Supplementary Material (ESI) for Chemical Communications
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A Highly Adaptable Catalyst/Substrate System for the Synthesis of Substituted Chromenes

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Supplementary Information

General:

All reactions were carried out under an atmosphere of nitrogen unless otherwise specified. Anhydrous solvents were transferred *via* syringe to flame-dried glassware, which had been cooled under a stream of dry nitrogen. Anhydrous tetrahydrofuran (THF), acetonitrile, ether, dichloromethane, and pentane were dried using a mBraun solvent purification system. Analytical thin layer chromatography (TLC) was performed using 250 μm Silica Gel 60 F254 pre-coated plates (EMD Chemicals Inc.). Flash column chromatography was performed using 230-400 Mesh 60Å Silica Gel (Whatman Inc.). The eluents employed are reported as volume:volume percentages. Melting points were recorded on a MEL-TEMP® capillary melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using Varian Unity Inova 500 MHz and Varian Mercury 300 MHz spectrometers. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or $CDCl_3$ (7.26 ppm). Coupling constants (J) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded using a Varian Unity Mercury 300 spectrometer at 75 MHz. Chemical shift is reported in ppm relative to the carbon resonance of $CDCl_3$ (77.00 ppm). Infrared spectra were obtained on a Perkin Elmer Spectrum RX-1 at 0.5 cm^{-1} resolution and are reported in wave numbers. High resolution mass spectra (HRMS) were obtained by The Mass Spectrometry Core Laboratory of University of Florida, and are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion (M+) or a suitable fragment ion.

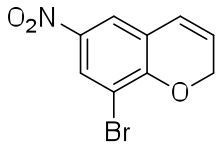
Compounds **6**,[1] **14**,[2] **16**,[3] **22**,[3] **24**,[4] **29**,[5] **31**,[6] **32**,[7] **33**,[8] **34**,[9] and **37**[10] have been described in the literature and when prepared here satisfactorily matched all previously reported data.

Representative procedure for the preparation of substrates

To a solution of salicylaldehyde derivative (1 mmol) in anhydrous THF (5 mL) was added dropwise vinyl magnesium bromide (1.0 M solution in THF, 2.5 mL, 2.5 eq) at -78°C. After TLC analysis indicated a complete conversion, the reaction was quenched with a saturated aqueous solution of NH_4Cl (5 mL) and warmed to room temperature. The crude mixture was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extract was dried over $MgSO_4$, purified by flash chromatography and immediately taken on to the next step.

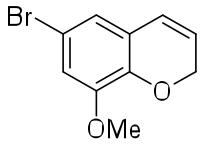
Representative procedure for the Au-catalyzed preparation of 2*H*-chromenes

Anhydrous THF (2.5 mL) was added to an aluminum foil covered, flame dried, flask containing **12** (26.5 mg, 0.05 mmol, 5.0 mol%), **10** (12.3 mg, 0.05 mL, 5.0 mol%), and activated 4 Å MS (80 mg). The heterogeneous mixture was vigorously stirred for 10 min and a solution of the corresponding *o*-(1-hydroxyallyl)phenol (1 mmol) in THF (2.5 mL) was added. The mixture was then immediately heated to reflux by immersing into an oil bath that has been preheated to 70°C. After TLC analysis indicated a complete reaction, the mixture was filtered through a short plug of silica with CH_2Cl_2 (4 mL). The solution of the crude product was concentrated in *vacuo*, and purified by flash chromatography (5% EtOAc/hexanes or 100% hexanes).



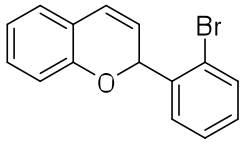
8-bromo-6-nitro-2H-chromene (18)

Pale yellow solid; mp 130-133 °C; R_f = 0.75 (20% EtOAc/hexanes); IR (neat) 3090, 2919, 1507, 1471, 1347, 1265, 1097, 902, 741, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.25 (d, J = 2.5 Hz, 1H), 7.78 (d, J = 2.5 Hz, 1H), 6.42 (dt, J = 10.0, 2.0 Hz, 1H), 5.91 (dt, J = 10.0, 3.3 Hz, 1H), 5.14 (dd, J = 3.3, 2.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 141.9, 128.8, 124.3, 122.9, 122.6, 121.1, 109.9, 67.9; HRMS (ESI) Calcd for $C_9H_7BrNO_3$ $(M+H)^+$: 255.9609; found 255.9599.



