

Supporting Information for:

**Nickel-Catalyzed Cycloaddition of Salicylic Acid Ketals to Alkynes
via Elimination of Ketones**

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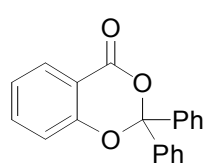
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Instrumentation and Chemicals

All manipulations of oxygen- and moisture-sensitive materials were conducted in a dry box or with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (^1H , 500 MHz; ^{13}C , 125.7 MHz) spectrometer using tetramethylsilane (^1H) as an internal standard. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration, and identification. GC-MS analyses and High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns (toluene as an eluent). Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. Infrared spectra (IR) spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. In-situ IR spectra were obtained with Mettler Toledo ReactIR 45M equipped with AgX Fiber (9.5 mm). Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F₂₅₄ (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO_4 solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–50 μm). Unless otherwise noted, commercially available reagents were used without purification. Toluene was purchased from Wako Pure Chemical Co. stored over slices of sodium. Bis(1,5-cyclooctadiene)nickel and trimethylphosphine were purchased from Strem Chemicals, Inc. Ketals were prepared according to the literatures.¹ *tert*-Butyldimethyl(5-(trimethylsilyl)pent-4-yn-2-yloxy)silane (**2f**) was prepared according to the literature.²

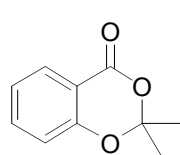
Characterization Data for Ketals.

2,2-Diphenyl-4*H*-benzo[*d*][1,3]dioxin-4-one (1a): [1433-60-9]



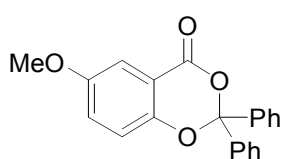
^1H NMR (CDCl_3) δ 7.85 (d, $J = 7.5$ Hz, 1H; Ar-H), 7.59 (m, 4H; Ar-H), 7.54 (dd, $J = 8.5, 7.5$ Hz, 1H; Ar-H), 7.36–7.30 (m, 6H; Ar-H), 7.16 (d, $J = 8.5$ Hz, 1H; Ar-H), 7.04 (dd, $J = 7.5, 7.5$ Hz, 1H; Ar-H). ^{13}C NMR (CDCl_3) δ 161.3 (C=O), 156.6 (C), 139.8 (C), 136.7 (CH), 130.0 (CH), 129.4 (CH), 128.7 (CH), 126.8 (CH), 123.2 (CH), 117.6 (CH), 115.2 (C), 107.1 (C).

2,2-Dimethyl-4*H*-benzo[*d*][1,3]dioxin-4-one (1b): [1433-61-0]



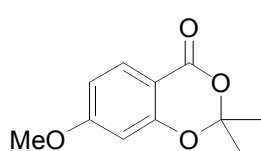
^1H NMR (CDCl_3) δ 7.95 (d, $J = 8.0$ Hz, 1H; Ar-H), 7.54 (dd, $J = 8.0, 7.5$ Hz, 1H; Ar-H), 7.10 (dd, $J = 7.5, 7.5$ Hz, 1H; Ar-H), 7.50 (d, $J = 8.0$ Hz, 1H; Ar-H), 1.72 (s, 6H; CH_3). ^{13}C NMR (CDCl_3) δ 161.3 (C=O), 156.2 (C), 136.5 (CH), 129.8 (CH), 122.8 (CH), 117.3 (CH), 113.8 (C), 106.5 (C), 26.0 (CH_3).

6-Methoxy-2,2-diphenyl-4*H*-benzo[*d*][1,3]dioxin-4-one (1c).



^1H NMR (CDCl_3) δ 7.59 (m, 4H; Ar-H), 7.37–7.30 (m, 6H; Ar-H), 7.28 (d, $J = 7.5$ Hz, 1H; Ar-H), 7.13–7.07 (m, 2H; Ar-H), 3.74 (s, 3H; CH_3O). ^{13}C NMR (CDCl_3) δ 161.5 (C=O), 155.1 (C), 150.8 (C), 139.9 (C), 129.3 (CH), 128.7 (CH), 126.7 (CH), 125.2 (CH), 118.8 (CH), 115.2 (C), 111.1 (CH), 107.1 (C), 55.9 (CH_3O). IR (KBr): 1740, 1614, 1595, 1497, 1452, 1439, 1341, 1298, 1275, 1263, 1240, 1204, 1184, 1175, 1136, 1076, 1061, 1038, 1018, 991, 762, 746, 739, 706 cm^{-1} . MS m/z (%): 333/332 (2/10) [M^+], 151/150 (9/100) [$\text{M}^+ - \text{Ph}_2\text{CO}$], 78/77 (1/8). HRMS Calcd for $\text{C}_{21}\text{H}_{16}\text{O}_4$: M^+ , 332.1049. Found: m/z 316.1048.

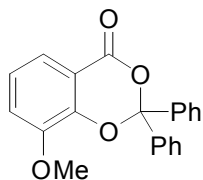
7-Methoxy-2,2-dimethyl-4*H*-benzo[*d*][1,3]dioxin-4-one (1d): [888723-96-4]



^1H NMR (CDCl_3) δ 7.83 (d, $J = 8.5$ Hz, 1H; Ar-H), 6.62 (dd, $J = 8.5, 2.0$ Hz, 1H; Ar-H), 6.39 (d, $J = 2.0$ Hz, 1H; Ar-H), 3.82 (s, 3H; CH_3O), 1.69 (s, 6H; CH_3). ^{13}C NMR (CDCl_3) δ 166.5 (C=O), 161.1

(C), 158.1 (C), 131.3 (CH), 110.4 (CH), 106.4 (C), 106.3 (C), 55.8 (CH₃-O), 25.9 (CH₃).

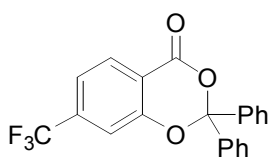
8-Methoxy-2,2-diphenyl-4*H*-benzo[*d*][1,3]dioxin-4-one (1e).



Mp. 130 °C (hexane/ethyl acetate). TLC: *R*_f 0.26 (hexane/ethyl acetate = 5/1). ¹H NMR (CDCl₃) δ 7.62 (d, *J* = 6.5 Hz, 4H; Ar-H), 7.43 (dd, *J* = 8.0, 1.5 Hz, 1H; Ar-H), 7.36–7.28 (m, 6H; Ar-H), 7.09 (dd, *J* = 8.0, 1.5 Hz, 1H; Ar-H), 6.96 (dd, *J* = 8.0, 8.0 Hz, 1H; Ar-H), 3.96 (s, 3H; CH₃O).

¹³C NMR (CDCl₃) δ 161.2 (C=O), 148.7 (C), 146.6 (C), 139.9 (C), 129.4 (CH), 128.7 (CH), 126.6 (CH), 122.8 (CH), 120.9 (CH), 118.0 (CH), 116.1 (C), 107.5 (C), 56.6 (CH₃-O). IR (KBr): 1740, 1614, 1595, 1497, 1452, 1439, 1341, 1298, 1275, 1263, 1240, 1204, 1184, 1175, 1136, 1076, 1061, 1038, 1018, 991, 762, 746, 739, 706 cm⁻¹. MS *m/z* (%): 333/332 (3/10) [M⁺], 182 (53), 152/151/150 (5/10/100) [M⁺-Ph₂CO], 122 (43), 105 (70), 77 (38). HRMS Calcd for C₂₁H₁₆O₄: M⁺, 332.1049. Found: *m/z* 332.1053.

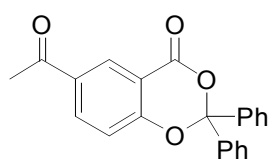
2,2-Diphenyl-7-(trifluoromethyl)-4*H*-benzo[*d*][1,3]dioxin-4-one (1f).



¹H NMR (CDCl₃) δ 7.99 (d, *J* = 8.5 Hz, 1H; Ar-H), 7.57 (m, 4H; Ar-H), 7.44 (s, 1H; Ar-H), 7.40–7.34 (m, 6H; Ar-H), 7.30 (d, *J* = 8.5 Hz, 4H; Ar-H). ¹³C NMR (CDCl₃) δ 160.1 (C=O), 156.6 (C), 139.1 (C), 138.0 (q, *J* = 33.1 Hz; C-CF₃), 131.0 (CH), 129.7 (CH),

128.9 (CH), 126.7 (CH), 123.0 (q, *J* = 274 Hz; CF₃), 119.8 (q, *J* = 3.4 Hz; C-CCF₃), 117.8 (C), 115.1 (q, *J* = 4.4 Hz; C-CCF₃), 107.9 (C). ¹⁹F NMR (CDCl₃) δ -64.1. IR (KBr): 1740, 1614, 1595, 1497, 1452, 1439, 1341, 1298, 1263, 1240, 1175, 1136, 1076, 1038, 1018, 991, 762, 746, 739, 706 cm⁻¹. MS *m/z* (%): 370/371 (34/8) [M⁺], 188/189 (10/100) [M⁺-Ph₂CO], 105 (54), 77 (24). HRMS Calcd for C₂₁H₁₃F₃O₃: M⁺, 370.0817. Found: *m/z* 370.0818.

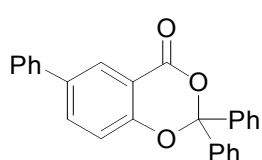
6-Acetyl-2,2-diphenyl-4*H*-benzo[*d*][1,3]dioxin-4-one (1g).



¹H NMR (CDCl₃) δ 8.42 (d, *J* = 2.0 Hz, 1H; Ar-H), 8.20 (dd, *J* = 8.5, 2.0 Hz, 1H; Ar-H), 7.58 (m, 4H; Ar-H), 7.39–7.32 (m, 6H; Ar-H), 7.60 (d, *J* = 8.5 Hz, 1H; Ar-H), 2.55 (s, 3H; CH₃). ¹³C NMR (CDCl₃) δ 195.8 (C=O), 160.6 (C=O), 160.0 (C), 139.2 (C), 136.3

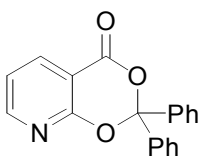
(CH), 132.4 (C), 131.1 (CH), 129.7 (CH), 128.9 (CH), 126.7 (CH), 118.3 (CH), 114.6 (C), 107.7 (C), 26.6 (CH₃). IR (KBr): 1755, 1597, 1586, 1431, 1314, 1215, 1125, 781, 762, 706 cm⁻¹. MS *m/z* (%): 345/344 (6/28) [M⁺], 163/162 (10/100) [M⁺-Ph₂CO], 148/147 (4/50), 105 (16), 78/77 (1/13). HRMS Calcd for C₂₂H₁₆O₄: M⁺, 344.1049. Found: *m/z* 344.1050.

2,2,6-triphenyl-4*H*-benzo[*d*][1,3]dioxin-4-one (1h).



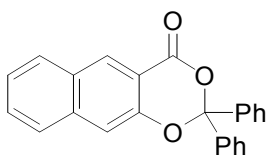
¹H NMR (CDCl₃) δ 8.09 (d, *J* = 2.0 Hz, 1H; Ar-H), 7.77 (dd, *J* = 8.5, 2.0 Hz, 1H; Ar-H), 7.62 (d, *J* = 6.5 Hz, 4H; Ar-H), 7.50 (d, *J* = 7.5 Hz, 2H; Ar-H), 7.41 (dd, *J* = 7.5, 8.5 Hz, 2H; Ar-H), 7.39–7.30 (m, 7H; Ar-H), 7.24 (d, *J* = 8.5 Hz, 1H; Ar-H). ¹³C NMR (CDCl₃) δ 161.3 (C=O), 155.9 (C), 140.0 (C), 139.0 (C), 136.4 (C), 135.3 (CH), 129.4 (CH), 129.0 (CH), 128.7 (CH), 128.1 (CH), 127.8 (CH), 126.8 (CH), 126.7 (CH), 118.0 (CH), 115.3 (C), 107.2 (C). IR (KBr): 1758, 1600, 1584, 1455, 1431, 1300, 1211, 1125, 781 cm⁻¹. MS *m/z* (%): 379/378 (2/8) [M⁺], 197/196 (13/100) [M⁺-Ph₂CO], 140/139 (7/13), 77 (4). HRMS Calcd for C₂₆H₁₈O₃: M⁺, 378.1256. Found: *m/z* 378.1259.

2,2-Diphenyl-4*H*-[1,3]dioxino[4,5-*b*]pyridin-4-one (1i).



Mp. 137 °C (hexane/ethyl acetate). TLC: R_f 0.18 (hexane/ethyl acetate = 5/1). ¹H NMR (CDCl₃) δ 8.51 (d, *J* = 5.0 Hz, 1H; Ar-H), 8.20 (d, *J* = 8.0 Hz, 1H; Ar-H), 7.65 (m, 4H; Ar-H), 7.38–7.30 (m, 6H; Ar-H), 7.10 (dd, *J* = 5.0, 8.0 Hz, 1H; Ar-H). ¹³C NMR (CDCl₃) δ 162.1 (C=O), 160.9 (C), 155.5 (CH), 139.7 (C), 139.4 (CH), 129.6 (CH), 128.9 (CH), 126.6 (CH), 120.2 (CH), 110.5 (C), 107.5 (C). IR (KBr): 1755, 1597, 1586, 1468, 1431, 1314, 1215, 1125, 781, 762, 706 cm⁻¹. MS *m/z* (%): 304/303 (1/4) [M⁺], 183/182 (12/71), 121 (2) [M⁺-Ph₂CO], 106/105 (7/100), 77 (47). HRMS Calcd for C₁₉H₁₃NO₃: M⁺, 303.0895. Found: *m/z* 303.0890.

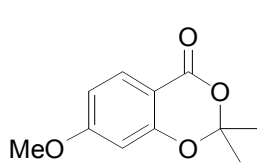
2,2-Diphenyl-4*H*-naphtho[2,3-*d*][1,3]dioxin-4-one (1j).



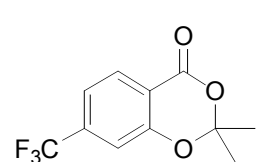
White powder. Mp. 210 °C (hexane/ethyl acetate). TLC: R_f 0.40 (hexane/ethyl acetate = 5/1). ¹H NMR (CDCl₃) δ 8.50 (s, 1H; Ar-H), 7.83 (d, *J* = 7.5 Hz, 1H; Ar-H), 7.77 (d, *J* = 8.5 Hz, 1H; Ar-H),

7.67–7.63 (m, 4H; Ar–H), 7.55 (dd, $J = 8.5, 7.5$ Hz, 1H; Ar–H), 7.53 (s, 1H; Ar–H), 7.40 (dd, $J = 7.0, 7.0$ Hz, 1H; Ar–H), 7.37–7.28 (m, 6H; Ar–H). ^{13}C NMR (CDCl_3) δ 161.8 (C=O), 151.8 (C), 140.0 (C), 137.9 (C), 132.7 (CH), 129.9 (CH), 129.8 (CH), 129.4 (CH), 128.8 (CH), 127.2 (CH), 126.9 (CH), 126.9 (C), 125.7 (CH), 115.3 (C), 113.5 (CH), 107.2 (C). IR (KBr): 1748, 1636, 1449, 1346, 1275, 1263, 1240, 1211, 974, 961, 766, 700, 474 cm^{-1} . MS m/z (%): 353/352 (2/7) [M^+], 183/182 (9/64), 171/170 (8/65) [$\text{M}^+ - \text{Ph}_2\text{CO}$], 142 (27), 105 (100), 77 (60). HRMS Calcd for $\text{C}_{24}\text{H}_{16}\text{O}_3$: M^+ , 352.1099. Found: m/z 352.1093.

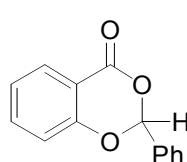
7-Methoxy-2,2-dimethyl-4*H*-benzo[*d*][1,3]dioxin-4-one (1b'): [888723-96-4]

 ^1H NMR (CDCl_3) δ 7.83 (d, $J = 8.5$ Hz, 1H; Ar–H), 6.62 (dd, $J = 8.5, 2.0$ Hz, 1H; Ar–H), 6.39 (d, $J = 2.0$ Hz, 1H; Ar–H), 3.82 (s, 3H; CH_3O), 1.69 (s, 6H; CH_3). ^{13}C NMR (CDCl_3) δ 166.5 (C=O), 161.1 (C), 158.1 (C), 131.3 (CH), 110.4 (CH), 106.4 (C), 106.3 (C), 55.8 (CH_3O), 25.9 (CH_3).

2,2-Dimethyl-7-(trifluoromethyl)-4*H*-benzo[*d*][1,3]dioxin-4-one (1b'').

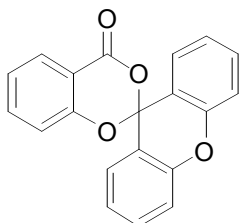
 TLC: R_f 0.50 (hexane/ethyl acetate = 5/1). ^1H NMR (CDCl_3) δ 8.09 (d, $J = 8.0$ Hz, 1H; Ar–H), 7.37 (d, $J = 8.0$ Hz, 1H; Ar–H), 7.25 (s, 1H; Ar–H), 1.76 (s, 6H; CH_3). ^{13}C NMR (CDCl_3) δ 160.0 (C=O), 156.3 (C), 138.0 (q, $J = 33.3$ Hz; C– CF_3), 130.8 (CH), 123.1 (q, $J = 273$ Hz; CF_3), 119.3 (q, $J = 3.8$ Hz; C– CCF_3), 116.5 (C), 115.0 (q, $J = 4.3$ Hz; C– CCF_3), 107.3 (C), 26.0 (CH_3). ^{19}F NMR (CDCl_3) δ -64.1. IR (neat): 1759, 1748, 1445, 1337, 1296, 1229, 1202, 1177, 1136, 1071, 1044, 947 cm^{-1} . MS m/z (%): 248/247/246 (10/70/100) [M^+], 228/227 (17/75) [$\text{M}^+ - \text{F}$], 190/189/188 (61/98/100) [$\text{M}^+ - \text{Me}_2\text{CO}$]. HRMS Calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{O}_3$: M^+ , 246.0504. Found: m/z 246.0511.

2-Phenyl-4*H*-benzo[*d*][1,3]dioxin-4-one: [5768-29-6]

 ^1H NMR (CDCl_3) δ 8.06 (d, $J = 7.5$ Hz, 1H; Ar–H), 7.67 (m, 2H; Ar–H), 7.62 (dd, $J = 7.5, 7.5$ Hz, 1H; Ar–H), 7.51–7.47 (m, 3H; Ar–H), 7.23 (dd, $J = 7.5, 7.5$ Hz, 1H; Ar–H), 7.13 (d, $J = 7.5$ Hz, 1H; Ar–H), 6.56 (s, 1H;

CH). ^{13}C NMR (CDCl_3) δ 162.1 (C=O), 158.4 (C), 136.6 (CH), 134.2 (CH), 130.6 (CH), 130.5 (C), 128.9 (CH), 126.8 (CH), 123.8 (CH), 117.1 (CH), 114.8 (C), 100.7 (CH).

4*H*-Spiro[benzo[*d*][1,3]dioxine-2,9'-xanthen]-4-one: [234075-37-7]

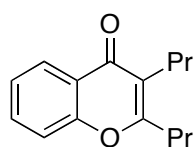


^1H NMR (CDCl_3) δ 8.10 (d, $J = 7.5$ Hz, 1H; Ar-H), 7.68 (d, 2H; Ar-H), 7.55 (dd, $J = 7.5, 7.5$ Hz, 1H; Ar-H), 7.48 (dd, $J = 7.5, 7.5$ Hz, 2H; Ar-H), 7.34 (d, $J = 8.5$ Hz, 2H; Ar-H), 7.21–7.15 (m, 3H; Ar-H), 6.88 (d, $J = 8.5$ Hz, 1H; Ar-H). ^{13}C NMR (CDCl_3) δ 160.3 (C=O), 155.8 (C), 151.0 (C), 137.2 (CH), 131.4 (CH), 129.7 (CH), 126.0 (CH), 123.7 (CH), 123.2 (CH), 120.3 (C), 117.4 (CH), 117.3 (CH), 113.5 (C), 99.0 (C).

Experimental Procedure and Characterization Data for Products.

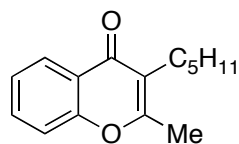
General procedure. The reaction was performed in a 15 mL sealed tube equipped with a Teflon-coated magnetic stirrer. A salicylic acid ketals (0.5 mmol) and an alkyne (1.0 mmol) were added to a solution of bis(1,5-dicyclooctadiene)nickel (14 mg, 0.05 mmol), tricyclohexylphosphine (14 mg, 0.05 mmol), and pyridine (0.5 mmol) in toluene (1.5 mL) in a dry box. The flask was taken outside the dry box and heated at 120 °C for the indicated time under argon atmosphere. The resulting reaction mixture was cooled to ambient temperature and filtered through a silica gel pad, concentrated in vacuo. The residue was purified by flash silica gel column chromatography (20 g, 2x15 cm, hexane/ethyl acetate = 5:1) to give the corresponding chromone.

2,3-Dipropyl-4H-chromen-4-one (3aa).



