Supporting Information for:

Alcohol-Assisted Phosphine Catalysis: One-Step Syntheses of Dihydropyrones from Aldehydes and Allenoates

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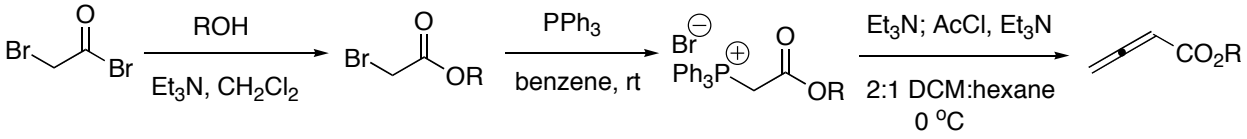
General Information: All reactions were performed under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dichloromethane was freshly distilled from CaH_2. All other anhydrous solvents were packaged in Sure/Seal™ bottles and used as received from Aldrich; chloroform was distilled from calcium chloride immediately prior to use. All aldehydes were purchased from Aldrich or Acros Organics. The liquid aldehydes were washed sequentially with saturated sodium bicarbonate and saturated sodium chloride and then distilled prior to use. Solid aldehydes were dissolved in dichloromethane, washed with saturated sodium bicarbonate, recrystallized from hexanes/ethyl acetate, and dried under vacuum over phosphorus pentoxide. All other reagents were used as received from commercial sources, with the halogenated alcohols stored over 4Å molecular sieves. Reactions were monitored through thin-layer chromatography (TLC) on 0.25-mm Silicycle silica gel plates (TLG-R10011B-323), visualized under UV light or with a permanganate or anisaldehyde stain. Flash column chromatography was performed using Silicycle Silia-P gel (50-μm particle size, R12030B) under compressed air. IR spectra were recorded on a Perkin–Elmer Paragon1000 FT-IR spectrometer. NMR spectra were obtained using a Bruker Avance-500 or AV-300 instrument calibrated to residual non-deuterated chloroform as the internal reference (7.26 ppm for ^{1}H NMR; 77.00 ppm for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift, multiplicity, and coupling constant (Hz) in the case of J_{CF} coupling. The following abbreviations are used to describe the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; app, apparent. Matrix-assisted laser desorption/ionization (MALDI) mass spectra were recorded using dihydroxybenzoic acid (DHB) as matrix and an Applied Biosystems Voyager-DE STR instrument operated in reflector mode with internal calibration to matrix at an accelerating voltage of 20 kV. An Agilent 6890N mass spectrometer

and an HP5 column were used for GC-MS analysis.

Allenoate Preparation

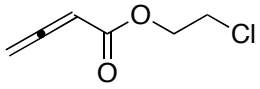
Methyl 2,3-butadienoate, isopropyl 2,3-butadienoate, and 2-fluoroethyl 2,3-butadienoate are known compounds prepared using a four-step procedure starting from bromoacetyl bromide and the corresponding alcohols; a Scheme, slightly modified from the published procedure, is outlined below.[1] Ethyl 2,3-butadienoate was prepared from ethyl bromoacetare, following published procedures. Spectral data for the new compound, 2-chloroethyl allenoate, is provided below.



General Procedure for the Preparation of 2,3-Butadienoates: As an example, the synthesis of 2-chloroethyl 2,3-butadienoate is described. Bromoacetyl bromide (38.0 mL, 0.435 mol) was added over 2 h to a solution of 2-chloroethyl alcohol (20.1 mL, 0.300 mol) and triethylamine (41.8 mL, 0.300 mol) in dichloromethane (500 mL) at 0 °C. The reaction mixture turned to a rust-red color upon addition of the bromide, and a white solid precipitated out. After stirring overnight, the reaction was quenched with water (200 mL); the organic phase was separated and extracted with water (200 mL). The organic phase was then dried (sodium sulfate) and the ester purified through vacuum distillation to give a colorless oil (47.03 g, 0.233 mol, 78%). The bromoester was dissolved in benzene (500 mL) and triphenylphosphine (61.231 g, 0.233 mol) was added. The reaction mixture was vigorously stirring at room temperature and monitored (TLC) for the disappearance of the bromide. The resulting white precipitate was filtered off and washed with benzene to give the phosphonium salt (102.7 g, 0.222 mol, 95%). Residual benzene was removed under vacuum in a 1-L round-bottom flask; a mixture of dichloromethane and hexane (2:1, 600 mL) was added, the flask was cooled in an ice bath at 0 °C, and then triethylamine (33.95 mL, 0.244 mol) was added. The mixture was stirred for 2 h, at which point

[1] (a) Zhu, X.-F.; Henry, C. E.; Wang, J.; Dudding, T.; Kwon, O. *Org. Lett.* **2005**, *7*, 1387. (b) Harvey, G. R.; Ratts, K. W. *J. Org. Chem.* **1966**, *31*, 3907. (c) Andrews, S. D.; Day, A. C.; Inwood, R. N. *J. Chem. Soc. Section C: Organic*, **1969**, 2443.

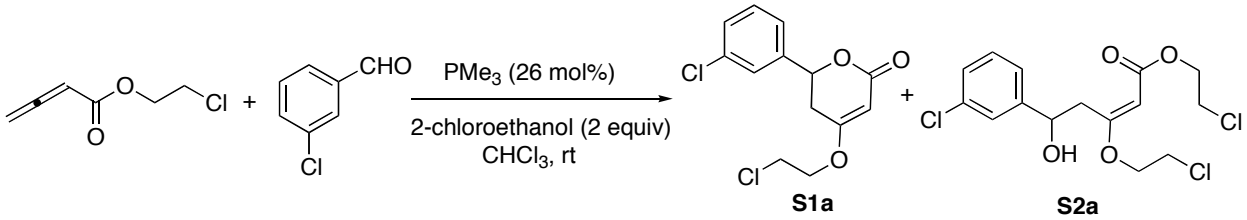
triethylamine (33.95 mL, 0.244 mol) was added, followed by the addition of acetyl chloride (17.3 mL, 0.244 mol) over 2 h. The reaction mixture was stirred in its ice bath overnight. The copious precipitate was filtered and rinsed with a mixture of hexane and dichloromethane (3:1). The resulting crude allenoate solution was concentrated to 200 mL; the additional solid precipitate was filtered off after the addition of hexane (200 mL). The resulting solution was concentrated at room temperature and the residue distilled (60 mmHg) to give the allenoate (10.49 g, 0.072 mol).



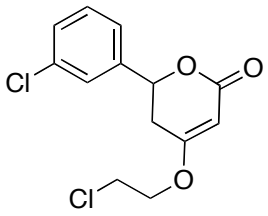
2-Chloroethyl 2,3-Butadienoate. Colorless liquid (23.9% overall yield); IR (neat) ν_{max} 1970, 1941, 1712, 1339, 1304, 1246, 1161, 854 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.61 (t, *J* = 6.5 Hz, 1H), 5.20 (d, *J* = 6.5 Hz, 2H), 4.33 (t, *J* = 5.8 Hz, 2H), 3.64 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.1, 165.2, 87.4, 79.6, 64.4, 41.4; MS (GC-MS) calcd for $C_6H_8O_2Cl^+$ $[M + H]^+$ 147.02, found 147.10.

Formation of Dihydropyrone in the Presence of Alcohols (Without *n*-Butyllithium)

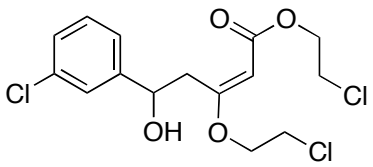
As an example, the experimental procedure for the reaction of 3-chlorobenzaldehyde with 2-chloroethyl 2,3-butadienoate in chloroform is described.



Dry chloroform (10 mL), neat 3-chlorobenzaldehyde (570 μL, 5.0 mmol), 2-chloroethanol (130 μL, 2.0 mmol), and trimethylphosphine (27 μL, 0.26 mmol) were added sequentially to a flame-dried flask under an argon atmosphere. Using a 250-μL syringe, 2-chloroethyl 2,3-butadienoate (146.6 mg, 1.0 mmol) was added dropwise to the mixture over 30 min. The orange-red solution obtained was stirred at room temperature until TLC (EtOAc/hexanes, 1:4; permanganate stain) indicated complete consumption of the allenoate. The reaction mixture was concentrated and the residue purified through flash column chromatography on silica gel (33–50% EtOAc in hexanes) to give **S1a** (95.4 mg, 33.2%) and **S2a** (29 mg, 7.8%).

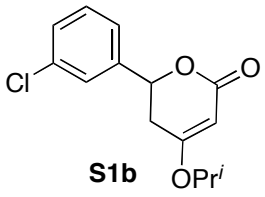


S1a **4-(2-Chloroethoxy)-6-(3-chlorophenyl)-5,6-dihydro-2*H*-pyran-2-one.** White solid (33%); m.p. 94 °C; IR (neat) ν_{max} 1712, 1626, 1406, 1374, 1223, 1184, 1075, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.29–7.36 (m, 3H), 5.40 (dd, *J* = 12, 4.2 Hz, 1H), 5.21 (d, *J* = 1.5 Hz, 1H), 4.17 (td, *J* = 5.4, 2.7 Hz, 2H), 3.77 (t, *J* = 5.4 Hz, 2H), 2.80 (ddd, *J* = 17.1, 12, 1.5 Hz, 1H), 2.64 (dd, *J* = 17.1, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 166.1, 140.1, 134.7, 130.1, 128.8, 126.2, 124.1, 91.6, 76.2, 68.8, 40.9, 34.8; MS (MALDI-TOF) calcd for $C_{13}H_{13}O_3Cl_2^+$ $[M + H]^+$ 287.02, found 287.04.

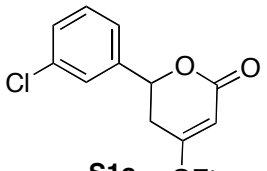


S2a **(*E*)-2-Chloroethyl 3-(2-Chloroethoxy)-5-(3-chlorophenyl)-5-hydroxypent-2-enoate.** Yellowish oil (7.8%); IR (neat) ν_{max} 1711, 1619, 1431, 1302, 1197, 1139, 1079, 1044 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.27–7.30 (m, 3H), 5.19 (s, 1H), 5.01 (dd, *J* = 9, 3.6 Hz, 1H), 4.37 (t, *J* = 5.7 Hz, 2H), 4.03 (t, *J* = 5.4 Hz, 2H), 3.66–3.72 (m, 4H), 3.26 (dd, *J* = 13.8, 9 Hz, 1H), 3.05 (dd, *J* = 13.7, 3.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 168.2, 146.0, 134.3, 129.7, 127.6, 125.8, 123.8, 93.7, 72.2, 68.3, 64.0, 42.0, 41.8, 41.0; MS (MALDI-TOF) calcd for $C_{15}H_{17}O_4Cl_3Na^+$ $[M + Na]^+$ 389.01; found 388.99.

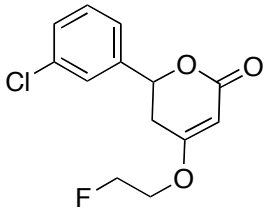
Spectral data for all additional dihydropyrones **S1** and three-component coupling products **S2** are provided below.



S1b **6-(3-Chlorophenyl)-4-isopropoxy-5,6-dihydro-2*H*-pyran-2-one.**[1]

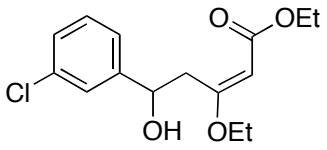


S1c **6-(3-Chlorophenyl)-4-ethoxy-5,6-dihydro-2*H*-pyran-2-one.**[2]



S1e **6-(3-Chlorophenyl)-4-(2-fluoroethoxy)-5,6-dihydro-*2H*-pyran-2-one.**

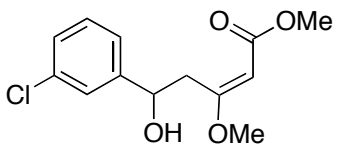
White solid (49%); m.p. 110 °C; IR (neat) ν_{max} 1712, 1625, 1391, 1291, 1226, 1185, 1073, 922 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.28–7.34 (m, 3H), 5.42 (dd, *J* = 12, 4 Hz, 1H), 5.25 (d, *J* = 1.5 Hz, 1H), 4.73 (dt, *J* = 48, 4 Hz, 2H), 4.09–4.24 (m, 2H), 2.84 (ddd, *J* = 17.5, 12, 1.5 Hz, 1H), 2.68 (dd, *J* = 17.5, 4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 165.9, 139.9, 134.6, 129.9, 128.7, 126.1, 123.9, 91.4, 80.5 (J_{CF} = 172 Hz), 76.2, 67.9 (J_{CF} = 20 Hz), 34.8; MS (MALDI-TOF) calcd for $C_{13}H_{13}O_3ClF^+$ $[M + H]^+$ 271.06, found 270.99.



S2c **(*E*)-Ethyl 5-(3-Chlorophenyl)-3-ethoxy-5-hydroxypent-2-enoate.**

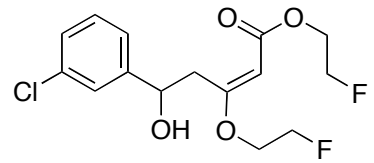
Yellow oil (15%); IR (neat) ν_{max} 2983, 1704, 1616, 1432, 1377, 1300, 1143, 1055 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.26 (m, 3H), 5.15 (s, 1H), 4.96 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.14–4.19 (m, 2H), 3.73–3.83 (m, 2H), 3.22 (dd, *J* = 13.8, 9.3 Hz, 1H), 2.92 (dd, *J* = 13.5, 3.5 Hz, 1H), 1.28 (t, *J* = 7.3 Hz, 3H), 1.27 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 169.6, 146.5, 134.0, 129.4, 127.2, 125.7, 123.7, 93.4, 72.2, 64.2, 60.1, 42.2, 14.2, 13.9; MS (MALDI-TOF) calcd for $C_{15}H_{19}O_4ClNa^+$ $[M + Na]^+$ 321.09, found 321.13.

[2] Fan, Q.; Lin, L.; Liu, J.; Huang, Y.; Feng, X.; Zhang, G. *Org. Lett.* **2004**, *6*, 2185.



S2d

(*E*)-Methyl 5-(3-Chlorophenyl)-5-hydroxy-3-methoxypent-2-enoate. Yellowish oil (30.1%); IR (neat) ν_{max} = 1710, 1623, 1439, 1376, 1290, 1196, 1142, 1055 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.21–7.31 (m, 3H), 5.21 (s, 1H), 4.96 (dd, *J* = 9.9, 3.3 Hz, 1H), 3.73 (s, 3H), 3.66 (s, 3H), 3.26 (dd, *J* = 13.7, 9.5 Hz, 1H), 2.90 (dd, *J* = 13.5, 3.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 169.7, 146.4, 134.1, 129.5, 127.3, 125.6, 123.6, 92.7, 72.2, 55.7, 51.3, 42.2; MS (MALDI-TOF) calcd for $C_{13}H_{15}O_4ClNa^+$ $[M + Na]^+$ 293.06, found 293.09.



