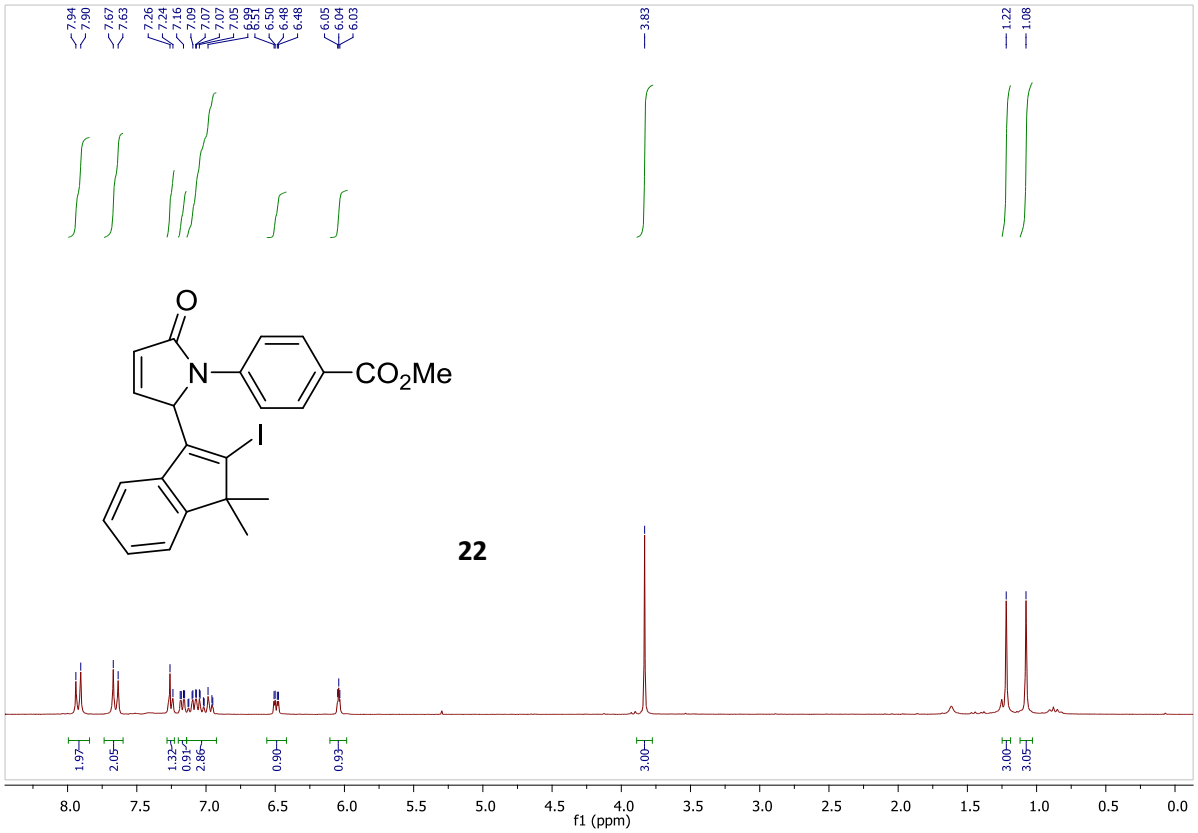

204.51
158.99
136.84
136.66
136.09
128.78
128.43
128.25
127.32
126.69
104.40
39.47
36.31
28.54
20.86
18.34
O---H
N
Ph
19
f1 (ppm)