Yield: >99%, yellow oil. TLC: R_f 0.43 (hexane/ethyl acetate=5/1). ^1H NMR (CDCl_3) δ 8.19 (d, $J = 7.5$, 1H; Ar-H), 7.57 (dd, $J = 7.5$, $J = 7.5$, 1H; Ar-H), 7.35 (d, $J = 8.5$, 1H; Ar-H), 7.31 (dd, $J = 8.5$, $J = 7.5$ Hz, 1H; Ar-H), 2.66 (t, $J = 7.0$ Hz, 2H; CH_2), 2.50 (t, $J = 8.0$ Hz, 2H; CH_2), 1.78 (tq, $J = 7.5$ Hz, $J = 7.0$ Hz, 2H; CH_2), 1.53 (tq, $J = 7.5$ Hz, $J = 7.0$ Hz, 2H; CH_2), 1.02 (t, $J = 7.5$ Hz, 3H; CH_3), 0.97 (t, $J = 7.5$ Hz, 3H; CH_3). ^{13}C NMR (CDCl_3) δ 178.0 (C=O), 165.5 (C-O), 156.1 (C-O), 133.0 (CH), 126.0 (CH), 124.5 (CH), 123.1 (CH), 121.4 (C), 117.1 (C), 33.8 (CH_2), 26.8 (CH_2), 22.7 (CH_2), 21.1 (CH_2), 14.3 (CH_3), 14.0 (CH_3). IR (neat): 2960, 1639, 1575, 1465, 1389, 1163, 759 cm^{-1} . MS m/z (%): 232/230/231 (6/36/6) [M^+], 216/215 (16/100) [$\text{M}^+ - \text{Me}$], 202/201 (6/10) [$\text{M}^+ - \text{Et}$], 188/187 (5/32) [$\text{M}^+ - \text{Pr}$], 121 (15). HRMS Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: M^+ , 230.1307. Found: m/z 230.1306.

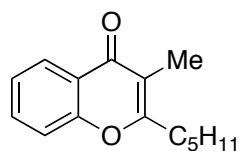
2-Methyl-3-pentyl-4H-chromen-4-one (3ab).



Yield: 42%, yellow oil. TLC: R_f 0.33 (hexane/ethyl acetate=5/1). ^1H NMR (CDCl_3) δ 8.11 (d, $J = 8.0$ Hz, 1H; Ar-H), 7.61 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 1H; Ar-H), 7.39 (d, $J = 8.5$ Hz, 1H; Ar-H), 7.35 (dd, $J = 8.5$ Hz, $J = 8.0$ Hz, 1H; Ar-H), 2.70 (t, $J = 7.5$ Hz, 2H; CH_2), 2.08 (s, 3H; CH_3), 1.74 (tt, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H; CH_2), 1.41-1.36 (m, 4H; CH_2), 0.92 (t, $J = 7.0$ Hz, 3H; CH_3). ^{13}C NMR

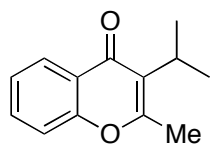
(CDCl₃) δ 178.4 (C=O), 165.6 (C-O), 156.1 (C-O), 133.1 (CH), 126.0 (CH), 124.6 (CH), 122.7 (C), 117.8 (CH), 116.7 (C), 32.3 (CH₂), 31.6 (CH₂), 27.0 (CH₂), 22.6 (CH₂), 14.1 (CH₃), 10.0 (CH₃). IR (neat): 2931, 1637, 1577, 1467, 1394, 1373, 1165, 759 cm⁻¹. MS m/z (%): 231/230/229 (5/27/2) [M⁺], 202/201 (7/47) [M⁺-Et], 188/187/185 (21/100/4) [M⁺-Pr], 121 (16). HRMS Calcd for C₁₅H₁₈O₂: M⁺, 230.1307. Found: m/z 230.1306.

3-Methyl-2-pentyl-4*H*-chromen-4-one (3ab').



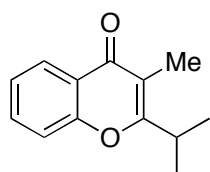
Yield: 42%, pale yellow oil. TLC: R_f 0.40 (hexane/ethyl acetate=5/1). ¹H NMR (CDCl₃) δ 8.19 (d, *J* = 8.0 Hz, 1H; Ar-H), 7.60 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H; Ar-H), 7.37 (d, *J* = 8.0 Hz, 1H; Ar-H), 7.34 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H; Ar-H), 2.53 (t, *J* = 7.5 Hz, 2H; CH₂), 2.42 (s, 3H; CH₃), 1.50 (tt, *J* = 7.5 Hz, *J* = 7.0 Hz, 2H; CH₂), 1.31-1.39 (m, 4H; CH₂), 0.90 (t, *J* = 7.0 Hz, 3H; CH₃). ¹³C NMR (CDCl₃) δ 177.8 (C=O), 162.3 (C-O), 156.1 (C-O), 133.1 (CH), 126.1 (CH), 124.6 (CH), 123.2 (C), 121.9 (CH), 117.7 (CH), 32.0 (CH₂), 28.7 (CH₂), 25.0 (CH₂), 22.8 (CH₂), 18.5 (CH₃), 14.3 (CH₃). IR (neat): 2931, 1639, 1465, 1400, 1168, 759 cm⁻¹. MS m/z (%): 230 (8) [M⁺], 216/215 (13/71) [M⁺-Me], 202/201 (11/52) [M⁺-Et], 188/187/185 (11/56/5) [M⁺-Pr], 125/124/123 (14/100/30) [M⁺-Bu], 121 (24). HRMS Calcd for C₁₅H₁₈O₂: M⁺, 230.1307. Found: m/z 230.1311.

3-Isopropyl-2-methyl-4*H*-chromen-4-one (3ac).



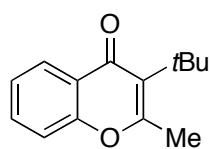
Yield: 49%, yellow oil. TLC: R_f 0.28 (hexane/ethyl acetate=5/1). ¹H NMR (CDCl₃) δ 8.19 (d, *J* = 8.0, 1H; Ar-H), 7.61 (dd, *J* = 8.5, *J* = 7.0, 1H; Ar-H), 7.41 (d, *J* = 8.5, 1H; Ar-H), 7.34 (dd, *J* = 8.5, *J* = 7.0 Hz, 1H; Ar-H), 3.25 (sept, *J* = 7.0 Hz, 1H; CH₂), 1.31 (d, *J* = 7.0 Hz, 6H; CH₂). ¹³C NMR (CDCl₃) δ 178.6 (C=O), 168.7 (C-O), 156.0 (C-O), 133.0 (CH), 126.0 (CH), 124.6 (CH), 122.7 (C), 117.8 (CH), 115.2 (C), 30.7 (CH), 19.8 (CH₃), 9.5 (CH₃). IR (neat): 2970, 1639, 1577, 1467, 1396, 1381, 1074, 759 cm⁻¹. MS m/z (%): 285/284/283 (7/30/10) [M⁺], 270/269 (12/59) [M⁺-Me], 202 (34), 187 (100). HRMS Calcd for C₁₃H₁₄O₂: M⁺, 202.0994. Found: m/z 202.0995.

2-Isopropyl-3-methyl-4*H*-chromen-4-one (3ac').



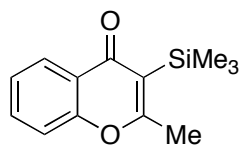
Yield: 49%, white powder. Mp. 113 °C (dichlorometane) TLC: R_f 0.45 (hexane/ethyl acetate=5/1). ^1H NMR (CDCl_3) δ 8.16 (d, $J = 7.5$, 1H; Ar-H), 7.57 (dd, $J = 8.5$, $J = 7.5$, 1H; Ar-H), 7.35-7.30 (m, 2H; Ar-H), 3.11 (sept, $J = 7.0$ Hz, 1H; CH), 2.44 (s, 3H; CH_3), 1.36 (d, $J = 7.0$ Hz, 6H; CH_3). ^{13}C NMR (CDCl_3) δ 177.6 (C=O), 161.5 (C-O), 155.5 (C-O), 132.7 (CH), 125.7 (CH), 125.5 (C), 124.4 (CH), 123.6 (C), 117.3 (CH), 27.0 (CH), 20.1 (CH_3), 18.7 (CH_3). IR (KBr): 2359, 1622, 1558, 1456, 1393, 1072, 765 cm^{-1} . MS m/z (%): 203/202/201 (8/46/24) [M^+], 188/187/185 (14/100/5) [$\text{M}^+ - \text{Me}$], 121 (20). HRMS Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2$: M^+ , 202.0994. Found: m/z 202.0992.

3-*tert*-Butyl-2-methyl-4*H*-chromen-4-one (3ad).



Yield: 64%, yellow oil. TLC: R_f 0.28 (hexane/ethyl acetate=5/1). ^1H NMR (CDCl_3) δ 8.19 (d, $J = 8.0$, 1H; Ar-H), 7.61 (dd, $J = 8.0$, $J = 7.5$, 1H; Ar-H), 7.22 (d, $J = 8.0$, 1H; Ar-H), 7.35 (dd, $J = 8.0$, $J = 7.5$ Hz, 1H; Ar-H), 2.24 (s, 3H; CH_3), 1.48 (s, 9H; CH_3). ^{13}C NMR (CDCl_3) δ 179.5 (C=O), 170.3 (C-O), 155.7 (C-O), 133.1 (CH), 125.9 (CH), 124.7 (CH), 122.0 (C), 117.8 (CH), 116.8 (C), 38.4 (C), 29.0 (CH_3), 11.1 (CH_3). IR (neat): 2965, 1633, 1568, 1469, 1361, 1134, 758 cm^{-1} . MS m/z (%): 217/216/215 (3/19/8) [M^+], 202/201 (17/100) [$\text{M}^+ - \text{Me}$], 121 (8). HRMS Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$: M^+ , 216.1150. Found: m/z 216.1152.

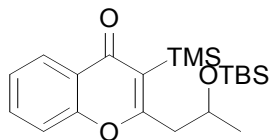
2-Methyl-3-(trimethylsilyl)-4*H*-chromen-4-one (3ae).



Yield: 91%, white powder. Mp. 136 °C (hexane). TLC: R_f 0.48 (hexane/ethyl acetate=5/1). ^1H NMR (CDCl_3) δ 8.09 (d, $J = 8.0$, 1H; Ar-H), 7.59 (dd, $J = 8.0$, $J = 8.0$, 1H; Ar-H), 7.34-7.30 (m, 2H; Ar-H), 2.44 (s, 3H; CH_3), 0.36 (s, 9H; Si- CH_3). ^{13}C NMR (CDCl_3) δ 182.2 (C=O), 169.1 (C-O), 156.2 (C-O), 133.3 (CH), 125.8 (CH), 124.9 (CH), 122.8 (C), 117.5 (CH), 21.8 (CH_3), 1.4 (Si- CH_3). IR (KBr): 2359, 1610, 1556, 1465, 1350, 858, 850, 771 cm^{-1} . MS m/z (%): 233/232/231 (2/14/1) [M^+], 219/218/217/216 (6/19/100/5) [$\text{M}^+ - \text{Me}$]. HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Si}$: M^+ , 232.0920. Found: m/z 232.0924. Anal Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Si}$: C, 67.20; H,

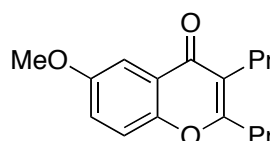
6.94. Found: C, 66.96; H, 6.98.

2-(2-(*tert*-Butyldimethylsilyloxy)propyl)-3-(trimethylsilyl)-4*H*-chromen-4-one (3af).



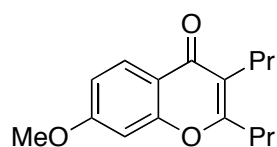
Yield: 81%, yellow oil. TLC: R_f 0.53 (hexane/ethyl acetate = 5/1). ^1H NMR (CDCl_3) δ 8.10 (d, J = 8.0 Hz, 1H; Ar-H), 7.59 (dd, J = 8.0, 7.5 Hz, 1H; Ar-H), 7.33 (m, 2H; Ar-H), 4.37 (m, 1H; CH), 2.91 (dd, J = 8.0, 8.0 Hz, 1H; CH_2), 2.74 (dd, J = 8.0, 4.5 Hz, 1H; CH_2), 1.27 (d, J = 6.0 Hz, 3H; CH_3), 0.76 (s, 9H; 3 CH_3), 0.38 (s, 9H; 3 CH_3), 0.02 (s, 3H; CH_3), -0.22 (s, 3H; CH_3). ^{13}C NMR (CDCl_3) δ 182.5 (C=O), 170.2 (C), 156.2 (C), 133.4 (CH), 125.8 (CH), 124.8 (CH), 122.9 (C), 118.7 (C), 117.4 (CH), 67.7 (CH-O), 44.4 (CH_2), 25.9 (3 CH_3), 24.5 (CH_3), 18.1 (C-Si), 1.7 (3 CH_3 -Si), -4.5 (CH_3 -Si), -4.8 (CH_3 -Si). IR (neat): 2930, 2361, 1634, 1614, 1557, 1468, 1350, 1248, 1130, 1076, 837, 764 cm^{-1} . MS m/z (%): 391/390 (1/2) [M^+], 376/375 (13/40) [M^+ -Me], 334/333 (95/100), 245/244/243 (65/42/89), 196/195 (22/73). HRMS Calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3\text{Si}_2$: M^+ , 390.2046. Found: m/z 390.2041.

6-Methoxy-2,3-dipropyl-4*H*-chromen-4-one (3ca).



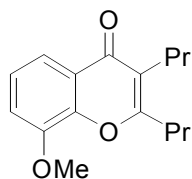
Yield: 90%, pale yellow powder. Mp. 40 $^\circ\text{C}$ (dichloromethane). TLC: R_f 0.28 (hexane/ethyl acetate-5/1). ^1H NMR (CDCl_3) δ 7.56 (s, 1H; Ar-H), 7.31 (d, J = 9.0, 1H; Ar-H), 7.20 (d, J = 7.5, 1H; Ar-H), 2.67 (t, J = 7.5 Hz, 2H; CH_2), 2.53 (t, J = 8.0 Hz, 2H; CH_2), 3.88 (s, 3H; CH_3), 1.78 (tq, J = 7.5 Hz, J = 7.0 Hz, 2H; CH_2), 1.54 (tq, J = 8.0 Hz, J = 7.5 Hz, 2H; CH_2), 1.03 (t, J = 7.5 Hz, 3H; CH_3), 0.96 (t, J = 7.0 Hz, 3H; CH_3). ^{13}C NMR (CDCl_3) δ 178.0 (C=O), 165.5 (C-O), 156.5 (C-O), 151.0 (CH), 123.6 (C), 123.2 (CH), 120.7 (C), 119.2 (CH), 105.0 (CH), 56.0 (CH_3), 33.9 (CH_2), 26.8 (CH_2), 22.7 (CH_2), 21.1 (CH_2), 14.4 (CH_3), 14.1 (CH_3). IR (KBr): 2962, 1631, 1612, 1581, 1485, 1378, 1026, 837, 775 cm^{-1} . MS m/z (%): 261/260/259 (7/36/8) [M^+], 247/246/245/243 (2/16/100/4) [M^+ -Me], 218/217/215 (4/31/7) [M^+ -Pr], 151 (8). HRMS Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: M^+ , 260.1412. Found: m/z 260.1413. Anal Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: C, 73.82; H, 7.74. Found: C, 73.79; H, 7.80.

7-Methoxy-2,3-dipropyl-4H-chromen-4-one (3da).



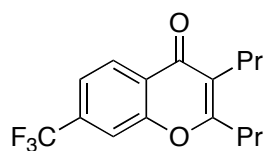
Yield: 66%, pale yellow oil. TLC: R_f 0.25 (hexane/ethyl acetate=5/1). ^1H NMR (CDCl_3) δ 8.08 (d, J = 9.0 Hz, 1H; Ar-H), 6.91 (d, J = 9.0 Hz, 1H; Ar-H), 6.72 (s, 1H; Ar-H), 3.89 (s, 3H; CH_3), 2.65 (t, J = 8.0 Hz, 2H; CH_2), 2.49 (t, 2H; CH_2), 1.78 (tq, J = 8.0 Hz, J = 7.0 Hz, 2H; CH_2), 1.52 (tq, J = 7.5 Hz, J = 7.5 Hz, 2H; CH_2), 1.03 (t, J = 7.0 Hz, 3H; CH_3), 0.98 (t, J = 7.5 Hz, 3H; CH_3). ^{13}C NMR (CDCl_3) δ 177.3 (C=O), 165.1 (C-O), 163.8 (C-O), 157.8 (CH), 127.5 (CH), 121.2 (C), 117.2 (C), 114.1 (CH), 99.9 (CH), 55.5 (CH_3), 33.9 (CH_2), 26.8 (CH_2), 22.8 (CH_2), 14.5 (CH_3), 14.2 (CH_3). IR (neat): 2960, 1633, 1575, 1440, 1386, 1168, 835, 783 cm^{-1} . MS m/z (%): 261/260/259 (7/34/8) [M^+], 247/246/245 (2/16/100) [$\text{M}^+ - \text{Me}$], 218/217/215 (5/26/8) [$\text{M}^+ - \text{Pr}$], 151 (12). HRMS Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: M^+ , 260.1412. Found: m/z 260.1412.

8-Methoxy-2,3-dipropyl-4H-chromen-4-one (3ea).



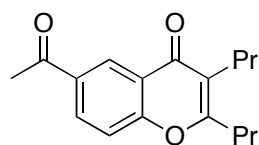
Yield: >99%, white powder. Mp. 76 °C (hexane/ethyl acetate). TLC: R_f 0.28 (hexane/ethyl acetate = 5/1). ^1H NMR (CDCl_3) δ 7.73 (d, J = 8.0 Hz, 1H; Ar-H), 7.30 (dd, J = 8.0, 8.0 Hz, 1H; Ar-H), 7.08 (d, J = 8.0 Hz, 1H; Ar-H), 3.95 (s, 3H; CH_3O), 2.71 (t, J = 7.5 Hz, 2H; CH_2), 2.51 (t, J = 7.5 Hz, 2H; CH_2), 1.81 (tq, J = 7.5, 7.0 Hz, 2H; CH_2), 1.53 (tq, J = 7.5, 7.0 Hz, 2H; CH_2), 1.04 (t, J = 7.0 Hz, 3H; CH_3), 0.97 (t, J = 7.0 Hz, 3H; CH_3). ^{13}C NMR (CDCl_3) δ 178.0 (C=O), 165.4 (C), 148.7 (C), 146.6 (C), 124.1 (CH), 124.1 (CH), 121.4 (C), 117.0 (CH), 113.7 (C), 56.5 ($\text{CH}_3\text{-O}$), 33.8 (CH_2), 26.8 (CH_2), 22.6 (CH_2), 21.2 (CH_2), 14.3 (CH_3), 14.1 (CH_3). IR (KBr): 2959, 2872, 1643, 1578, 1491, 1456, 1433, 1391, 1271, 1221, 1184, 1173, 1090, 1072, 760 cm^{-1} . MS m/z (%): 261/260 (9/57) [M^+], 246/245 (25/100) [$\text{M}^+ - \text{Me}$], 232/231 (9/12) [$\text{M}^+ - \text{Et}$], 218/217 (8/54) [$\text{M}^+ - \text{Pr}$], 151 (22). HRMS Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: M^+ , 260.1412. Found: m/z 260.1413.

2,3-Dipropyl-7-(trifluoromethyl)-4H-chromen-4-one (3fa).



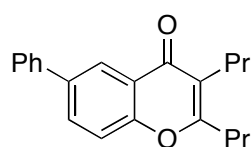
Yield: >99%, yellow oil. TLC: R_f 0.50 (hexane/ethyl acetate=5/1). ^1H NMR (CDCl_3) δ 8.29 (d, J = 8.5 Hz 1H; Ar-H), 7.68 (s, 1H; Ar-H), 7.55 (d, J = 8.5 Hz, 1H; Ar-H), 2.69 (t, J = 7.0 Hz, 2H; CH_2), 2.51 (t, J = 7.5 Hz, 2H; CH_2), 1.80 (tq, J = 7.5 Hz, J = 7.0 Hz, 2H; CH_2), 1.53 (tq, J = 7.5 Hz, J = 7.5 Hz, 2H; CH_2), 1.04 (t, J = 7.5 Hz, 3H; CH_3), 0.98 (t, J = 7.5 Hz, 3H; CH_3). ^{13}C NMR (CDCl_3) δ 177.1 (C=O), 166.5 (C-O), 155.4 (C-O), 134.7 (q, J = 32.9 Hz; C- CF_3), 127.4 (CH), 125.1 (C), 123.4 (q, J = 271.6 Hz; CF_3), 122.3 (C), 120.8 (q, J = 3.4 Hz; C- CCF_3), 115.7 (q, J = 3.9 Hz; C- CCF_3), 33.8 (CH_2), 26.8 (CH_2), 22.6 (CH_2), 21.0 (CH_2), 14.3 (CH_3), 14.0 (CH_3). ^{19}F NMR δ -63.6. IR (neat): 2962, 1649, 1573, 1438, 1319, 1166, 1134, 1062, 927, 881, 792 cm^{-1} . MS m/z (%): 299/298/297 (6/32/7) [M^+], 284/283 (17/100) [$\text{M}^+ - \text{Me}$], 256/255/253 (6/18/6) [$\text{M}^+ - \text{Pr}$], 189 (9). HRMS Calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{O}_2$: M^+ , 298.1181. Found: m/z 298.1180. Anal Calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{O}_2$: C, 64.42; H, 5.74. Found: C, 64.52; H, 5.88.

6-Ethanoyl-2,3-dipropyl-4H-chromen-4-one (3ga).



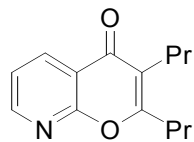
Yield: 75%, white powder. Mp. 78 $^{\circ}\text{C}$ (hexane). TLC: R_f 0.15 (hexane/ethyl acetate=5/1). ^1H NMR (CDCl_3) δ 8.73 (s, 1H; Ar-H), 8.24 (d, J = 9.0, 1H; Ar-H), 7.44 (d, J = 9.0 Hz 1H; Ar-H), 2.70 (t, J = 7.5 Hz 2H; CH_2), 2.68 (s, 3H; CH_3), 2.52 (t, J = 7.5 Hz 2H; CH_2), 1.80 (tq, J = 7.5 Hz, J = 7.5 Hz, 2H; CH_2), 1.52 (tq, J = 7.5 Hz, J = 7.5 Hz, 2H; CH_2), 1.04 (t, J = 7.5 Hz, 3H; CH_3), 0.99 (t, J = 7.5 Hz, 3H; CH_3). ^{13}C NMR (CDCl_3) δ 196.9 (C=O), 177.7 (C=O), 166.0 (C-O), 158.7 (C-O), 133.4 (C), 132.1 (CH), 127.9 (CH), 124.4 (C), 122.1 (CH), 118.6 (CH), 33.8 (CH_2), 26.8 (CH_3), 26.7 (CH_2), 22.6 (CH_2), 21.0 (CH_2), 14.3 (CH_3), 14.1 (CH_3). IR (KBr): 2963, 1683, 1639, 1440, 1357, 1255, 852 cm^{-1} . MS m/z (%): 273/272/271 (7/36/6) [M^+], 259/258/257 (2/17/100) [$\text{M}^+ - \text{Me}$], 230/229 (6/31) [$\text{M}^+ - \text{Pr}$], 163 (9), 147 (6). HRMS Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$: M^+ , 272.1412. Found: m/z 272.1411. Anal Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$: C, 74.97; H, 7.40. Found: C, 74.77; H, 7.45.