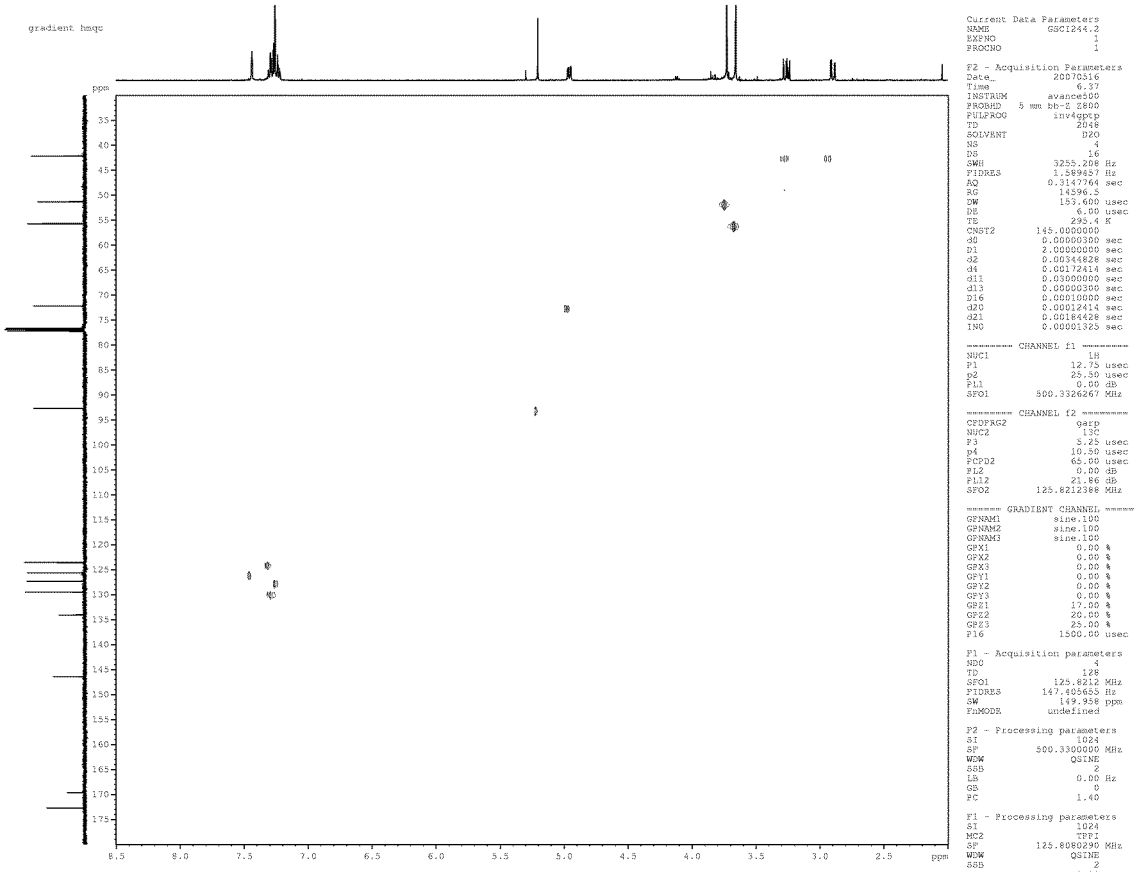
S2e

(*E*)-2-Fluoroethyl 5-(3-Chlorophenyl)-3-(2-fluoroethoxy)-5-hydroxypent-2-enoate. Yellowish oil (5.8%); IR (neat) ν_{max} 1713, 1622, 1435, 1387, 1289, 1145, 1075, 1049 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.23–7.30 (m, 3H), 5.23 (s, 1H), 5.01 (dd, *J* = 9, 3.6 Hz, 1H), 4.64 (dm, *J* = 47 Hz, 4H), 4.38 (ddd, *J* = 29, 4.8, 3.6 Hz, 2H), 4.01 (ddt, *J* = 28, 5.3, 2.6 Hz, 2H), 3.29 (dd, *J* = 13.7, 9.1 Hz, 1H), 3.03 (dd, *J* = 13.7, 3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 168.4, 146.0, 134.1, 129.5, 127.4, 125.7, 123.7, 93.6, 81.3 (J_{CF} = 171 Hz), 80.6 (J_{CF} = 172 Hz), 72.1, 67.4 (J_{CF} = 20.5), 63.1 (J_{CF} = 20 Hz), 41.9; MS (MALDI-TOF) calcd for $C_{15}H_{17}O_4ClF_2Na^+$ $[M + Na]^+$ 357.07, found 357.12.

The structures of the three-component coupling products were assigned based on their 2D-NMR spectra. The HMQC and NOESY spectra of the methyl ester **S2d** are provided below. The 1D ^1H and ^{13}C NMR spectra are appended to this Supporting Information.[3]

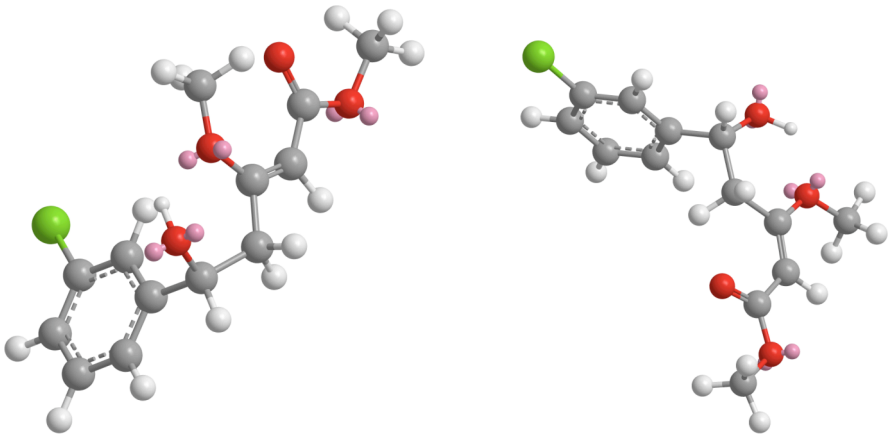
[3] For the spectral data of the *Z*-isomer, see: Fan, Q.; Lin, L.; Liu, J.; Huang, Y.; Feng, X. *Eur. J. Org. Chem.* **2005**, 3542.

Example HMQC-NMR Spectrum: Non-Cyclized Side Product S2d

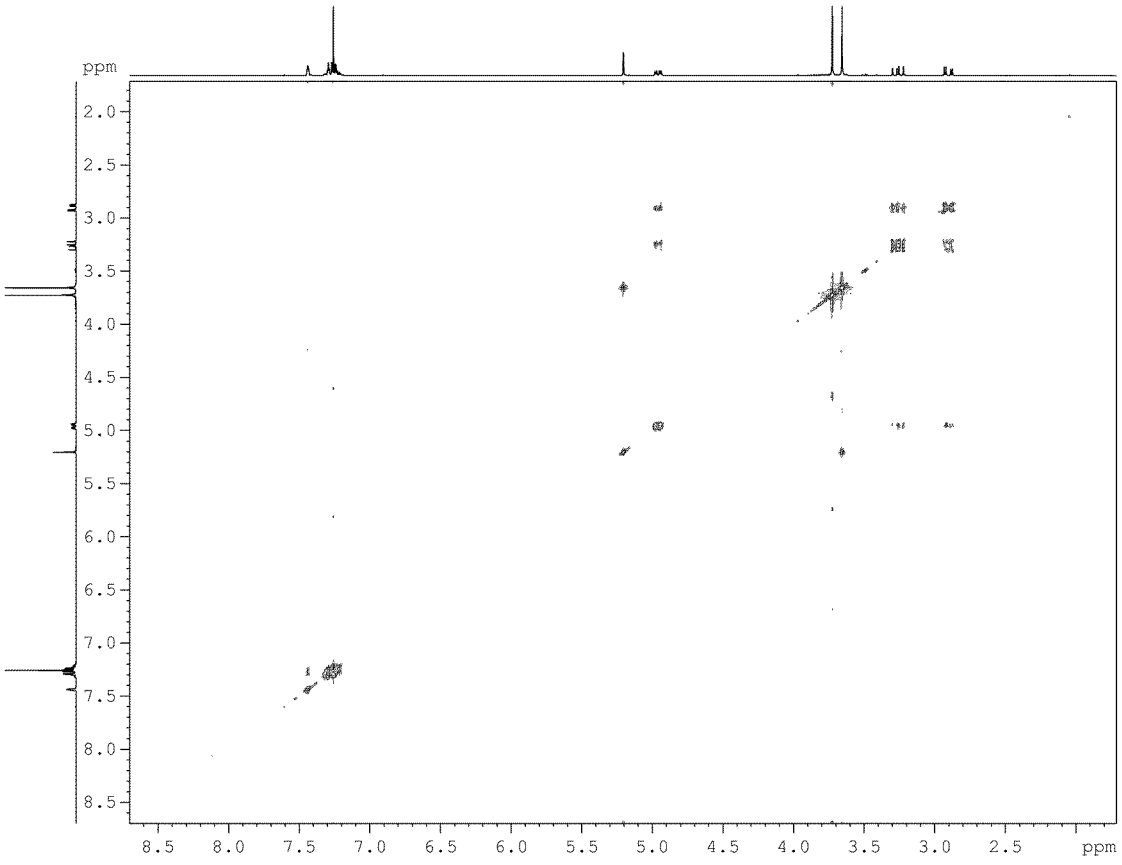


There is an NOE observed between the methyl enol ether protons and the adjacent vinyl proton. Although there could be ambiguity in the assignment of the peaks for the methyl enol ether and the methyl ester—and, consequently, a misconstrued NOE assignment—a brief look at the MM2 optimized geometries (see below) of the possible *E* and *Z* isomers lends support to our assignment. With the *E*-enoate stereochemistry, an NOE is expected between the enol ether's methyl and vinyl protons, with the methyl ester directed away from the vinyl proton. For the *Z*-enoate stereochemistry, it is clear that an NOE should be observed between the allylic and vinylic protons, with no NOE peak likely between either of the methyl protons and the vinyl proton. Therefore, the stereochemistry of the double bond in question, as well as the assignment of the peaks corresponding to the methyl ester and methyl enol ether, can be determined with confidence.

Optimized MM2 Geometries of the *E* and *Z* Isomers of S2d

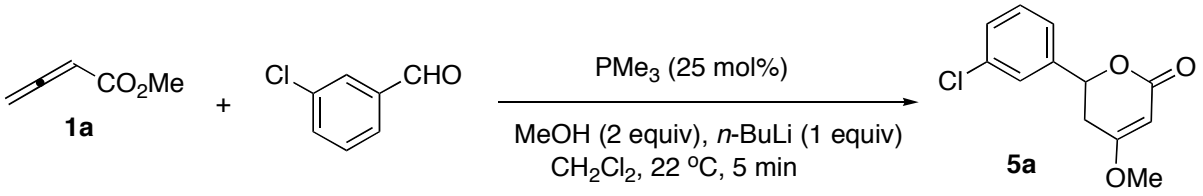


NOESY-NMR Spectrum: Non-Cyclized Side Product S2d (Suggesting *E* Stereochemistry)



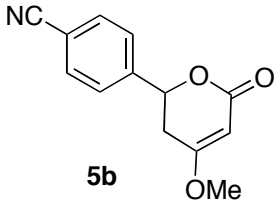
Optimized Experimental Procedure for the Formation of Dihydropyrones

As an example, the experimental procedure for the reaction of 3-chlorobenzaldehyde with methyl 2,3-butadienoate in dichloromethane is described.

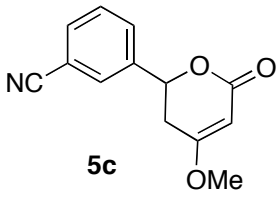


Dry dichloromethane (10 mL), methanol (81 μL, 2.0 mmol), *n*-butyllithium (1.5 M in hexanes, 0.667 mL), and neat 3-chlorobenzaldehyde (570 μL, 5.0 mmol) were added to a flame-dried flask under an argon atmosphere with rapid stirring. Immediately following the addition of trimethylphosphine (26 μL, 0.25 mmol), methyl 2,3-butadienoate (98.1 mg) was added dropwise over 30 min using a 250-μL microsyringe. The orange-red solution was stirred at room temperature for 5 min, at which point TLC (EtOAc/hexanes, 1:4; permanganate stain) indicated complete consumption of the butadienoate. The reaction mixture was neutralized and extracted with a mixture of saturated ammonium chloride and saturated sodium chloride (1:1, 20 mL); the aqueous layer was back-extracted with dichloromethane (10 mL). The organic layer was concentrated and the residue purified through flash column chromatography on silica gel (33–50% EtOAc/hexanes) to give 6-(3-chlorophenyl)-4-methoxy-5,6-dihydro-*2H*-pyran-2-one (**5a**; 169.9 mg, 71.2%) as a white solid; m.p. 96 °C; IR (neat) ν_{max} 2923, 1714, 1625, 1385, 1288, 1228, 1074, 1031 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.28–7.34 (m, 3H), 5.40 (dd, *J* = 11.9, 4.1 Hz, 1H), 5.24 (d, *J* = 1.5 Hz, 1H), 3.78 (s, 3H), 2.77 (ddd, *J* = 17.1, 12, 1.5 Hz, 1H), 2.59 (dd, *J* = 17.1, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 166.5, 140.3, 134.7, 130.1, 128.8, 126.3, 124.1, 90.7, 76.3, 56.3, 35.0; MS (MALDI-TOF) calcd for $C_{12}H_{12}O_3Cl^+$ $[M + H]^+$ 239.05, found 239.08.

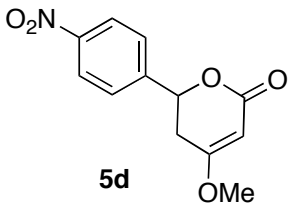
Spectral data for all additional dihydropyrones are provided below.



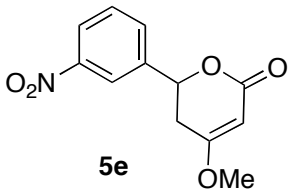
5b **4-Methoxy-6-(4-cyanophenyl)-5,6-dihydro-2*H*-pyran-2-one.** White solid (67.7%); m.p. 158 °C; IR (neat) ν_{max} 2229, 1715, 1628, 1385, 1290, 1228, 1082, 831 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8 Hz, 2H), 7.54 (d, *J* = 8 Hz, 2H), 5.47 (dd, *J* = 11.5, 4 Hz, 1H), 5.24 (s, 1H), 3.78 (s, 3H), 2.74 (dd, *J* = 17, 12 Hz, 1H), 2.63 (dd, *J* = 17, 4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 165.9, 143.3, 132.5, 126.5, 118.2, 112.4, 90.5, 75.9, 56.3, 34.7; MS (MALDI-TOF) calcd for $C_{13}H_{12}O_3N$ $[M + H]^+$ 230.08, found 230.03.