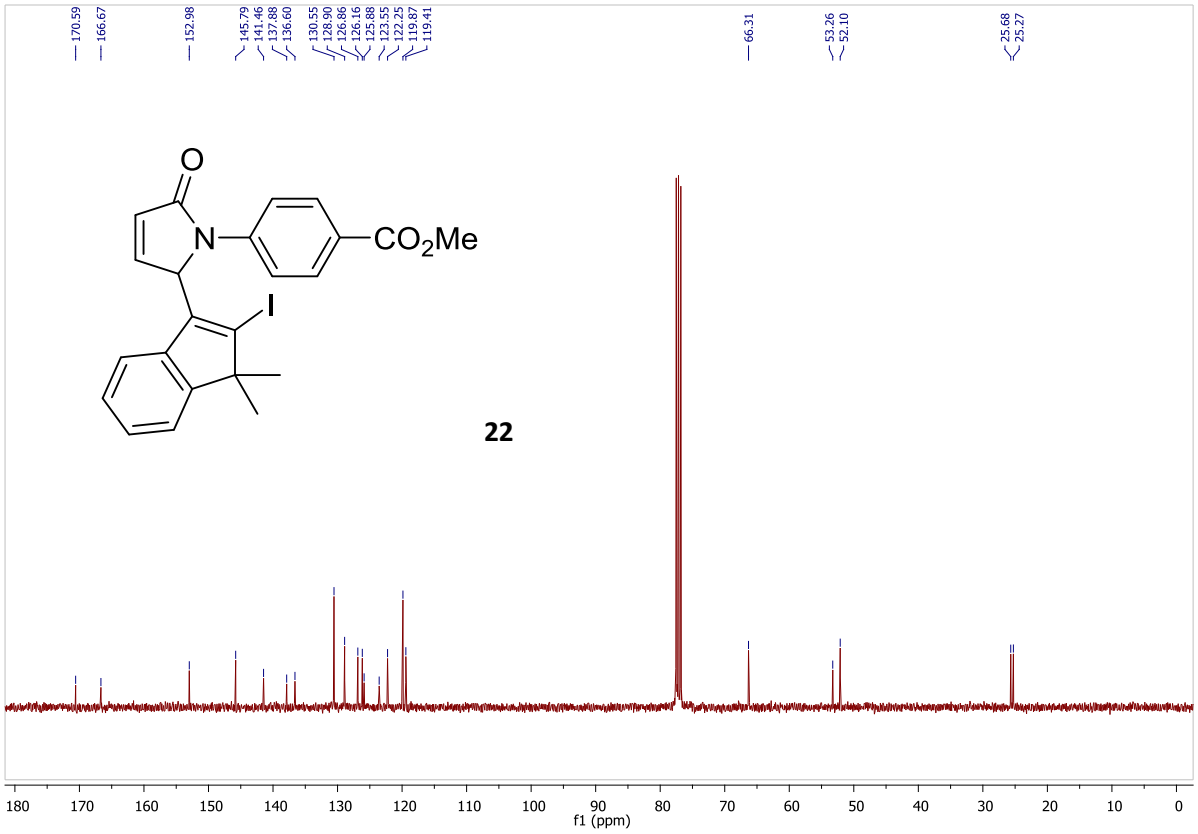

7.46
7.44
7.41
7.38
7.36
7.28
7.26
7.15
7.07
7.05
6.76
6.75
4.04
3.09
3.05
2.86
2.83
2.80
2.77
2.74
2.15
O
Ph
PhHN
Ph
O
20
4.24
1.45
9.21
2.12
1.00
1.02
2.02
2.96
f1 (ppm)


207.92
201.19
169.80
140.33
137.72
128.92
128.87
128.80
127.66
127.23
127.19
52.05
50.32
45.10
30.26
O
Ph
PhHN
Ph
O
20
f1 (ppm)


7.85
7.84
7.83
7.82
7.32
7.30
7.29
7.28
7.28
7.27
7.26
7.14
6.58
6.57
5.44
4.87
4.87
O
Ph
N
Ph
Ph
21
1.01
2.13
9.44
2.15
1.09
2.02
0.94
1.00
1.00
f1 (ppm)


206.82
157.99
147.25
146.55
140.93
134.95
132.67
129.02
128.88
128.79
128.64
127.41
127.28
127.12
122.56
121.17
107.69
80.18
65.25
O
Ph
N
Ph
Ph
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.94
7.90
7.67
7.63
7.26
7.24
7.16
7.09
7.07
7.07
7.05
6.89
6.51
6.50
6.48
6.48
6.05
6.04
6.03
3.83
1.22
1.08
O
N
CO2Me
I
22
1.97
2.05
1.32
0.91
2.86
0.90
0.93
3.00
3.00
3.05
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)


170.59
166.67
152.98
145.79
141.46
137.88
136.60
130.55
128.90
126.86
126.16
125.88
123.55
122.25
119.87
119.41
66.31
53.26
52.10
25.68
25.27
O
N
CO2Me
I
22
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)