6-Phenyl-2,3-dipropyl-4H-chromen-4-one (3ha).



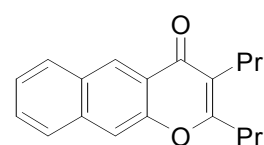
Yield: 75%, yellow oil. TLC: R_f 0.43 (hexane/ethyl acetate=5/1). ^1H NMR (CDCl_3) δ 8.44 (s, 1H; Ar-H), 7.84 (d, J = 8.5, 1H; Ar-H), 7.64-7.66 (m, 2H; Ph-H), 7.40-7.50 (m, 3H; Ph-H), 7.36 (d, J = 8.5 Hz, 2H; Ar-H), 2.70 (t, J = 7.5 Hz, 2H; CH_2), 2.55 (t, J = 7.5 Hz, 2H; CH_2), 1.81 (tq, J = 7.5 Hz, J = 7.5 Hz, 2H; CH_2), 1.56 (tq, J = 7.5 Hz, J = 7.5 Hz, 2H; CH_2), 1.04 (t, J = 7.5 Hz, 3H; CH_3), 1.00 (t, J = 7.0 Hz, 3H; CH_3). ^{13}C NMR (CDCl_3) δ 178.1 (C=O), 165.6 (C-O), 155.5 (C-O), 139.8 (C), 137.6 (C), 131.9 (CH), 129.0 (CH), 127.7 (CH), 127.3 (CH), 123.9 (CH), 123.1 (C), 121.4 (C), 118.2 (CH), 33.8 (CH_2), 26.8 (CH_2), 22.7 (CH_2), 21.1 (CH_2), 14.3 (CH_3), 14.1 (CH_3). IR (neat): 2960, 1639, 1572, 1475, 1373, 1155, 827, 763, 698 cm^{-1} . MS m/z (%): 307/306/305 (10/41/5) [M^+], 293/292/291 (3/22/100) [$\text{M}^+ - \text{Me}$], 264/263 (8/36) [$\text{M}^+ - \text{Pr}$], 197 (14), 139 (22). HRMS Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2$: M^+ , 306.1620. Found: m/z 306.1618. Anal Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2$: C, 82.32; H, 7.24. Found: C, 82.08; H, 7.23.

2,3-Dipropyl-4H-pyrano[2,3-*b*]pyridin-4-one (3ia).



Yield: 38%, yellow oil. TLC: R_f 0.20 (hexane/ethyl acetate = 5/1). ^1H NMR (CDCl_3) δ 8.64 (d, J = 4.5 Hz, 1H; Ar-H), 8.56 (d, J = 7.5 Hz, 1H; Ar-H), 7.39 (dd, J = 4.5, 7.5 Hz, 1H; Ar-H), 2.74 (t, J = 7.5 Hz, 2H; CH_2), 2.52 (t, J = 7.5 Hz, 2H; CH_2), 1.85 (tq, J = 7.5, 7.5 Hz, 2H; CH_2), 1.54 (tq, J = 7.5, 7.5 Hz, 2H; CH_2), 1.05 (t, J = 7.5 Hz, 3H; CH_3), 0.99 (t, J = 7.5 Hz, 3H; CH_3). ^{13}C NMR (CDCl_3) δ 178.6 (C=O), 166.4 (C), 160.6 (C), 152.8 (CH), 136.8 (CH), 122.1 (C), 121.7 (CH), 117.8 (C), 33.9 (CH_2), 26.8 (CH_2), 22.6 (CH_2), 21.1 (CH_2), 14.3 (CH_3), 14.1 (CH_3). IR (neat): 2963, 1643, 1622, 1599, 1423, 1393, 1163, 785 cm^{-1} . MS m/z (%): 231/230 (9/62) [M^+], 217/216 (27/100) [$\text{M}^+ - \text{Me}$], 203/202 (13/7) [$\text{M}^+ - \text{Et}$], 189/188 (7/57) [$\text{M}^+ - \text{Pr}$], 122 (36). HRMS Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2$: M^+ , 231.1259. Found: m/z 231.1263.

2,3-Dipropyl-4H-benzo[*g*]chromen-4-one (3ja).



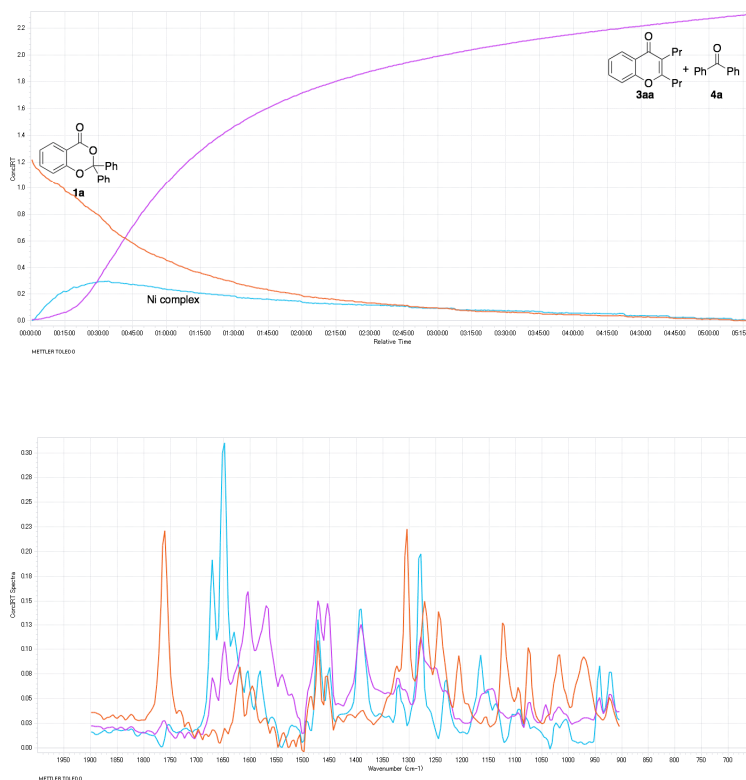
Yield: >99%, white powder. Mp. 64 °C (hexane). TLC: R_f 0.45 (hexane/ethyl acetate = 5/1). ^1H NMR (CDCl_3) δ 8.76 (s, 1H; Ar-H), 8.02 (d, J = 8.0 Hz, 1H; Ar-H), 7.86 (d, J = 8.0 Hz, 1H; Ar-H), 7.81

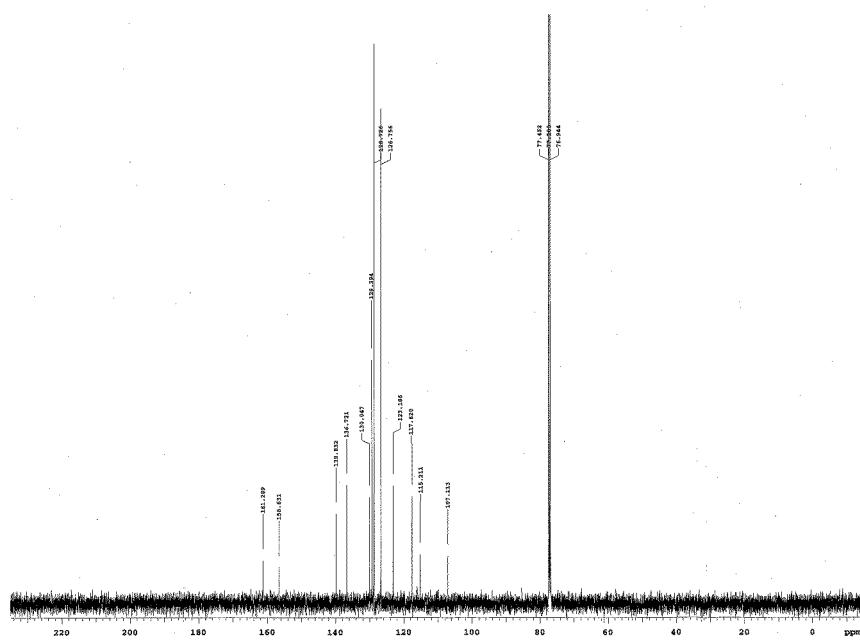
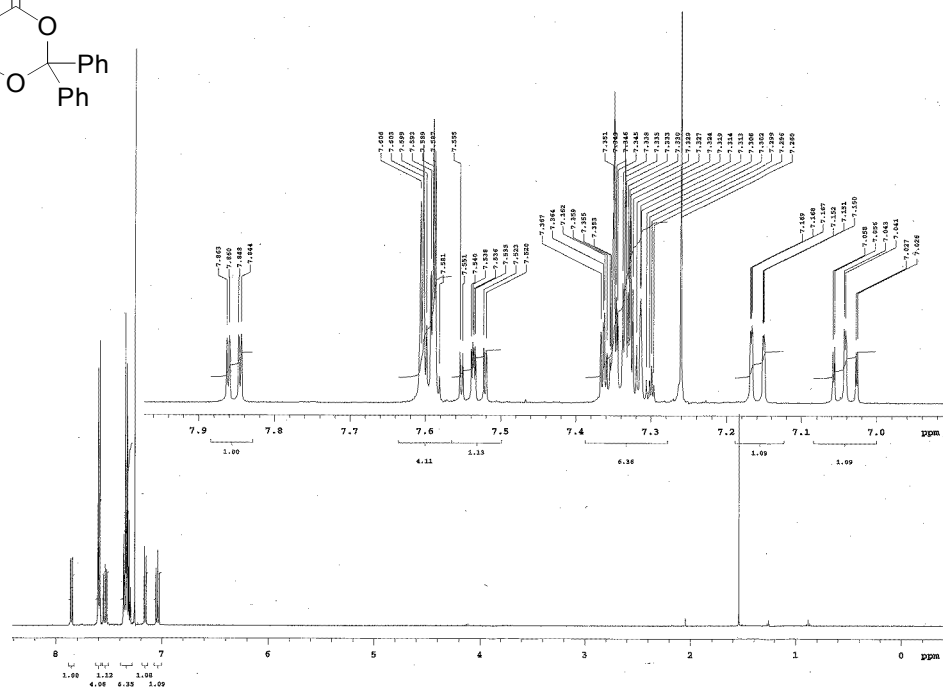
(s, 1H; Ar-H), 7.56 (dd, $J = 8.0, 7.0$ Hz, 1H; Ar-H), 7.47 (dd, $J = 7.0, 8.0$ Hz, 1H; Ar-H), 2.72 (t, $J = 7.5$ Hz, 2H; CH₂), 2.56 (t, $J = 7.5$ Hz, 2H; CH₂), 1.85 (tq, $J = 7.5, 7.5$ Hz, 2H; CH₂), 1.57 (tq, $J = 7.5, 7.5$ Hz, 2H; CH₂), 1.07 (t, $J = 7.5$ Hz, 3H; CH₃), 1.01 (t, $J = 7.5$ Hz, 3H; CH₃). ¹³C NMR (CDCl₃) δ 178.9 (C=O), 166.6 (C), 152.6 (C), 135.8 (C), 130.3 (C), 129.8 (CH), 128.5 (CH), 127.2 (CH), 127.0 (CH), 125.6 (CH), 122.3 (C), 119.8 (C), 113.6 (CH), 34.1 (CH₂), 26.9 (CH₂), 22.9 (CH₂), 21.1 (CH₂), 14.4 (CH₃), 14.1 (CH₃). IR (KBr): 2961, 1647, 1624, 1464, 1395, 1167, 745 cm⁻¹. MS m/z (%): 281/280 (17/78) [M⁺], 266/265 (38/100) [M⁺-Me], 252/251 (13/17) [M⁺-Et], 238/237 (12/66) [M⁺-Pr], 171 (24). HRMS Calcd for C₁₉H₂₀O₂: M⁺, 280.1463. Found: m/z 280.1459.

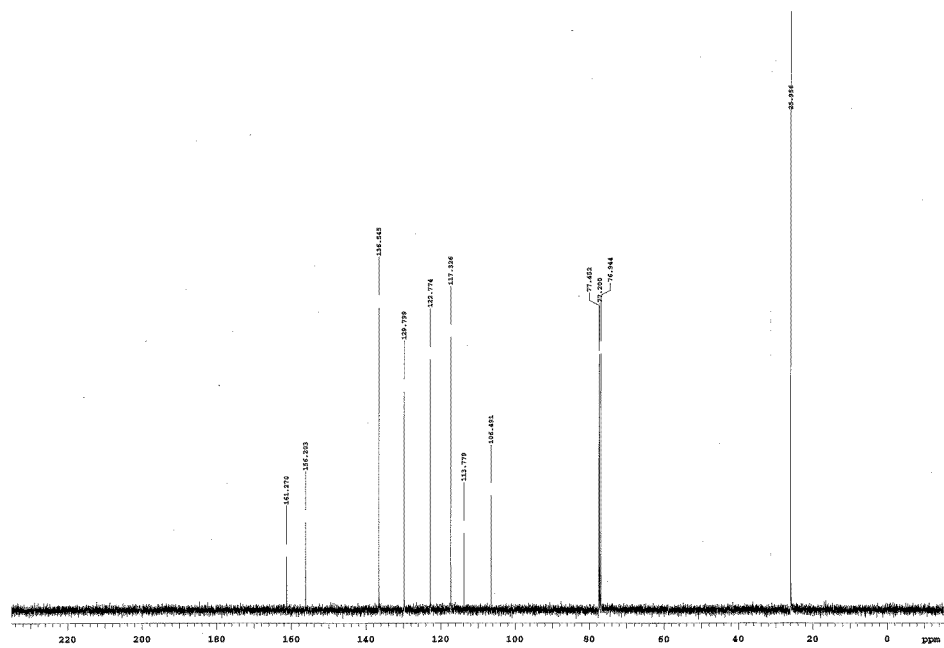
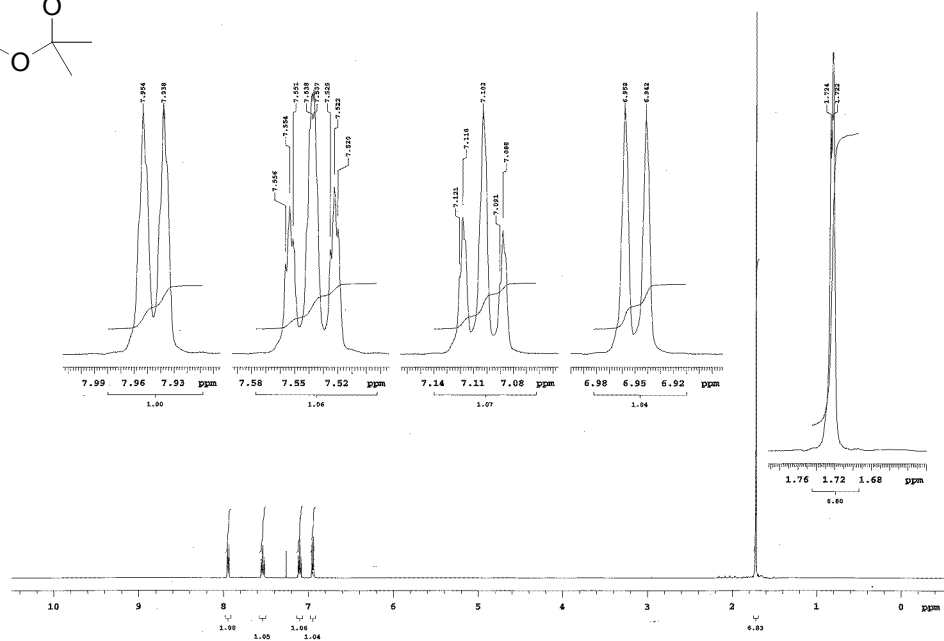
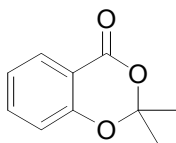
In-situ IR Spectra Analysis

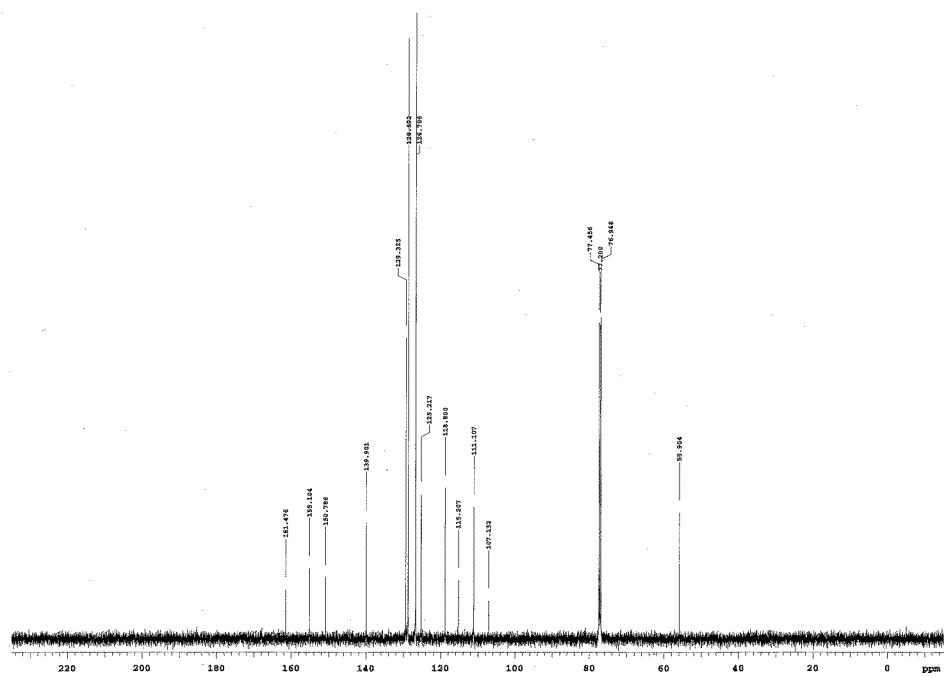
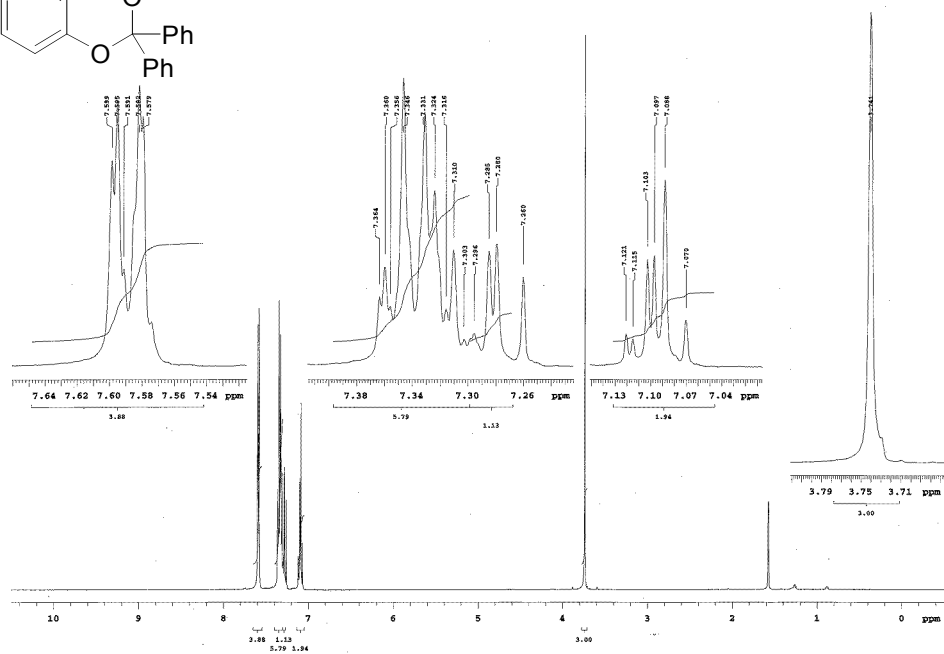
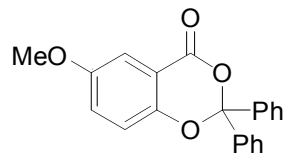
Procedure for the large-scale reaction.