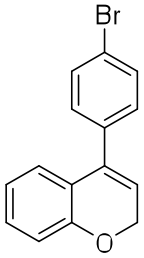
6-bromo-8-methoxy-2*H*-chromene (20)

Colorless oil; R_f = 0.64 (10% EtOAc/hexanes); IR (neat) 2917, 2849, 1567, 1480, 1271, 1215, 1033, 845 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.87 (d, J = 2.0 Hz, 1H), 6.75 (d, J = 2.0 Hz, 1H), 6.33 (dt, J = 10.0, 2.0 Hz, 1H), 5.82 (dt, J = 10.0, 3.5 Hz, 1H), 4.88 (dd, J = 3.5, 2.0 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.7, 142.1, 124.4, 123.8, 123.3, 121.7, 115.4, 113.0, 66.0, 56.5; HRMS (ESI) Calcd for $C_{10}H_8BrO_2$ $(M-H)^+$: 238.9708; found 238.9713.



2-(2-bromophenyl)-2*H*-chromene (28)

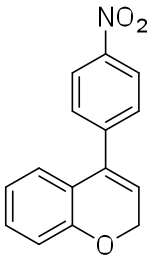
Colorless oil; R_f = 0.15 (hexanes); IR (neat) 1684, 1653, 1560, 1507, 1457, 1227, 1203, 1112, 1020, 748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.61 (dd, J = 8.0, 1.5 Hz, 1H), 7.57 (dd, J = 8.0, 1.0 Hz, 1H), 7.30 (ddt, J = 7.8, 1.5, 0.5 Hz, 1H), 7.15 (m, 2H), 7.00 (dd, J = 7.5, 1.5 Hz, 1H), 6.87 (dt, J = 7.5, 1.0 Hz, 1H), 6.82 (dd, J = 8.0, 0.5 Hz, 1H), 6.51 (ddd, J = 10.0, 2.0, 0.5 Hz, 1H), 6.33 (dd, J = 3.5, 2.5, 1H), 5.79 (dd, J = 10.0, 3.5, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 140.2, 133.1, 129.8, 129.8, 128.9, 128.1, 126.9, 124.3, 124.0, 121.7, 121.6, 121.2, 116.0, 76.4; HRMS (ESI) Calcd for $C_{15}H_{12}BrO$ $(M+H)^+$: 287.0072; found 287.0078.



4-(4-bromophenyl)-2*H*-chromene (35)

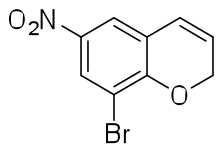
Colorless oil; R_f = 0.55 (5% EtOAc/hexanes); IR (neat) 3047, 2964, 2832, 1481, 1447, 1222, 1114, 1066, 1011, 805, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 7.16 (dt, J = 7.8, 2.0 Hz, 1H), 6.89 (m, 3H), 5.78 (t, J = 4.0 Hz, 1H), 4.83 (d, J = 4.0 Hz,

2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 137.4, 136.4, 131.8, 130.5, 129.7, 125.8, 123.5, 122.0, 121.5, 120.5, 116.5, 65.3; HRMS (ESI) Calcd for $C_{15}H_{11}BrO$ $(M)^+$: 285.9993; found 285.9999.



4-(4-nitrophenyl)-2*H*-chromene (36)

