

Electronic Supplementary Information

Rhodium(III)-catalysed decarbonylative coupling of maleic anhydrides with alkynes

Takanori Matsuda* and Kentaro Suzuki

*Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku,
Tokyo 162-8601, Japan*

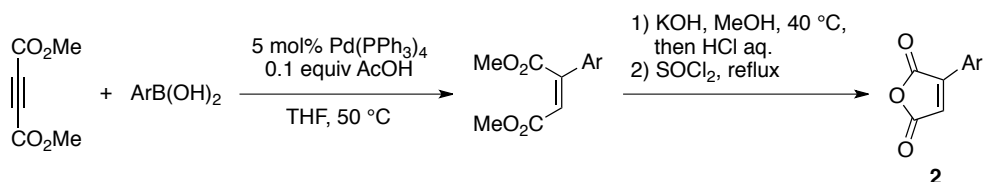
E-mail: mtd@rs.tus.ac.jp

General. All reactions were carried out with standard Schlenk techniques under a nitrogen atmosphere. Column chromatography was performed on Wakogel[®] C-200 (75–150 μm). Preparative thin-layer chromatography was performed on Wakogel[®] B-5F. Proton chemical shifts were referenced to residual CHCl_3 signal at 7.26 ppm. Carbon chemical shifts were referenced to CDCl_3 at 77.0 ppm. Melting points were not corrected.

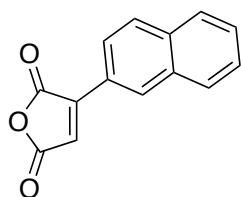
Materials: Preparation of Substituted Maleic Anhydrides 2. Substrates **2** were synthesised by palladium-catalysed addition of arylboronic acids to dimethyl acetylenedicarboxylate,¹ and subsequent hydrolysis followed by dehydration.²

1 A. K. Gupta, K. S. Kim and C. H. Oh, *Synlett*, 2005, 457.

2 M. K. Sahoo, S. B. Mhaske and N. P. Argade, *Synthesis*, 2003, 346.



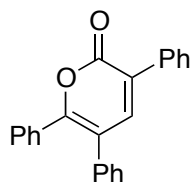
All other commercially available chemical resources were used as received without further purification.



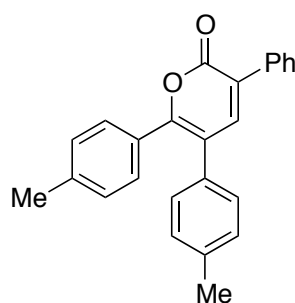
3-(Naphthalen-2-yl)furan-2,5-dione (2d). Yellow solid, mp 159–160 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.07 (s, 1H), 7.56–7.66 (m, 2H), 7.79 (dd, $J = 8.5, 1.5$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 8.5$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 8.74 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 124.0, 124.07, 124.10, 127.4, 127.8, 129.0, 129.3, 129.7, 131.0, 132.8, 134.8, 146.5, 163.7, 164.7; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_8\text{NaO}_3$ $[\text{M} + \text{H}]^+$ 247.0366, found 247.0363; IR (ν/cm^{-1}): 1828, 1766, 1227, 910.

General Procedure for Rhodium(III)-Catalysed Decarbonylative Coupling of Maleic Anhydrides **2 with Alkynes **1**.** A Schlenk tube was charged with $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (5.0 μmol), $\text{Cu}(\text{OAc})_2$ (0.150 mmol), alkyne **1** (0.100 mmol) and maleic anhydride **2** (0.150 mmol), and the tube was evacuated and backfilled with nitrogen. *t*-Amyl alcohol (1.0 mL) was added via a syringe through the septum, and the mixture was heated at 120 °C with stirring for the indicated period of time. The reaction mixture was cooled to room temperature and then filtered through a plug of Florisil[®] washing with

hexane–AcOEt (1:1), and the filtrate was concentrated. The residue was purified by preparative TLC on silica gel to afford pyrone **3**.



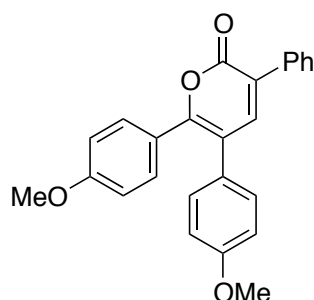
3,5,6-Triphenyl-2H-pyran-2-one (3a). According to the general procedure, **1a** (17.8 mg, 0.100 mmol), **2a** (26.1 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 2 h. Purification by preparative TLC on silica gel (hexane:acetone = 3:1) afforded **3a** (27.5 mg, 0.085 mmol, 85%) as a yellow solid. Mp 143–144 °C (lit. 140–142 °C;^{3a} 143–145 °C;^{3b} 141–143 °C^{3c}); ¹H NMR (301 MHz, CDCl₃) δ 7.22–7.48 (m, 13H), 7.63 (s, 1H), 7.74–7.80 (m, 2H). The spectral data matched those reported in the literature.³



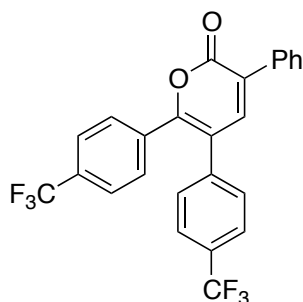
5,6-Bis(4-methylphenyl)-3-phenyl-2H-pyran-2-one (3b). According to the general procedure, **1b** (20.6 mg, 0.100 mmol), **2a** (25.9 mg, 0.149 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 2 h. Purification by preparative TLC on silica gel (hexane:acetone = 5:1) afforded **3b** (30.4 mg, 0.086 mmol, 86%) as a yellow solid. Mp 156–

3 (a) R. C. Larock, M. J. Doty and X. Han, *J. Org. Chem.*, 1999, **64**, 8770; (b) S. Mochida, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2009, **74**, 6295; (c) M. Itoh, M. Shimizu, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2013, **78**, 11427.

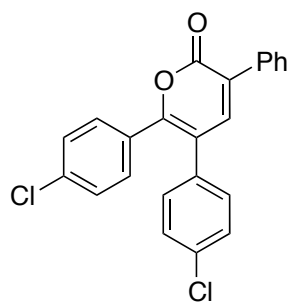
157 °C; ^1H NMR (500 MHz, CDCl_3) δ 2.33 (s, 3H), 2.38 (s, 3H), 7.07 (d, J = 8.0 Hz, 2H), 7.14–7.18 (m, 4H), 7.34 (d, J = 8.0 Hz, 2H), 7.35–7.40 (m, 1H), 7.41–7.46 (m, 2H), 7.60 (s, 1H), 7.73–7.77 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 21.2, 21.4, 118.1, 125.0, 128.2, 128.4, 128.5, 128.9, 129.0, 129.1, 129.7, 133.6, 134.6, 137.7, 140.1, 144.7, 156.8, 161.4; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ 375.1356, found 375.1360; IR (ν/cm^{-1}): 1728, 1504, 1180, 825.



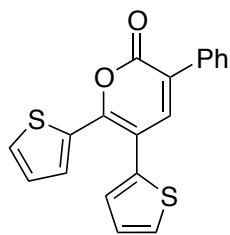
5,6-Bis(4-methoxyphenyl)-3-phenyl-2H-pyran-2-one (3c). According to the general procedure, **1c** (23.8 mg, 0.100 mmol), **2a** (25.8 mg, 0.148 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (4.2 mg, 5.0 μmol , 5 mol% Rh) and $\text{Cu}(\text{OAc})_2$ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 3 h. Purification by preparative TLC on silica gel (hexane:acetone = 3:1) afforded **3c** (32.7 mg, 0.085 mmol, 85%) as a yellow solid. Mp 158–159 °C (lit.^{3c} 157–158 °C); ^1H NMR (301 MHz, CDCl_3) δ 3.87 (s, 3H), 3.90 (s, 3H), 6.81–6.90 (m, 2H), 6.92–7.03 (m, 2H), 7.21–7.30 (m, 2H), 7.40–7.55 (m, 5H), 7.65 (s, 1H), 7.78–7.88 (m, 2H). The spectral data matched those reported in the literature.^{3c}



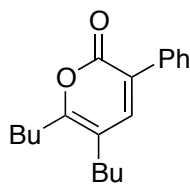
3-Phenyl-5,6-bis[4-(trifluoromethyl)phenyl]-2H-pyran-2-one (3d). According to the general procedure, **1d** (31.4 mg, 0.100 mmol), **2a** (26.3 mg, 0.151 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 5 h. Purification by preparative TLC on silica gel (hexane:acetone = 5:1) afforded **3d** (34.3 mg, 0.075 mmol, 75%) as a yellow solid. Mp 67–68 °C (lit.^{3c} 65–66 °C); ¹H NMR (500 MHz, CDCl₃) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.40–7.48 (m, 3H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 2H), 7.58 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.73–7.77 (m, 2H). The spectral data matched those reported in the literature.^{3c}



5,6-Bis(4-chlorophenyl)-3-phenyl-2H-pyran-2-one (3e). According to the general procedure, **1e** (24.6 mg, 0.100 mmol), **2a** (26.1 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 5 h. Purification by preparative TLC on silica gel (hexane:acetone = 4:1) afforded **3e** (32.3 mg, 0.082 mmol, 83%) as a yellow solid. Mp 150–151 °C (lit.^{3c} 150–151 °C); ¹H NMR (500 MHz, CDCl₃) δ 7.15–7.19 (m, 2H), 7.23–7.27 (m, 2H), 7.31–7.36 (m, 4H), 7.36–7.45 (m, 3H), 7.54 (s, 1H), 7.70–7.74 (m, 2H). The spectral data matched those reported in the literature.^{3c}

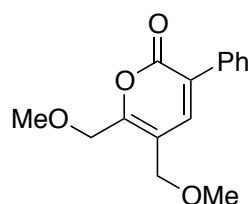


3-Phenyl-5,6-di(2-thienyl)-2H-pyran-2-one (3f). According to the general procedure, **1f** (19.0 mg, 0.100 mmol), **2a** (26.1 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 19 h. Purification by preparative TLC on silica gel (hexane:acetone = 5:1) afforded **3f** (2.0 mg, 0.006 mmol, 6%) as a brown solid. Mp 165–166 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.00 (dd, *J* = 5.5, 4.0 Hz, 1H), 7.13 (dd, *J* = 3.5, 1.0 Hz, 1H), 7.16 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.35–7.45 (m, 4H), 7.47 (dd, *J* = 3.5, 1.0 Hz, 1H), 7.51–7.56 (m, 2H), 7.72–7.75 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 109.7, 123.9, 127.4, 128.0, 128.07, 128.10, 128.5, 128.6, 129.1, 130.4, 130.6, 133.7, 134.1, 136.0, 144.3, 153.4, 160.1; HRMS (ESI) calcd for C₁₉H₁₂NaO₂S₂ [M + Na]⁺ 359.0171, found 359.0173; IR (ν/cm⁻¹): 1712, 1519, 1496, 717.

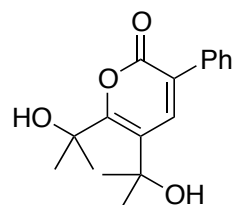


5,6-Dibutyl-3-phenyl-2H-pyran-2-one (3g). According to the general procedure, **1g** (13.8 mg, 0.100 mmol), **2a** (26.1 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 3 h. Purification by preparative TLC on silica gel (hexane:acetone = 10:1) afforded **3g** (21.5 mg, 0.076 mmol, 76%) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 0.957 (t, *J* = 7.5 Hz, 3H), 0.962 (t, *J* = 7.3 Hz, 3H), 1.35–1.45 (m, 4H), 1.47–1.55 (m, 2H), 1.66–1.76 (m, 2H), 2.34–2.38 (m, 2H), 2.52–2.57 (m, 2H), 7.31 (s, 1H), 7.32–7.36 (m, 1H),

7.38–7.42 (m, 2H), 7.64–7.67 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 13.8, 13.9, 22.3, 22.5, 29.1, 29.9, 30.4, 32.5, 115.8, 124.8, 128.1, 128.2, 128.3, 135.0, 143.8, 161.0, 162.3; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{24}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ 307.1669, found 307.1668; IR (ν/cm^{-1}): 2954, 2931, 1712, 1558.