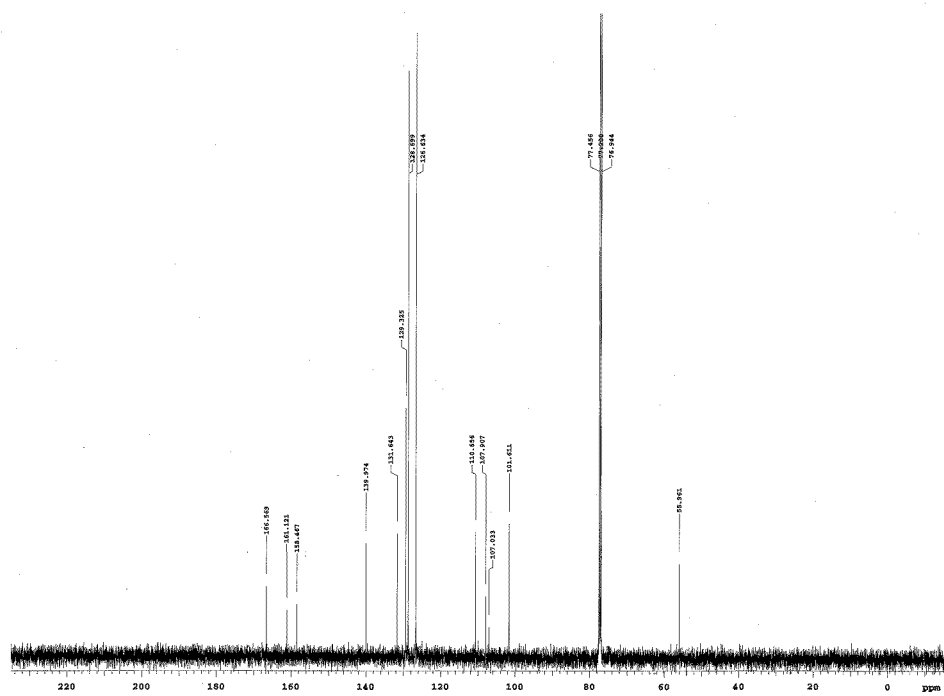
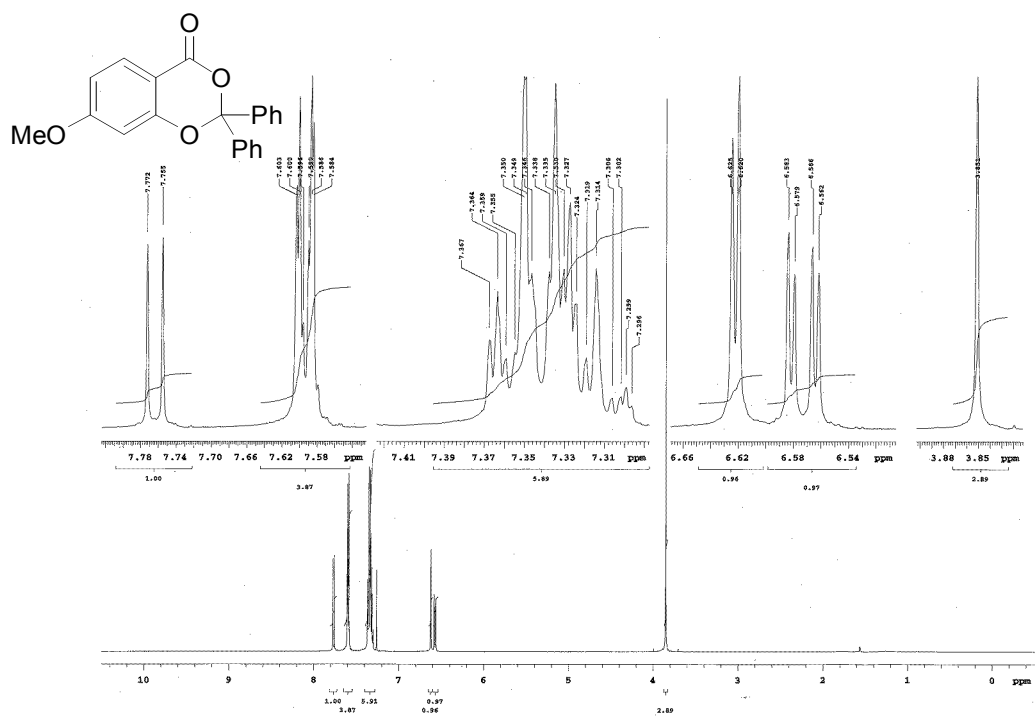
The reaction was performed in a 50 mL round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and Dimroth reflux condenser. The top of condenser was connected with a balloon filled with argon gas (ca. 1 atm). Salicylic acid ketals (**1a**) (10 mmol, 3.02 g) and **2a** (12 mmol, 1.76 mL) were added to a solution of bis(1,5-dicyclooctadiene)nickel (138 mg, 0.5 mmol), pyridine (10 mmol), and tricyclohexylphosphine (0.5 mmol) in toluene (20 mL) in a dry box. The flask was taken outside the dry box. The ReactIR™ probe was inserted directly into the reaction mixture. The measurement was started when the temperature of the reaction mixture was stabilized at 100 °C. After 6 h, the resulting reaction mixture was cooled to ambient temperature and filtered through a silica gel pad, concentrated in vacuo. The residue was purified by flash silica gel column chromatography (50 g, 2x25 cm, hexane/ethyl acetate = 5:1) to give **3aa** in 99% yield and benzophenone (**4a**) in 99% yield.

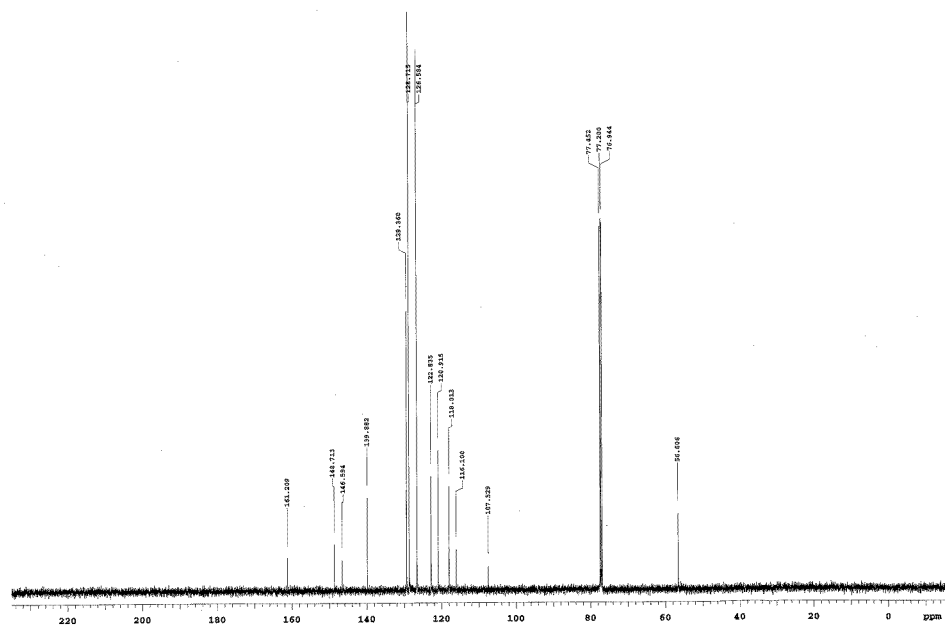
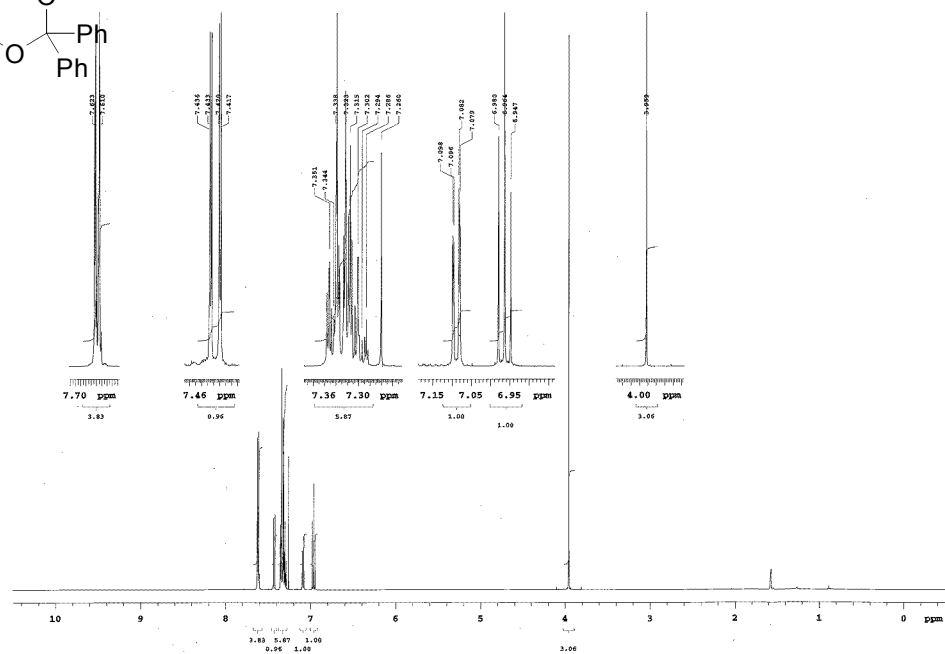
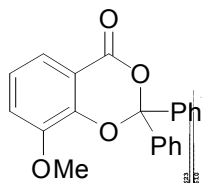


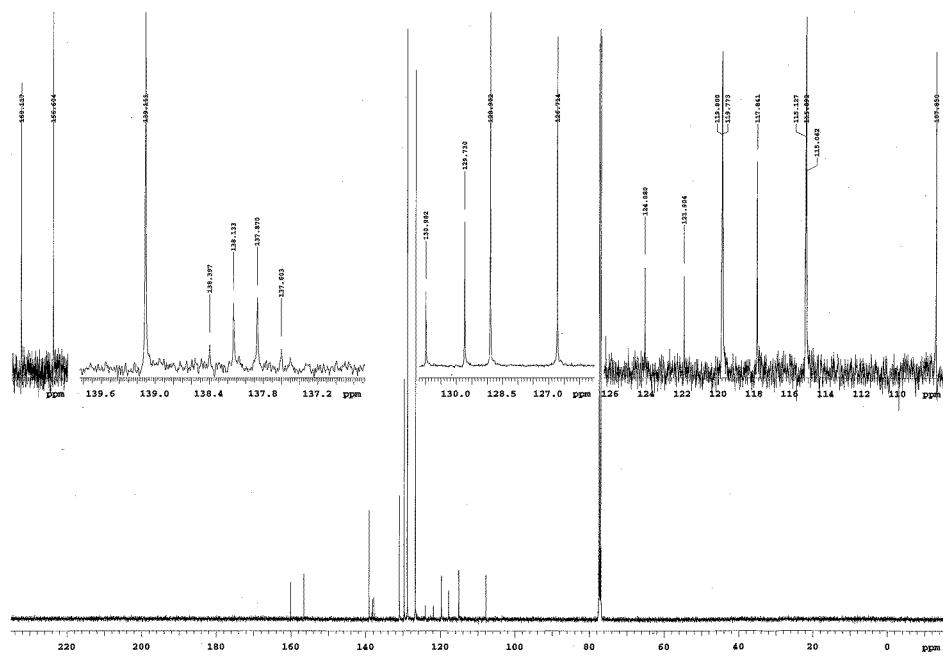
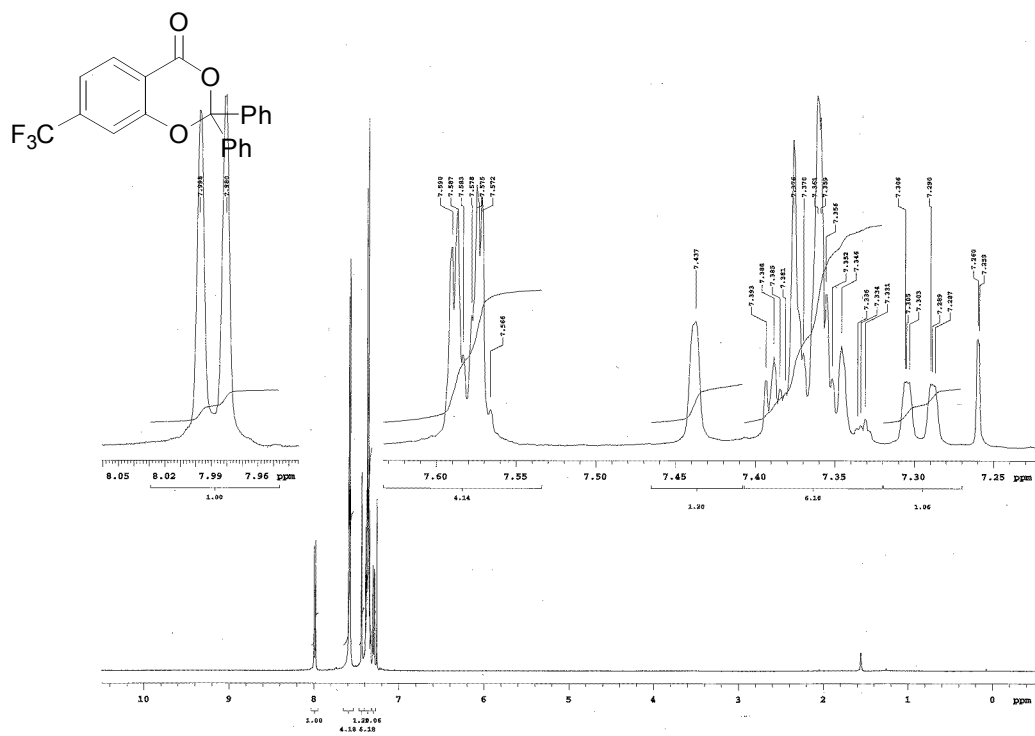
O=C1OC(c2ccccc2)(c3ccccc3)OC1c4ccccc4

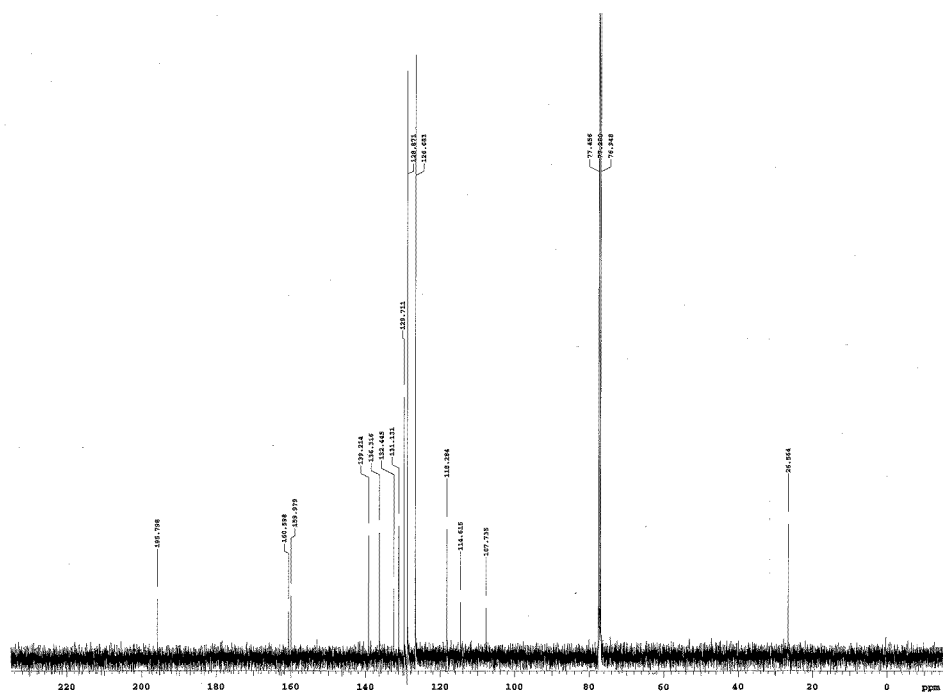


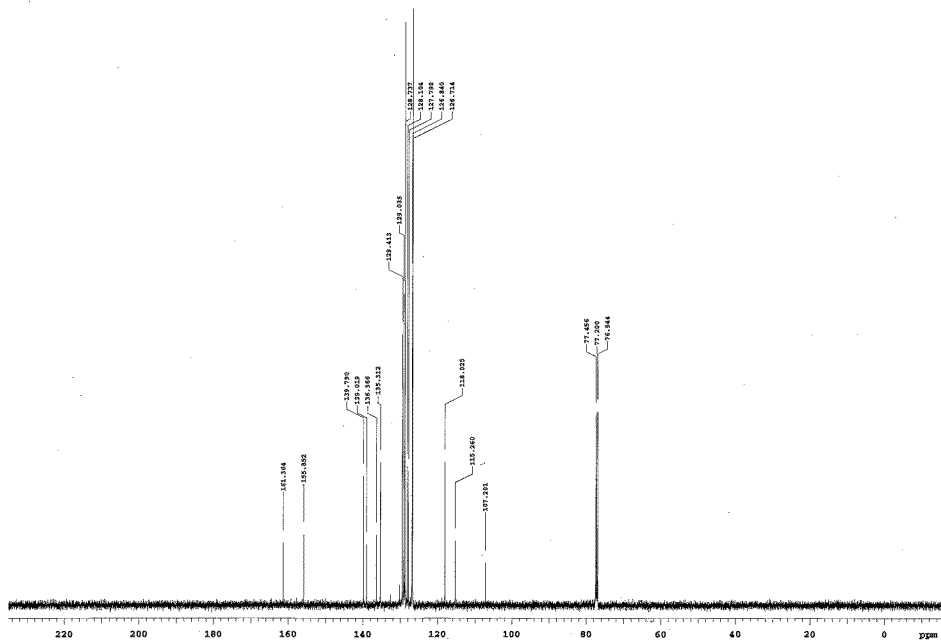
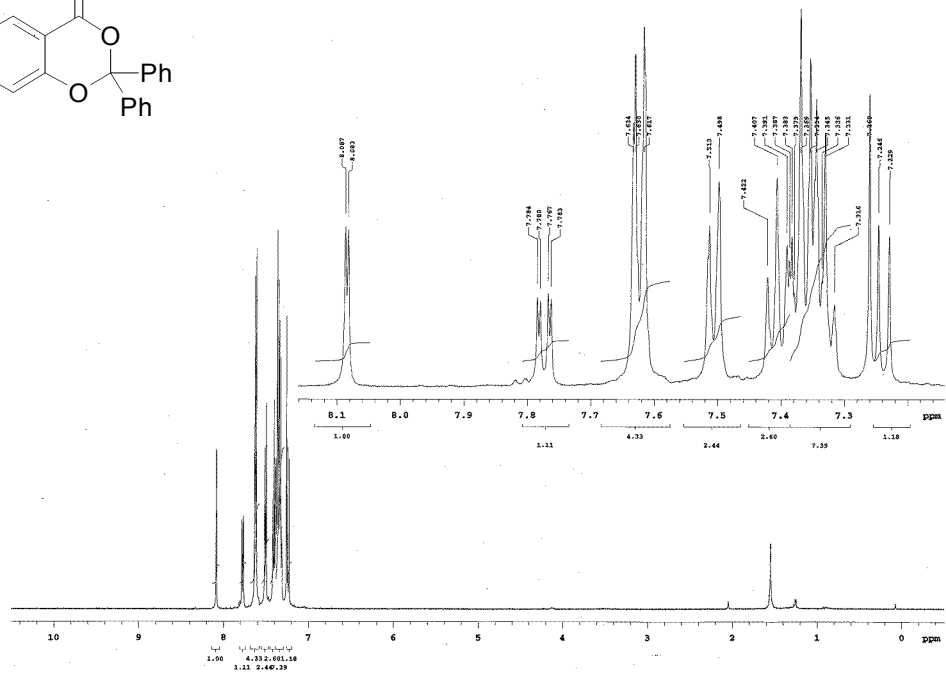
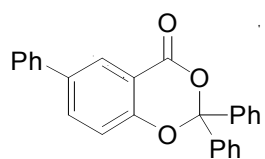


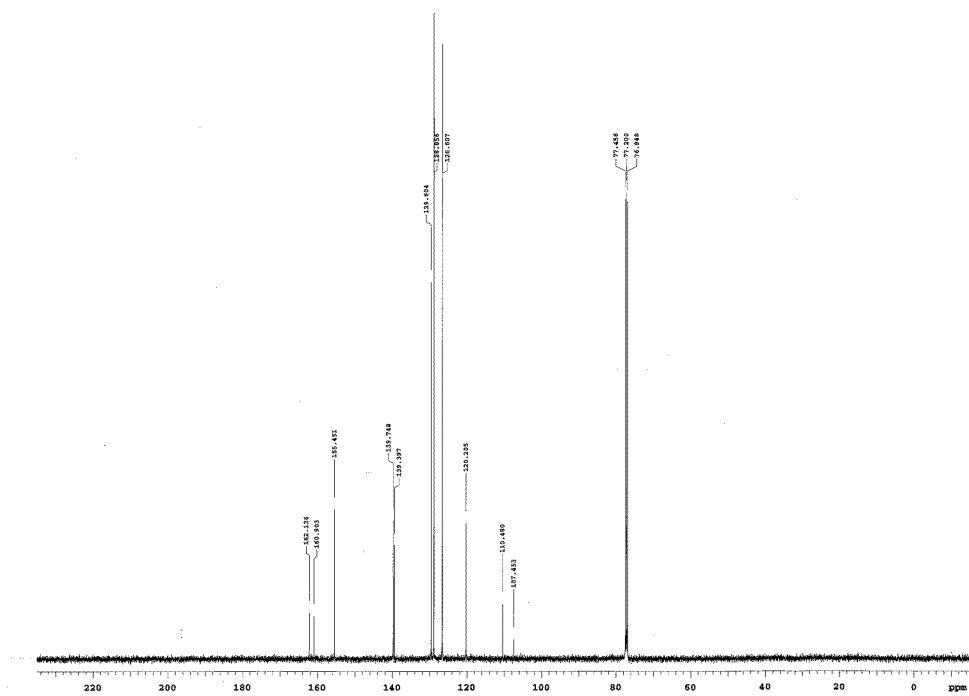
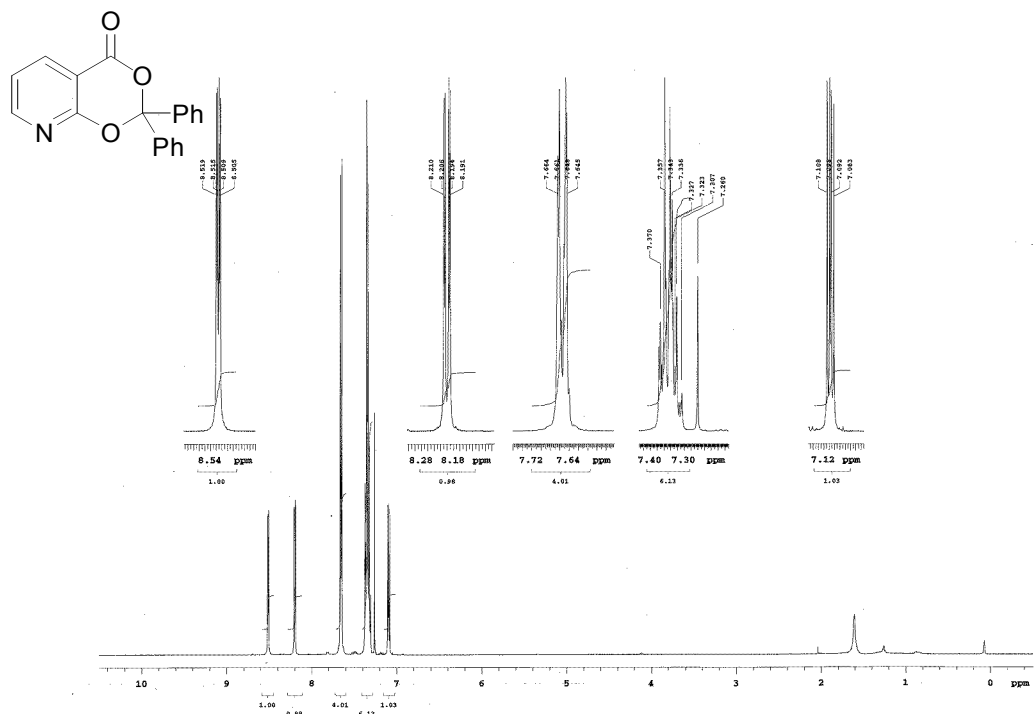