Yellow solid; mp 88-92 °C; R_f = 0.35 (10% EtOAc/hexanes); IR (neat) 2849, 1597, 1516, 1484, 1346, 1224, 853, 761, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 7.0 Hz, 2H), 7.52 (d, J = 7.0 Hz, 2H), 7.20 (dt, J = 7.0, 2.0 Hz, 1H), 6.90 (m, 3H), 5.91 (t, J = 4.0 Hz, 1H), 4.88 (d, J = 4.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 145.2, 135.9, 130.2, 129.7, 125.6, 124.0, 122.8, 122.2, 121.7, 116.8, 100.0, 65.2; HRMS (ESI) Calcd for $C_{15}H_{12}NO_3$ $(M+H)^+$: 254.0817; found 254.0814.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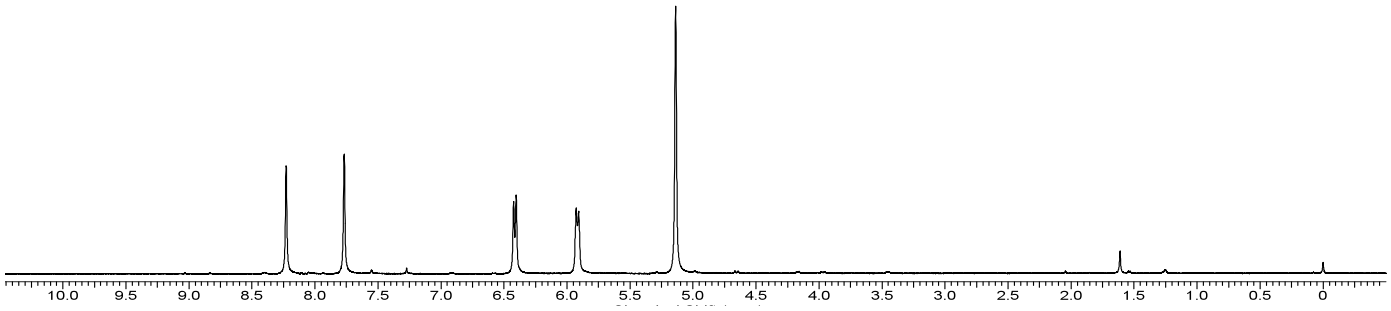
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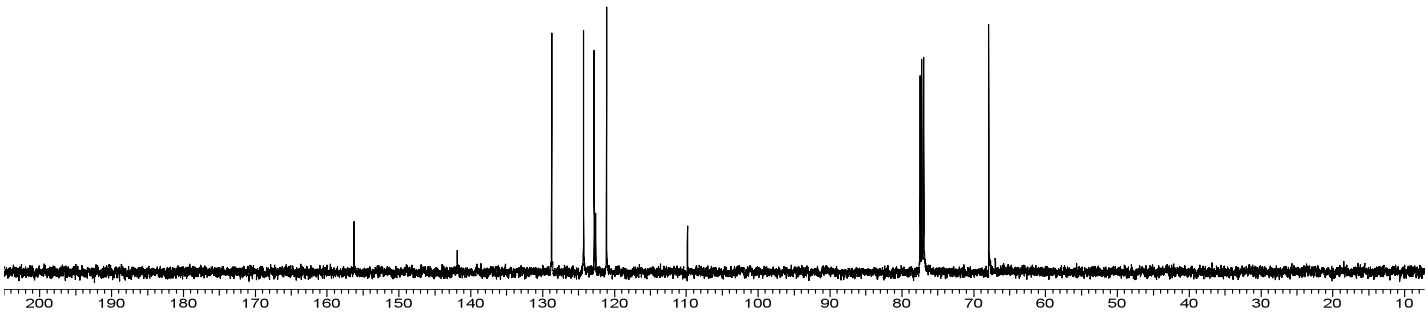
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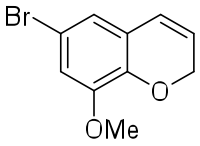