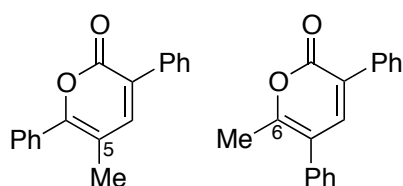


5,6-Bis(methoxymethyl)-3-phenyl-2H-pyran-2-one (3h). According to the general procedure, **1h** (11.4 mg, 0.100 mmol), **2a** (26.1 mg, 0.150 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (4.2 mg, 5.0 μmol , 5 mol% Rh) and Ag_2CO_3 (41.3 mg, 0.15 mmol) were reacted in DMF (1.0 mL) at 120 $^\circ\text{C}$ for 5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 2:1) afforded **3h** (15.0 mg, 0.058 mmol, 58%) as a yellow solid. Mp 55–57 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 3.40 (s, 3H), 3.45 (s, 3H), 4.32 (s, 2H), 4.34 (s, 2H), 7.34–7.44 (m, 3H), 7.54 (s, 1H), 7.65–7.69 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 58.3, 59.0, 68.1, 68.5, 115.7, 127.6, 128.2, 128.4, 128.7, 134.2, 141.6, 157.0, 161.0; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 283.0941, found 283.0939; IR (ν/cm^{-1}): 1728, 1188, 1088.



5,6-Bis(2-hydroxypropan-2-yl)-3-phenyl-2H-pyran-2-one (3i). According to the general procedure, **1i** (14.2 mg, 0.100 mmol), **2a** (26.1 mg, 0.150 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (4.2 mg, 5.0 μmol , 5 mol% Rh) and Ag_2CO_3 (41.3 mg, 0.150 mmol) were reacted in DMF (1.0 mL) at 120 $^\circ\text{C}$ for 5 h. Purification by preparative TLC on silica gel

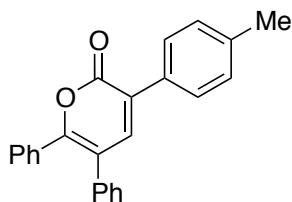
(hexane:AcOEt = 2:1) afforded **3i** (13.5 mg, 0.047 mmol, 47%) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 1.65 (s, 6H), 1.67 (s, 6H), 7.35–7.45 (m, 4H), 7.61–7.65 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 30.1, 32.0, 72.3, 74.0, 122.8, 124.7, 128.0, 128.5, 128.6, 134.3, 142.1, 160.5, 165.0; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 311.1254, found 311.1253; IR (ν/cm^{-1}): 3294, 1720, 1689, 1227.



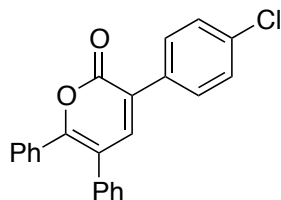
5-Methyl-3,6-diphenyl-2H-pyran-2-one (3j) and 6-methyl-3,5-diphenyl-2H-pyran-2-one (3'j). According to the general procedure, **1j** (11.3 mg, 0.097 mmol), **2a** (26.3 mg, 0.151 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (4.2 mg, 5.0 μmol , 5 mol% Rh) and $\text{Cu}(\text{OAc})_2$ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 $^\circ\text{C}$ for 5 h. Purification by preparative TLC on silica gel (hexane:acetone = 4:1) afforded a mixture of **3j** and **3'j** (17.5 mg, 0.067 mmol, 69%, **3j**:**3'j** = 69:31 by ^1H NMR). The major isomer **3j** could be isolated as a pure compound.

3j: pale yellow solid, Mp 137–138 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 2.26 (s, 3H), 7.35–7.50 (m, 7H), 7.63–7.67 (m, 2H), 7.71–7.75 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 17.0, 111.9, 125.8, 128.2, 128.36, 128.42, 128.5, 128.7, 129.8, 132.3, 134.6, 145.2, 156.5, 161.7; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{14}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ 285.0886, found 285.0890; IR (ν/cm^{-1}): 1705, 1550, 694.

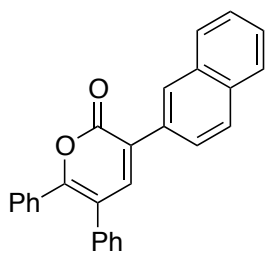
3'j: ^1H NMR (500 MHz, CDCl_3) δ 2.33 (s, 3H), 7.30–7.33 (m, 2H), 7.35–7.51 (m, 7H), 7.68–7.71 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 18.3, 118.7, 124.8, 127.9, 128.1, 128.4, 128.80, 128.84, 134.5, 135.9, 143.4, 158.3, 161.8.



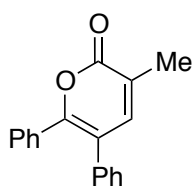
3-(4-Methylphenyl)-5,6-diphenyl-2H-pyran-2-one (3k). According to the general procedure, **1a** (17.8 mg, 0.100 mmol), **2b** (28.2 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.1 mg, 4.9 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 2 h. Purification by preparative TLC on silica gel (hexane:acetone = 5:1) afforded **3k** (28.3 mg, 0.084 mmol, 84%) as a yellow solid. Mp 170–171 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.40 (s, 3H), 7.23–7.28 (m, 6H), 7.29–7.38 (m, 4H), 7.40–7.43 (m, 2H), 7.60 (s, 1H), 7.65–7.68 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 21.3, 118.6, 125.6, 127.9, 128.07, 128.13, 129.0, 129.16, 129.19, 129.24, 129.8, 131.5, 132.0, 136.5, 138.7, 143.7, 156.4, 161.4; HRMS (ESI) calcd for C₂₄H₁₈NaO₂ [M + Na]⁺ 361.1199, found 361.1196; IR (ν/cm⁻¹): 1712, 1543, 771, 702.



3-(4-Chlorophenyl)-5,6-diphenyl-2H-pyran-2-one (3l). According to the general procedure, **1a** (17.8 mg, 0.100 mmol), **2c** (31.2 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.1 mg, 0.149 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 5 h. Purification by preparative TLC on silica gel (hexane:acetone = 5:1) afforded **3l** (33.0 mg, 0.092 mmol, 92%) as a yellow solid. Mp 161–162 °C (lit.^{3b} 160–161 °C); ¹H NMR (300 MHz, CDCl₃) δ 7.21–7.45 (m, 12H), 7.61 (s, 1H), 7.69–7.76 (m, 2H). The spectral data matched those reported in the literature.^{3b}

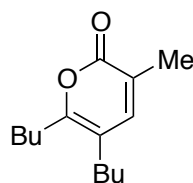


3-(2-Naphthyl)-5,6-diphenyl-2H-pyran-2-one (3m). According to the General Procedure, **1a** (17.8 mg, 0.100 mmol), **2d** (33.6 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 5 h. Purification by preparative TLC on silica gel (hexane:acetone = 5:1) afforded **3m** (34.2 mg, 0.091 mmol, 91%) as a yellow solid. Mp 165–166 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.26–7.31 (m, 4H), 7.31–7.40 (m, 4H), 7.43–7.47 (m, 2H), 7.47–7.53 (m, 2H), 7.76 (s, 1H), 7.83–7.87 (m, 2H), 7.88–7.92 (m, 2H), 8.32–8.34 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 118.7, 125.4, 125.6, 126.3, 126.6, 127.6, 127.8, 127.98, 128.05, 128.2, 128.5, 129.0, 129.2, 129.3, 129.9, 131.7, 131.9, 133.19, 133.23, 136.5, 144.5, 156.8, 161.3; HRMS (ESI) calcd for C₂₇H₁₈NaO₂ [M + Na]⁺ 397.1199, found 397.1203; IR (ν/cm⁻¹): 1720, 1535, 771, 694.

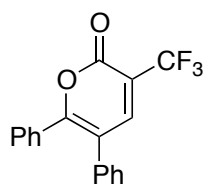


3-Methyl-5,6-diphenyl-2H-pyran-2-one (3n). According to the general procedure, **1a** (17.8 mg, 0.100 mmol), **2e** (17.1 mg, 0.153 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 8 h. Purification by preparative TLC on silica gel (hexane:acetone = 3:1) afforded **3n** (22.0 mg, 0.084 mmol, 84%) as a yellow solid. Mp 120–121 °C (lit. 124–126 °C^{3b}; 127–128 °C^{3c}); ¹H NMR (300 MHz, CDCl₃) δ 2.16 (d, *J* = 1.2 Hz, 3H), 7.11–7.34

(m, 11H). The spectral data matched those reported in the literature.^{3b,c,4}



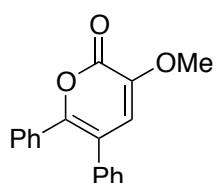
5,6-Dibutyl-3-methyl-2H-pyran-2-one (3o). According to the general procedure, **1g** (13.8 mg, 0.100 mmol), **2e** (16.8 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.1 mg, 0.149 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane:acetone = 5:1) afforded **3o** (15.1 mg, 0.068 mmol, 68%) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 0.91 (t, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.0 Hz, 3H), 1.29–1.39 (m, 4H), 1.40–1.47 (m, 2H), 1.57–1.66 (m, 2H), 2.05 (s, 3H), 2.24 (t, *J* = 7.2 Hz, 2H), 2.45 (t, *J* = 8.0 Hz, 2H), 6.96 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 13.8, 13.9, 16.4, 22.3, 22.4, 28.9, 29.9, 30.1, 32.4, 115.1, 122.4, 143.3, 158.9, 164.3; HRMS (ESI) calcd for C₁₄H₂₂NaO₂ [M + Na]⁺ 245.1512, found 245.1516; IR (ν/cm⁻¹): 2954, 2870, 1712, 1458, 1080.



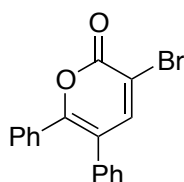
5,6-Diphenyl-3-(trifluoromethyl)-2H-pyran-2-one (3p). According to the general procedure, **1a** (17.8 mg, 0.100 mmol), **2f** (24.9 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Ag₂CO₃ (41.4 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 20 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) afforded **3p** (22.6 mg, 0.071 mmol, 72%) as a pale yellow oil. ¹H NMR (500 MHz,

4 (a) L. Ackermann, J. Pospech, K. Graczyk and K. Rauch, *Org. Lett.*, 2012, **14**, 930; (b) Q. Li, Y. Yan, X. Wang, B. Gong, X. Tang, J. Shi, H. E. Xu and W. Yi, *RSC Adv.*, 2013, **3**, 23402.

CDCl₃) δ 7.17–7.23 (m, 2H), 7.25–7.30 (m, 2H), 7.34–7.42 (m, 6H), 7.88 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 114.9 (q, ²J_{C-F} = 33.6 Hz), 116.8, 121.7 (q, ¹J_{C-F} = 271.5 Hz) 128.4, 128.5, 129.1, 129.3, 129.4, 130.9, 131.1, 134.9, 147.3 (q, ³J_{C-F} = 4.4 Hz), 156.7, 161.6; HRMS (ESI) calcd for C₁₈H₁₁FN₂O₂ [M + Na]⁺ 339.0603, found 339.0603; IR (ν /cm⁻¹): 1751, 1543, 1273, 1142, 702.

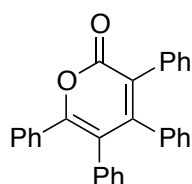


3-Methoxy-5,6-diphenyl-2H-pyran-2-one (3q). According to the general procedure, **1a** (17.8 mg, 0.100 mmol), **2g** (19.2 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μ mol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane:acetone = 5:1) afforded **3q** (23.0 mg, 0.083 mmol, 83%) as a yellow solid. Mp 131–132 °C; ¹H NMR (301 MHz, CDCl₃) δ 3.91 (s, 3H), 6.65 (s, 1H), 7.20–7.40 (m, 10H); ¹³C NMR (75.6 MHz, CDCl₃) δ 56.3, 117.4, 118.0, 127.9, 128.0, 128.8, 128.9, 129.0, 129.2, 131.9, 136.7, 144.2, 149.1, 158.5; HRMS (ESI) calcd for C₁₈H₁₄NaO₃ [M + Na]⁺ 301.0835, found 301.0838; IR (ν /cm⁻¹): 1728, 1628, 1342, 1227, 1126, 702.

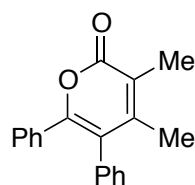


3-Bromo-5,6-diphenyl-2H-pyran-2-one (3r). According to the general procedure, **1a** (17.8 mg, 0.100 mmol), **2h** (35.4 mg, 0.200 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μ mol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 3 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1)

afforded **3r** (17.7 mg, 0.054 mmol, 54%) as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.16–7.21 (m, 2H), 7.22–7.27 (m, 2H), 7.30–7.38 (m, 6H), 7.84 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 109.8, 118.5, 128.26, 128.31, 129.09, 129.13, 130.3, 131.3, 135.1, 148.7, 157.4, 158.3; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{11}\text{BrNaO}_2$ $[\text{M} + \text{Na}]^+$ 348.9835, found 348.9837; IR (ν/cm^{-1}): 1728, 764, 694.