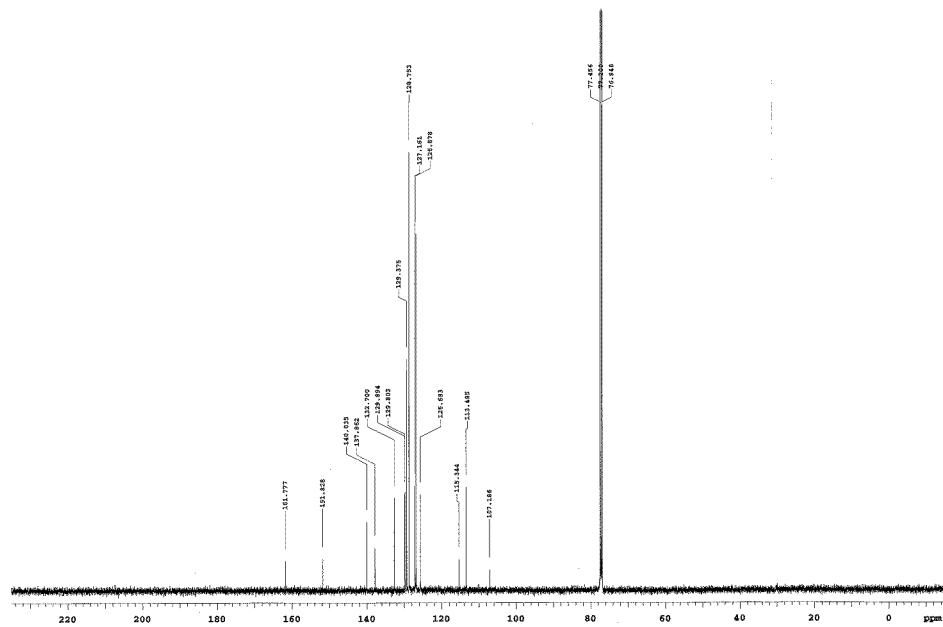
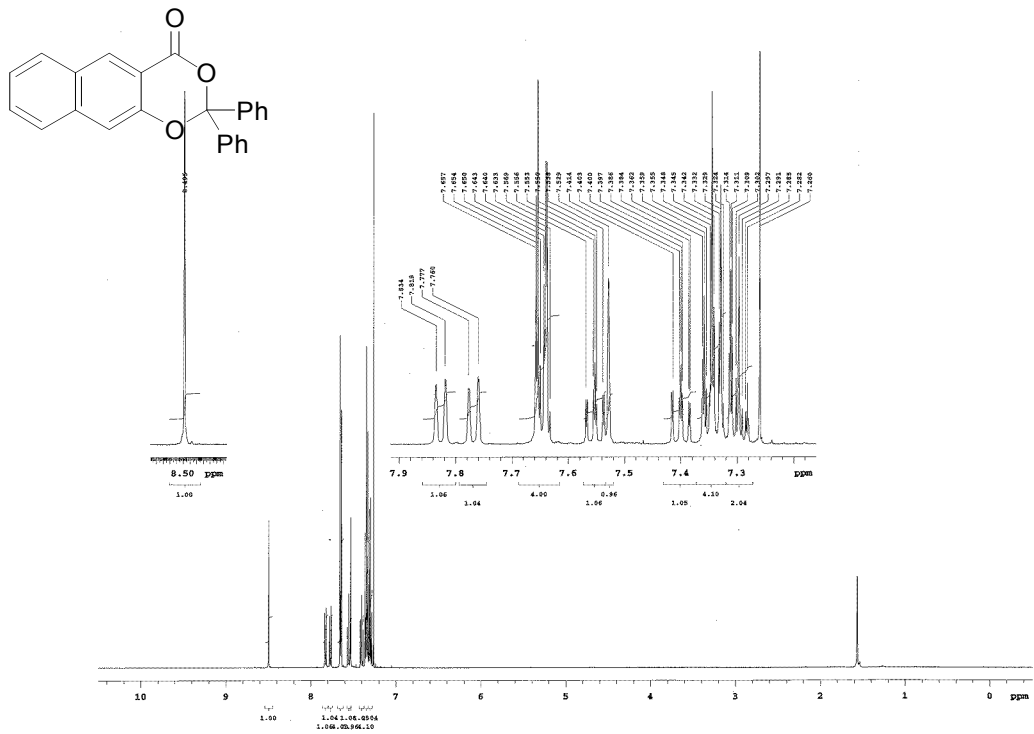


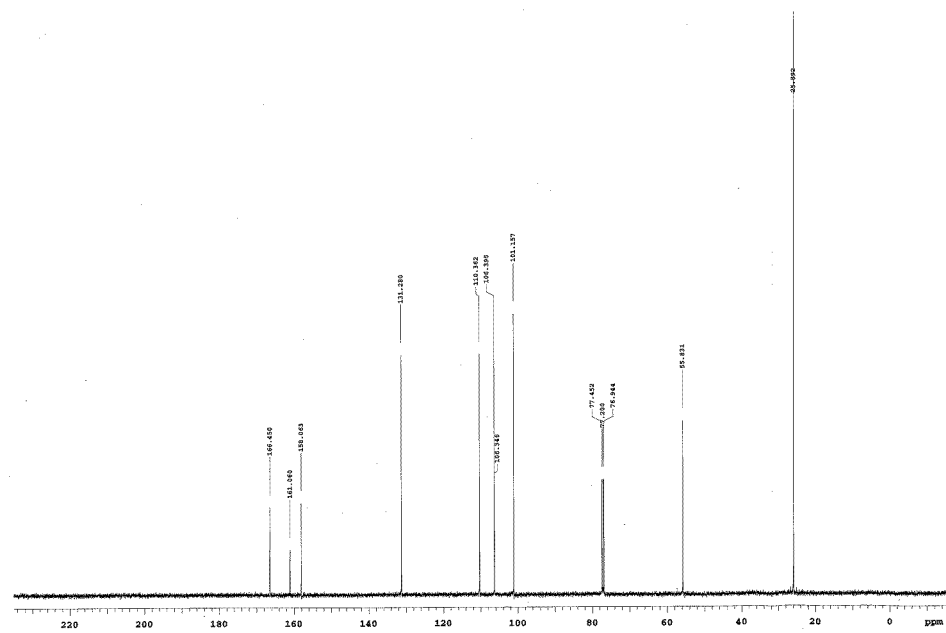
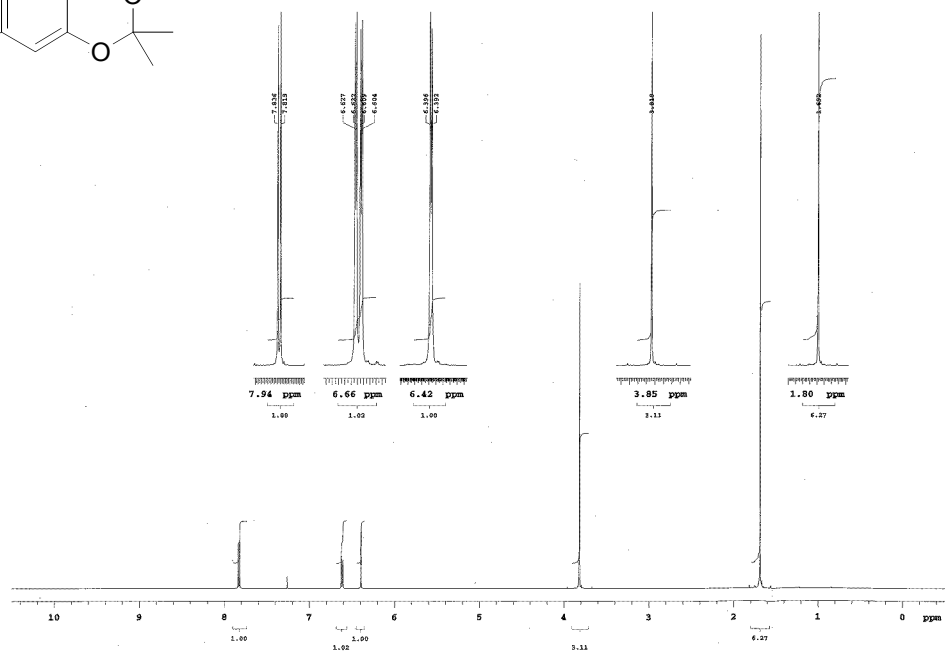
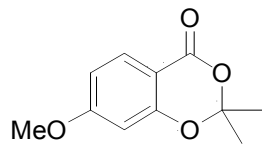


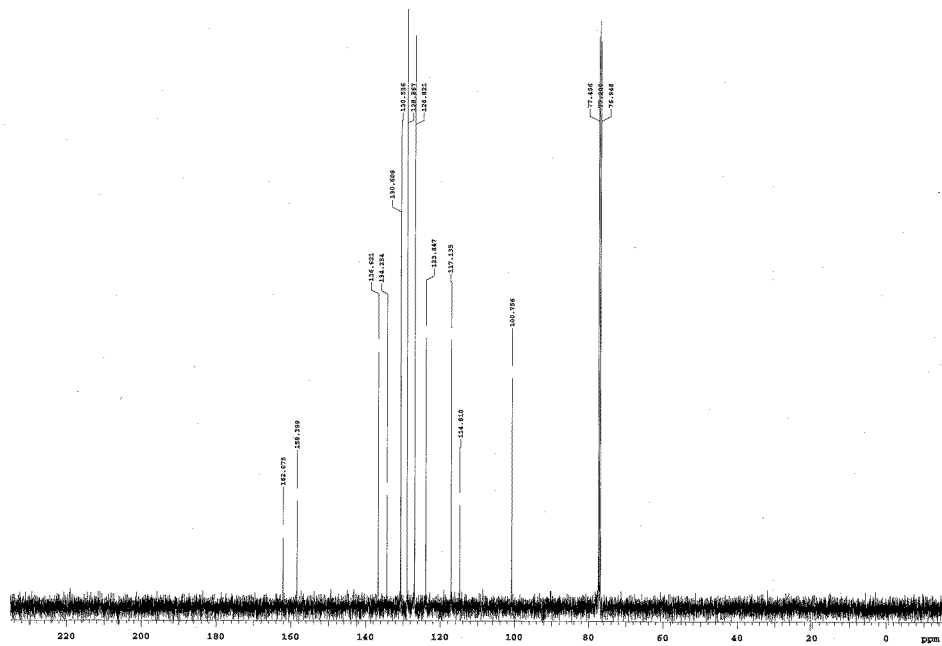
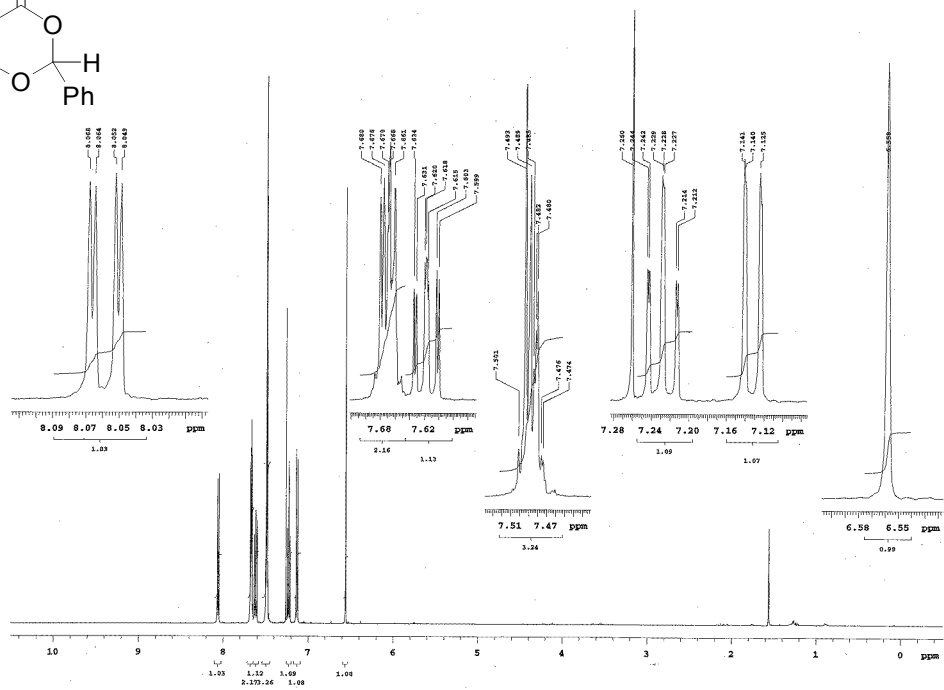
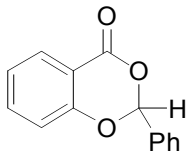


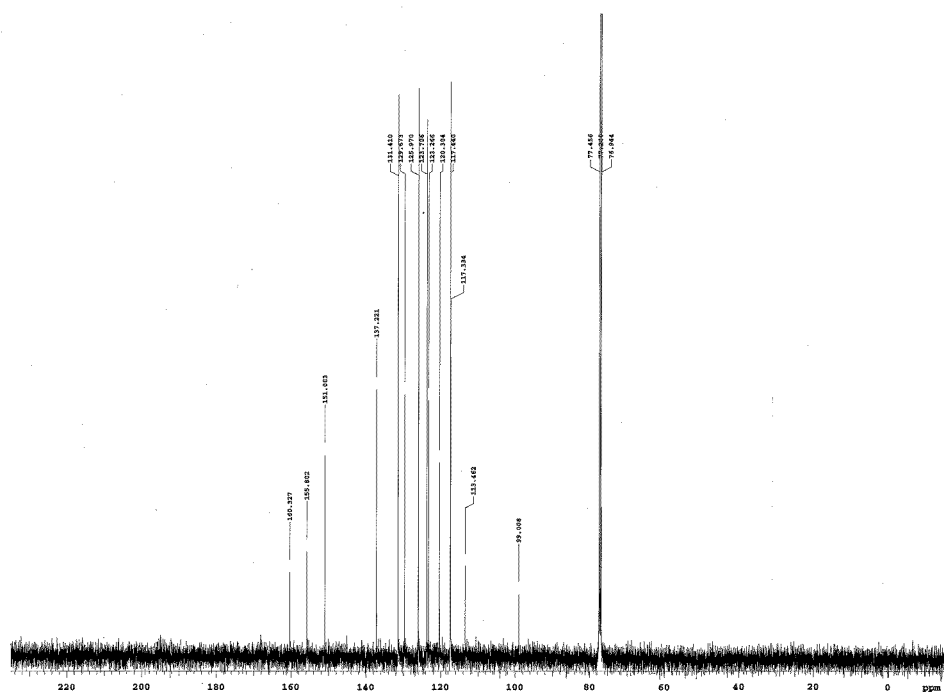
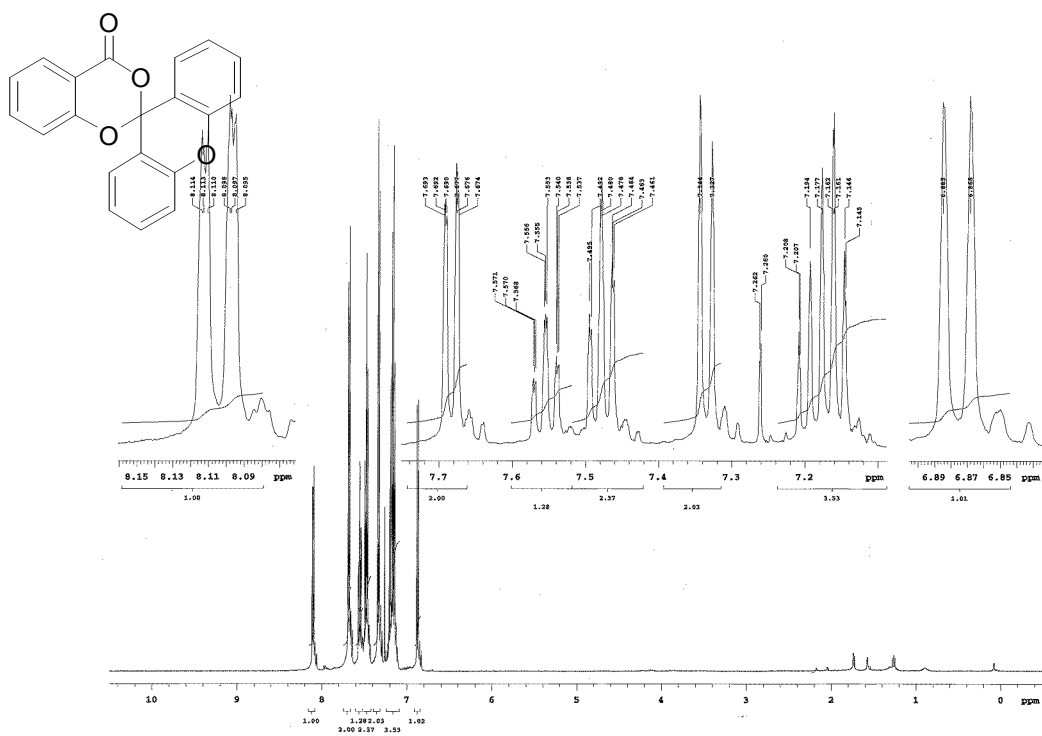


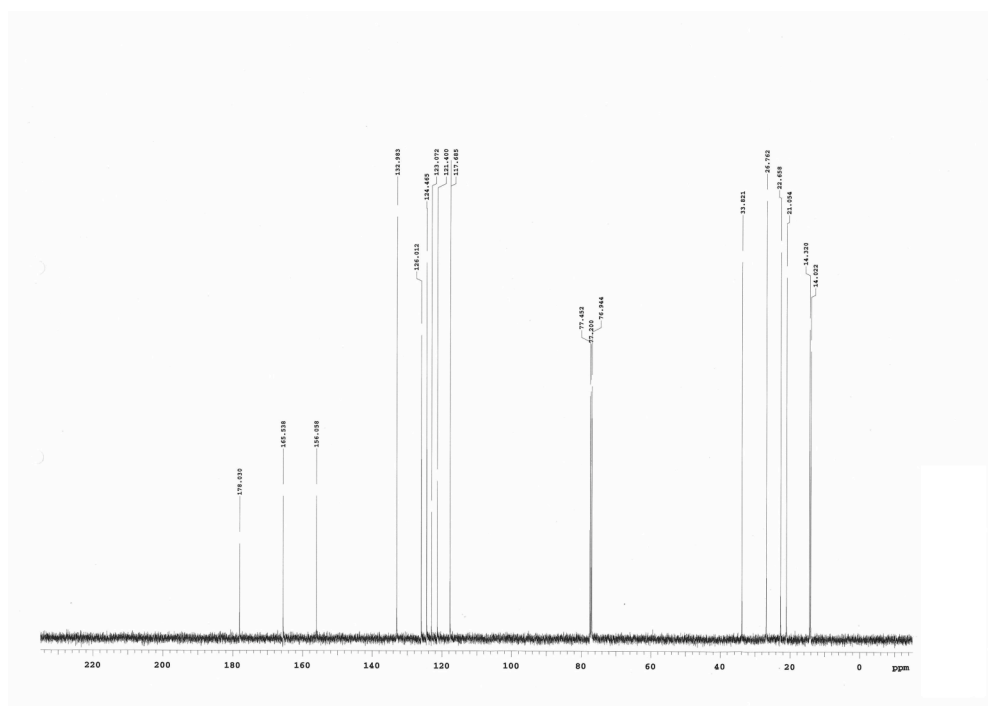
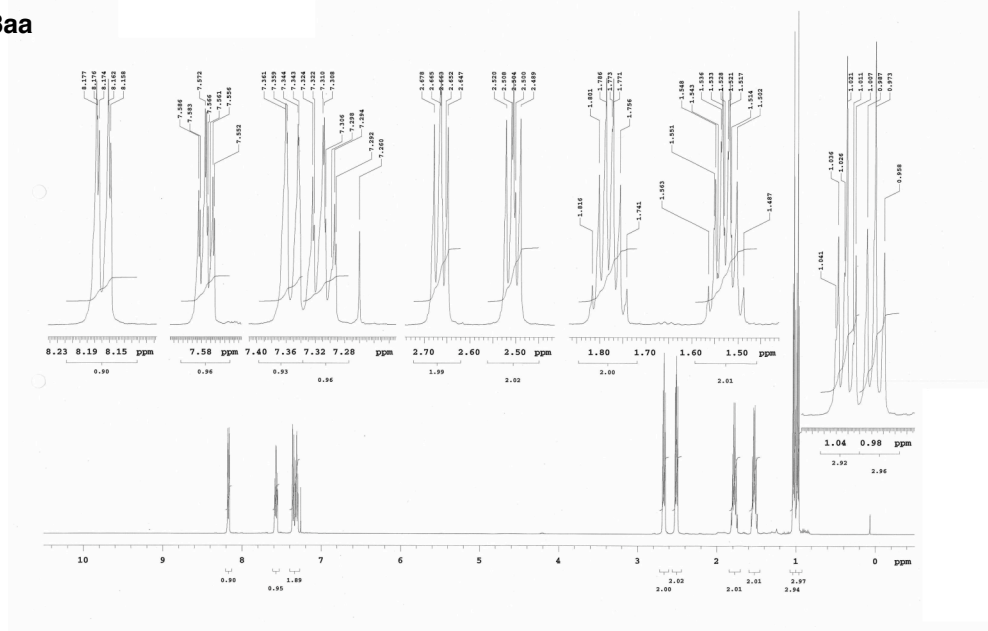
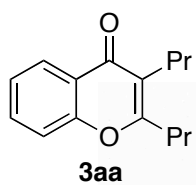