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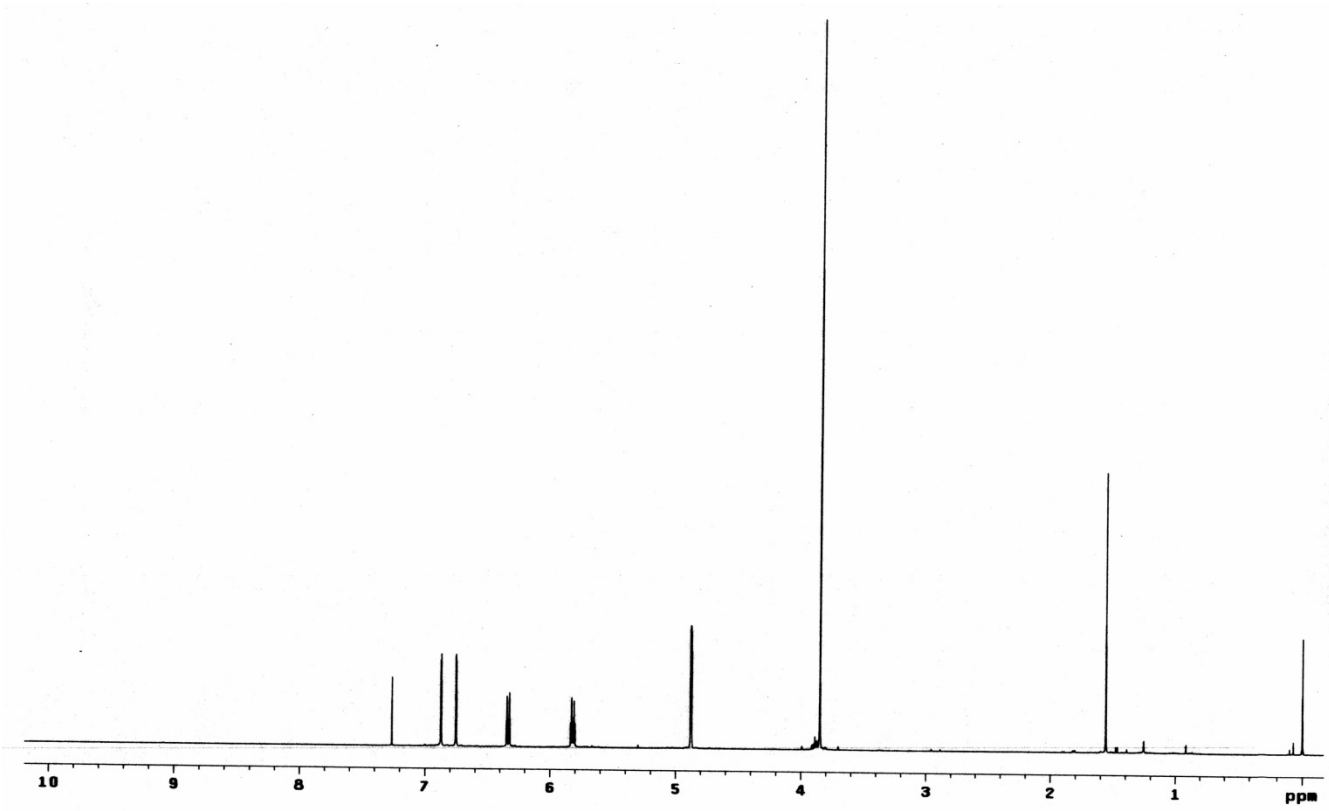