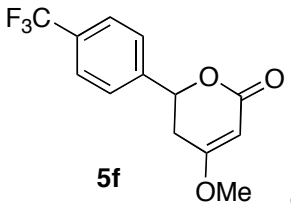
5c **4-Methoxy-6-(3-cyanophenyl)-5,6-dihydro-2*H*-pyran-2-one.** White solid (83.0%); m.p. 137 °C; IR (neat) ν_{max} 1715, 1386, 1227, 1076, 1033, 805, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.66 (m, 2H), 7.52 (t, *J* = 8 Hz, 1H), 5.45 (dd, *J* = 12, 4 Hz, 1H), 5.25 (d, *J* = 1.5 Hz, 1H), 3.79 (s, 3H), 2.77 (ddd, *J* = 17, 12, 1.5 Hz, 1H), 2.63 (dd, *J* = 17, 4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 165.9, 139.8, 132.1, 130.2, 129.6, 129.4, 118.2, 112.9, 90.5, 75.7, 56.3, 34.7; MS (MALDI-TOF) calcd for $C_{13}H_{12}O_3N^+$ $[M + H]^+$ 230.08, found 230.11.



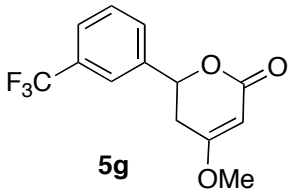
5d **4-Methoxy-6-(4-nitrophenyl)-5,6-dihydro-2*H*-pyran-2-one.** White solid (39.9%); m.p. 150 °C; IR (neat) ν_{max} 1716, 1624, 1522, 1351, 1230, 1078, 1033, 859 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9 Hz, 2H), 7.61 (d, *J* =9 Hz, 2H), 5.53 (dd, *J* = 12, 4 Hz, 1H), 5.26 (d, *J* = 1.5 Hz, 1H), 3.79 (s, 3H), 2.77 (ddd, *J* = 17, 12, 1.5 Hz, 1H), 2.66 (dd, *J* = 17, 4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 165.9, 147.8, 145.2, 126.7, 123.9, 90.5, 75.7, 56.3, 34.7; MS (MALDI-TOF) calcd for $C_{12}H_{12}O_5N^+$ $[M + H]^+$ 250.07, found 250.08.



5e **4-Methoxy-6-(3-nitrophenyl)-5,6-dihydro-2*H*-pyran-2-one.** White solid (73.7%); m.p. 146 °C; IR (neat) ν_{max} 1715, 1625, 1532, 1353, 1228, 1074, 816, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.23 (d, *J* = 6.5 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 8 Hz, 1H), 5.53 (dd, *J* = 12, 4 Hz, 1H), 5.28 (d, *J* = 1.5 Hz, 1H), 3.81 (s, 3H), 2.84 (dd, *J* = 12, 1.5 Hz, 1H), 2.68 (dd, *J* = 17, 4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 165.8, 148.3, 140.3, 131.9, 129.8, 123.5, 120.9, 90.5, 75.7, 56.3, 34.8; MS (MALDI-TOF) calcd for $C_{12}H_{12}O_5N^+$ $[M + H]^+$ 250.07, found 250.09.

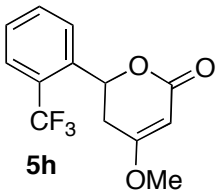


5f **4-Methoxy-6-(4-trifluoromethylphenyl)-5,6-dihydro-2*H*-pyran-2-one.** White solid (63.3%); m.p. 109 °C; IR (neat) ν_{max} 1717, 1625, 1388, 1327, 1231, 1168, 1123, 1067 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8 Hz, 2H), 5.49 (dd, *J* = 12 Hz, 4 Hz, 1H), 5.25 (d, *J* = 1.5 Hz, 1H), 3.78 (s, 3H), 2.77 (ddd, *J* = 17, 12, 1.5 Hz, 1H), 2.63 (dd, *J* = 17, 4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 166.2, 142.1, 130.7 (q, J_{CF} = 32.4 Hz), 126.1, 125.6 (q, J_{CF} = 3.7 Hz), 123.8 (q, J_{CF} = 270.5 Hz), 90.5, 76.1, 56.2, 34.8; MS (MALDI-TOF) calcd for $C_{13}H_{12}O_3F_3$ $[M + H]^+$ 273.08, found 273.10.

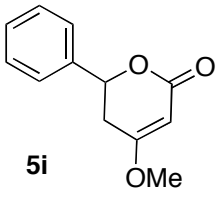


5g **4-Methoxy-6-(3-trifluoromethyl)-5,6-dihydro-2*H*-pyran-2-one.** White solid (74%); m.p. 71 °C; IR (neat) ν_{max} 1716, 1624, 1330, 1229, 1125, 1074, 806, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.62 (d, *J* = 8 Hz, 2H), 7.54 (t, *J* = 8 Hz, 1H), 5.49 (dd, *J* = 12, 4 Hz, 1H), 5.27 (d, *J* = 1.5 Hz, 1H), 3.80 (s, 3H), 2.81 (ddd, *J* = 17, 12, 1.5 Hz, 1H), 2.64 (dd, *J* = 17, 4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 166.3, 139.2, 131.0 (q, J_{CF} = 32 Hz), 129.2 (2H), 125.4 (q, J_{CF} = 4 Hz), 123.7 (q, J_{CF} = 271 Hz), 122.7 (q, J_{CF} = 4 Hz), 90.5, 76.2,

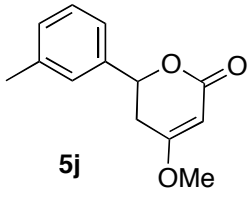
56.2, 34.9; MS (MALDI-TOF) calcd for $C_{13}H_{12}O_3F_3^+$ [M + H]$^+$ 273.08, found 273.00.



5h **4-Methoxy-6-(2-trifluoromethylphenyl)-5,6-dihydro-2*H*-pyran-2-one.** White solid (57.5%); m.p. 123 °C; IR (neat) ν_{max} 1721, 1625, 1374, 1315, 1231, 1166, 1120, 1027 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8 Hz, 1H), 7.62–7.67 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 5.79 (dd, *J* = 12.5, 3.5 Hz, 1H), 5.27 (d, *J* = 2 Hz, 1H), 3.79 (s, 3H), 2.73 (ddd, *J* = 17.2, 12.8, 1.8 Hz, 1H), 2.57 (dd, *J* = 17, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 166.4, 137.1 (q, J_{CF} = 1.4 Hz), 132.4 (q, J_{CF} = 1.1 Hz), 128.6, 128.2, 126.9 (q, J_{CF} = 30.4 Hz), 125.6 (q, J_{CF} = 5.7 Hz), 124.0 (q, J_{CF} = 274.1 Hz), 90.3, 73.4, 56.2, 35.8; MS (MALDI-TOF) calcd for $C_{13}H_{12}O_3F_3$ [M + H]$^+$ 273.08, found 273.12.

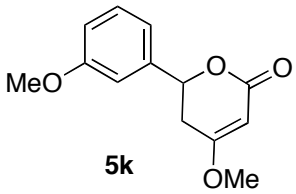


5i **4-Methoxy-6-phenyl-5,6-dihydro-2*H*-pyran-2-one.**[4]

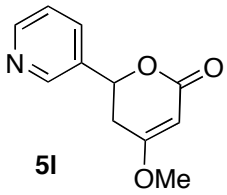


5j **4-Methoxy-6-(3-methylphenyl)-5,6-dihydro-2*H*-pyran-2-one.** White solid (36.2%); m.p. 87 °C; IR (neat) ν_{max} 1711, 1625, 1391, 1291, 1225, 1072, 924, 885 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 7.19–7.15 (m, 2H), 5.39 (dd, *J* = 12.5 Hz, 4 Hz, 1H), 5.24 (d, *J* = 1.5 Hz, 1H), 3.78, 2.82 (ddd, *J* = 17, 12, 1.5 Hz, 1H), 2.58 (dd, *J* = 17, 4 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 166.8, 138.4, 138.1, 129.2, 128.4, 126.6, 122.9, 90.5, 77.1, 56.0, 35.0, 21.3; MS (MALDI-TOF) calcd for $C_{13}H_{14}O_3^+$ [M + H]$^+$ 219.10, found 219.11.

[4] Dugger, R. W.; Heathcock, C. H. *J. Org. Chem.* **1980**, *45*, 1181.

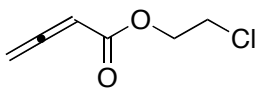


5k **4-Methoxy-6-(3-methylphenyl)-5,6-dihydro-2*H*-pyran-2-one.**[5]



5l **4-Methoxy-6-(pyrid-3-yl)-5,6-dihydro-2*H*-pyran-2-one.** Yellow solid (44.0%); m.p. 113 °C; IR (neat) ν_{max} 1710, 1622, 1392, 1228, 1076, 1023, 916, 820 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.61 (d, *J* = 3.5, 1H), 7.81 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.35 (dd, *J* = 8, 5 Hz, 1H), 5.48 (dd, 12.2, 3.8 Hz, 1H), 5.26 (d, *J* = 1.5 Hz, 1H), 3.79 (s, 3H), 2.83 (ddd, *J* = 17.3, 12.3, 1.8 Hz, 1H), 2.63 (dd, 17, 4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 166.2, 150.0, 147.5, 133.8, 133.7, 123.5, 90.6, 74.8, 56.2, 34.6; MS (MALDI-TOF) calcd for $C_{11}H_{12}O_3N^+$ $[M + H]^+$ 206.08, found 206.08.

[5] Du, H.; Zhao, D.; Ding, K. *Chem. Eur. J.* **2004**, *10*, 5964.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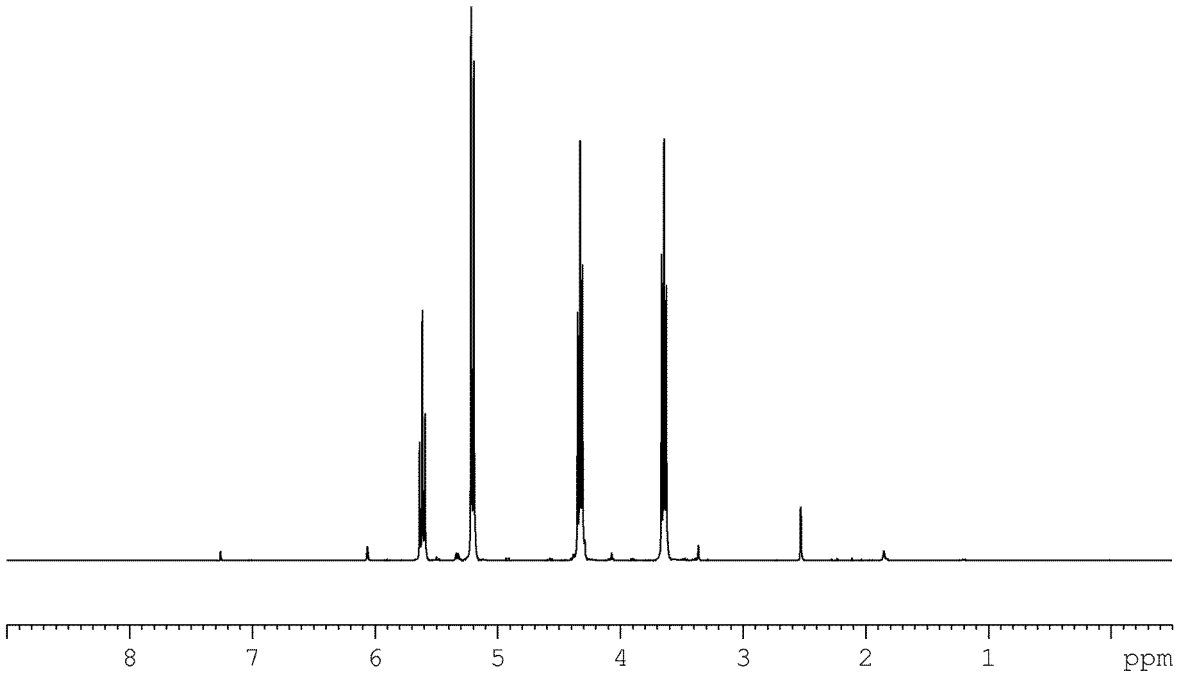
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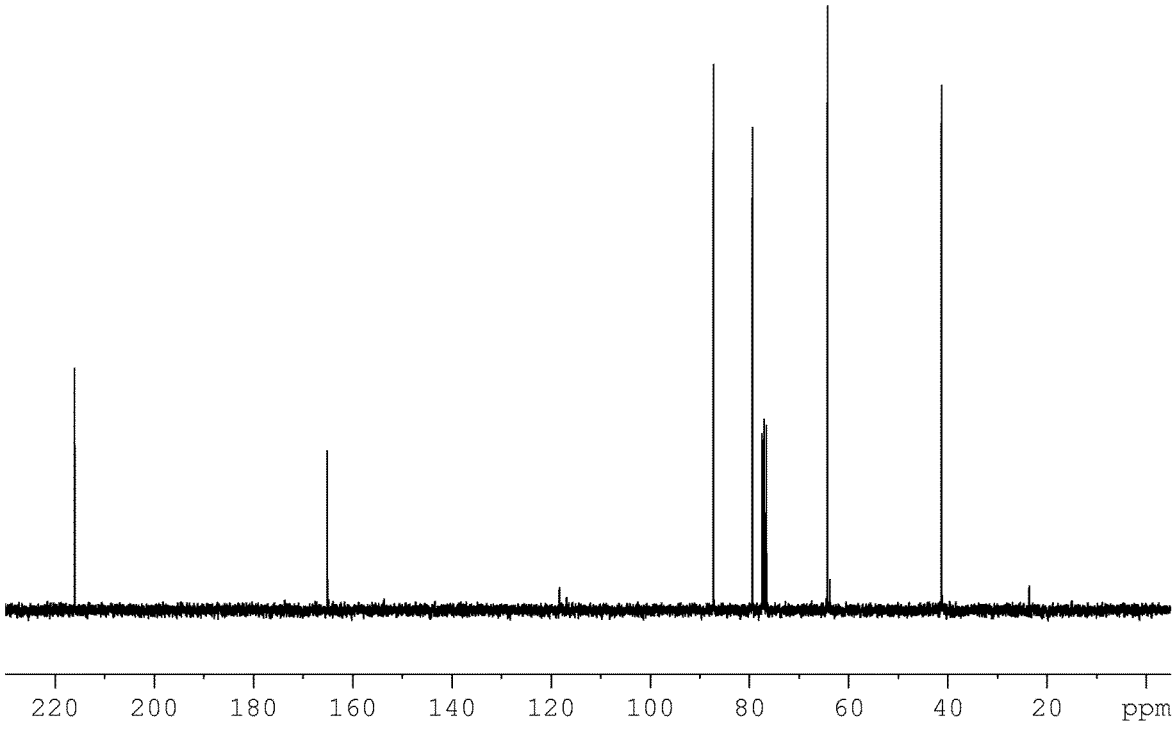
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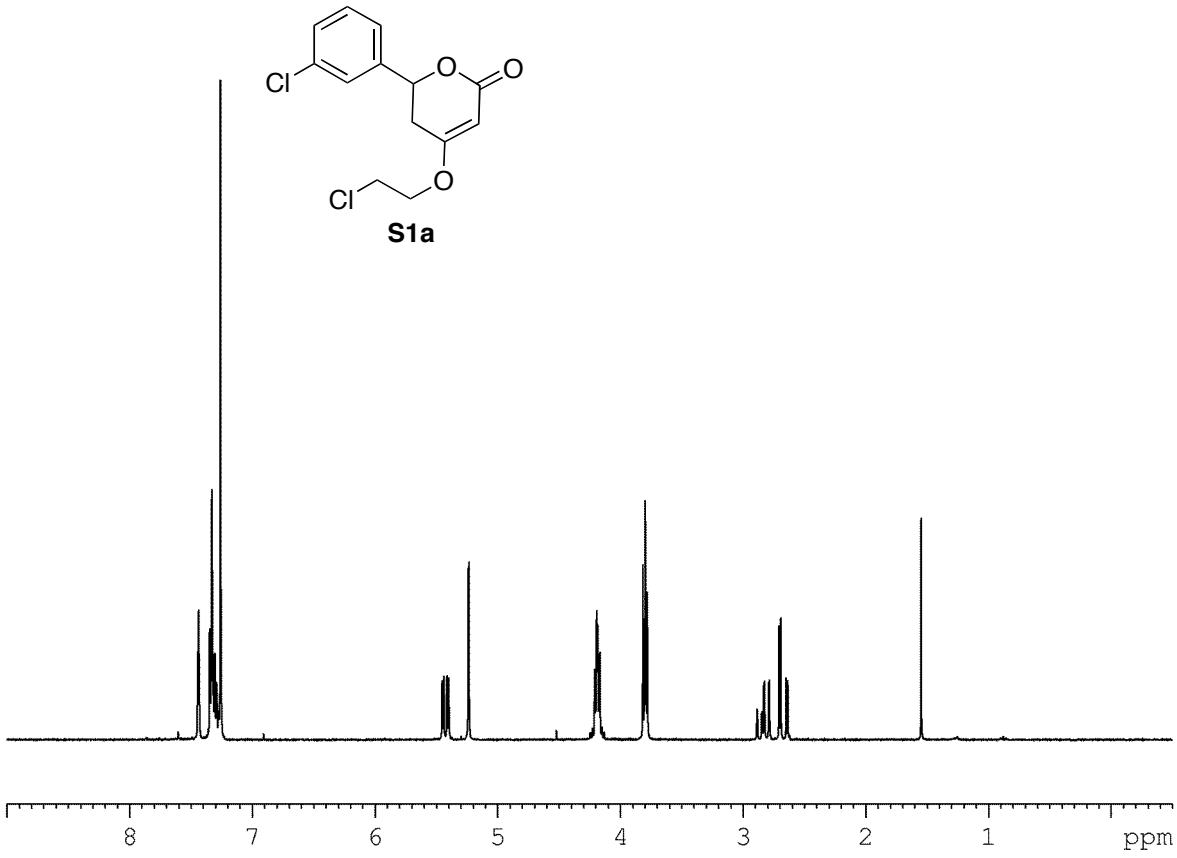