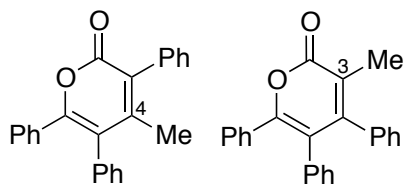


3,4,5,6-Tetraphenyl-2H-pyran-2-one (3s). According to the general procedure, **1a** (17.8 mg, 0.100 mmol), **2i** (37.5 mg, 0.150 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (4.2 mg, 5.0 μmol , 5 mol% Rh) and $\text{Cu}(\text{OAc})_2$ (27.3 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 $^\circ\text{C}$ for 30 h. Purification by preparative TLC on silica gel (hexane:acetone = 10:1) afforded **3s** (8.0 mg, 0.020 mmol, 20%) as a yellow solid. Mp 160–161 $^\circ\text{C}$ (lit. 165–167 $^\circ\text{C}^{3a}$, 163–165 $^\circ\text{C}^{3b}$); ^1H NMR (500 MHz, CDCl_3) δ 6.71–6.75 (m, 2H), 6.85–6.89 (m, 2H), 6.92–7.00 (m, 3H), 7.22 (m, 9H), 7.23–7.29 (m, 2H), 7.30–7.35 (m, 2H). The spectral data matched those reported in the literature.^{3b}



3,4-Dimethyl-5,6-diphenyl-2H-pyran-2-one (3t). According to the General Procedure, **1a** (17.8 mg, 0.100 mmol), **2j** (18.9 mg, 0.150 mmol), $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$ (4.2 mg, 5.0 μmol , 5 mol% Rh), $\text{Cu}(\text{OAc})_2$ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 $^\circ\text{C}$ for 6 h. Purification by preparative TLC on silica gel (hexane:acetone = 5:1) afforded **3t** (9.7 mg, 0.035 mmol, 35%) as a yellow solid. Mp 115–116 $^\circ\text{C}$ (lit.^{3b} 117–119 $^\circ\text{C}$); ^1H

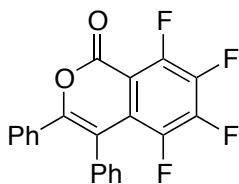
NMR (500 MHz, CDCl₃) δ 1.91 (s, 3H), 2.18 (s, 3H), 7.10–7.17 (m, 4H), 7.18–7.24 (m, 3H), 7.32–7.37 (m, 3H). The spectral data matched those reported in the literature.^{3a,b}



4-Methyl-3,5,6-triphenyl-2H-pyran-2-one (3u) and 3-methyl-4,5,6-triphenyl-2H-pyran-2-one (3'u). According to the General Procedure, **1a** (17.8 mg, 0.100 mmol), **2i** (28.2 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μ mol, 5 mol% Rh), Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane:acetone = 3:1) afforded **3u** (5.0 mg, 0.015 mmol, 15%) and **3'u** (3.2 mg, 0.009 mmol, 9%).

3u: pale yellow solid, Mp 158–159 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.81 (s, 3H), 7.16–7.25 (m, 5H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.34–7.40 (m, 6H), 7.43–7.48 (m, 2H); ¹³C NMR (126 MHz) δ 19.9, 120.3, 125.0, 127.8, 128.0, 128.5, 128.9, 129.1, 129.3, 130.0, 130.7, 132.5, 134.6, 135.3, 152.4, 155.7, 161.9; HRMS (ESI) calcd for C₂₄H₁₈NaO₂ [M + Na]⁺ 361.1199, found 361.1198; IR (ν /cm⁻¹): 1705, 1535, 756, 702.

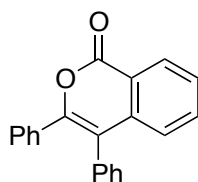
3'u: pale yellow solid, Mp 167–168 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.99 (s, 3H), 6.83 (d, *J* = 6.0 Hz, 2H), 6.91 (d, *J* = 6.0 Hz, 2H), 7.00–7.08 (m, 3H), 7.14–7.24 (m, 6H), 7.25–7.29 (m, 2H). The spectral data matched those reported in the literature.⁵



5,6,7,8-Tetrafluoro-3,4-diphenyl-1H-isochromen-1-one (3v). According to the

⁵ Y. Kuninobu, A. Kawata, M. Nishi, H. Takata and K. Takai, *Chem. Commun.*, 2008, 6360.

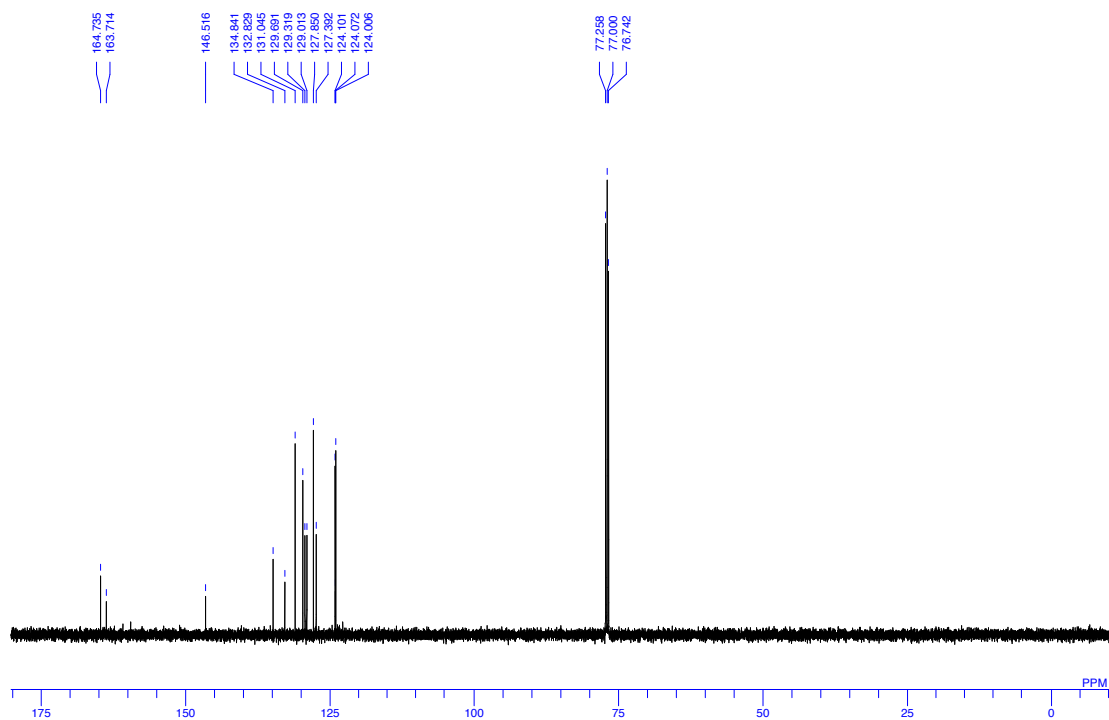
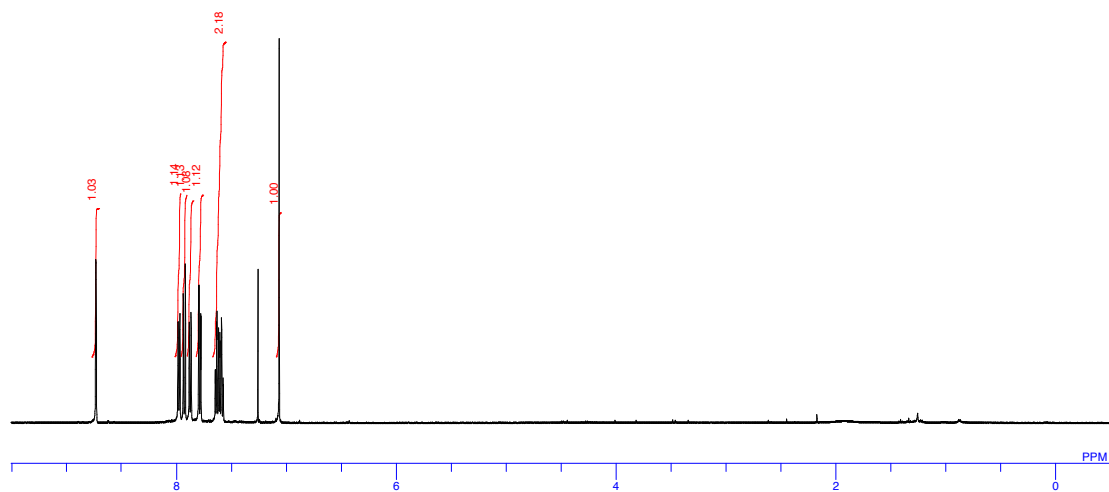
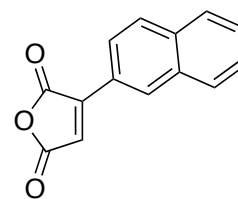
general procedure, **1a** (17.8 mg, 0.100 mmol), **2l** (33.0 mg, 0.150 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 3 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) afforded **3v** (18.8 mg, 0.051 mmol, 51%) as a yellow solid. Mp >240 °C; ¹H NMR (500 MHz, CDCl₃) δ 6.72–6.76 (m, 2H), 6.77–6.86 (m, 3H), 7.11–7.19 (m, 5H); ¹³C NMR (126 MHz, CDCl₃) δ 118.8, 125.6, 126.46, 126.51, 126.96, 129.7, 130.8, 138.8, 137.8 (m), 138.8, 139.8 (m), 140.0, 142.1, 142.4 (m), 144.5 (m); HRMS (ESI) calcd for C₂₁H₁₀F₄NaO₂ [M + Na]⁺ 393.0509, found 393.0504; IR (ν/cm⁻¹): 1658, 1520, 1496, 1442, 1381, 694.