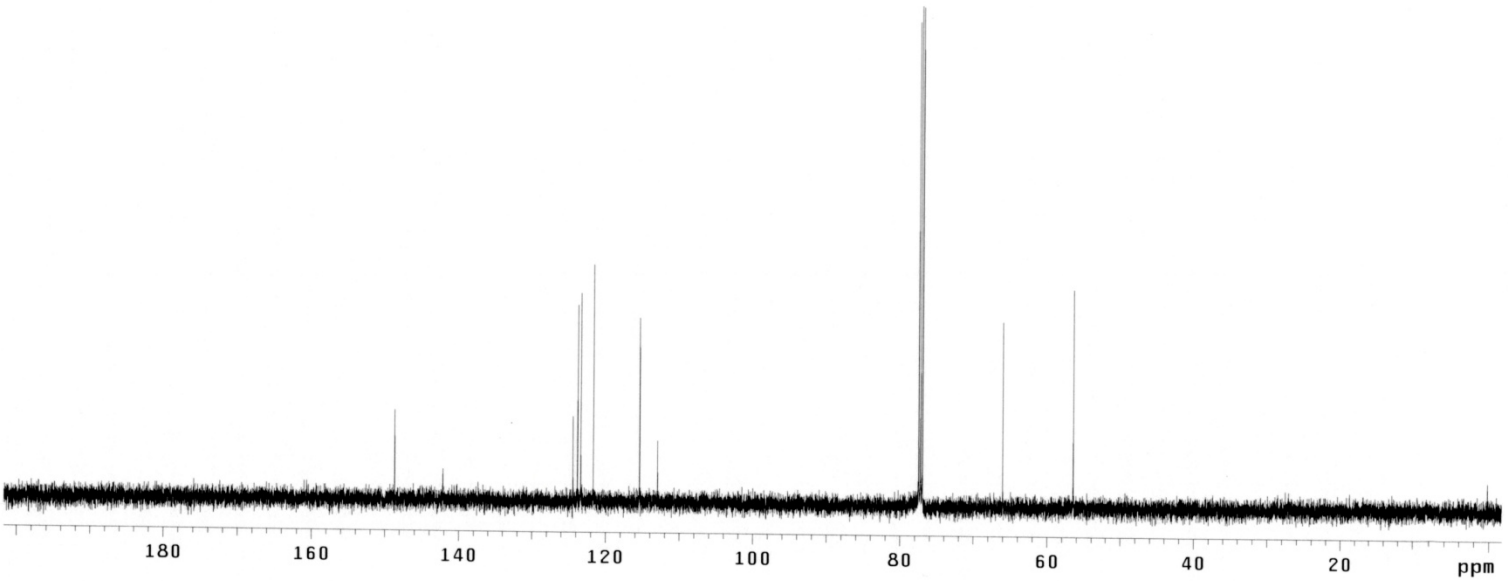

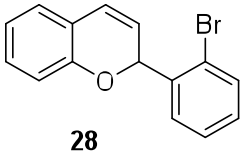

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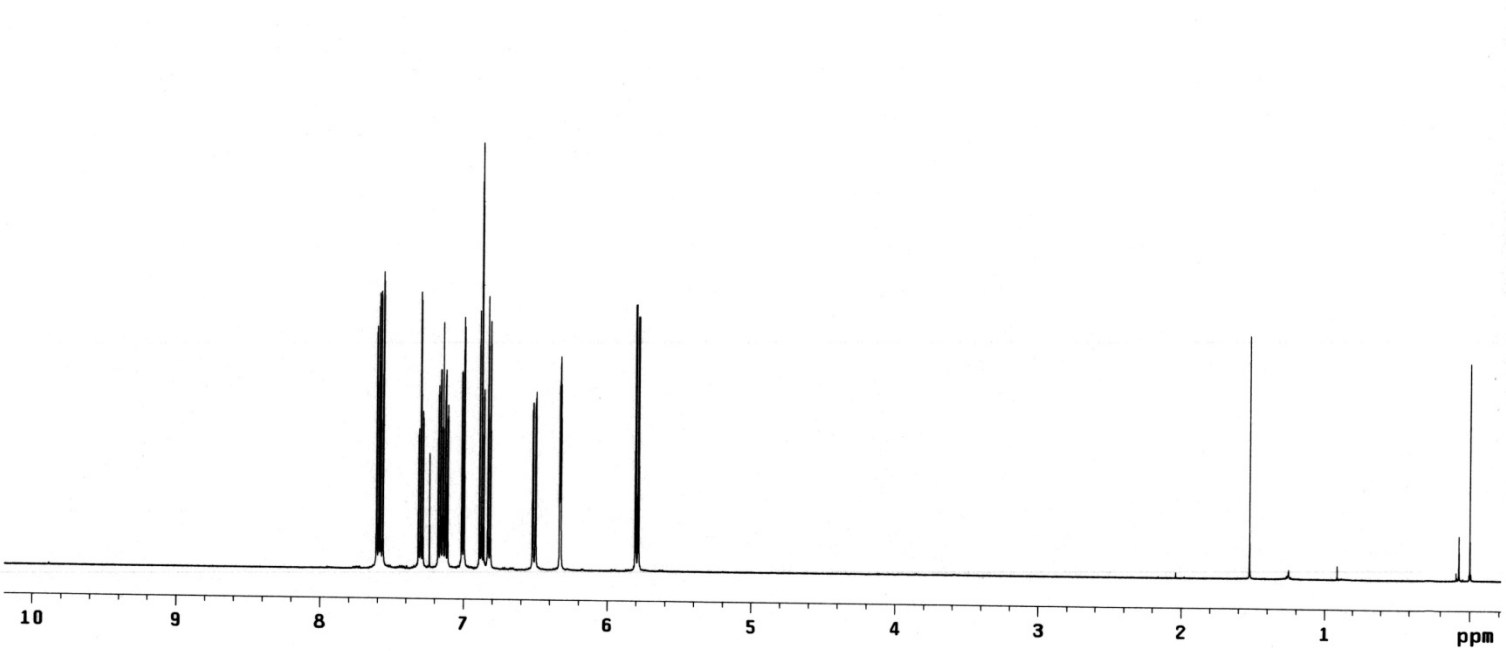