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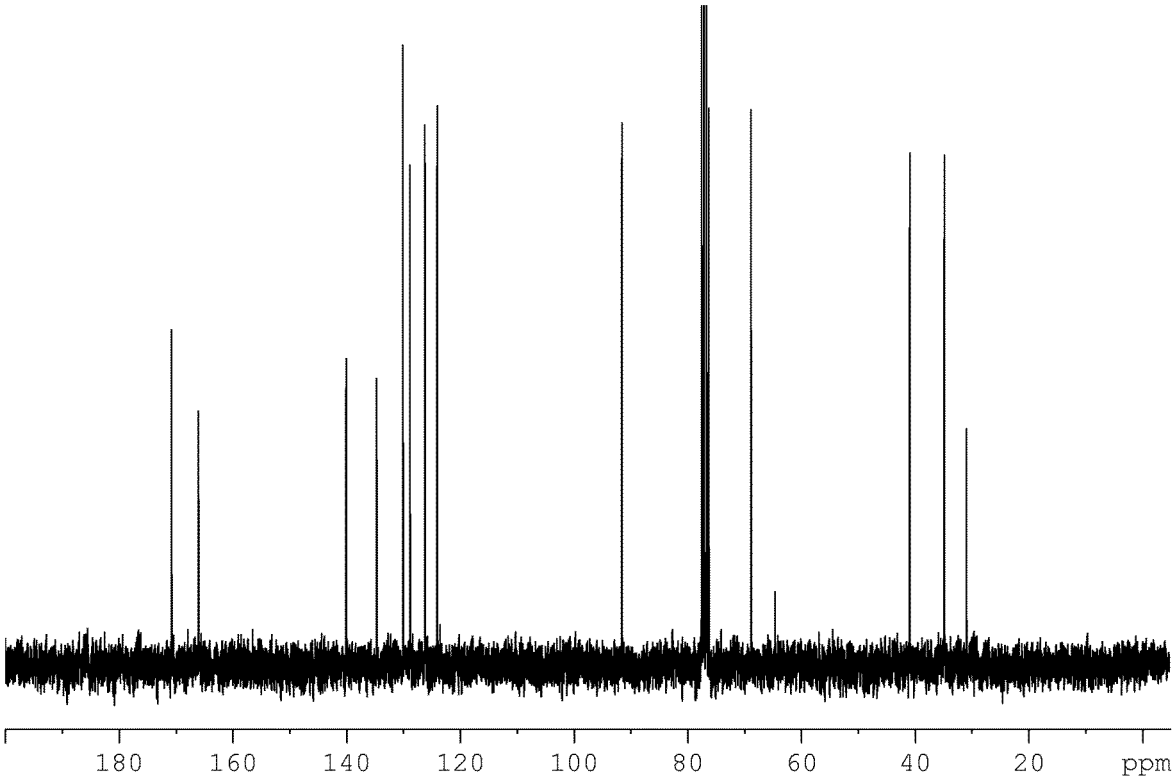
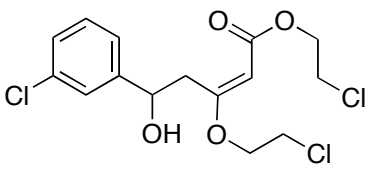
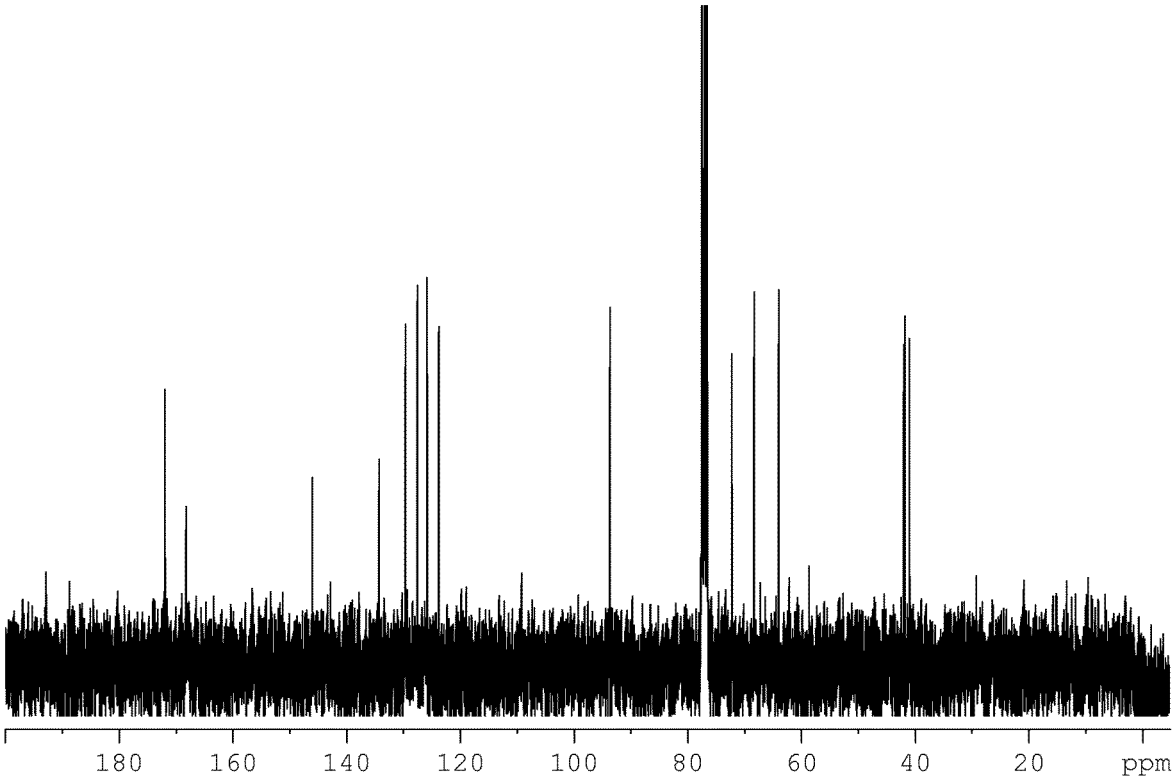
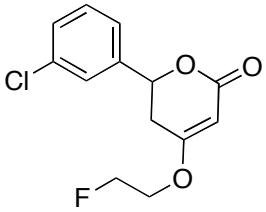