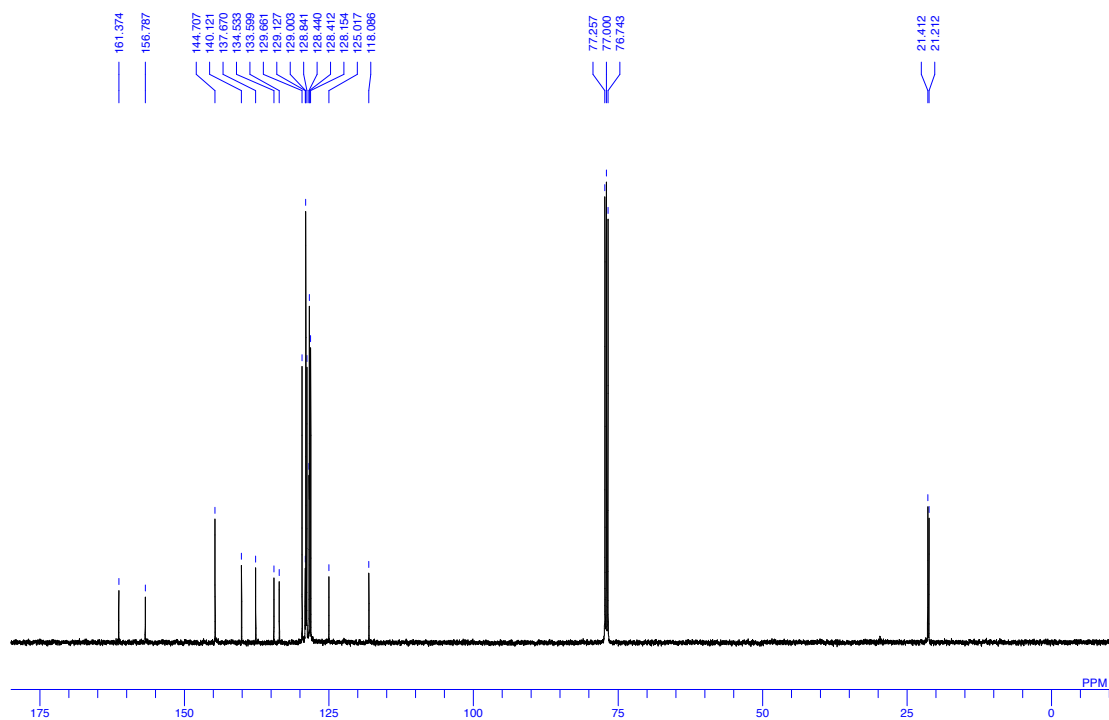
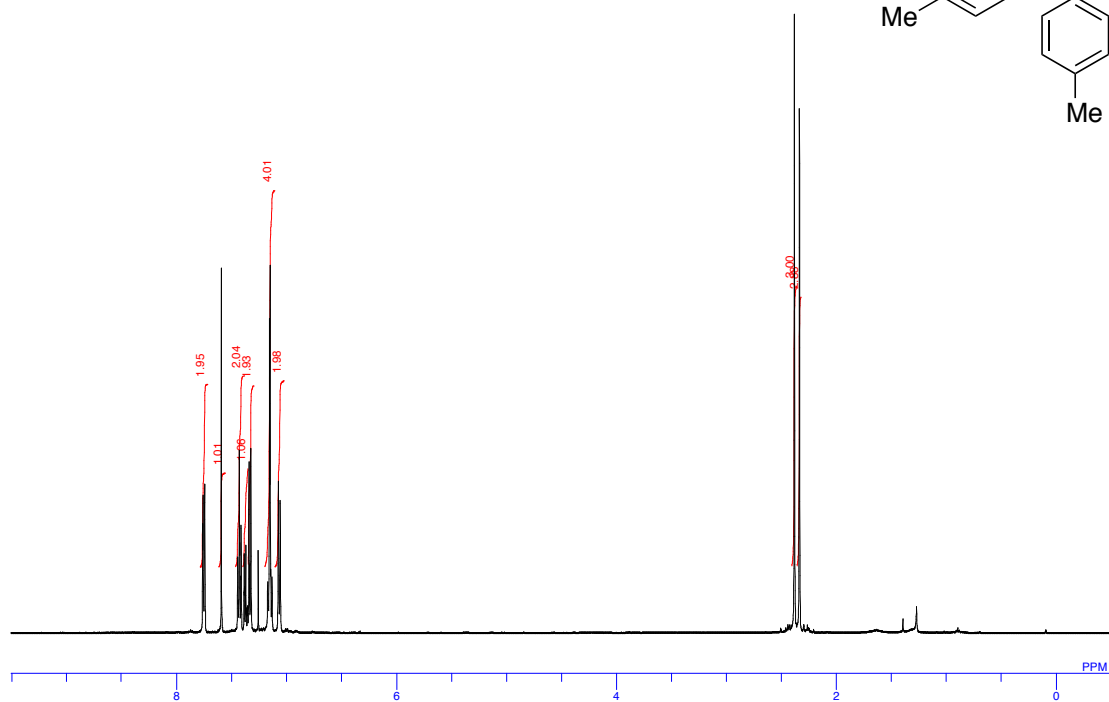
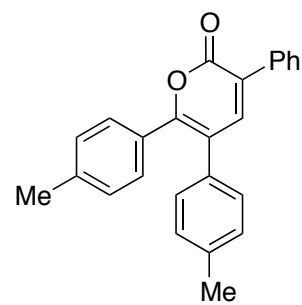
3,4-Diphenyl-1H-isochromen-1-one (3w). According to the general procedure, **1a** (17.8 mg, 0.100 mmol), **2q** (22.6 mg, 0.100 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (4.2 mg, 5.0 μmol, 5 mol% Rh) and Cu(OAc)₂ (27.2 mg, 0.150 mmol) were reacted in *t*-AmOH (1.0 mL) at 120 °C for 1 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 5:1) afforded **3w** (26.8 mg, 0.090 mmol, 90%) as a pale yellow solid. Mp 172–173 °C (lit. 170–171 °C^{6a}; 172–174 °C^{6b}); ¹H NMR (500 MHz, CDCl₃) δ 7.23–7.36 (m, 6H), 7.38–7.43 (m, 2H), 7.44–7.52 (m, 3H), 7.57–7.62 (m, 1H), 7.68–7.73 (m, 1H), 8.46–8.50 (m, 1H). The spectral data matched those reported in the literature.⁶

⁶ (a) T. Yao and R. C. Larock, *J. Org. Chem.*, 2003, **68**, 5936; (b) K. Ueura, T. Satoh and M. Miura, *Org. Lett.*, 2007, **9**, 1407; (c) Y. Kajita, T. Kurahashi and S. Matsubara, *J. Am. Chem. Soc.*, 2008, **130**, 17226.

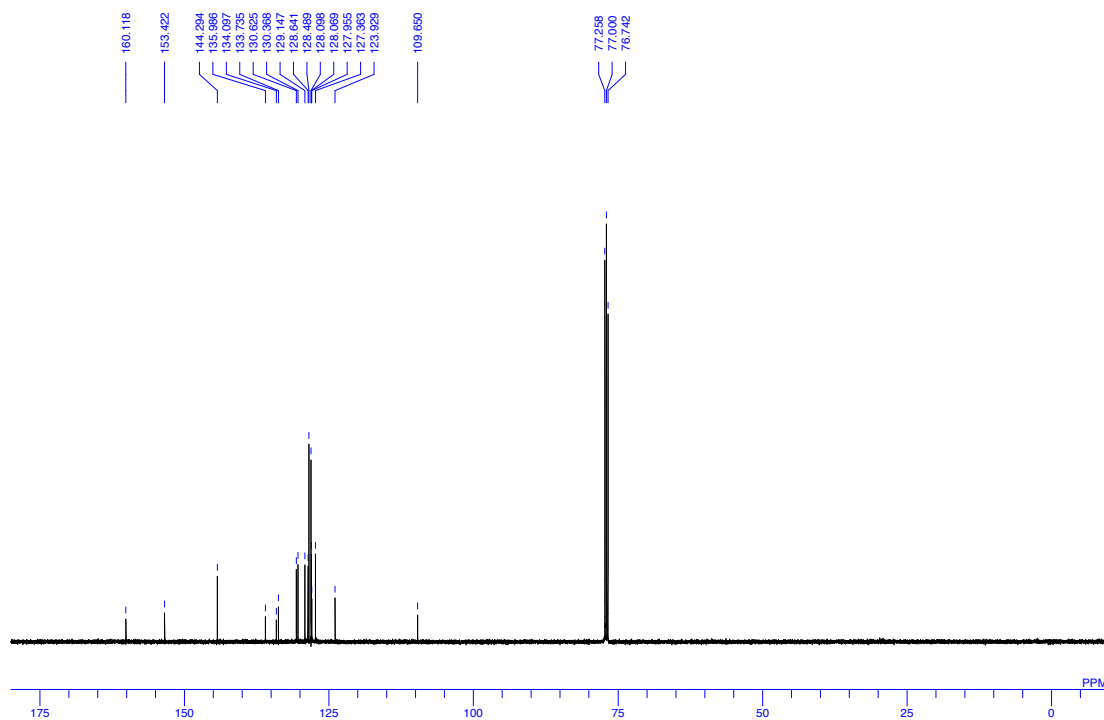
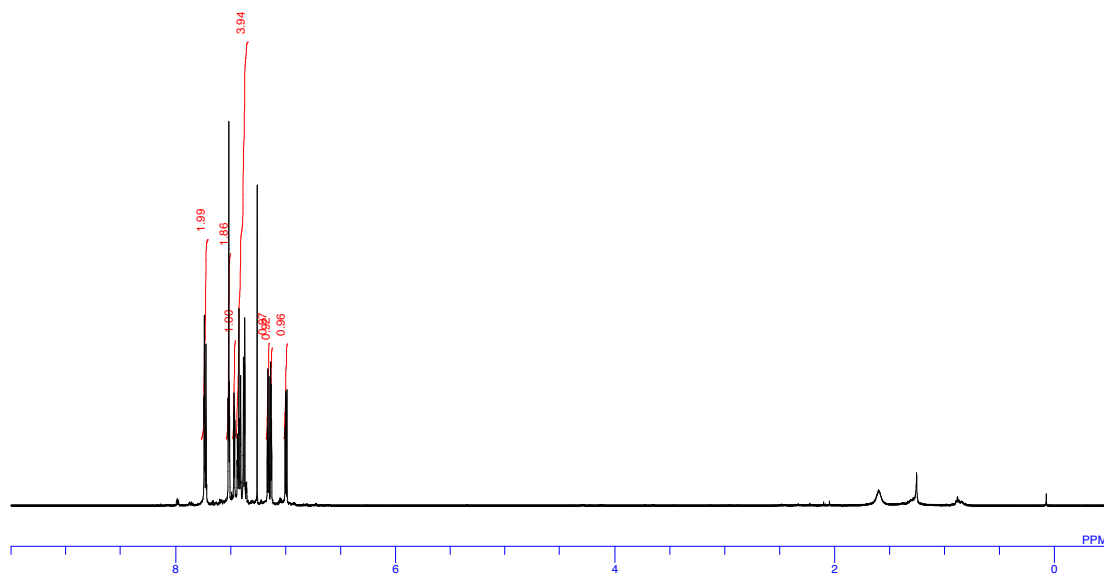
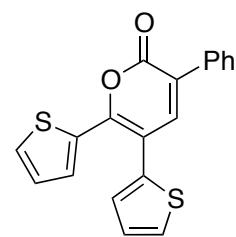
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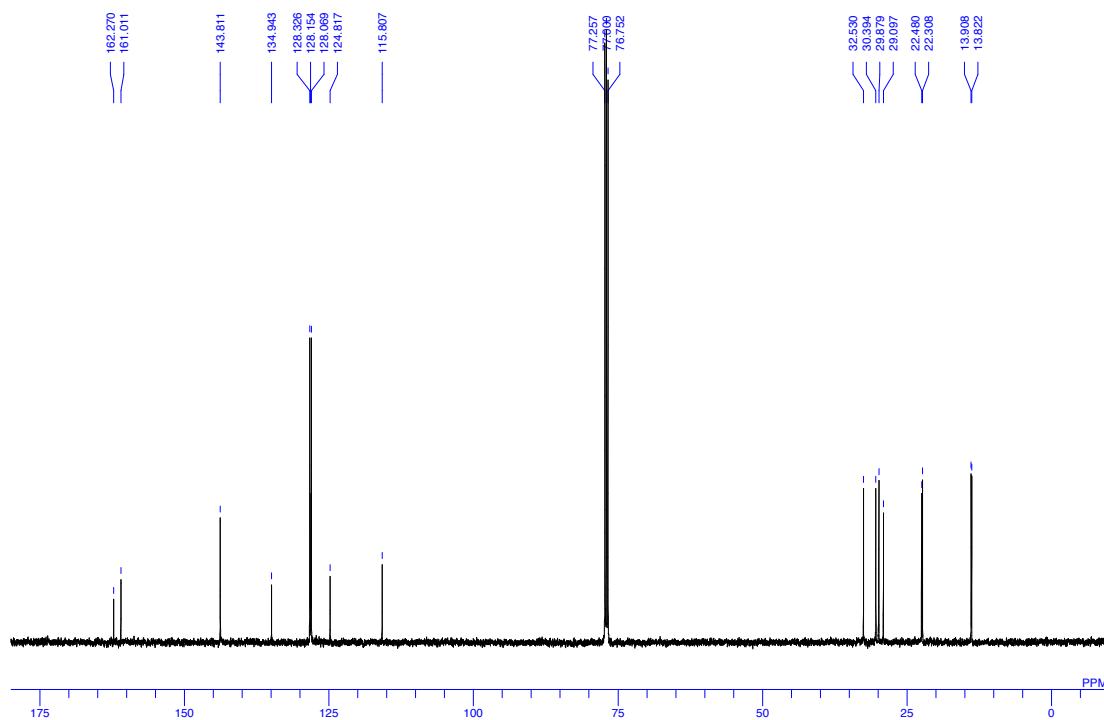
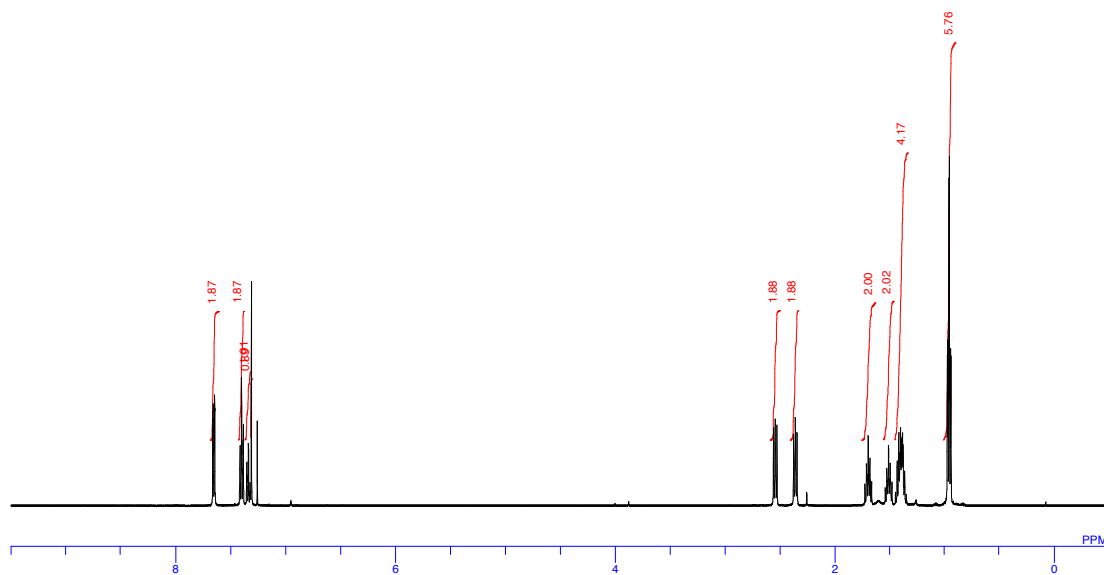
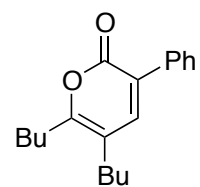
3b