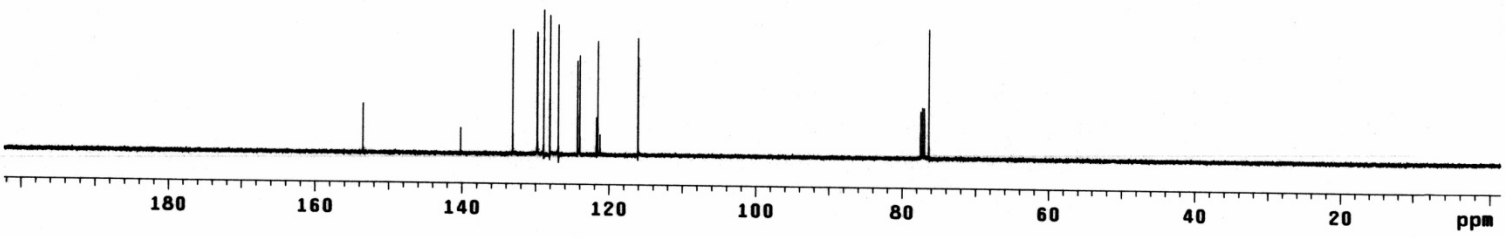

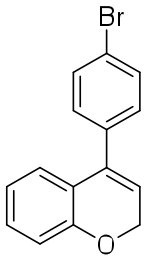

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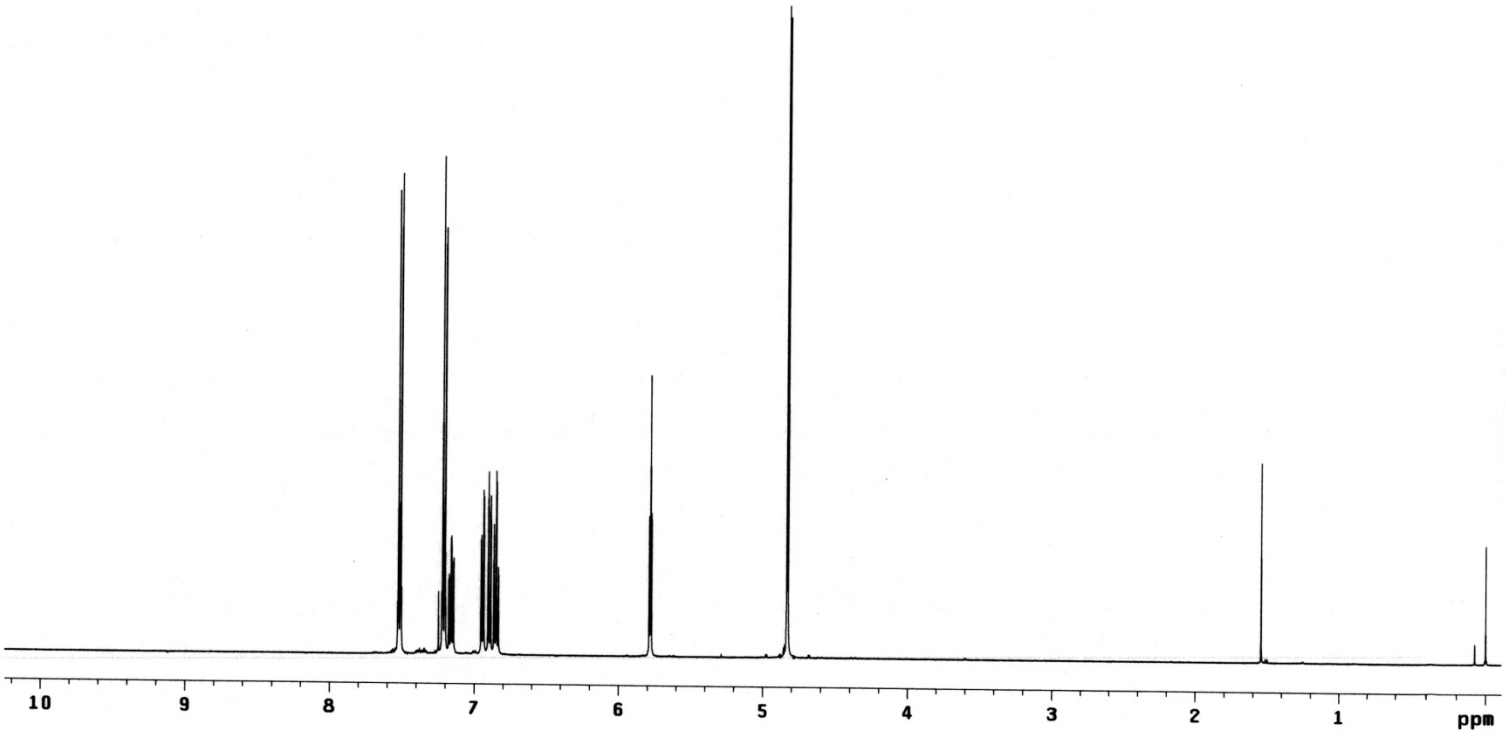