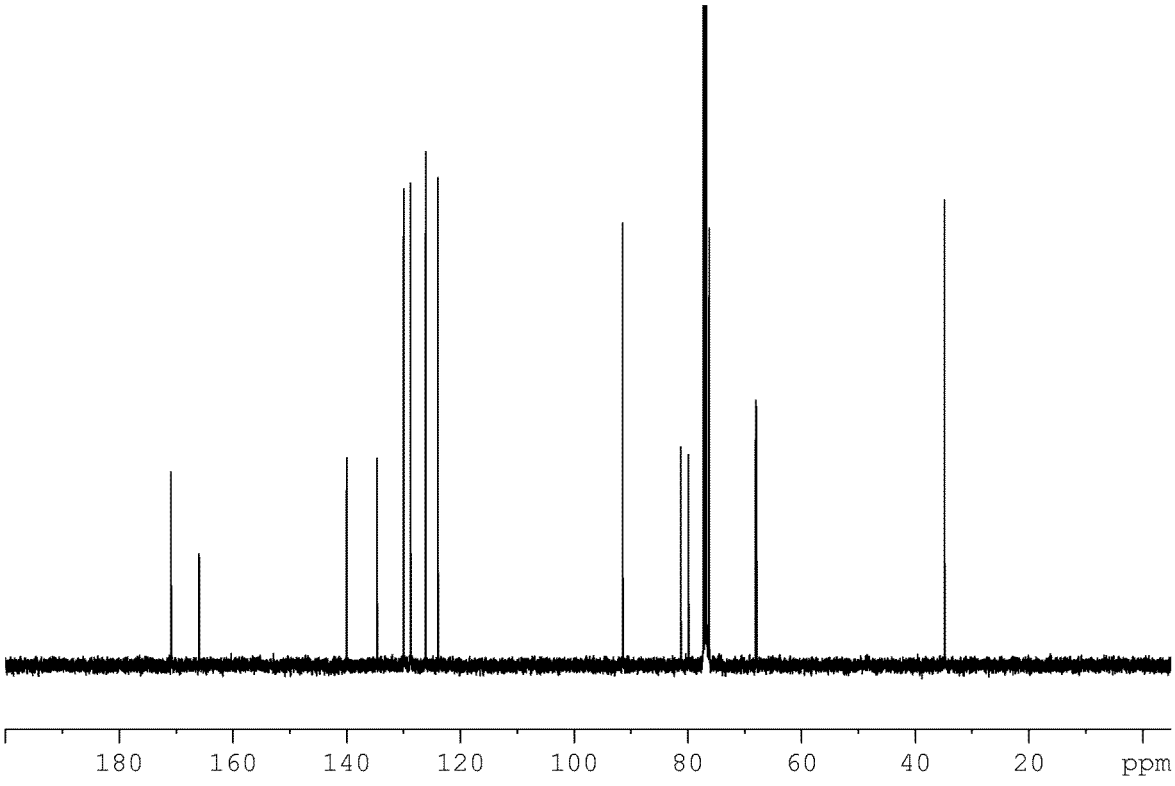


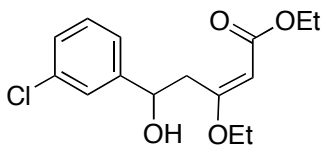
S2a



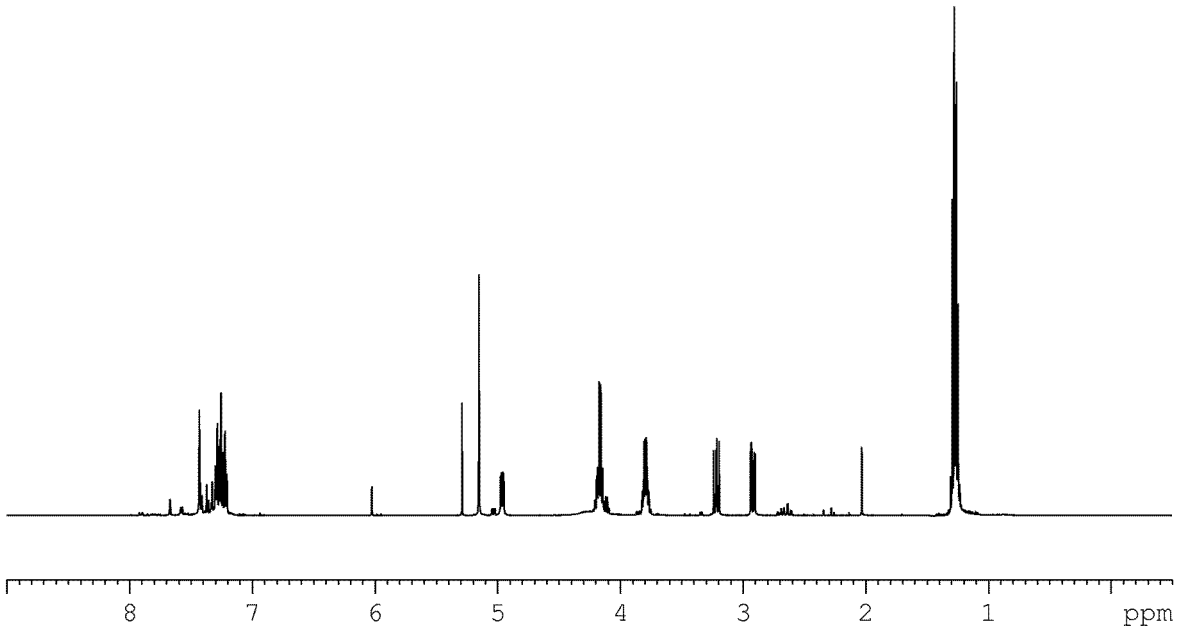


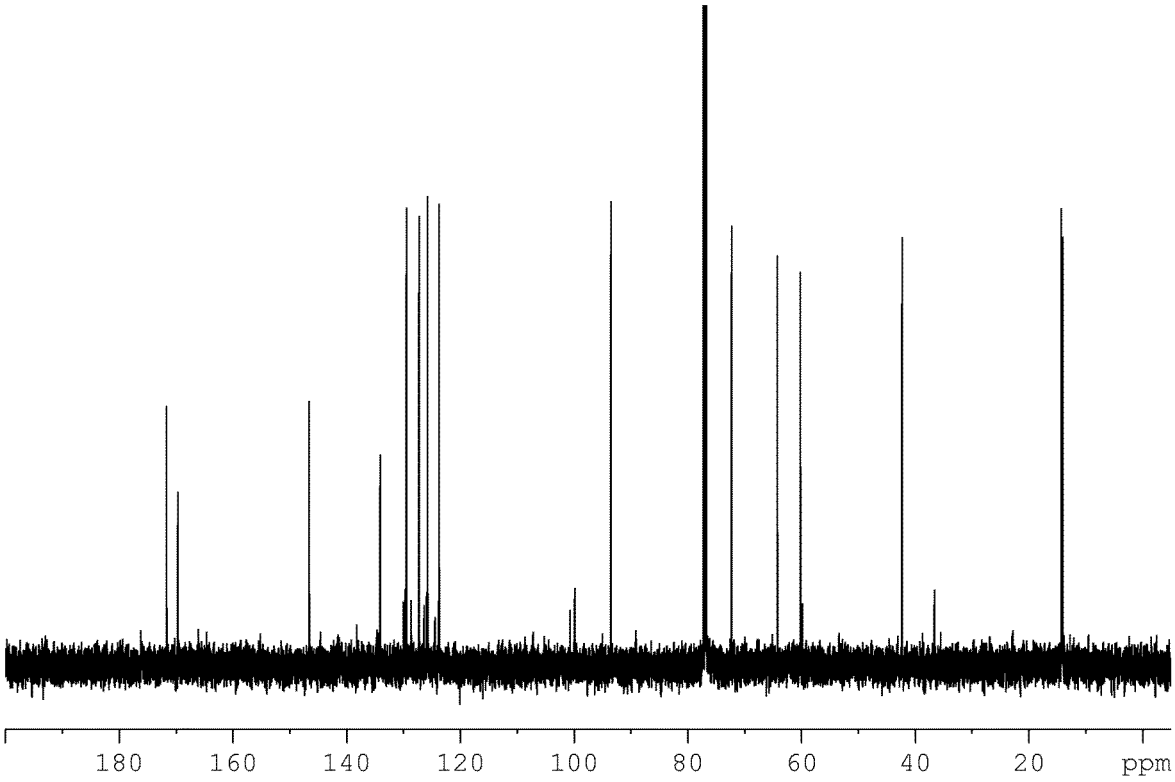
S1e

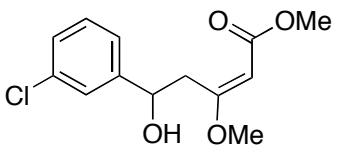




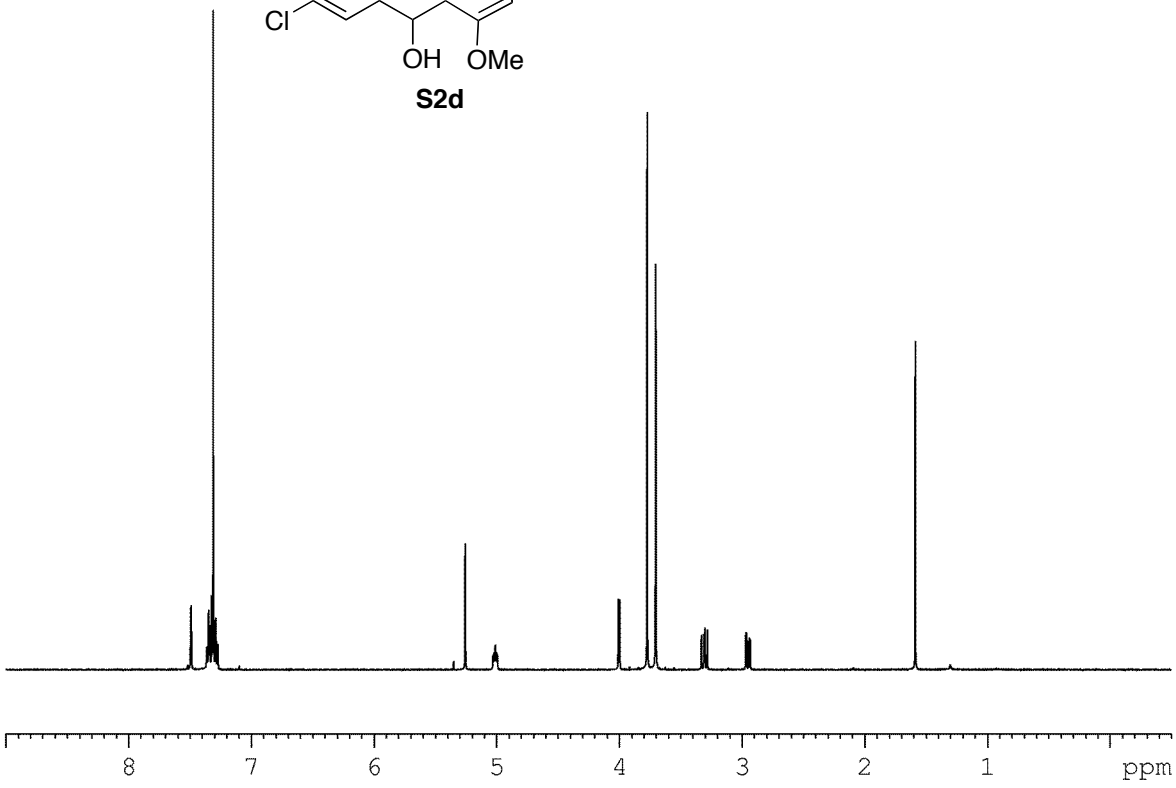
S2c

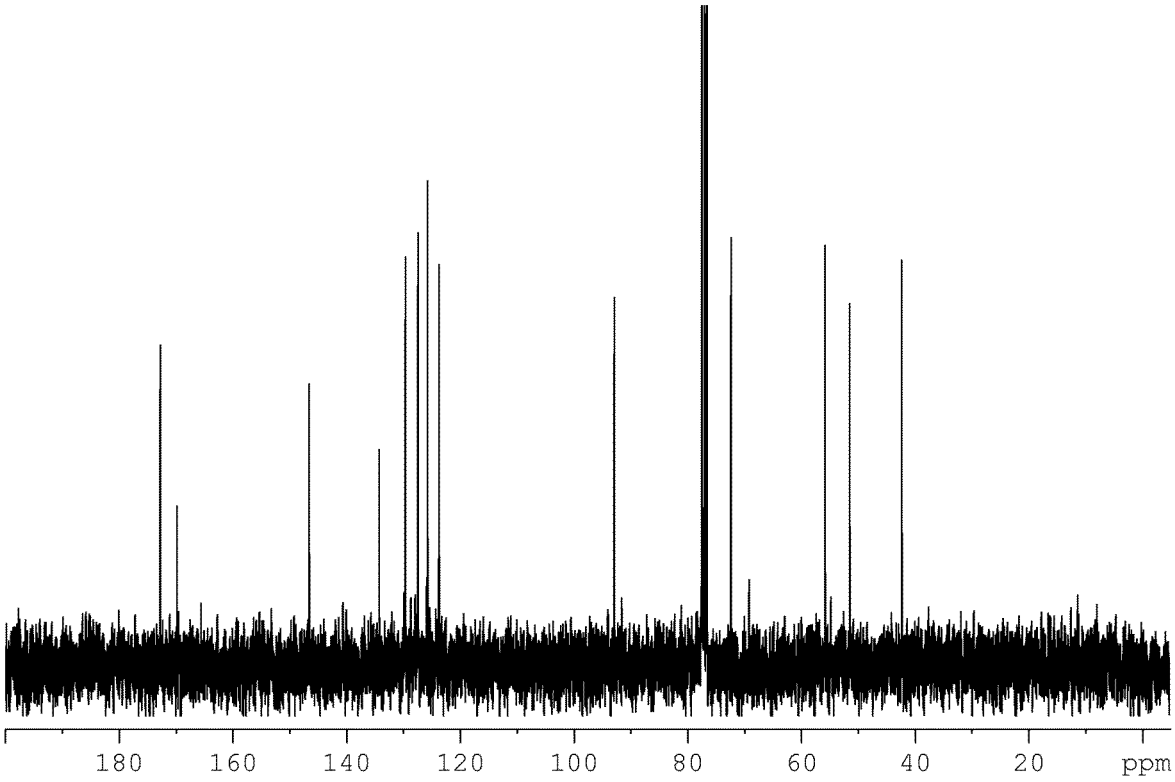


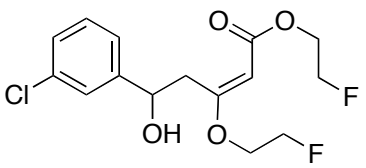




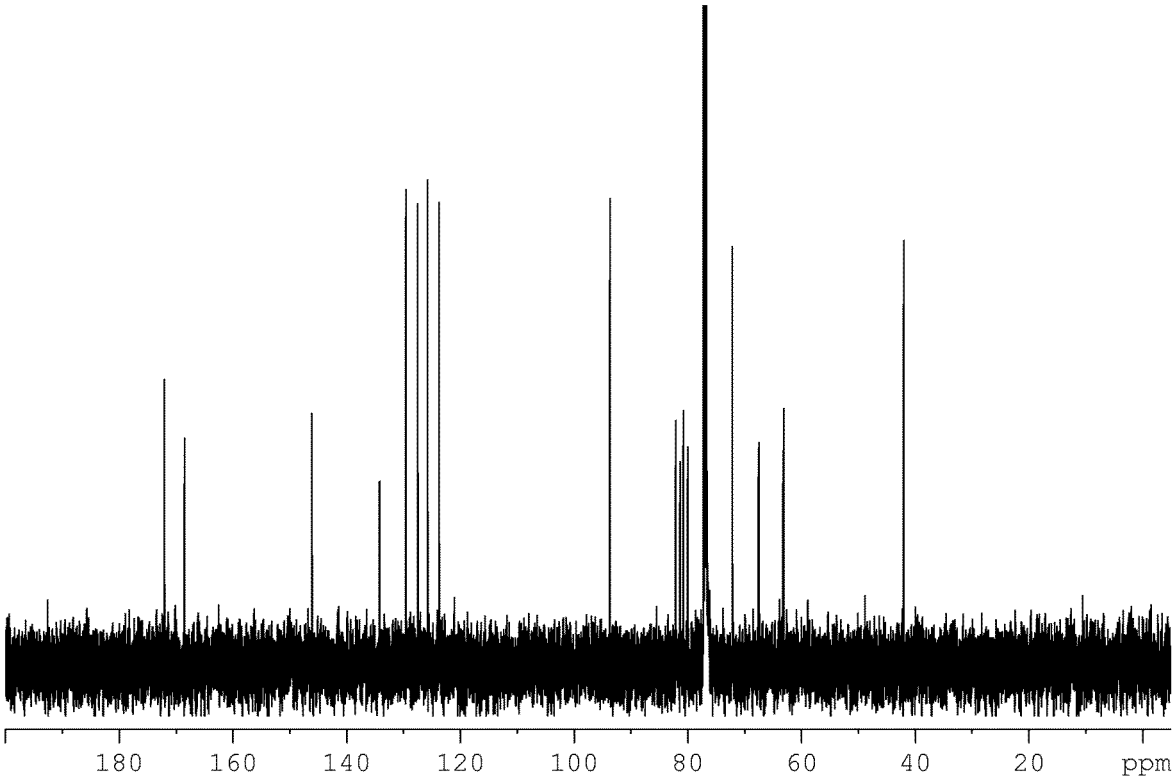
S2d