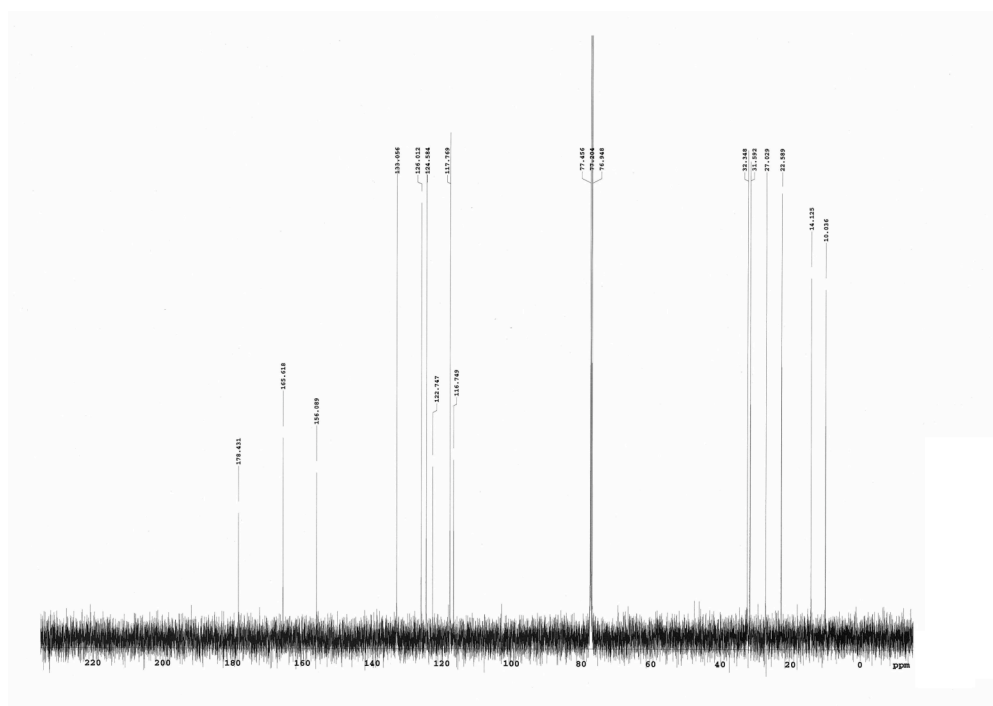
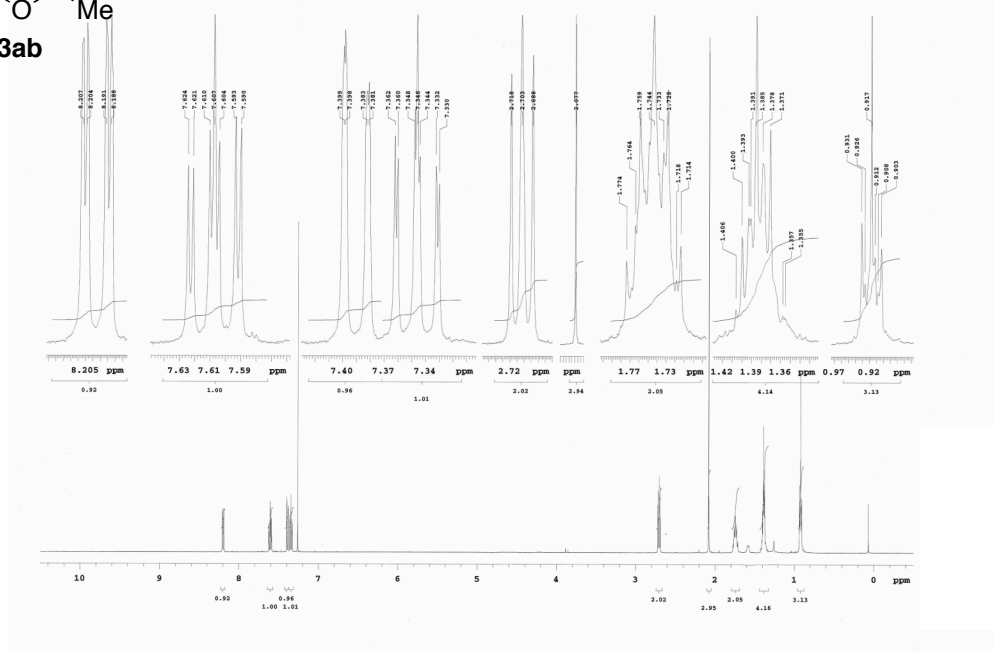
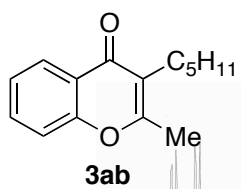


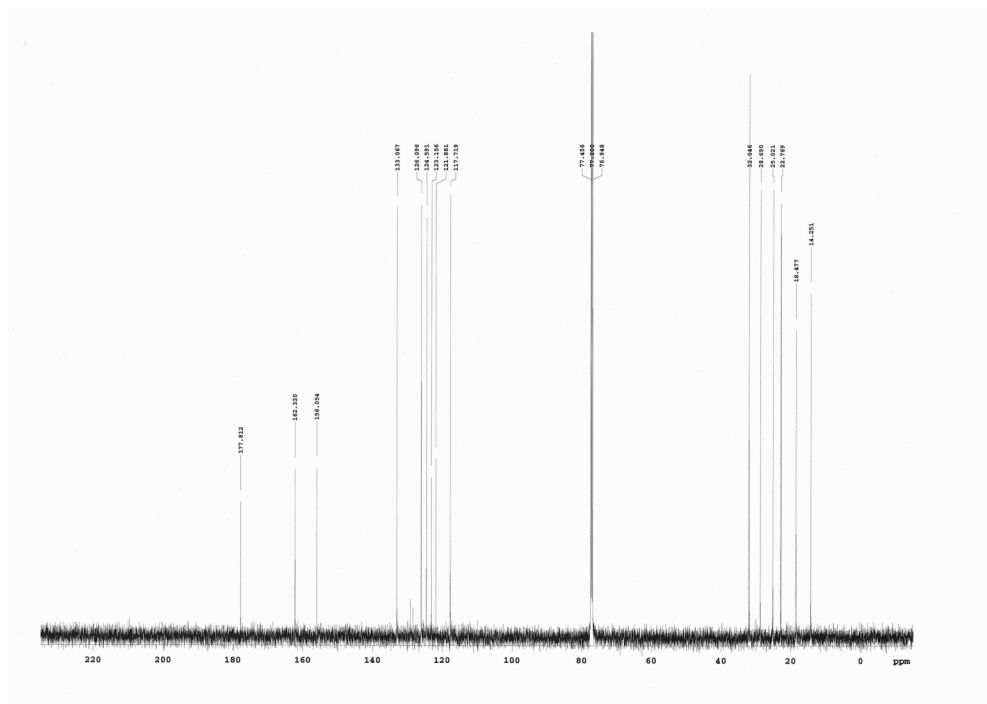
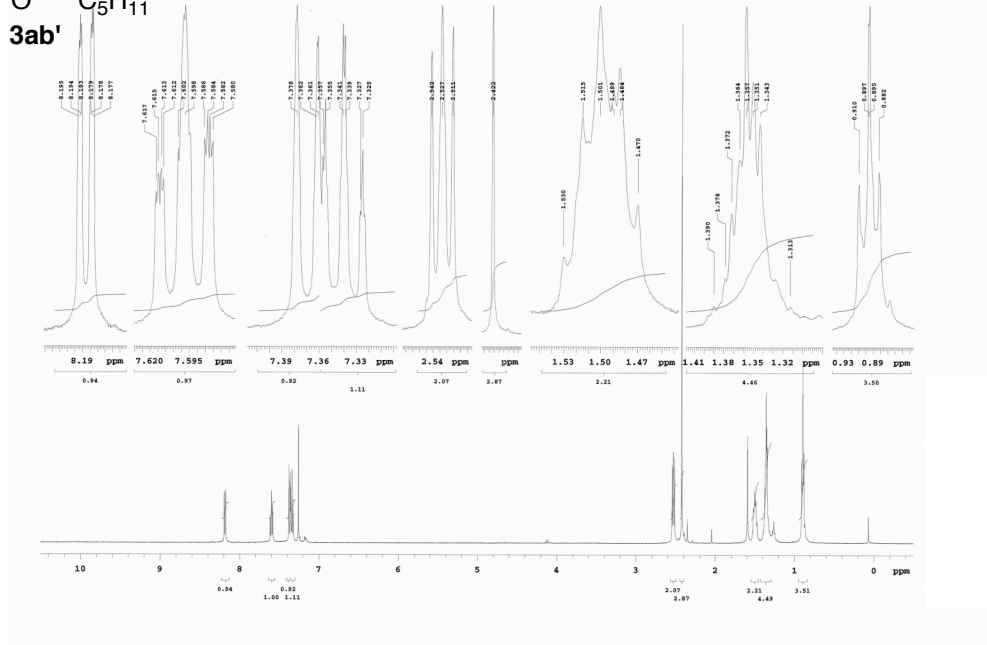
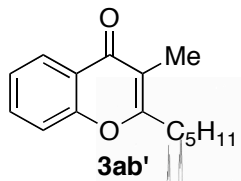


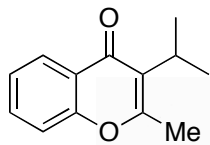




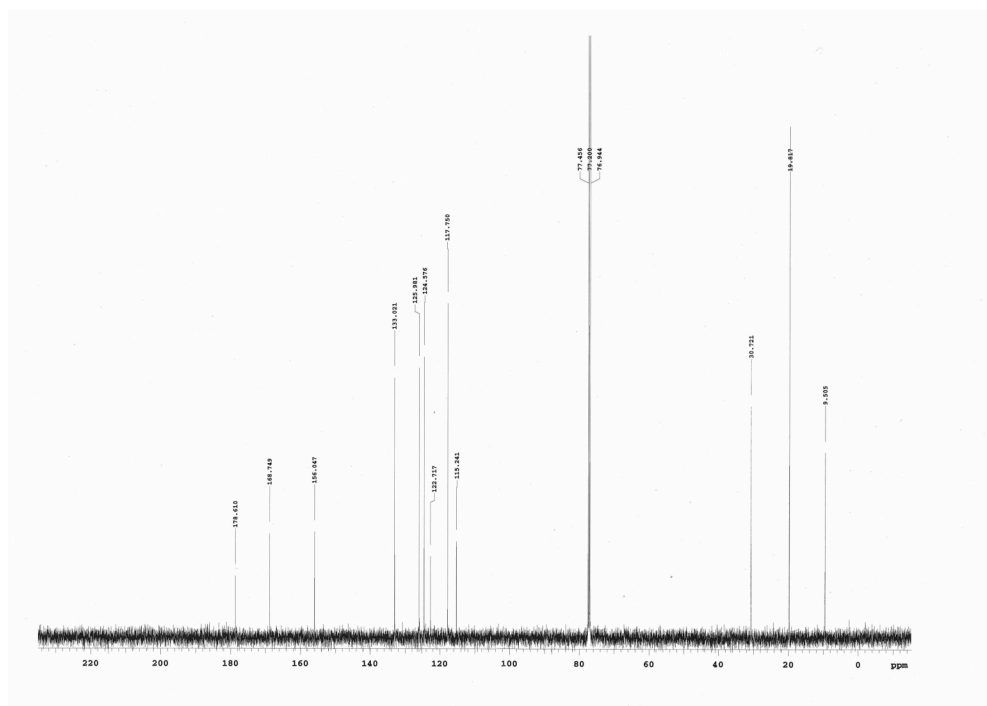
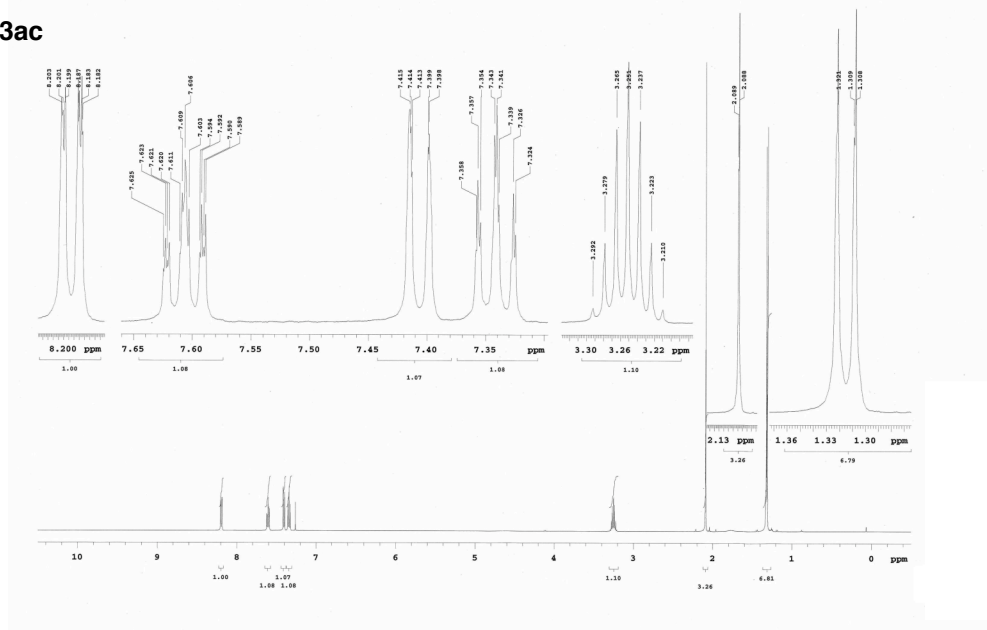


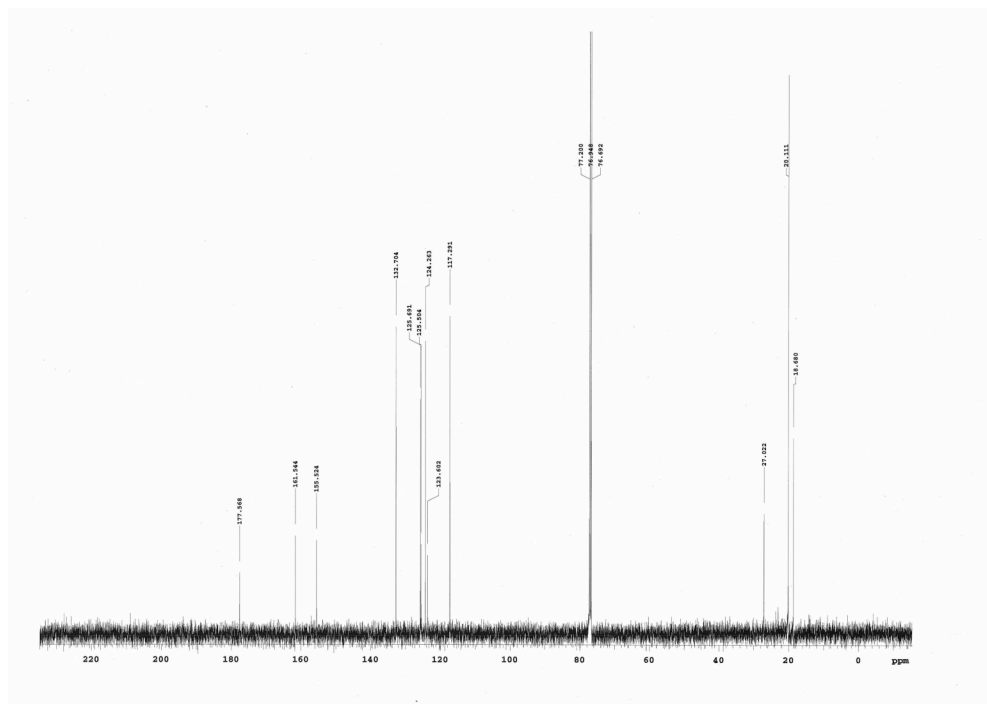
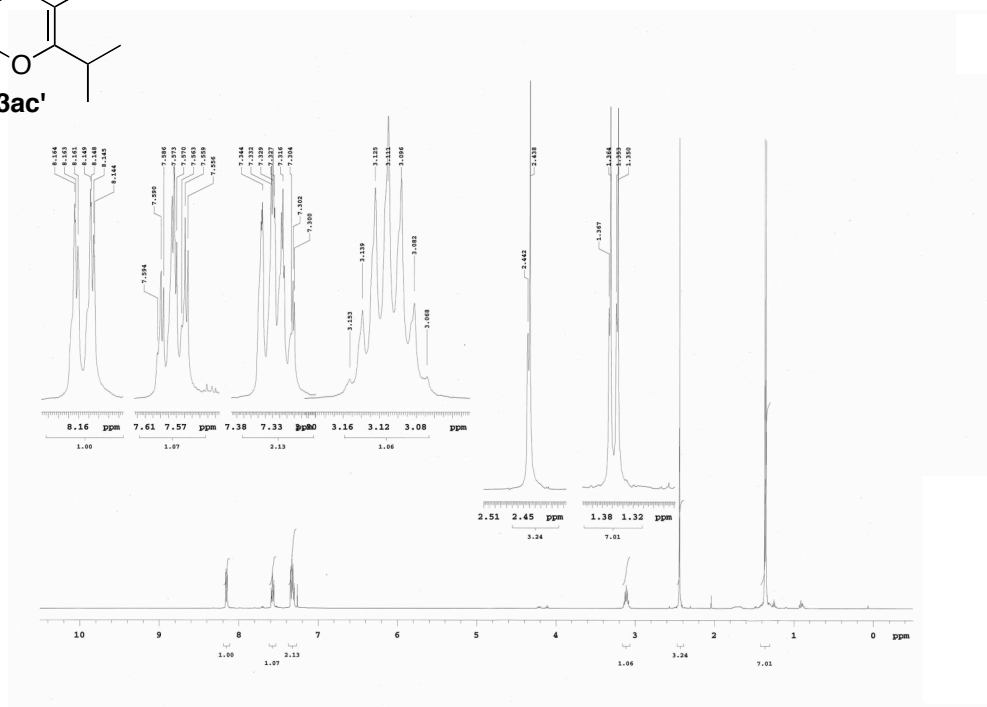
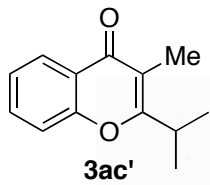


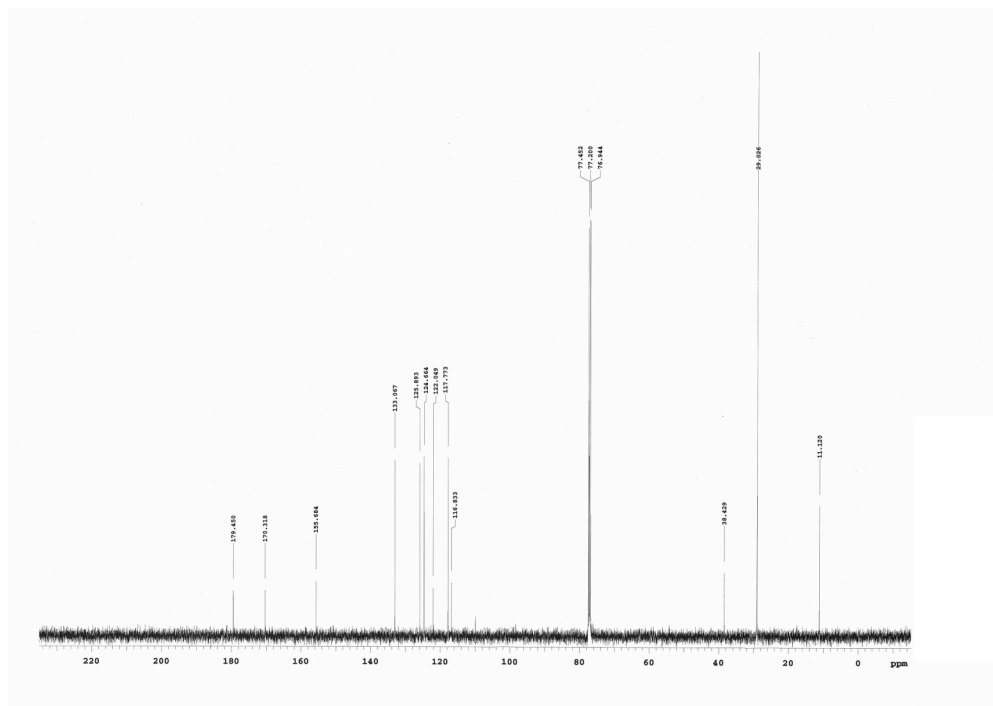
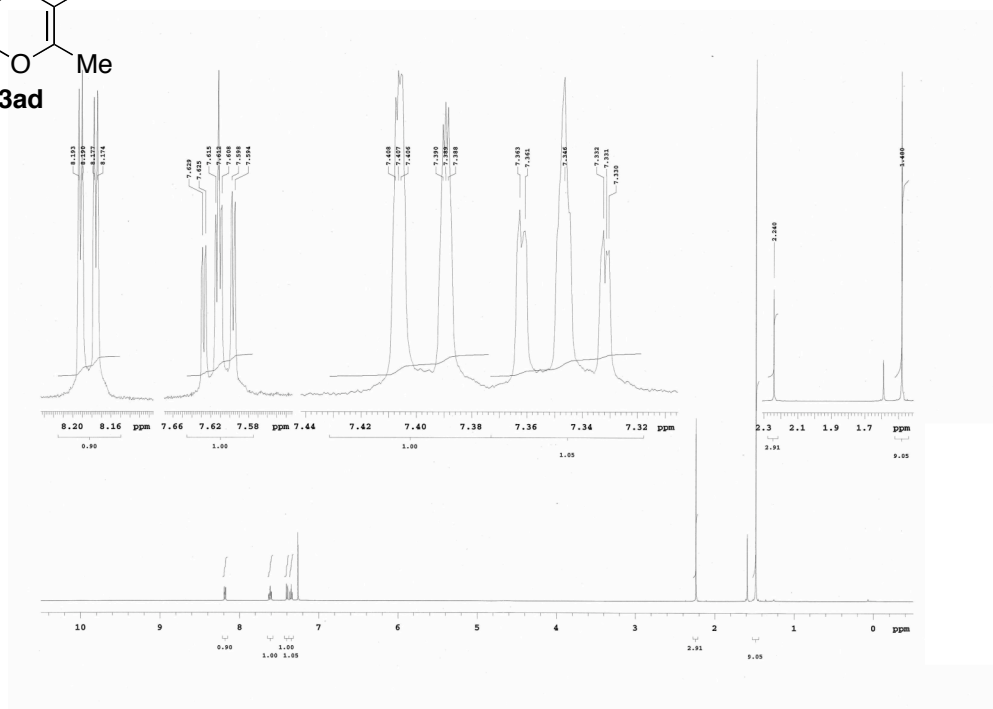
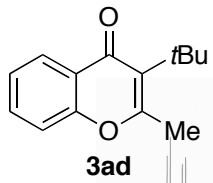