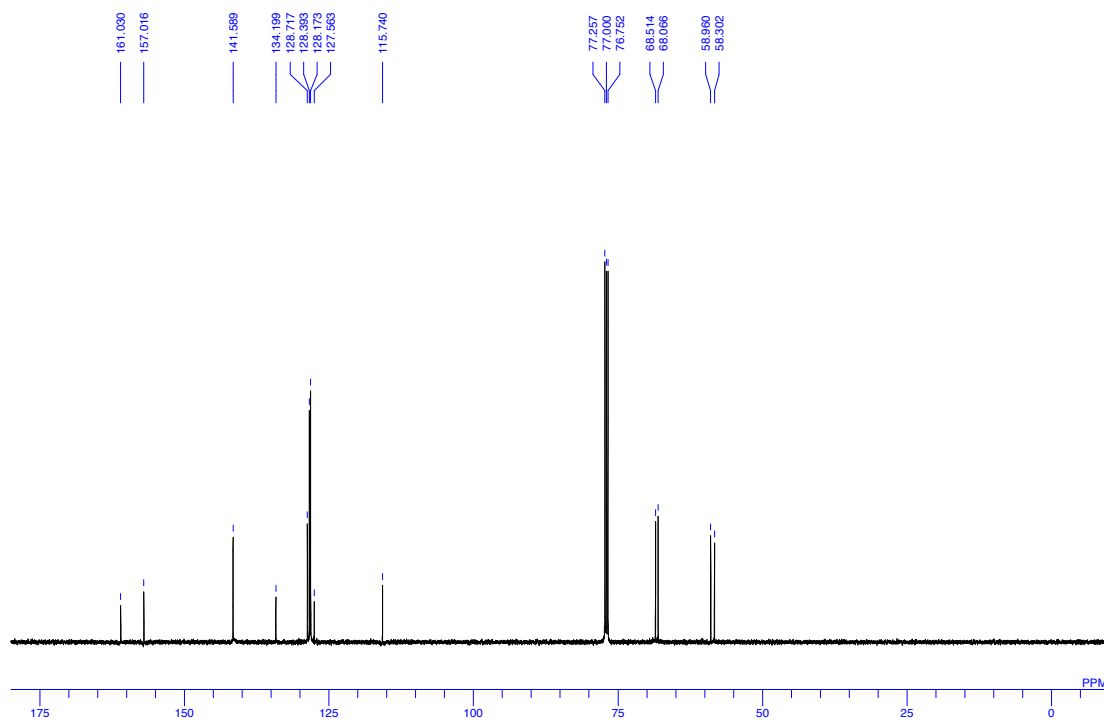
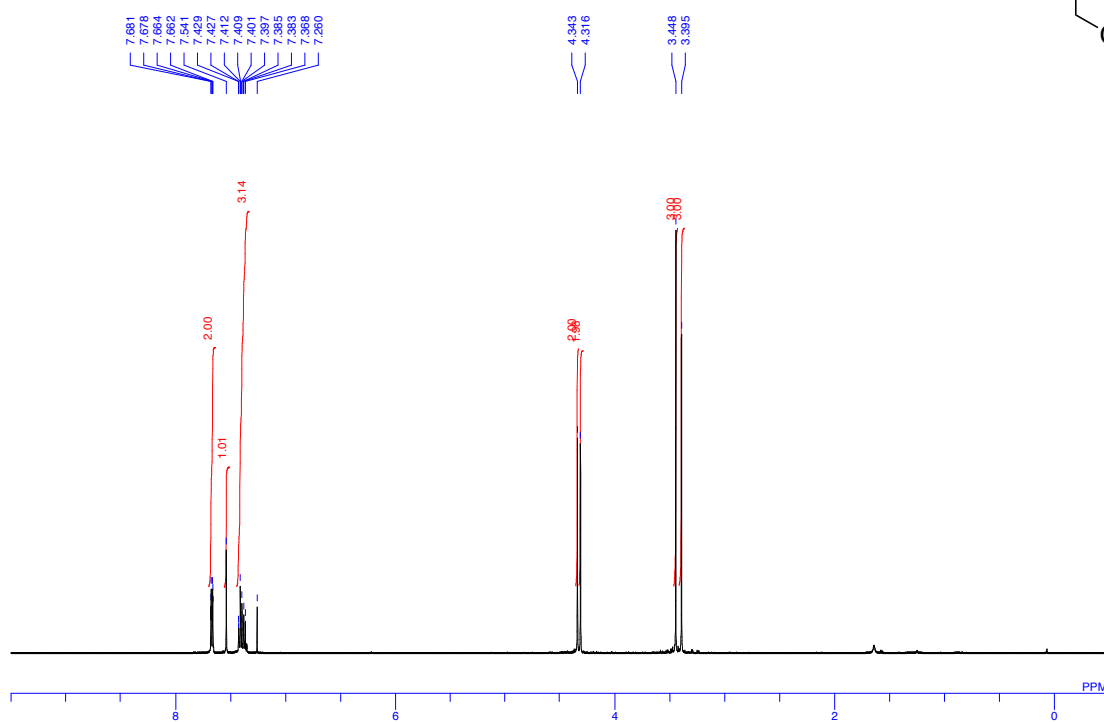
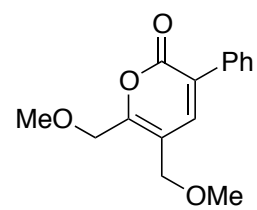
3f