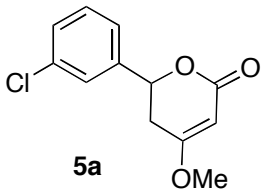




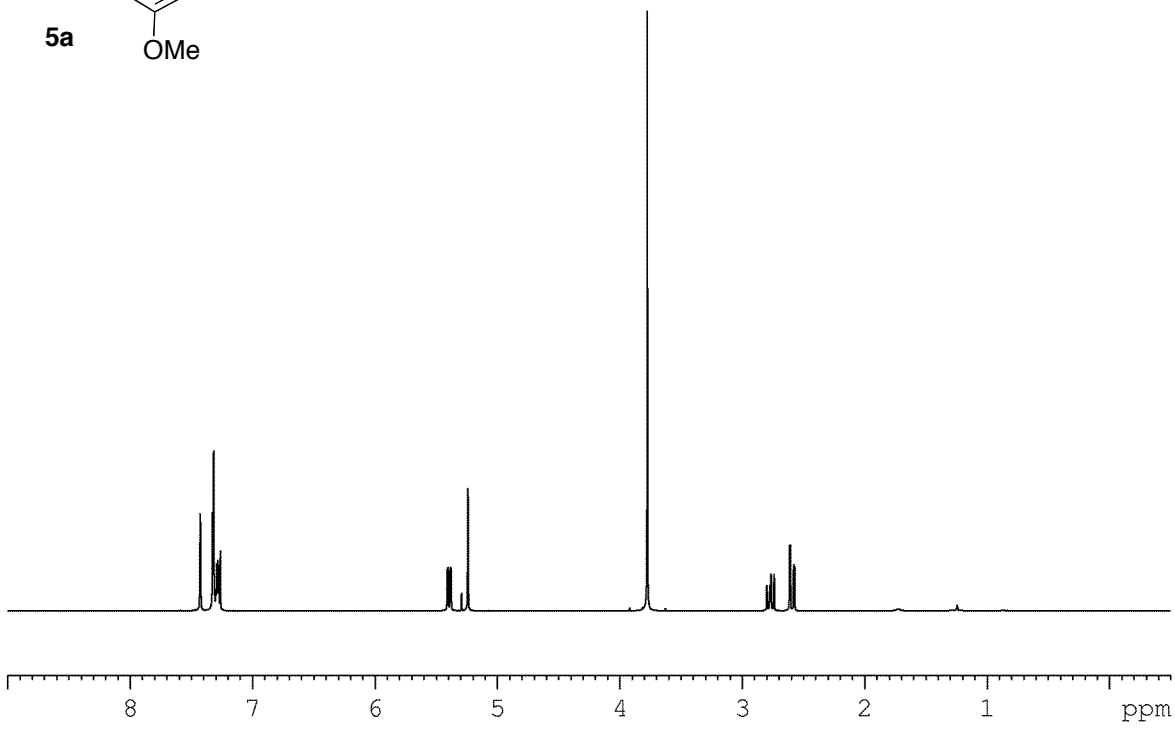


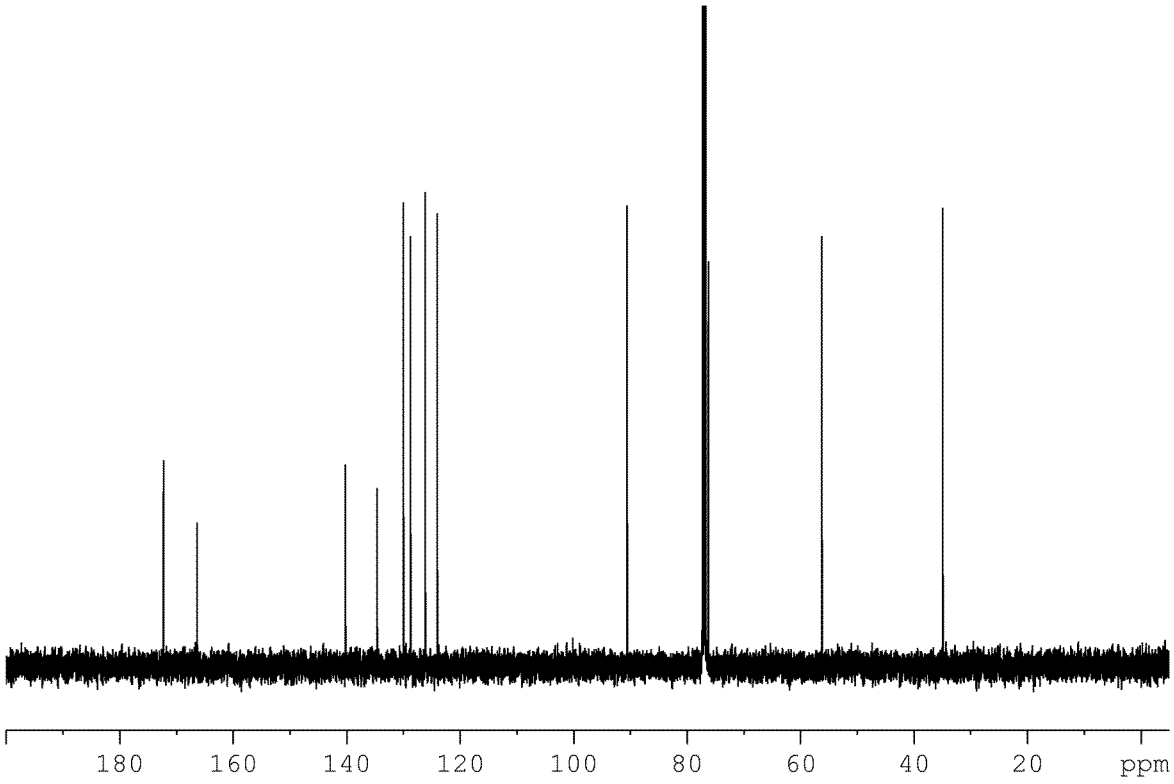
S2e

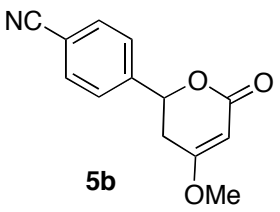




5a







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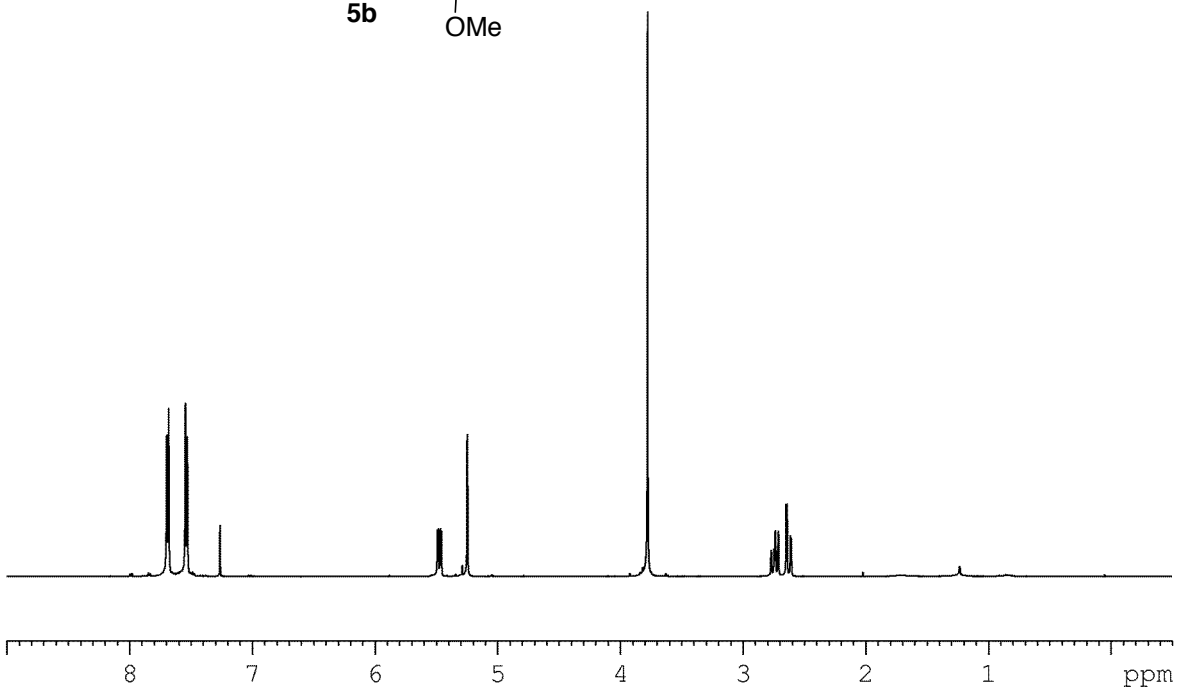
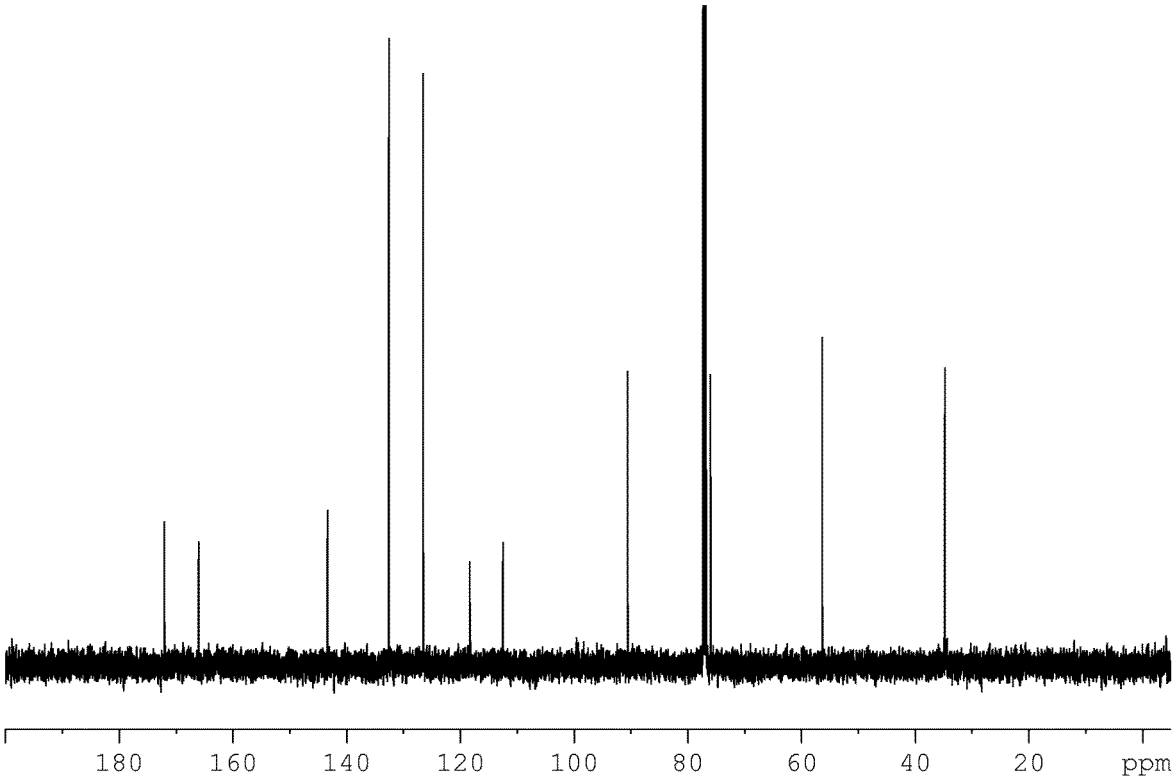
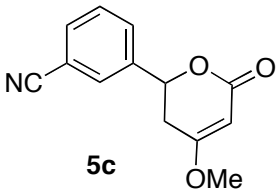
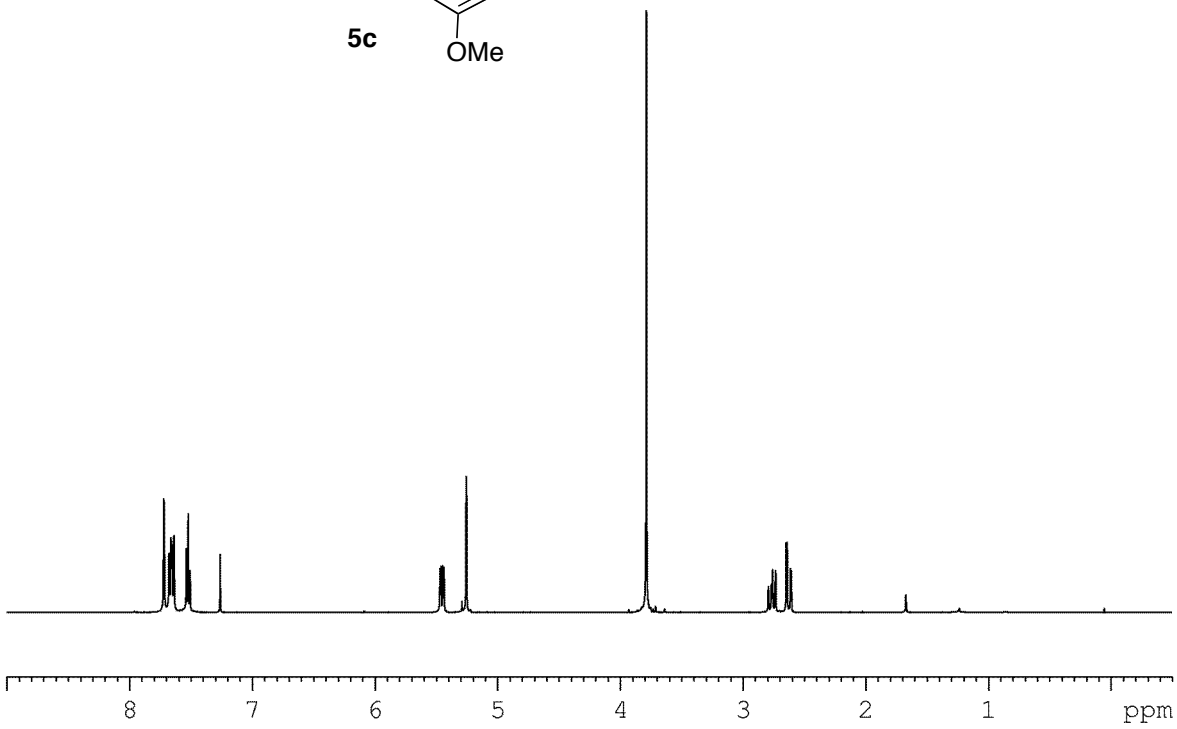
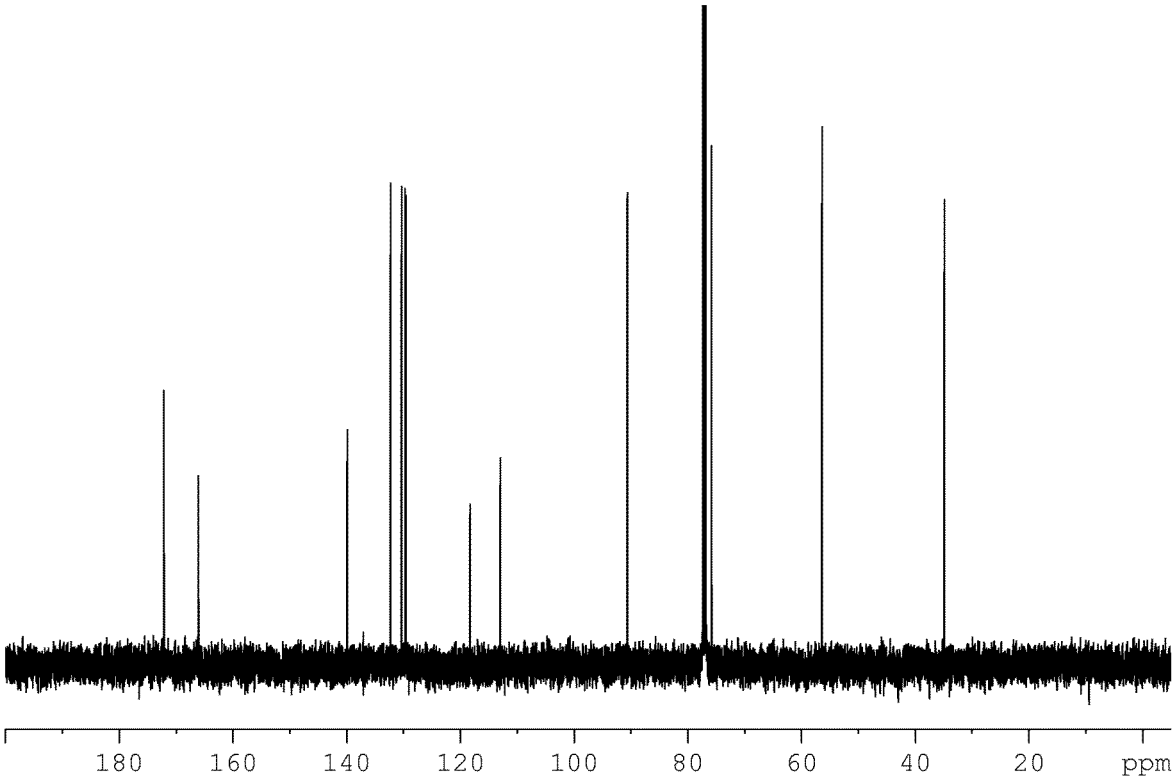