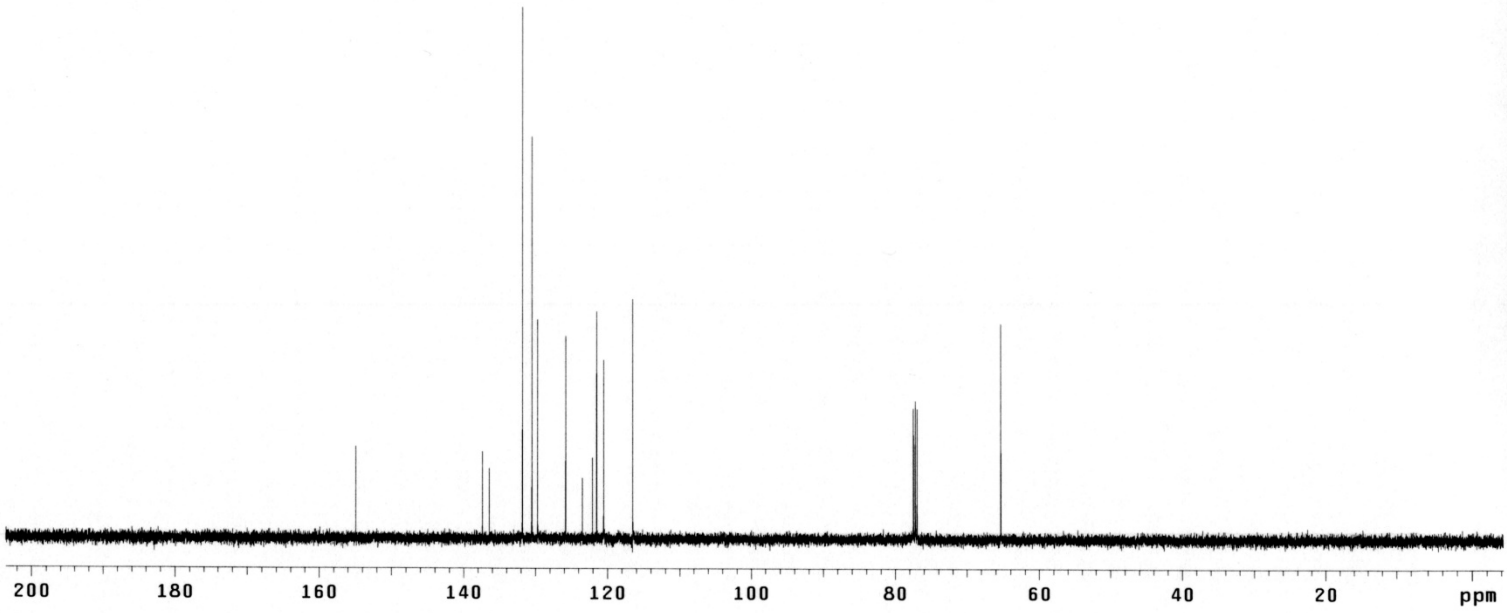

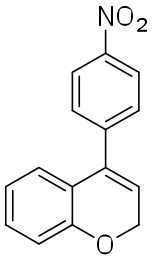

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