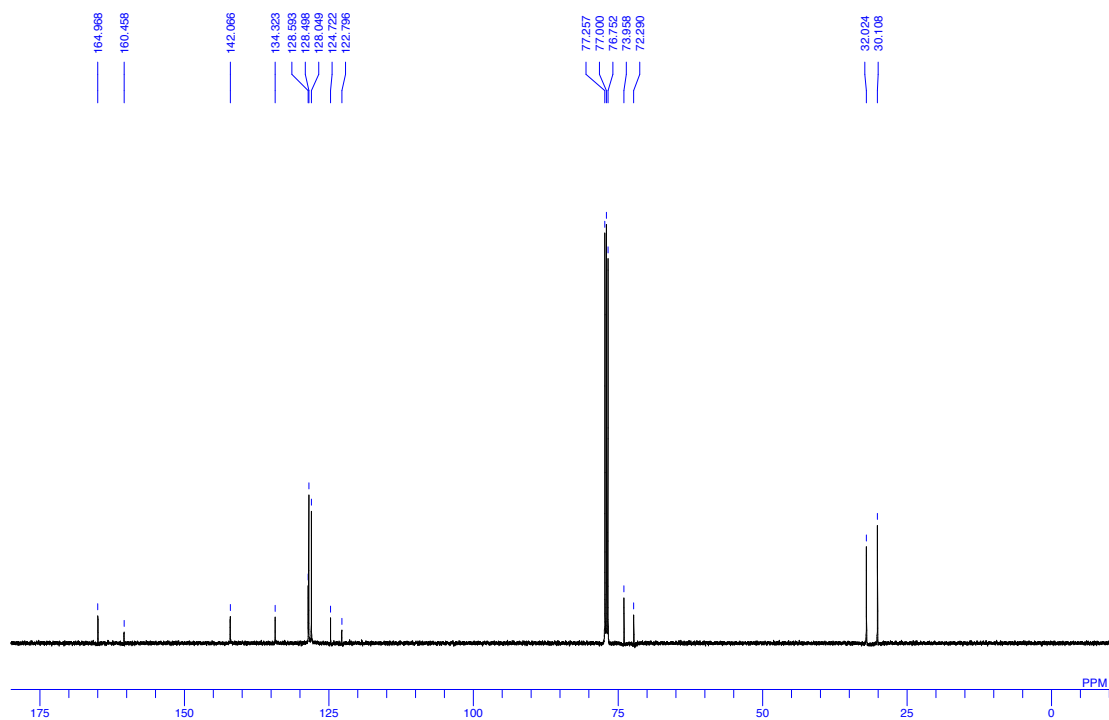
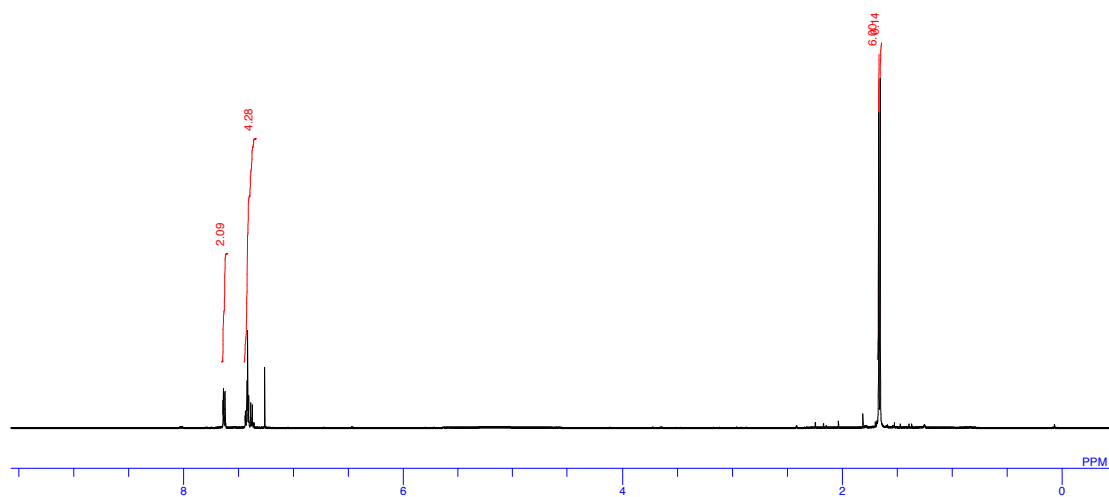
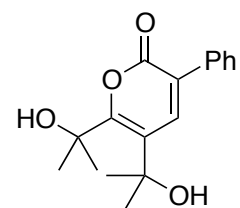
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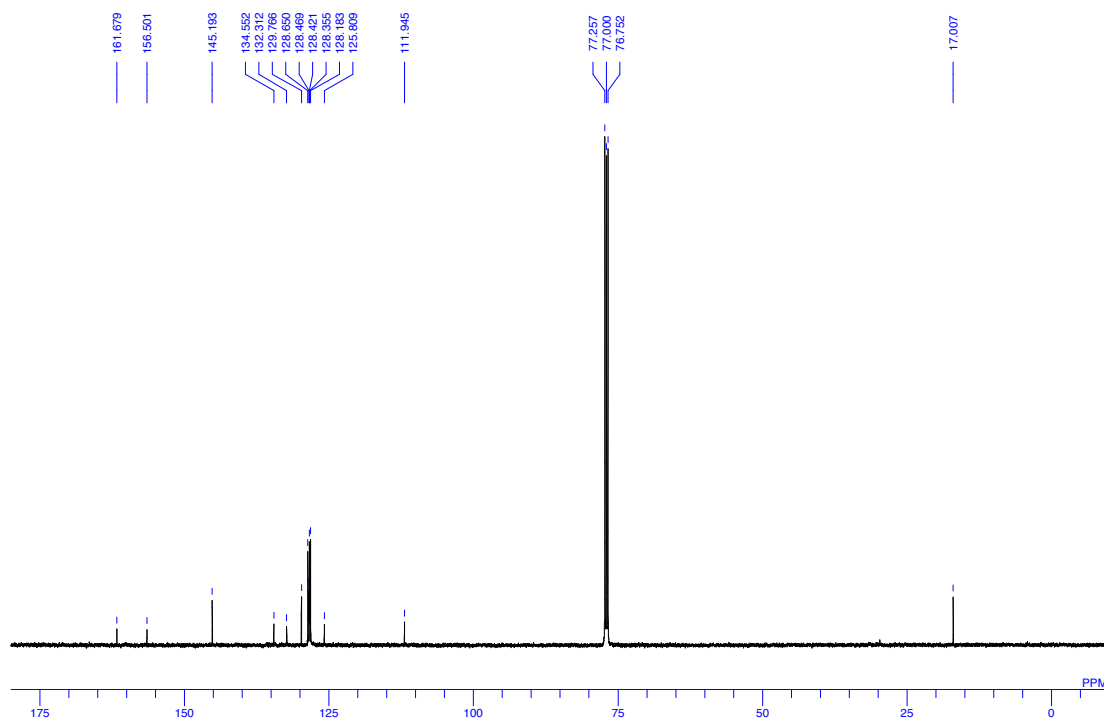
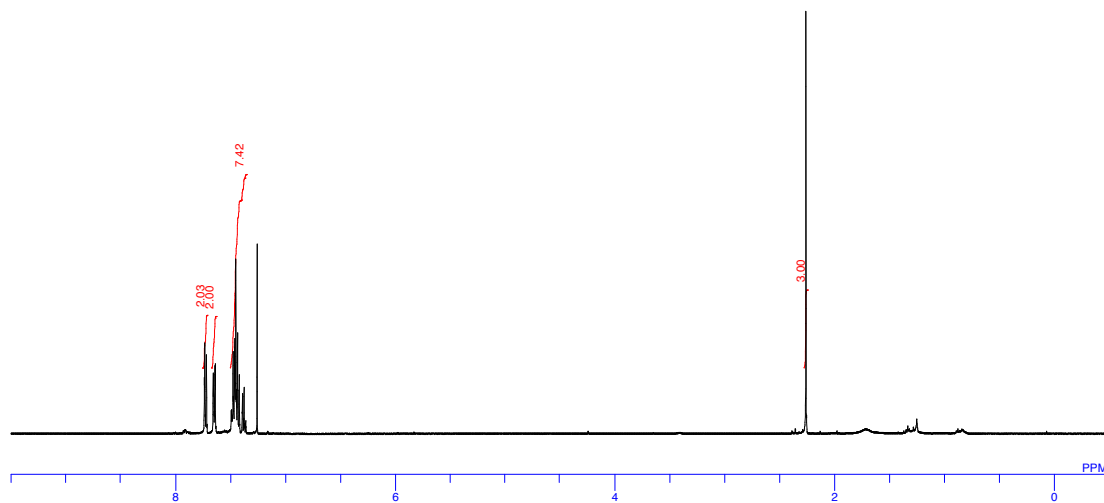
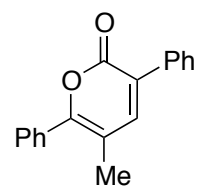
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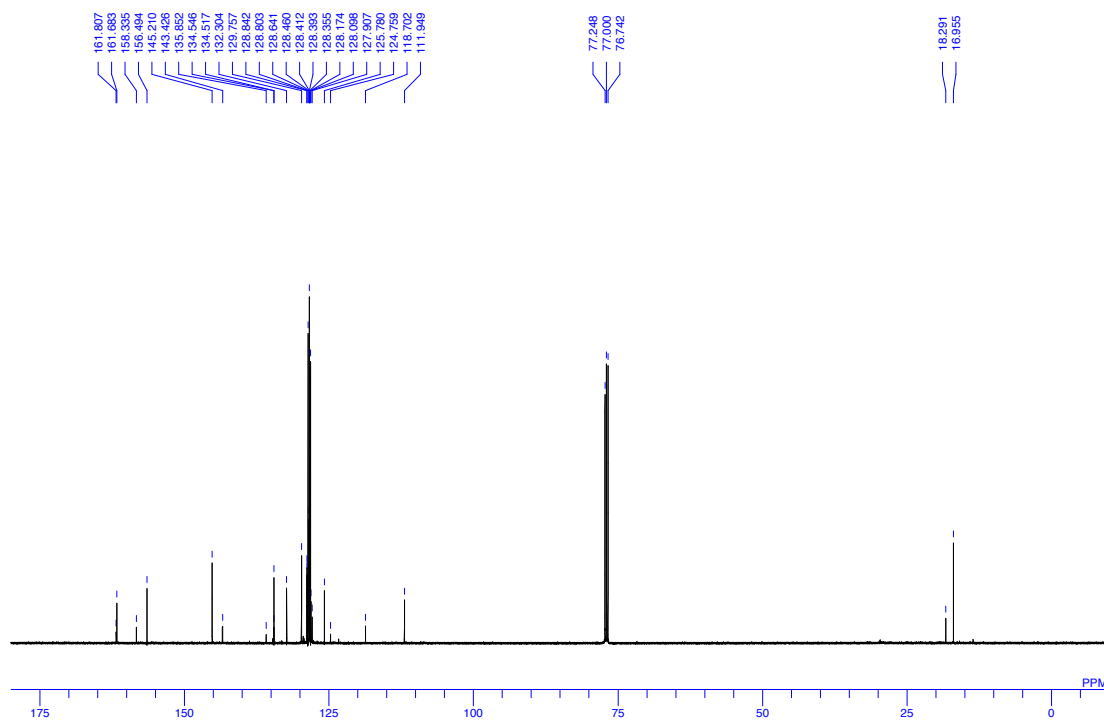
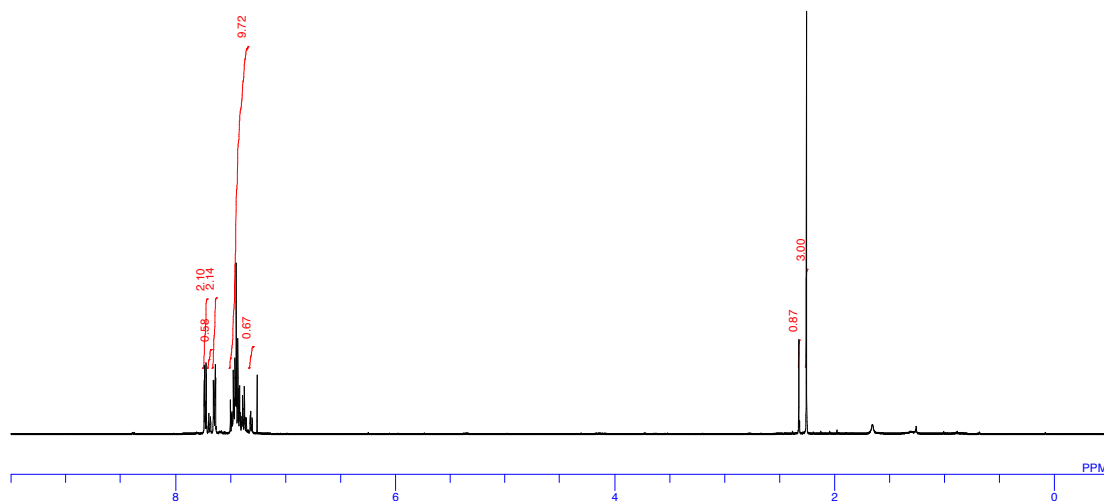
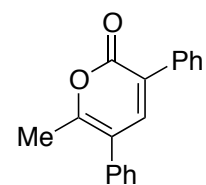
3i



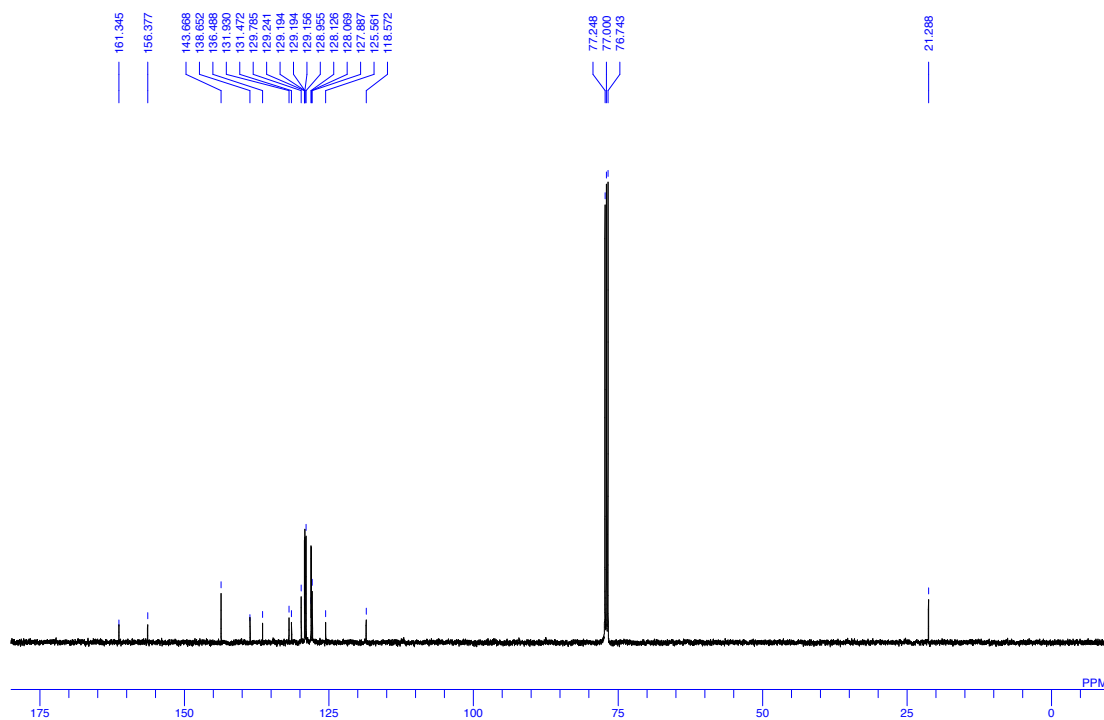
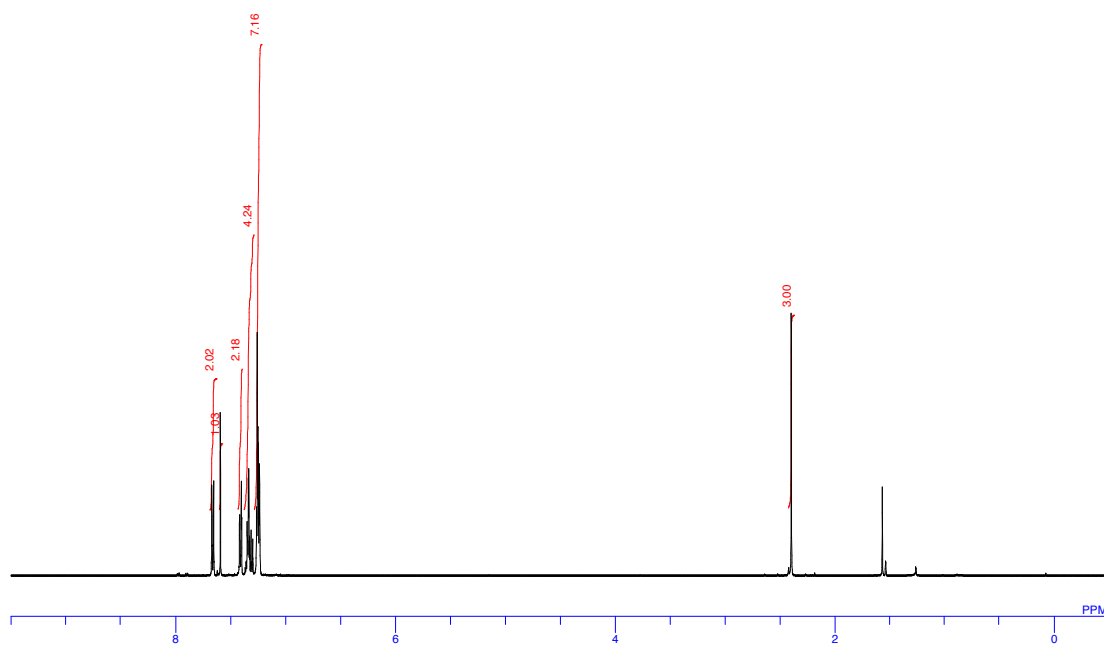
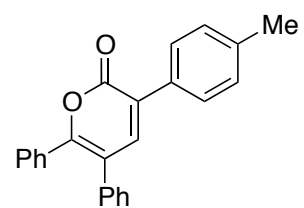
3j