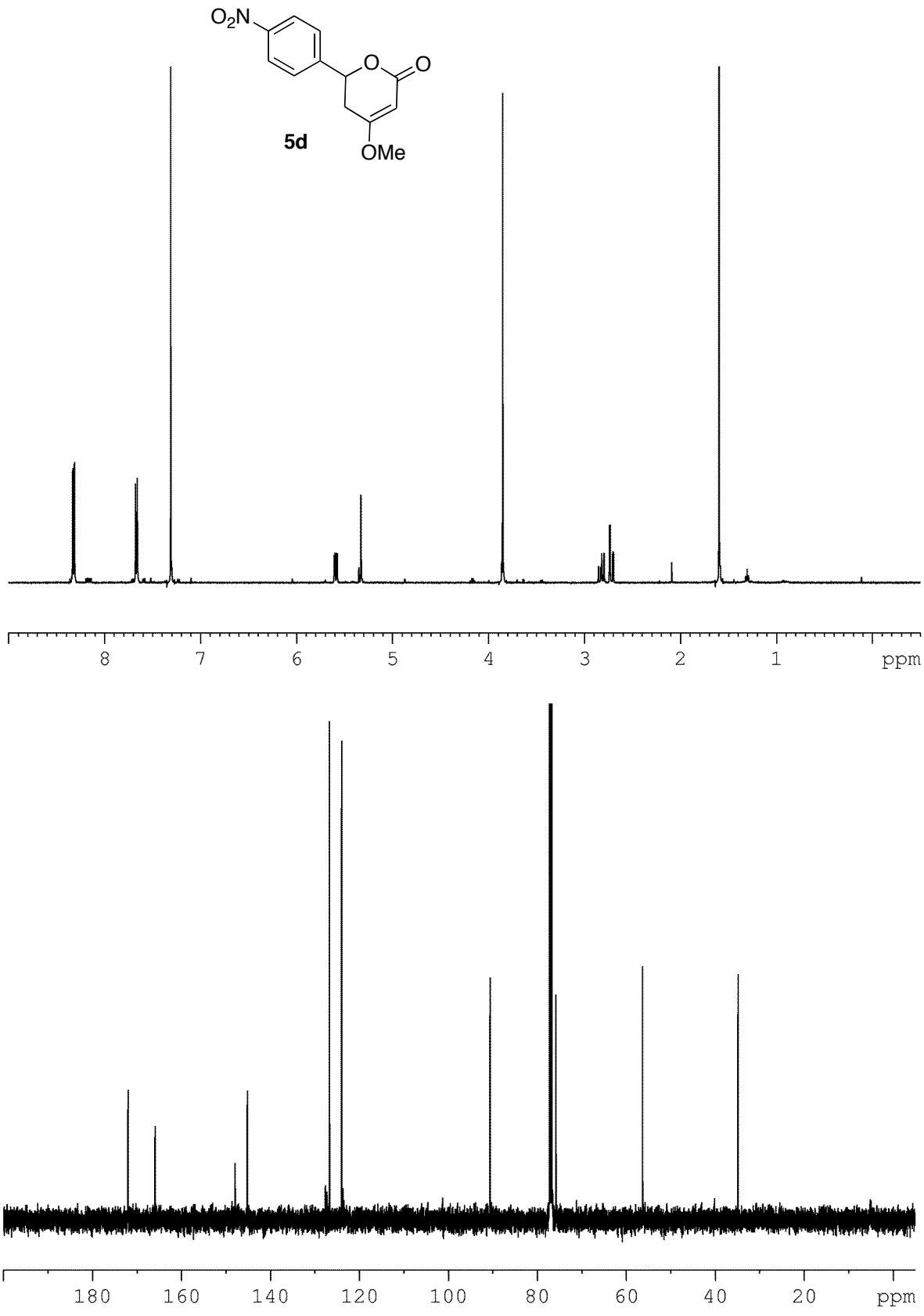




5c



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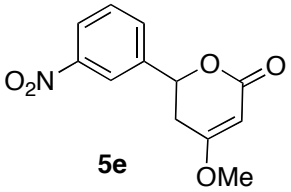
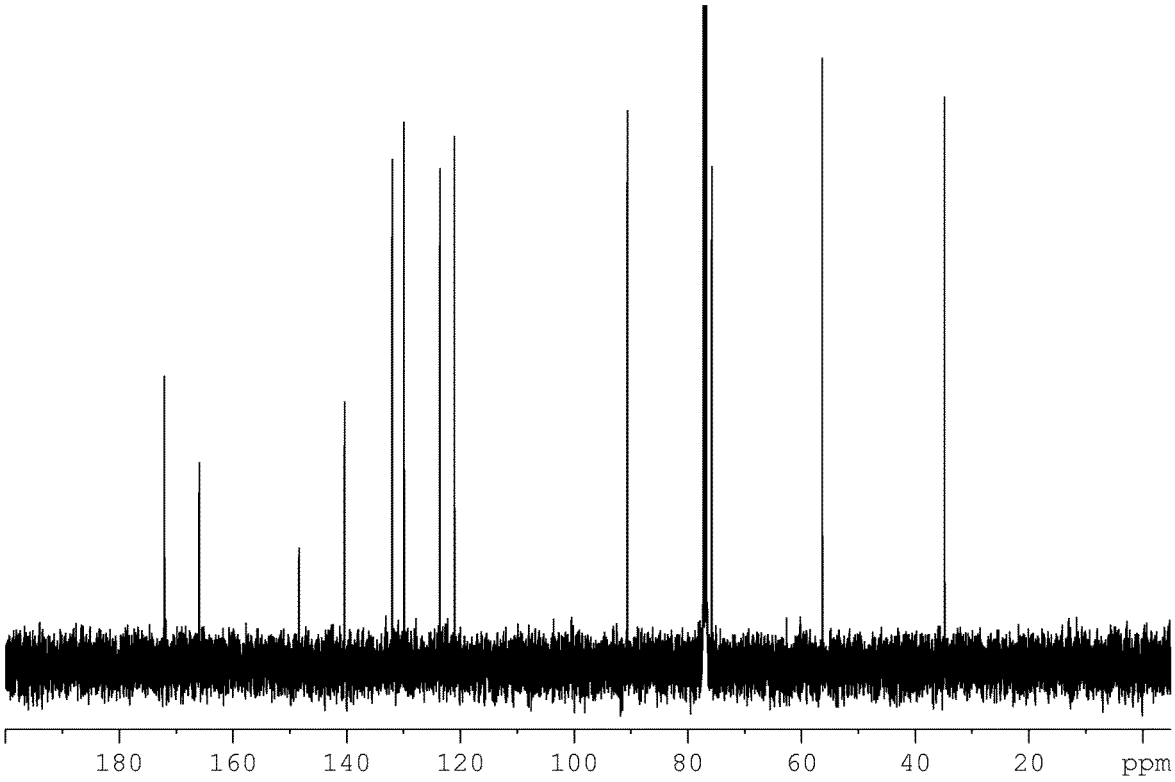
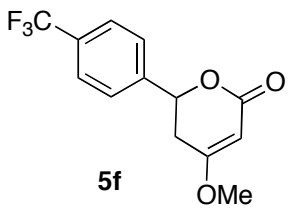


5e





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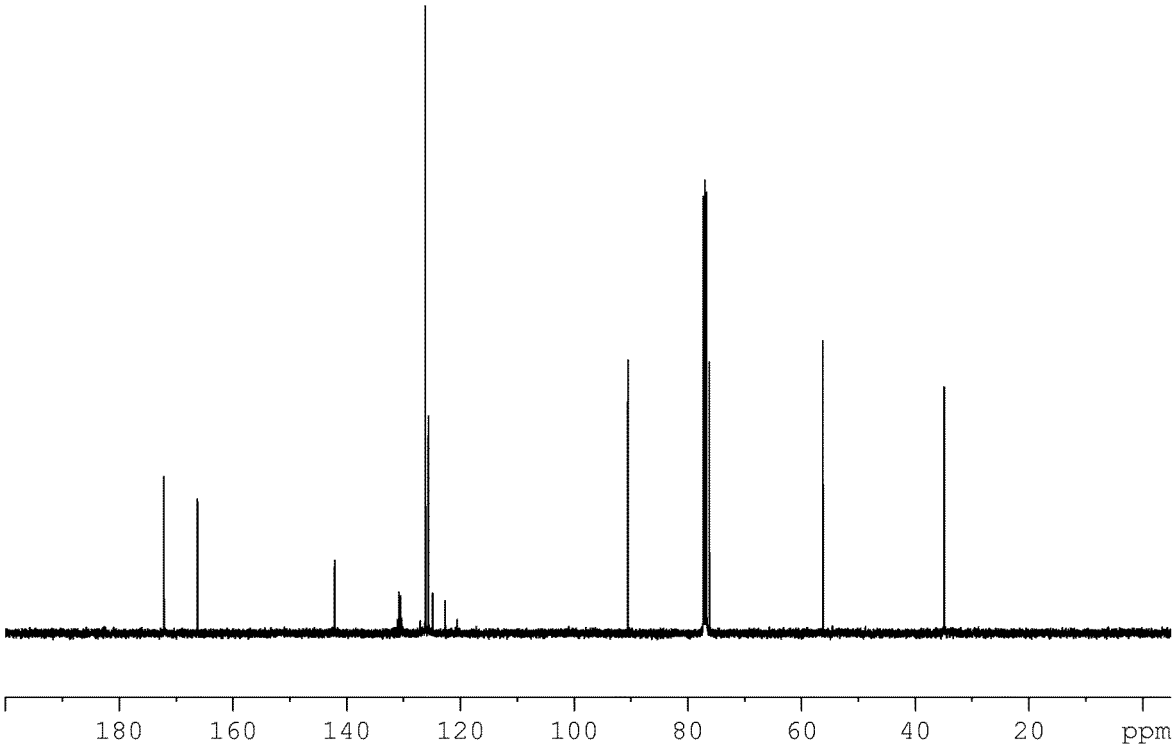

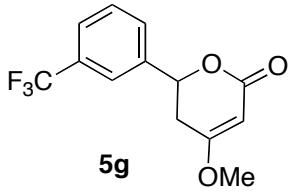

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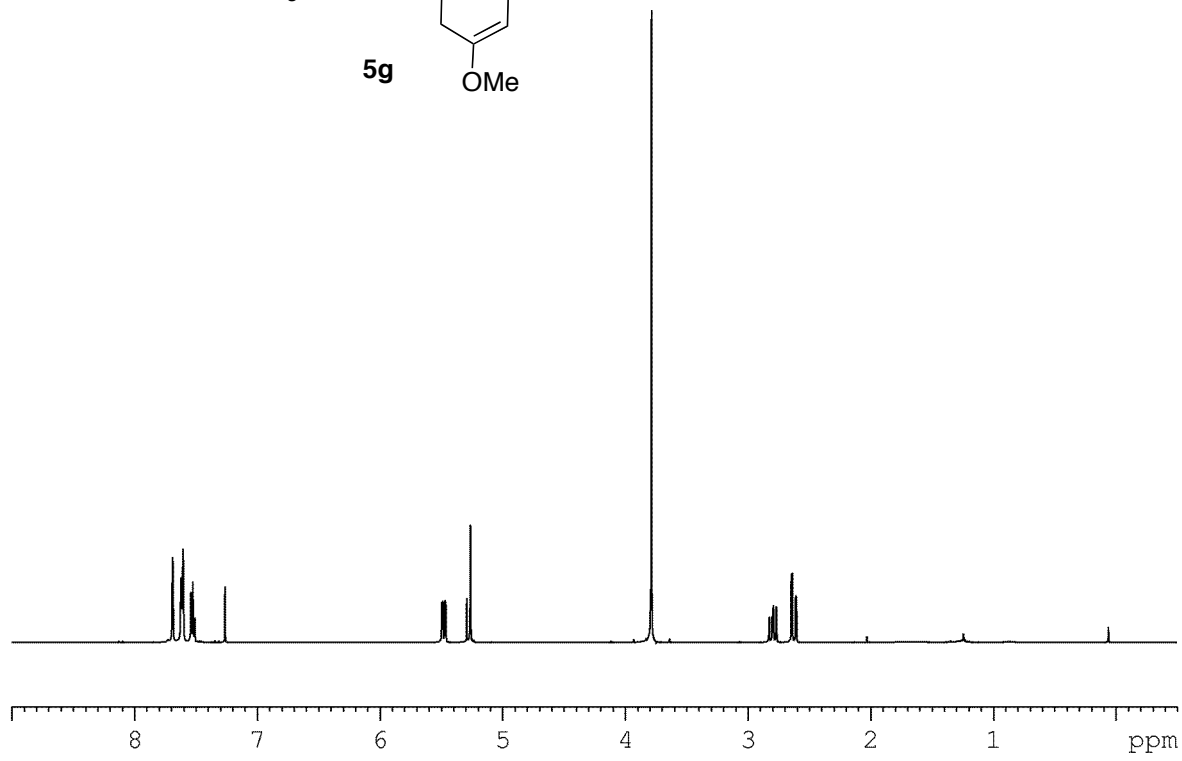

