– Supporting Information –

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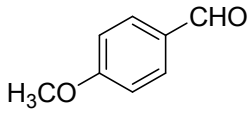
1. General Information

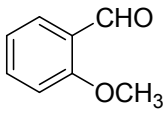
All reactions were carried out under air atmosphere unless otherwise noted. All reagents and solvents were obtained from commercial suppliers such as $FeCl_3$ (anhydrous, 98% pure) from Alfa Aesar, TMDSO (CAS: 3277-26-7, 98% pure) from Energy Chemical and Adamas-beta®, and used without further purification. Reactions were monitored by TLC on silica gel plates (GF254). ^1H (400 MHz) and ^{13}C NMR spectra (100 MHz) of solutions in $CDCl_3$ or DMSO-d_6 were recorded on a Bruker Avance 400 NMR spectrometer. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals ($CDCl_3$: δ_H 7.26 and δ_C 77.0 ppm; DMSO-d_6: δ_H 2.50 and δ_C 39.50 ppm). The signals of water were observed at about 1.58 ppm in $CDCl_3$ and 3.33 ppm in DMSO-d_6, respectively. Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants, *J,* were reported in hertz unit (Hz). HRMS was performed on a Q-TOF mass spectrometer. Infrared spectra of neat substances were recorded on a Thermo Nicolet Corporation GC-FTIR NEXUS670 spectrometer. ICP-AES analysis was measured on a Prodigy (LEEMAN LABS INC.) machine. GC-MS were determined with Agilent 7890-5975C.

2. Products from Fe-Catalyzed Aerobic C-C Bond Cleavage

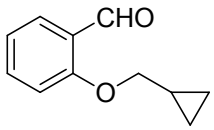
General Procedure: A 25 mL flask was charged with $FeCl_3$ (0.025 mmol, 4.1 mg), olefin (0.25 mmol), EtOH (2 mL), and TMDSO (0.75 mmol, 135 μL). The reaction mixture was stirred under air atmosphere at room temperature until the reaction was complete (observed by TLC). The resulting reaction solution was directly purified by column chromatography (Petroleum ether/ ethyl acetate) on silica gel to afford the corresponding product.



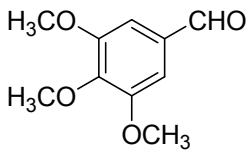
4-Methoxybenzaldehyde (2a): *Following the general procedure*, **2a** was isolated as a yellow oil (29.9mg, 88%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1 H), 7.83 (d, *J* = 8.8 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.88 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 164.6, 131.9, 1 29.9, 114.3, 55.5 ppm.



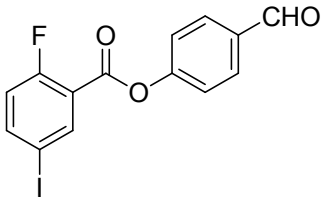
2-Methoxybenzaldehyde (2b): *Following the general procedure*, **2b** was isolated as a yellow oil (31.0mg, 91%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.47 (s, 1 H), 7.84-7.82 (m, 1 H), 7.58-7.53 (m, 1 H), 7.05-6.98 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 161.8, 135.9, 128.5, 124. 8, 120.6, 111.6, 55.6 ppm.



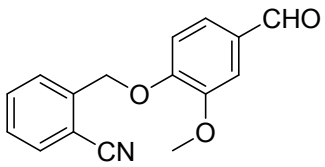
2-(Cyclopropylmethoxy)benzaldehyde (2c): *Following the general procedure*, **2c** was isolated a s a yellow oil (34.3mg, 78%), known compound. The NMR spectroscopic data agree with thos e described in ref.[S2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.55 (s, 1 H), 7.82 (dd, *J* =7.6 Hz, 1.6 Hz, 1 H), 7.53-7.49 (m, 1 H), 7.01-6.97 (m, 1 H), 6.93 (d, *J* =8.4 Hz, 1 H), 3.92 (d, *J* =7.2 Hz, 2 H), 1.33-1.25 (m, 1 H), 0.68-0.63 (m, 2 H), 0.39-0.3 5 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 161.4, 135.8, 128.1, 125.0, 120.5, 11 2.8, 73.2, 10.0, 3.1 ppm.



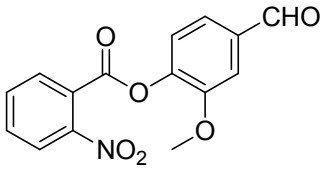
3,4,5-Trimethoxybenzaldehyde (2d): *Following the general procedure*, **2d** was isolated as a white solid (38.3mg, 78%), known compound. The NMR spectroscopic data agree with those d escribed in ref.[S3]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1 H), 7.12 (s, 2 H), 3.93 (s, 3 H), 3.92 ppm (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 153.6, 143.5, 131.6, 106.6, 61.0, 5 6.2 ppm. Mp: 69.1-70.8 ^{o}C.