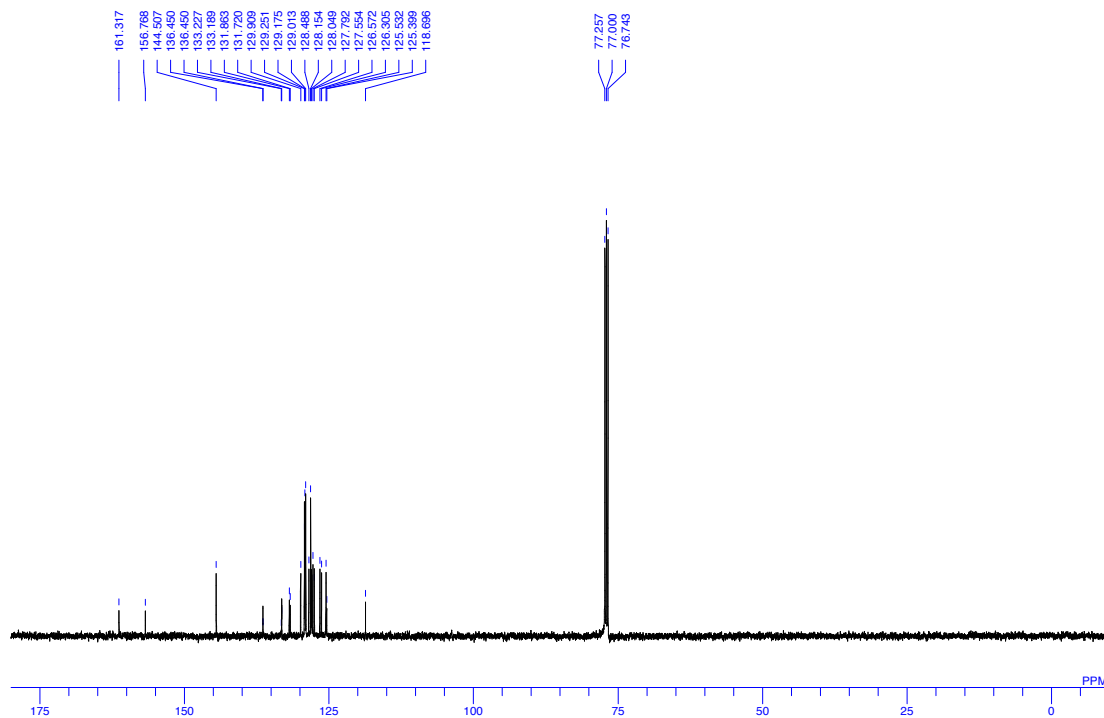
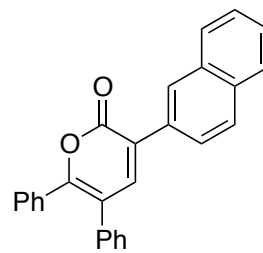
3'j (mixture with **3j**)



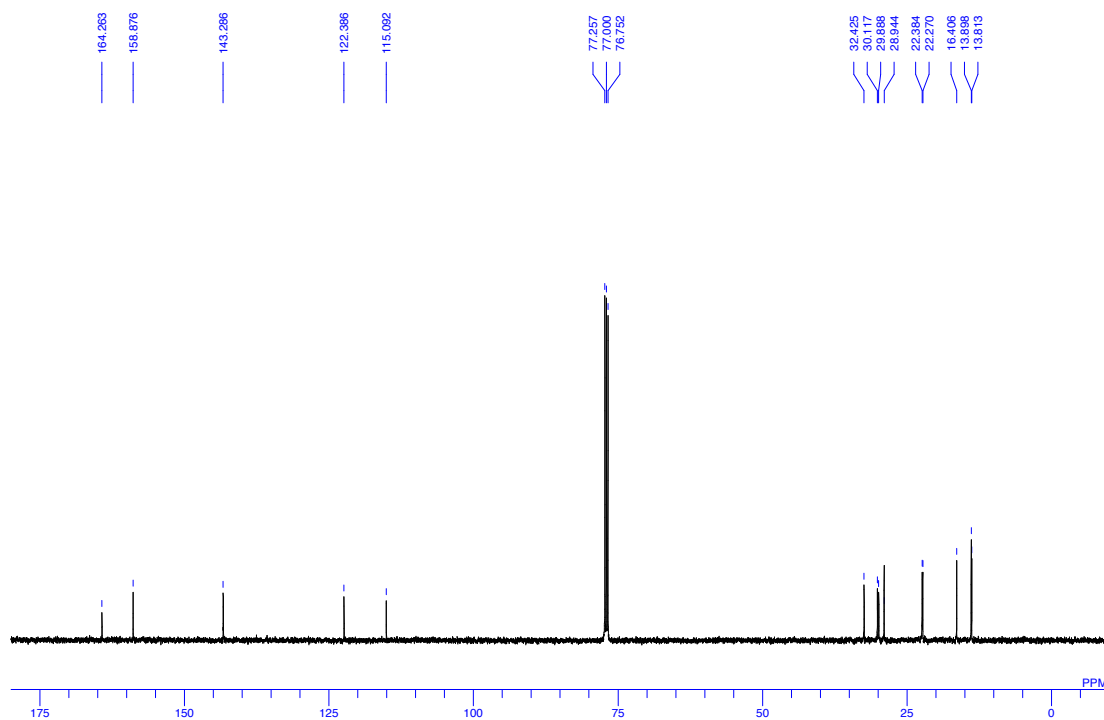
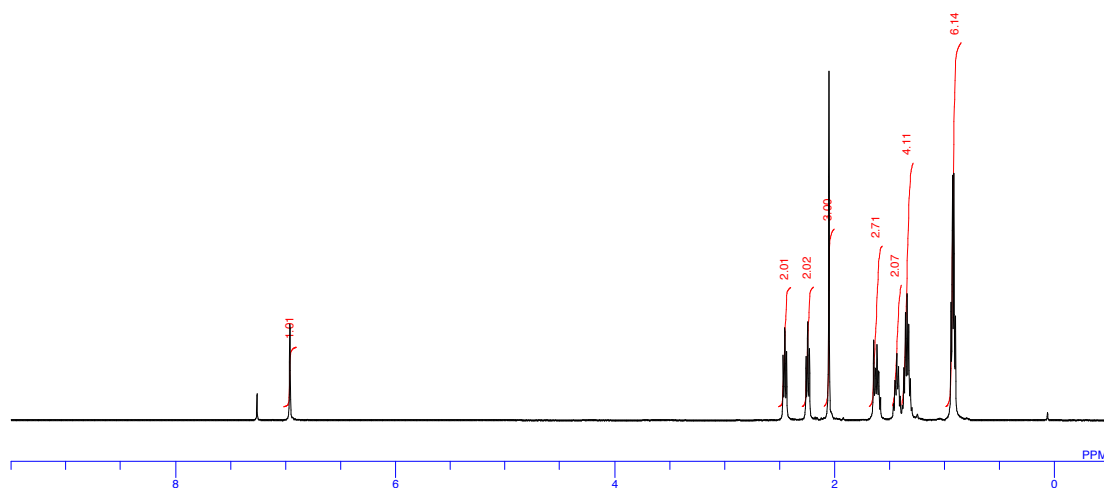
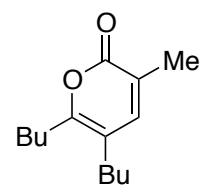
3k