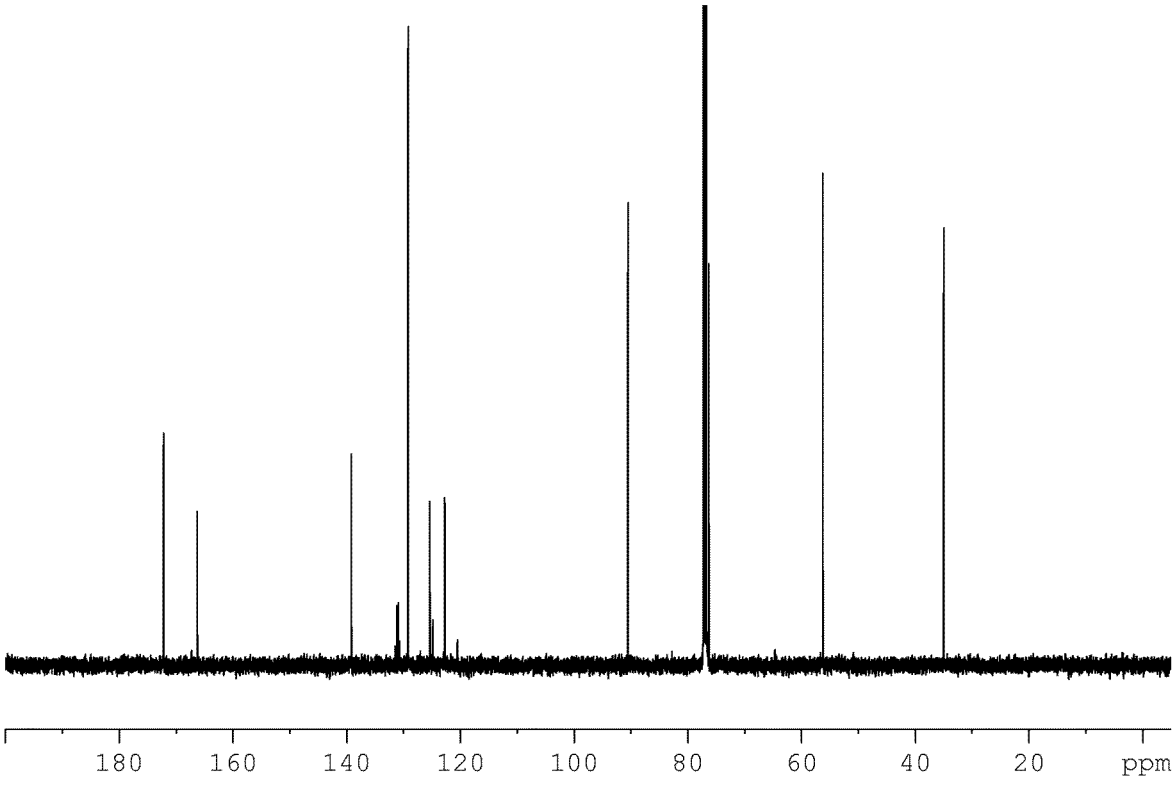

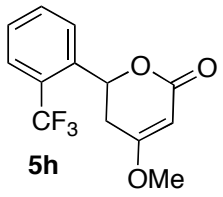

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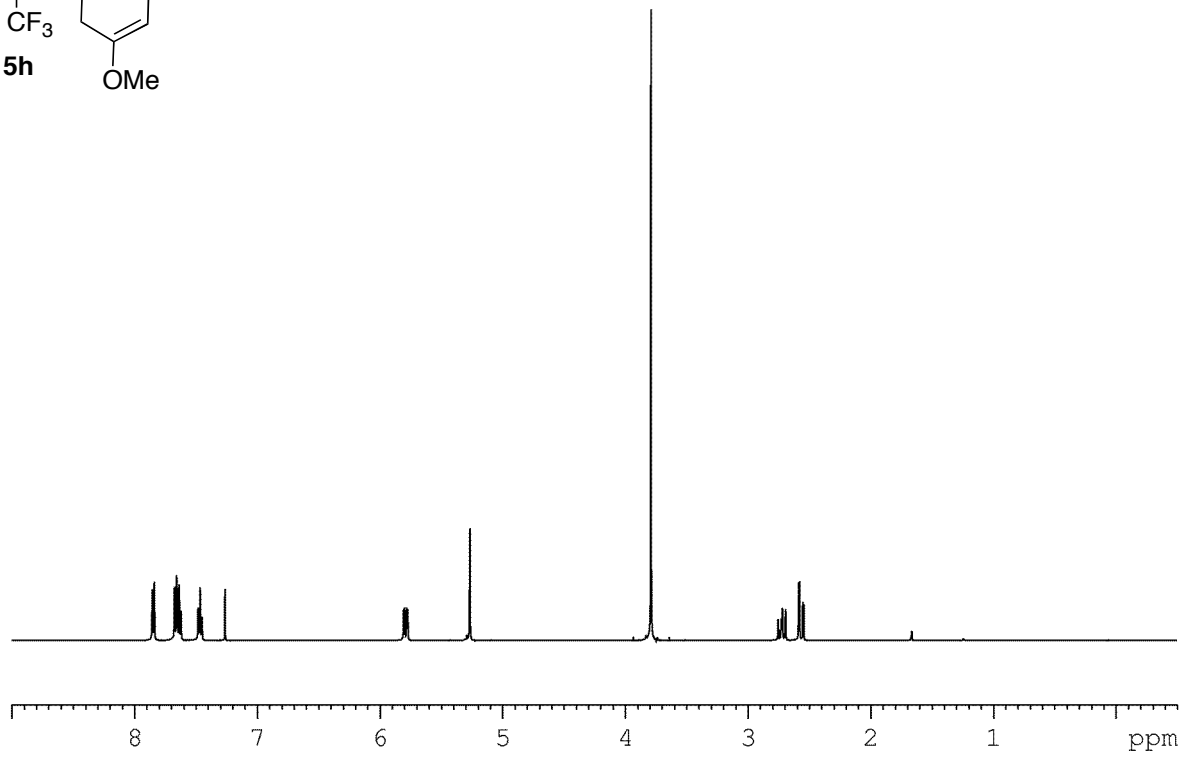

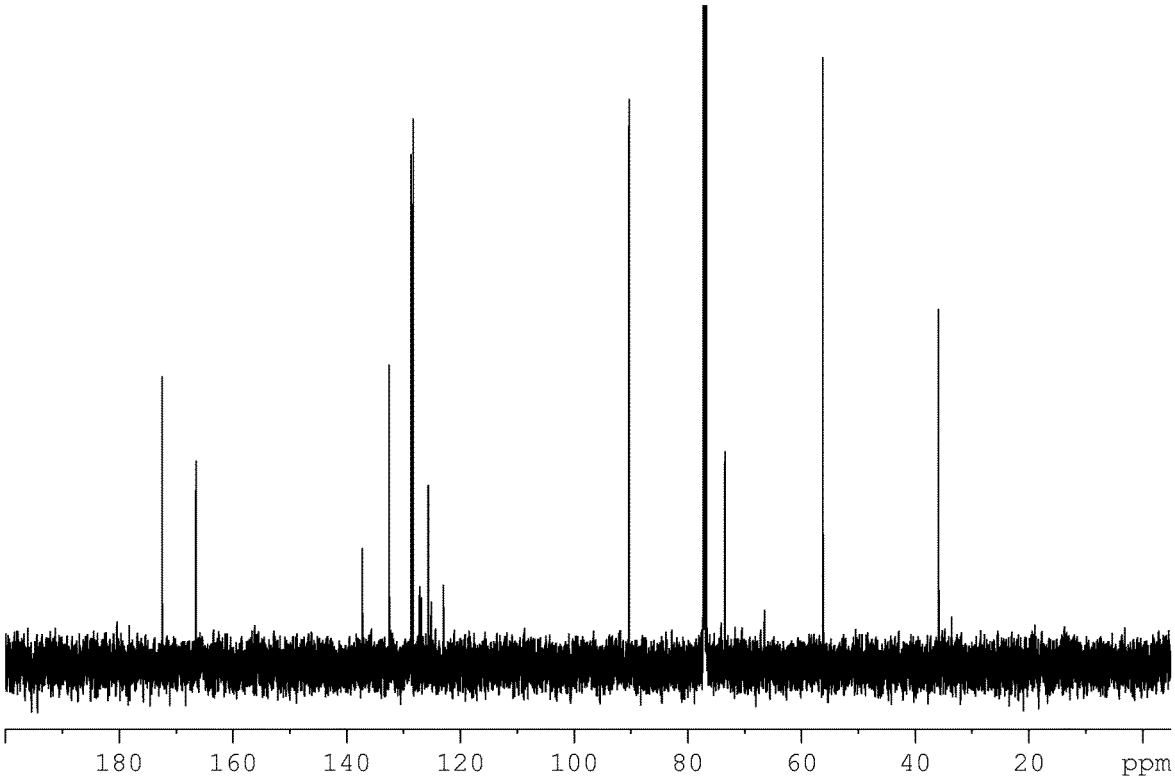

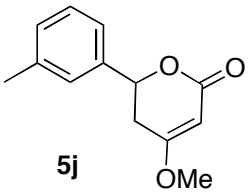

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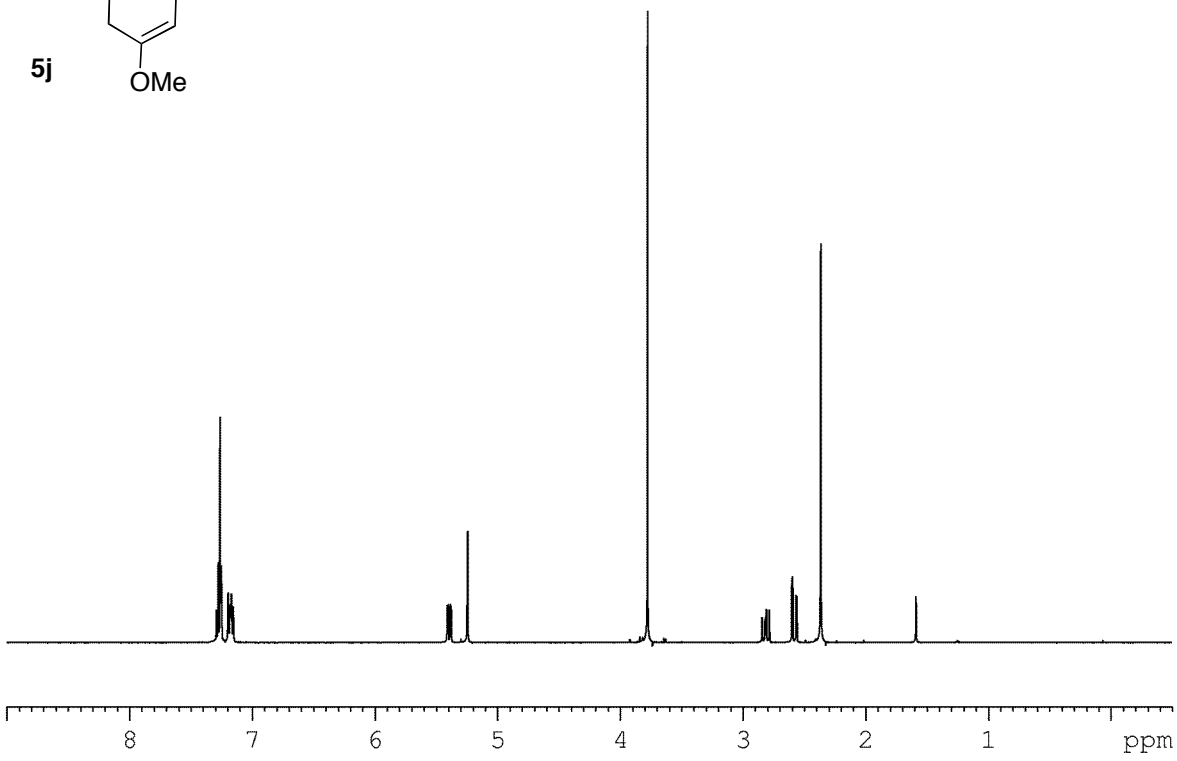

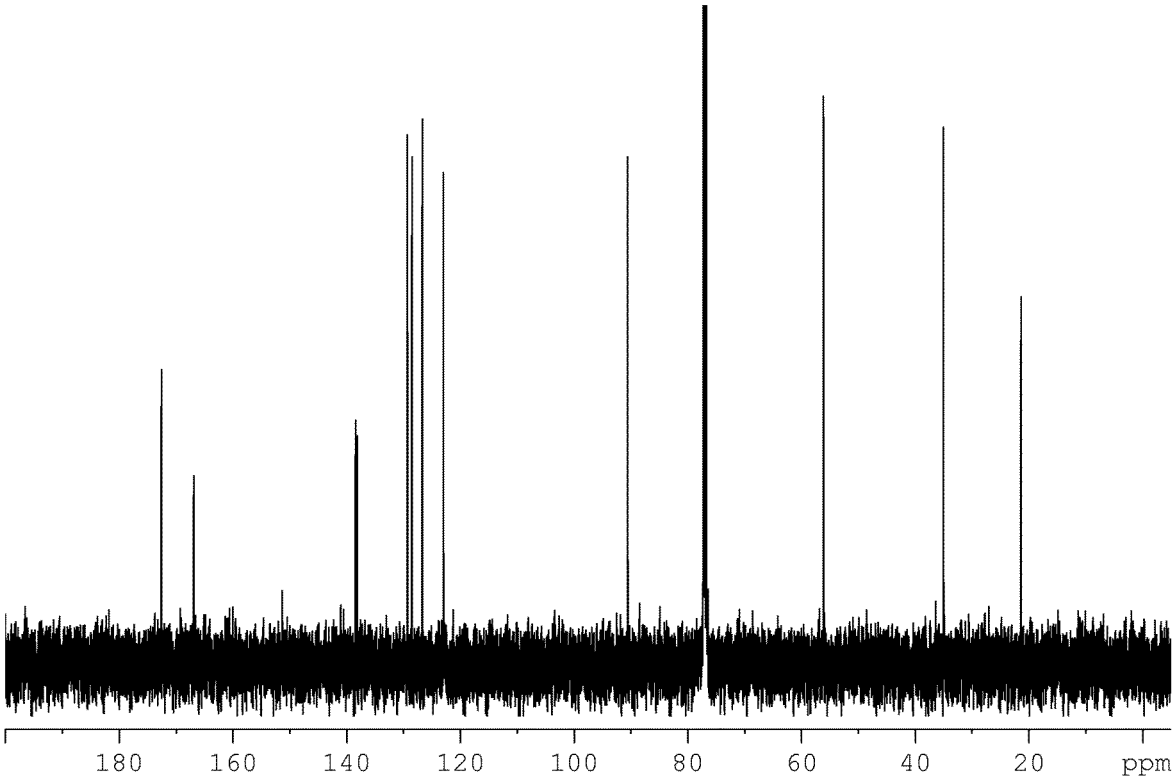

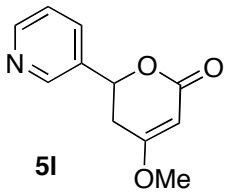

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