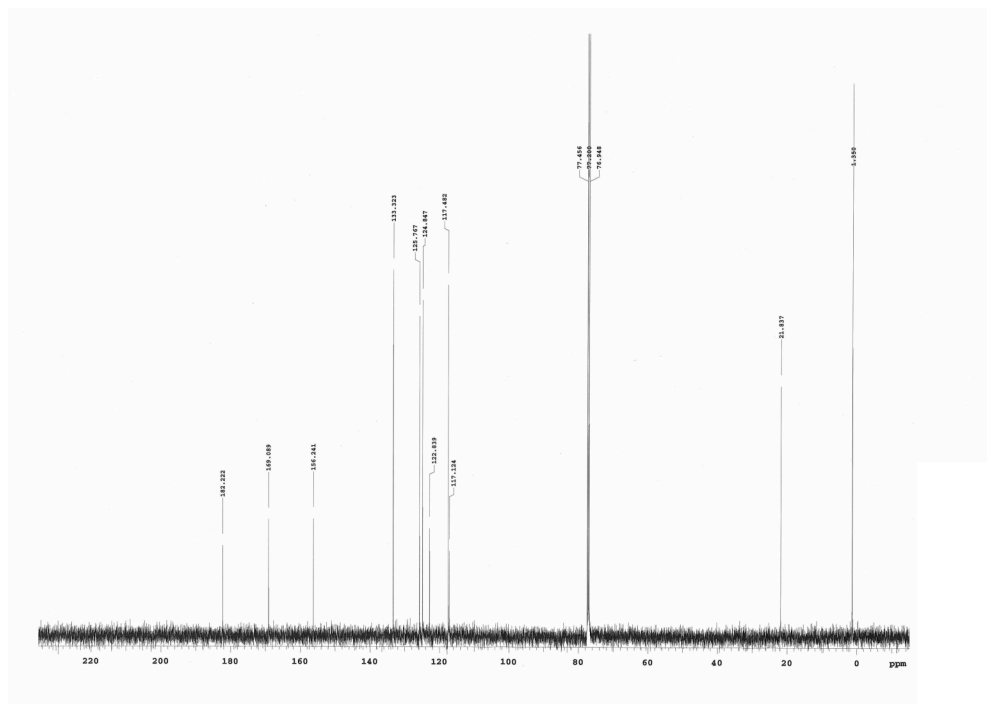
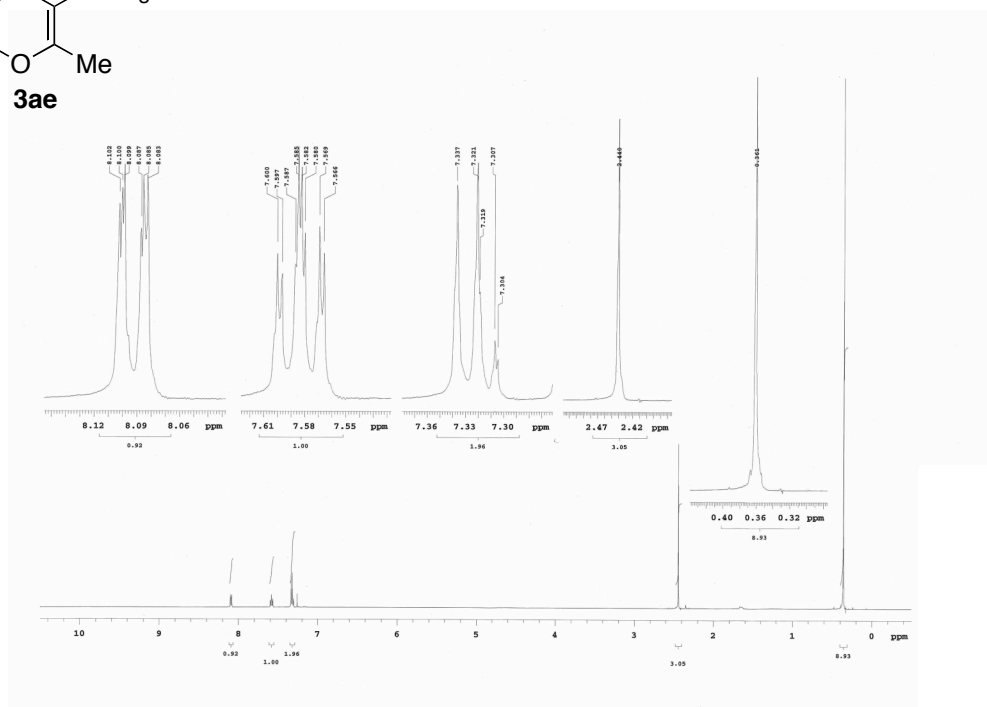
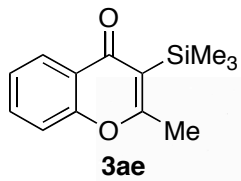


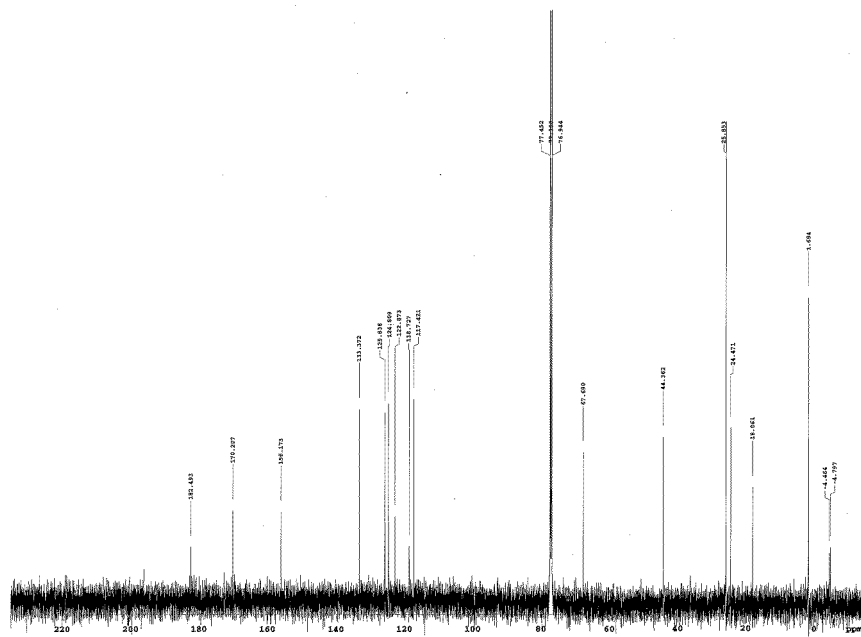
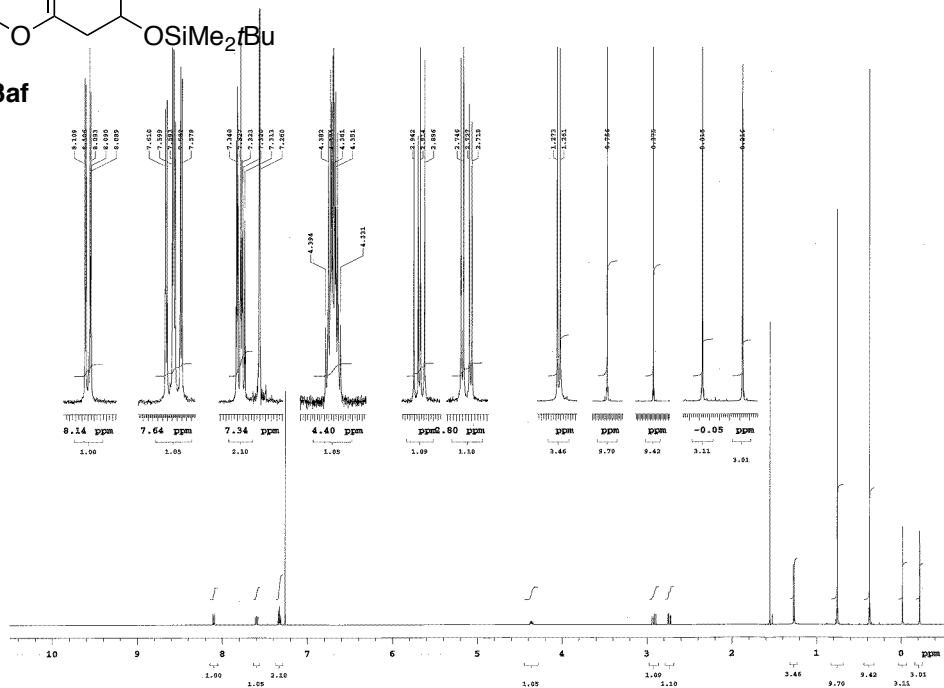
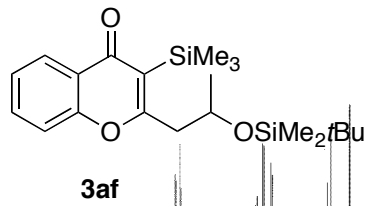
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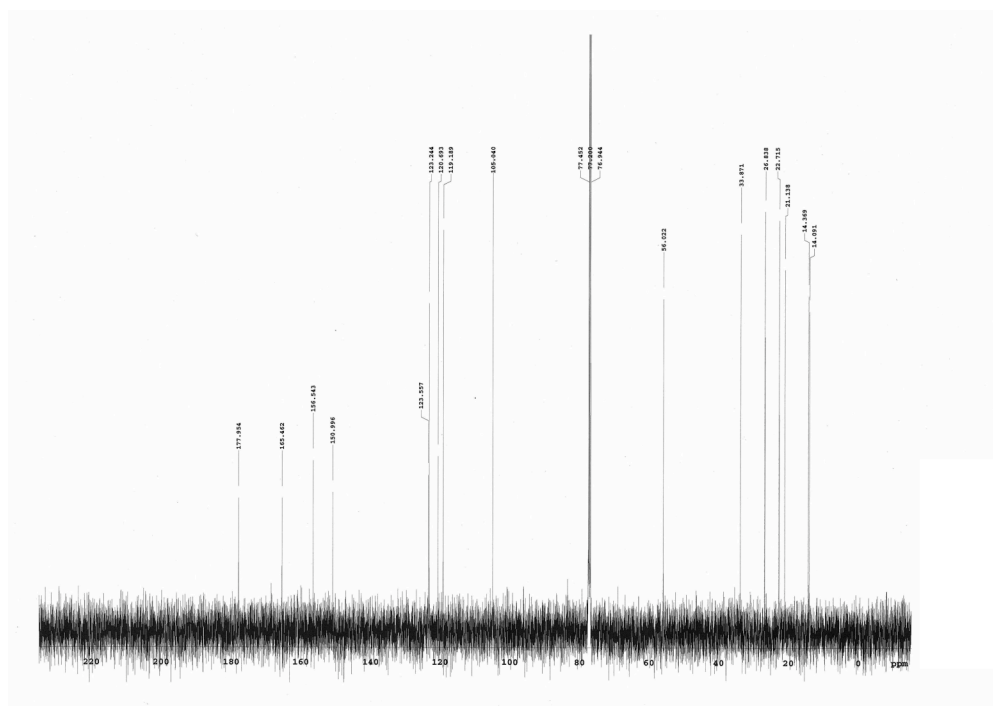
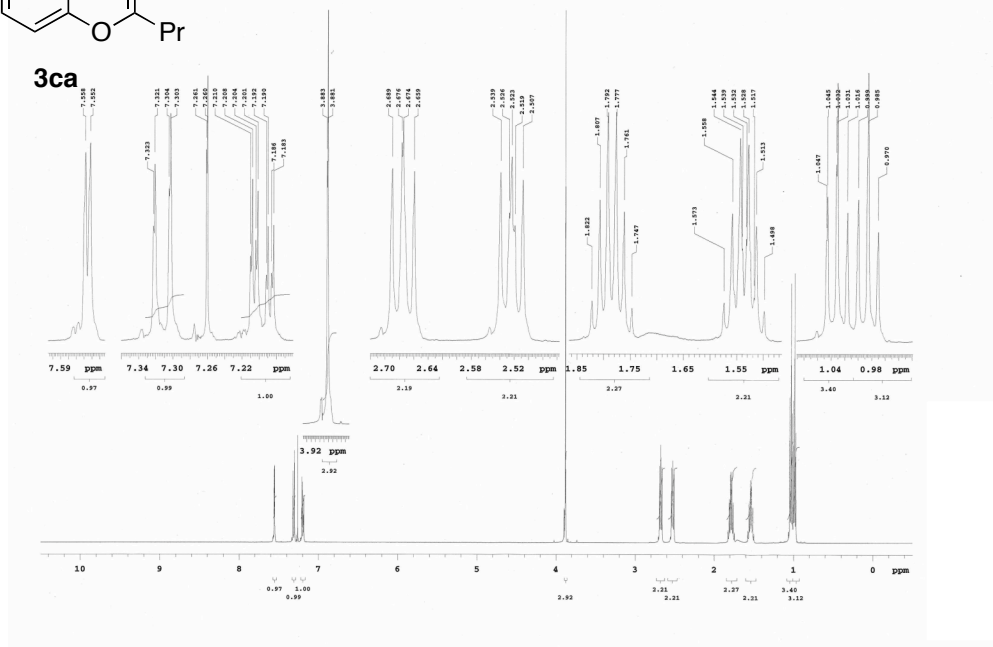
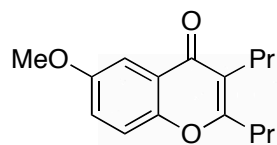


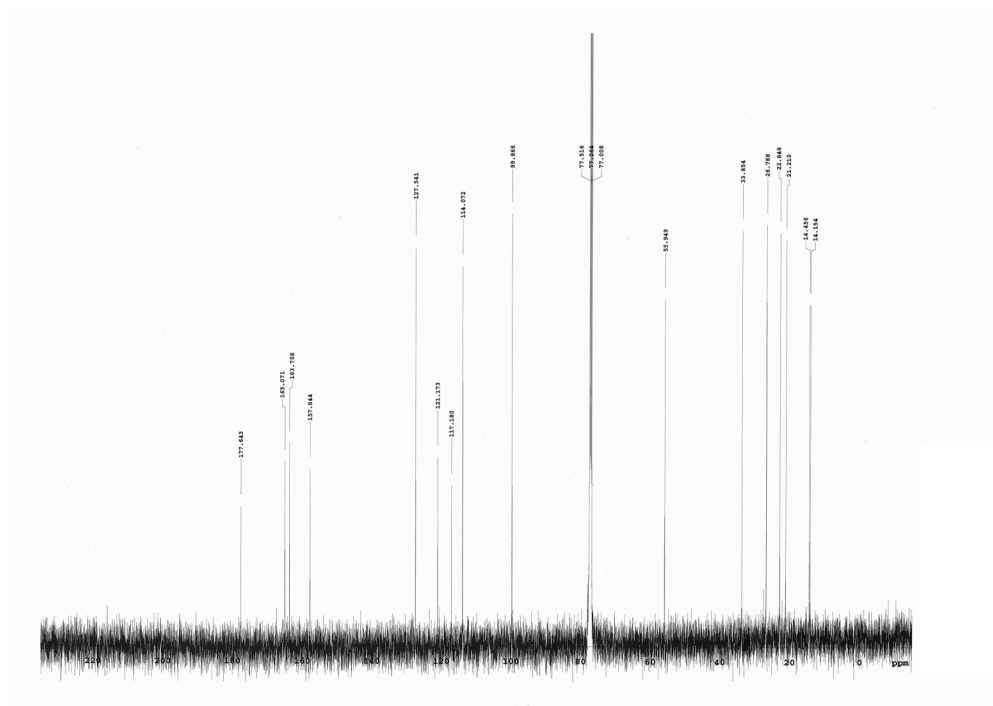
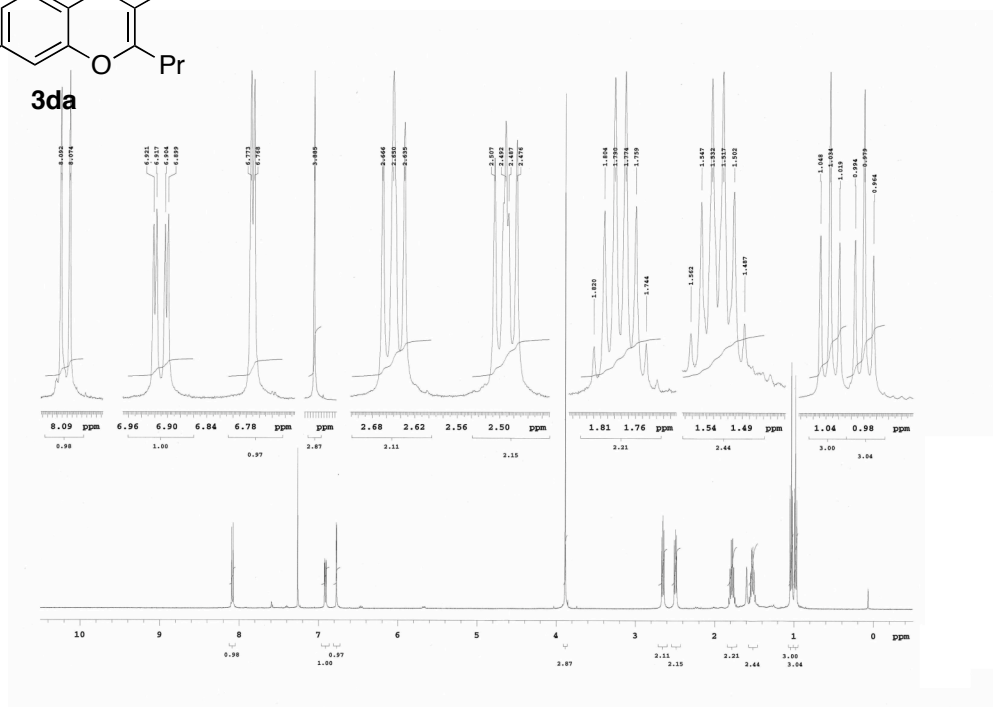
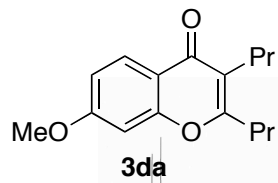