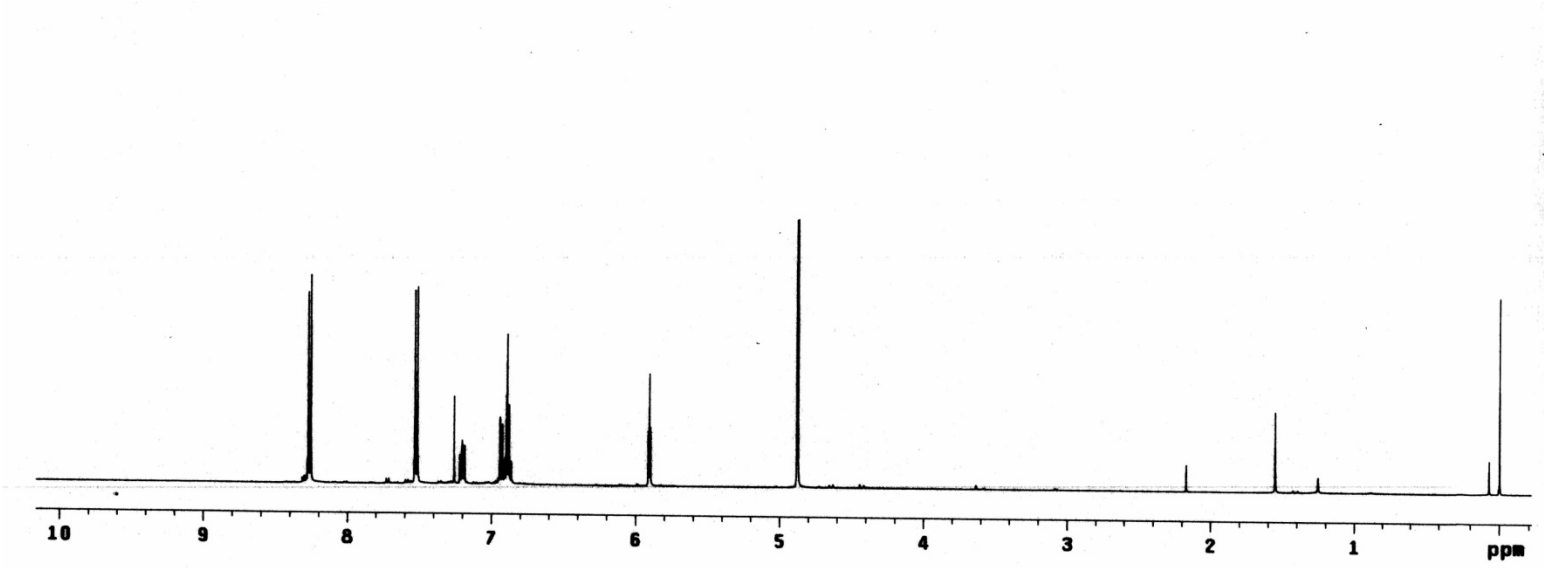

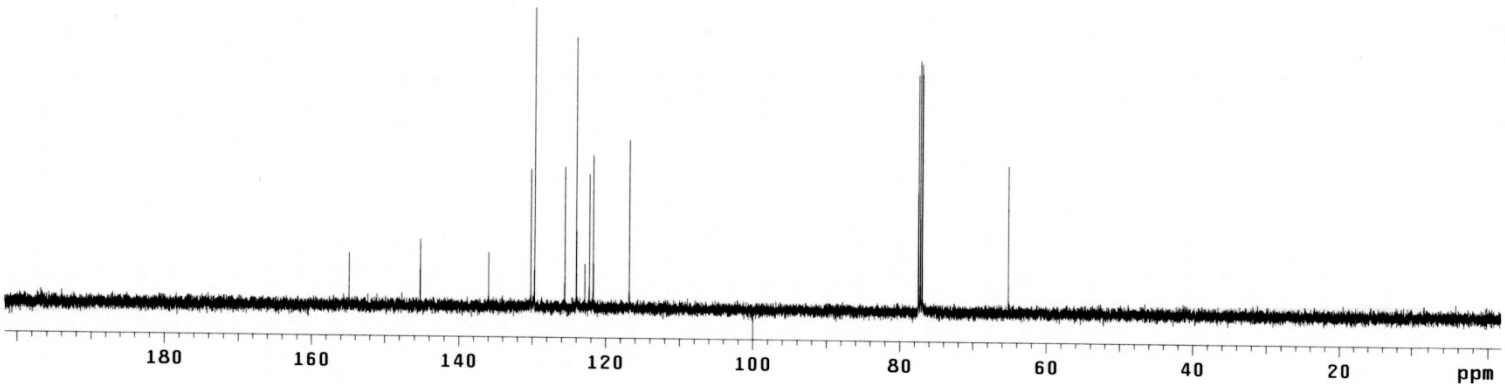

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