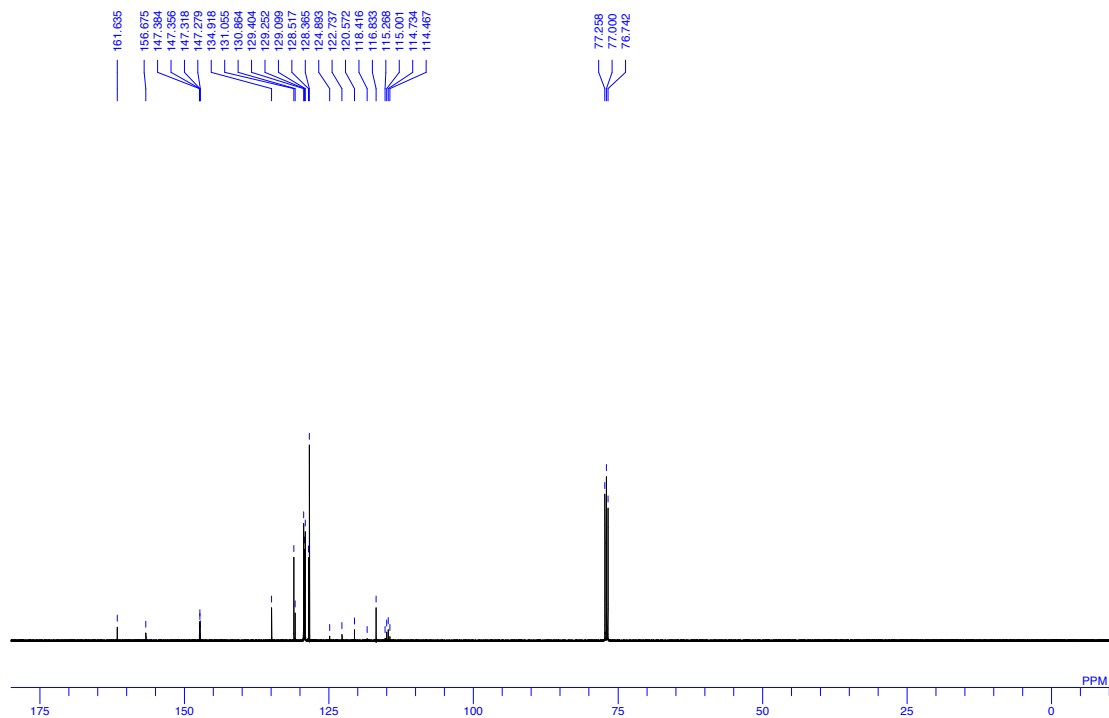
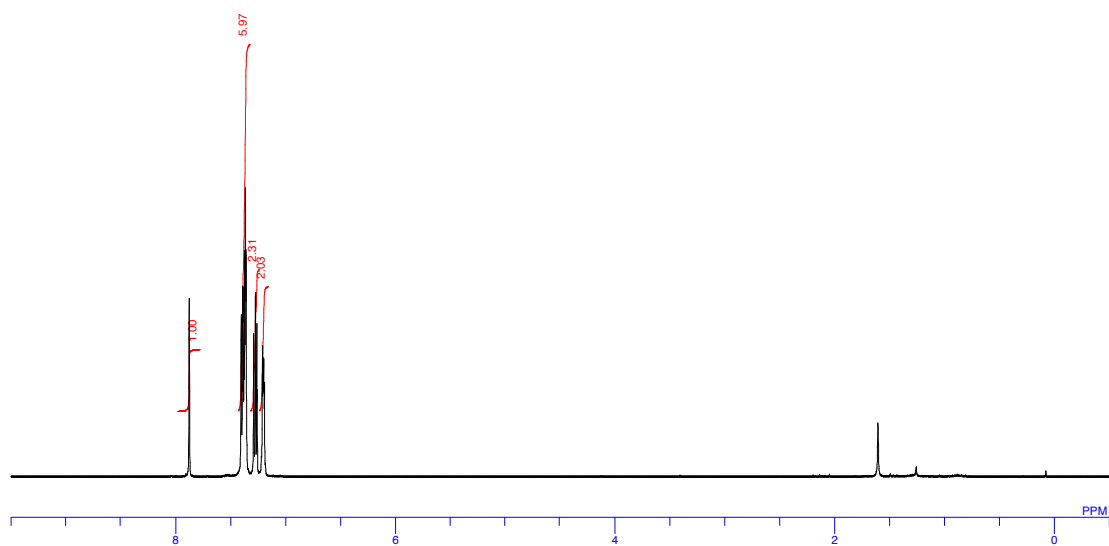
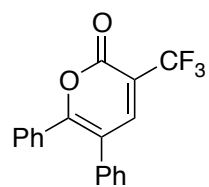
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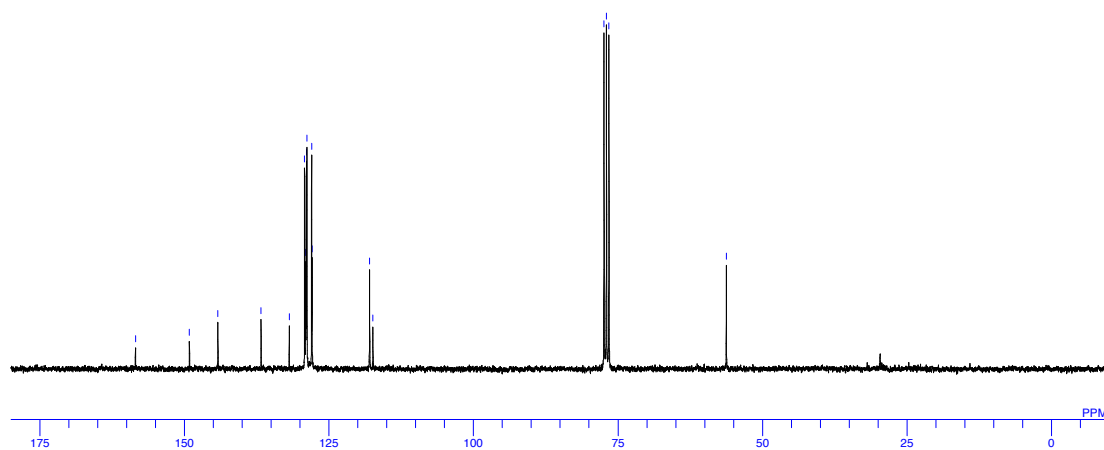
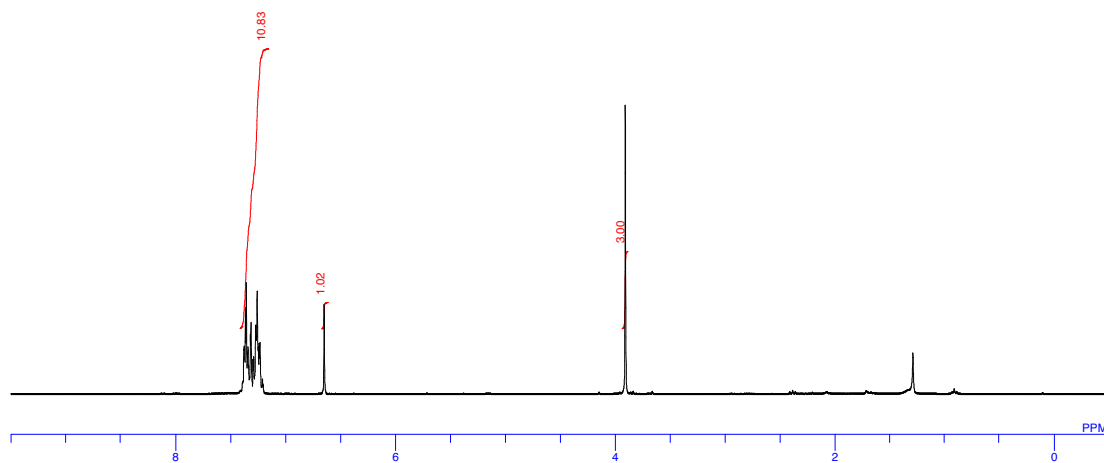
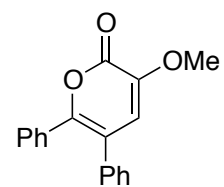
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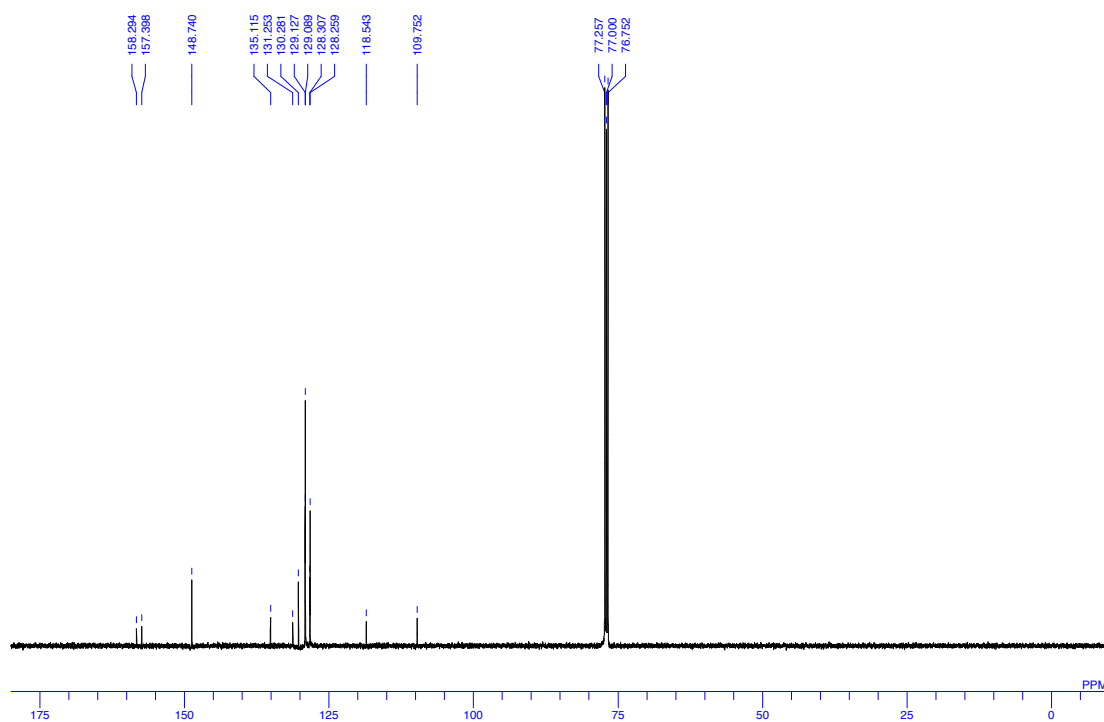
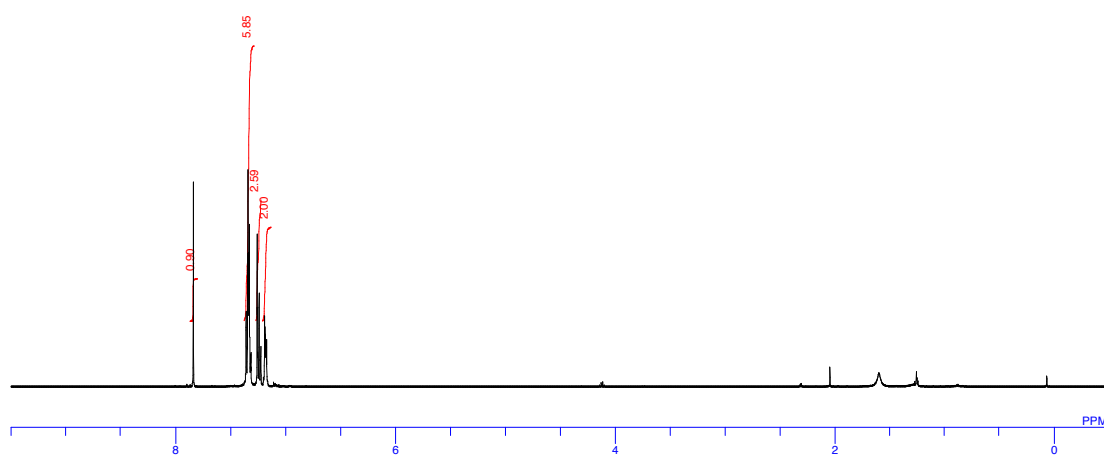
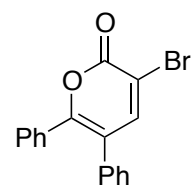
3p



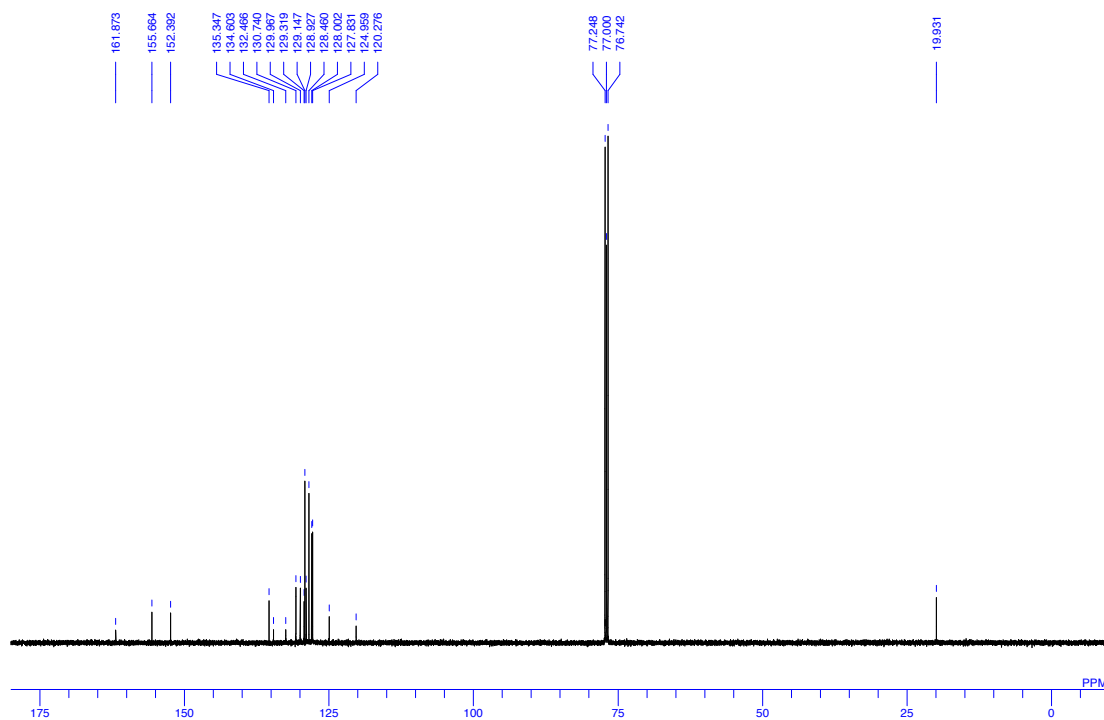
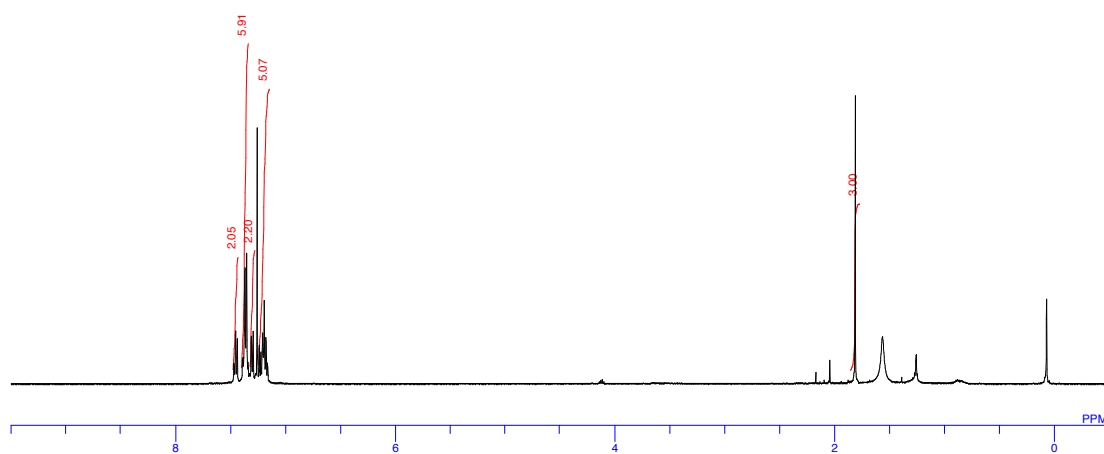
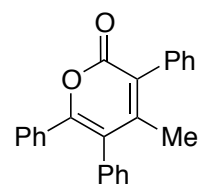
3q



3r



3u



3v