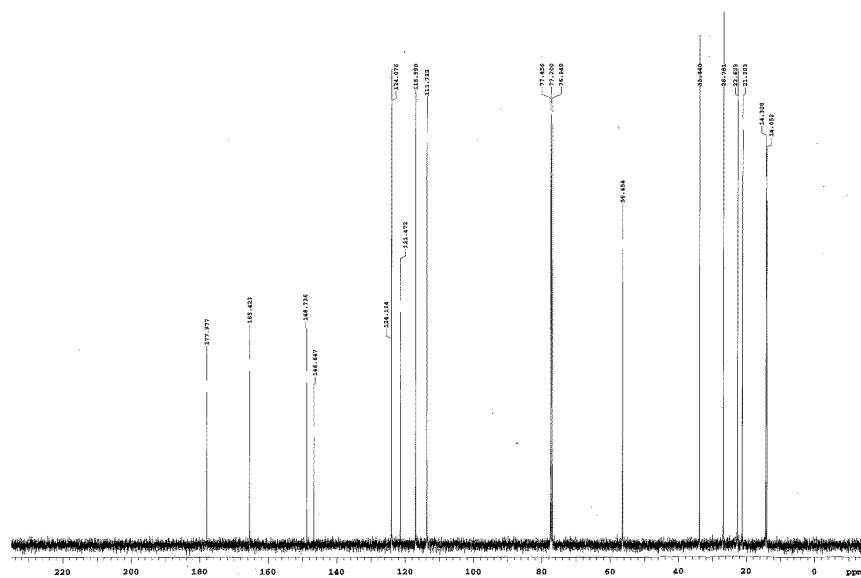
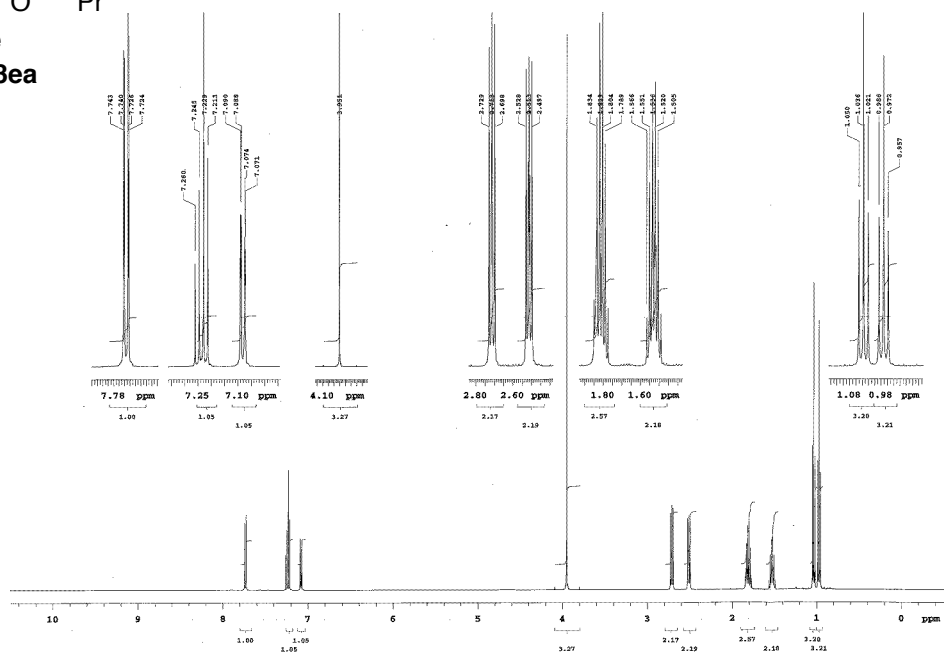
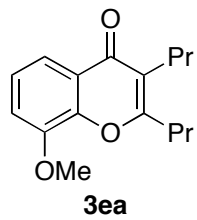


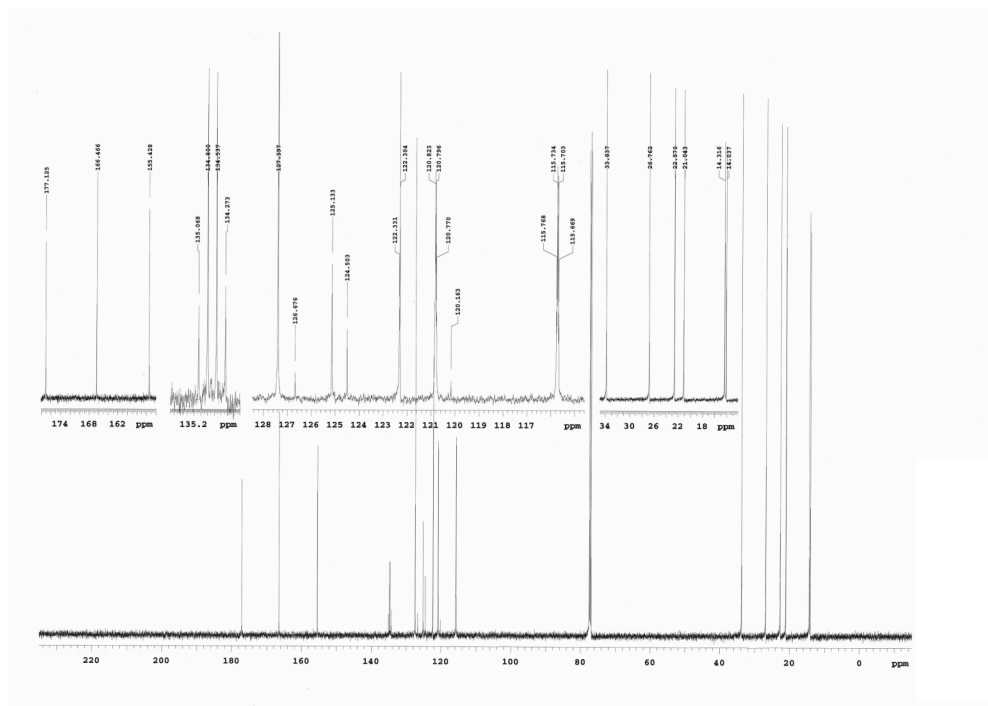
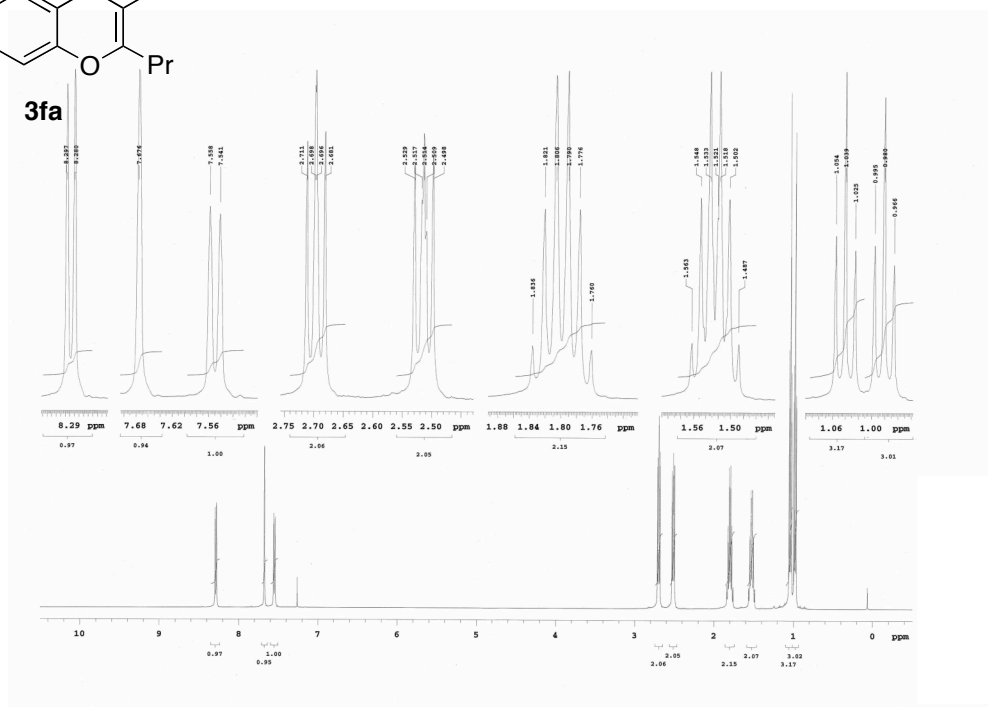
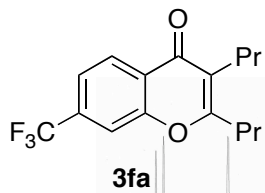


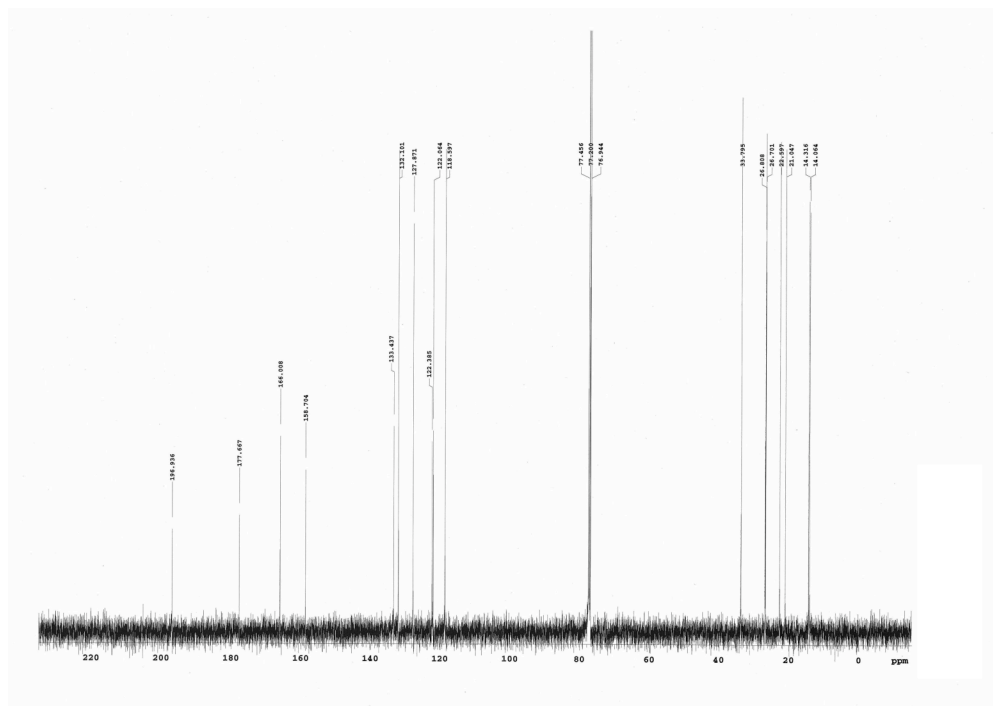
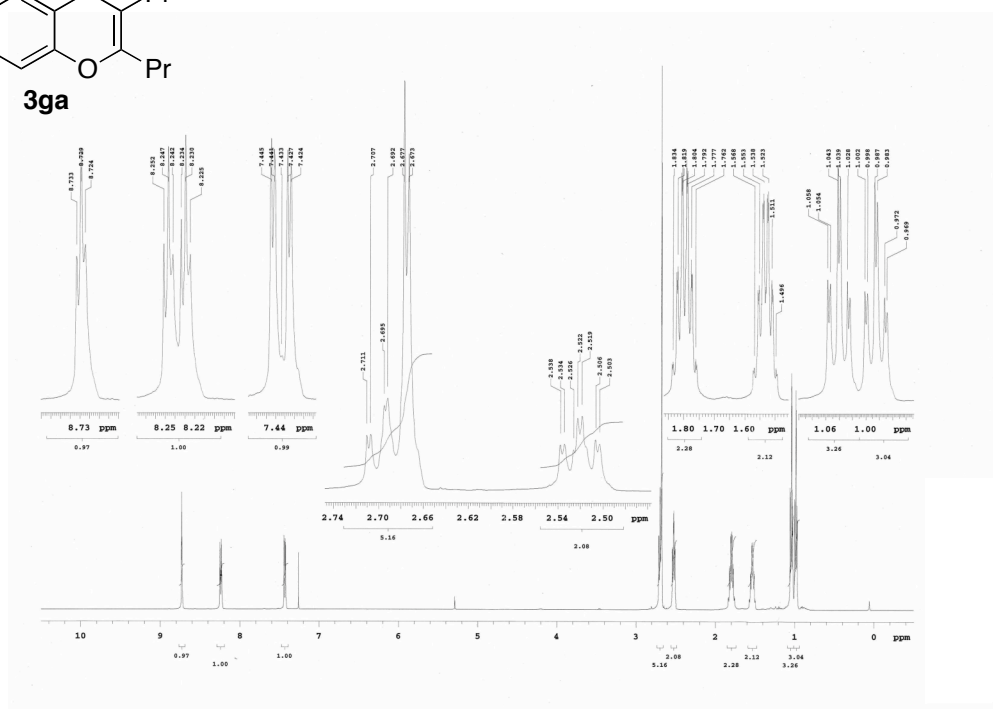
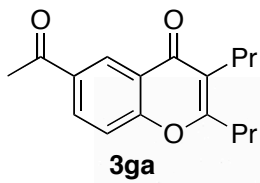




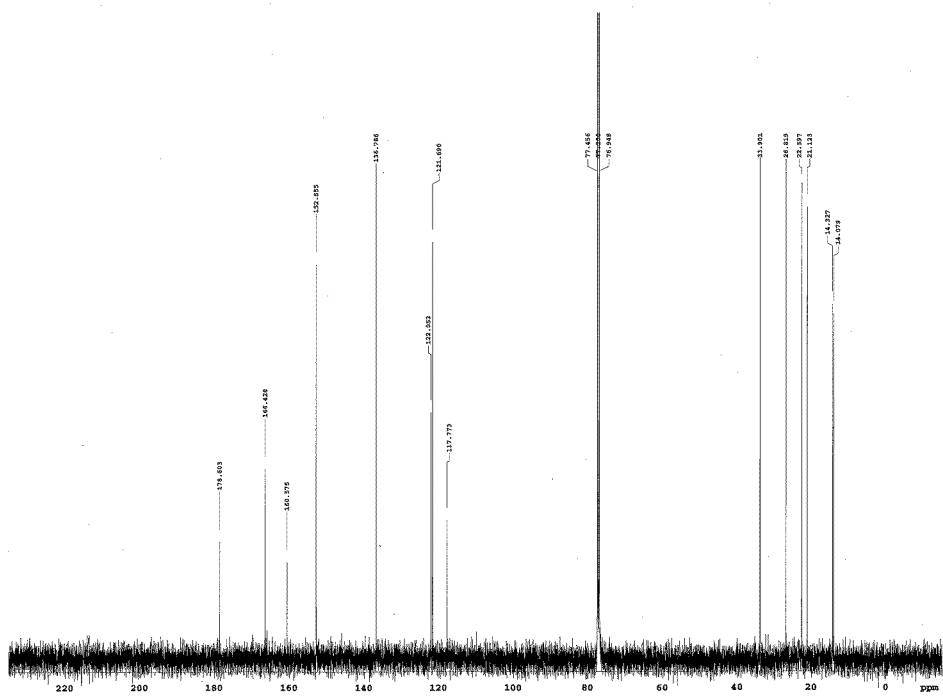
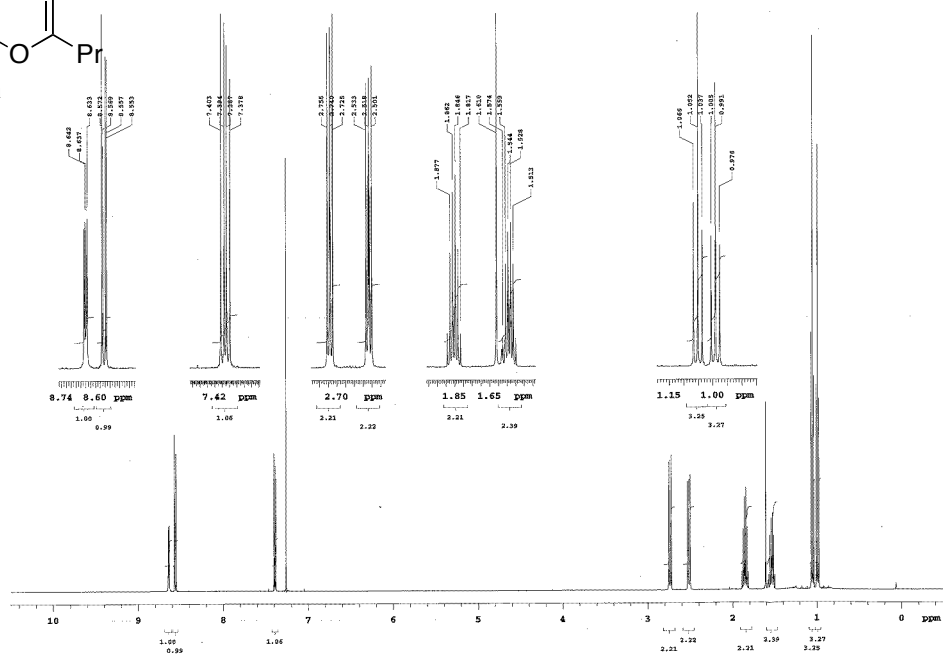
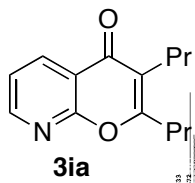


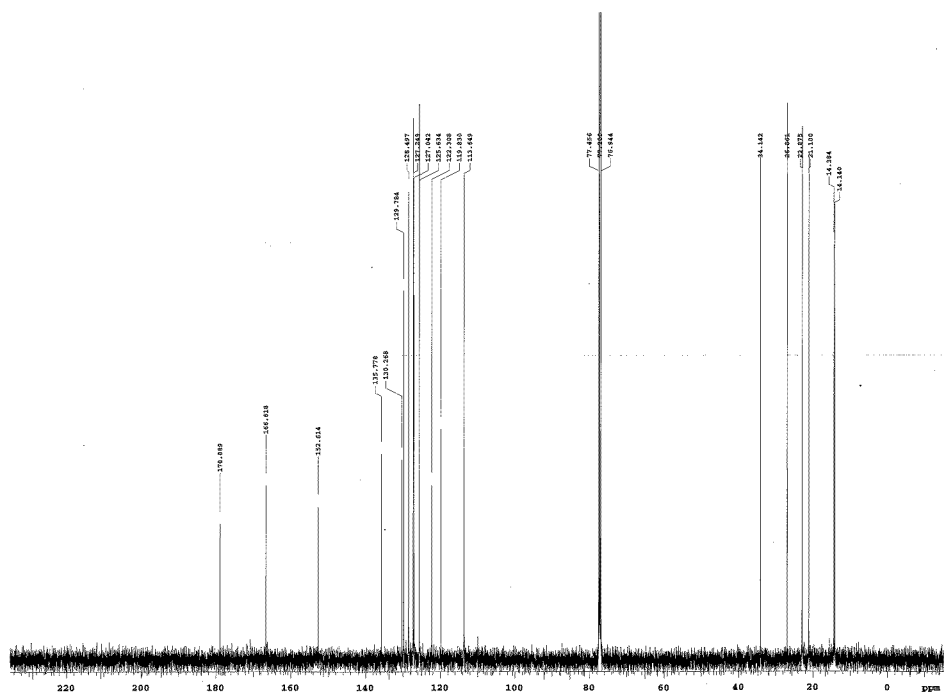
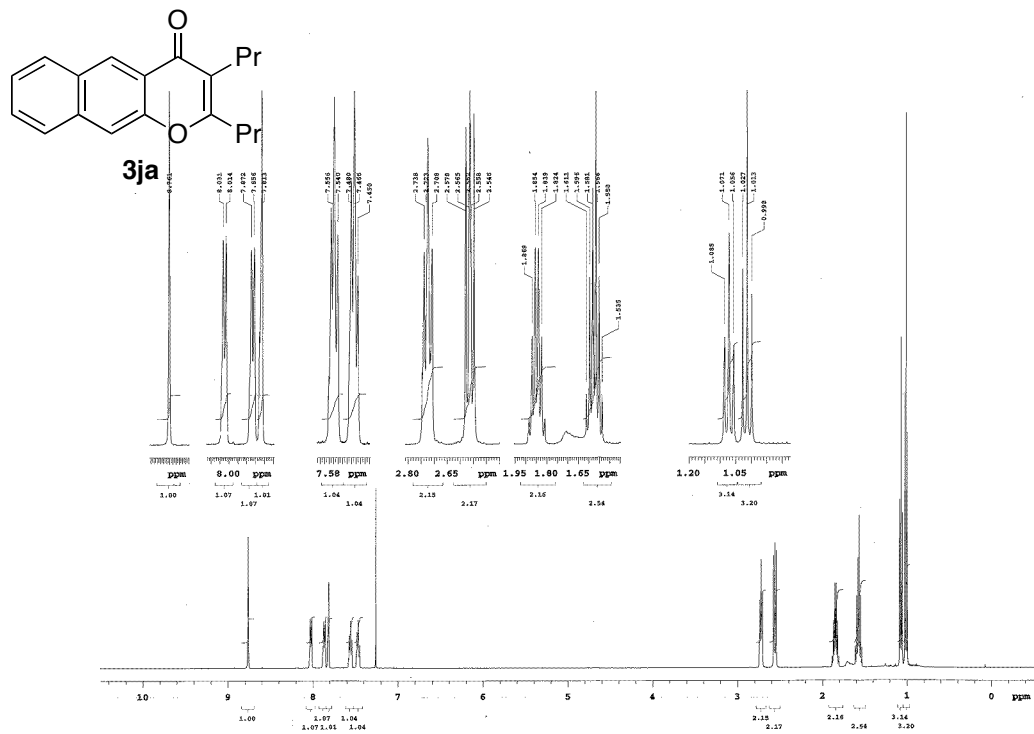












Optimization of the Reaction Conditions

Table S1. Optimization of Leaving Molecule^a

$\text{1} + \text{Pr} \equiv \text{Pr} \xrightarrow[\text{toluene, 120 } ^\circ\text{C, 24 h}]{\text{Ni(cod)}_2 (10 \text{ mol } \%), \text{PCy}_3 (10 \text{ mol } \%), \text{pyridine (100 mol } \%)} \text{3}$

2a (2.0 equiv.)

R ¹	R ²	R ³	3 yield (%) ^b
H	Me	Me	61
MeO	Me	Me	60
CF ₃	Me	Me	99
H	Ph	Ph	99
MeO	Ph	Ph	66
CF ₃	Ph	Ph	99
H	Ph	H	14
H			24

^aAll reactions were carried out using Ni(cod)₂ (10 mol %), PCy₃ (10 mol %), pyridine (100 mol %), **1** (0.5 mmol), and **2** (1.0 mmol) in 2 mL of toluene at 120 °C for 24 h in sealed tube. ^bIsolated yields.

Table S2. Optimization of Amount of Alkyne^a

$\text{1a} + \text{Pr} \equiv \text{Pr} \xrightarrow[\text{toluene, 120 } ^\circ\text{C, 24 h}]{\text{Ni(cod)}_2 (10 \text{ mol } \%), \text{PCy}_3 (10 \text{ mol } \%), \text{pyridine (100 mol } \%)} \text{3aa}$

2a (equive.)	3aa yield (%) ^b
1.0	95
1.5	97
2.0	99
3.0	99

^aAll reactions were carried out using Ni(cod)₂ (10 mol %), PCy₃ (10 mol %), pyridine (100 mol %), **1a** (0.5 mmol), and **2a** in 2 mL of toluene at 120 °C for 24 h in sealed tube. ^bIsolated yields.

References

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