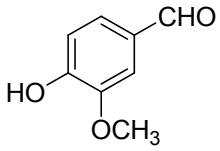
4-Formylphenyl 2-fluoro-5-iodobenzoate (2e):*Following the general procedure*, **2e** was isolated as a white solid (57.3mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1 H), 8.40 (dd, *J* = 6.8 Hz, 2.4 Hz, 1 H), 8.00-7.97 (m, 2 H), 7.93-7.89 (m, 1 H), 7.44-7.40 (m, 2 H), 7.02 pp m (dd, *J* = 10.4 Hz, 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 163.5, 160.9, 160. 6 (d, *J* = 3.9 Hz), 154.9, 144.4 (d, *J* = 9.1 Hz), 140.9, 134.2, 131.3, 122.4, 119.5 (d, *J* = 23. 0 Hz), 86.7 (d, *J* = 3.9 Hz) ppm; HRMS (ESI) calcd. for $C_{14}H_8FIO_3H^+$ [M + H^+] m/z 370.95 749, found 370.95715; IR (KBr, cm^{-1}): ν_{max} 1744, 1684, 1595, 1476, 1270, 1235, 1210, 823, 8 03, 508. Mp: 106.0-107.8 °C.



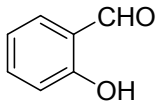
2-((4-Formyl-2-methoxyphenoxy)methyl)benzonitrile (2f): *Following the general procedure*, **2f** was isolated as a yellow solid (53.4mg, 80%), known compound. (CAS: 443289-08-5). ^{1}H NM R (400 MHz, $CDCl_3$): δ 9.87 (s, 1 H), 7.72 (d, *J* =8.0 Hz, 2 H), 7.67-7.63 (m, 1 H), 7.47-7. 43 (m, 3 H), 7.04 (d, *J* =8.0 Hz, 1 H), 5.42 (s, 2 H), 3.96 ppm (s, 3 H); ^{13}C NMR (100 M Hz, $CDCl_3$): δ 190.9, 152.8, 150.2, 139.6, 133.3, 132.9, 131.0, 128.7, 128.3, 126.5, 116.9, 112. 7, 110.9, 109.5, 68.3, 56.1 ppm. Mp: 101.5-102.9 °C.



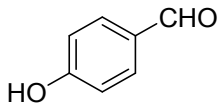
4-Formyl-2-methoxyphenyl 2-nitrobenzoate (2g): *Following the general procedure*, **2g** was isolated as a white solid (46.7mg, 62%), known compound. (CAS: 432011-37-5). ^{1}H NMR (40 0 MHz, $CDCl_3$): δ 9.99 (s, 1 H), 8.05 (dd, *J* =7.6 Hz, 0.8 Hz, 1 H), 7.95 (dd, *J* =7.6 Hz, 1. 6 Hz, 1 H), 7.81-7.76 (m, 1 H), 7.75-7.71 (m, 1 H), 7.56-7.54 (m, 2 H), 7.47 (d, *J* =8.4 Hz, 1 H), 3.95 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 162.9, 152.0, 148.0, 144.1, 135.6, 133.3, 132.3, 130.2, 126.7, 124.9, 124.2, 123.3, 110.8, 56.2 ppm. Mp: 111.0-112.5 °C.



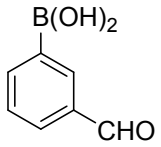
4-Hydroxy-3-methoxybenzaldehyde (2h): *Following the general procedure*, **2h** was isolated as a white solid (31.8 mg, 84%), known compound. The NMR spectroscopic data agree with thos e described in ref.[S4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1 H), 7.43-7.40 (m, 2 H), 7.05 -7.02 (m, 1 H), 6.31 (br, 1 H), 7.05-6.98 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190. 9, 151.7, 147.1, 129.8, 127.5, 114.4, 108.7, 56.0 ppm. Mp: 70.2-72.0 °C.



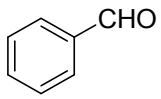
2-Hydroxybenzaldehyde (2i): *Following the general procedure*, **2i** was isolated as a yellow oil (25.9mg, 85%), known compound. The NMR spectroscopic data agree with those described in ref. [S3]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.02 (s, 1 H), 9.89 (s, 1 H), 7.56-7.50 (m, 2 H), 7. 03-6.97 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 161.6, 136.9, 133.7, 120.6, 119.8 , 117.5 ppm.



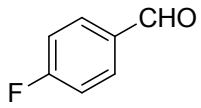
4-Hydroxybenzaldehyde (2j):*Following the general procedure*, **2j** was isolated as a white solid (26.2mg, 86%), known compound. The NMR spectroscopic data agree with those described in ref.[S3]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1 H), 7.86-7.83 (m, 2 H), 7.02-6.99 (m, 2 H), 6.57 ppm (br, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 161.7, 132.6, 129.7, 116.0 ppm. Mp: 102.0-104.0 °C.



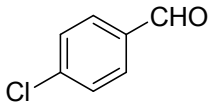
(3-Formylphenyl)boronic acid (2k): *Following the general procedure*, **2k** was isolated as a white solid (33.6 mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[S5]. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.07 (s, 1 H), 8.40 (s, 1 H), 8.18 (d t, J = 7.6 Hz, 1.2 Hz, 1 H), 7.97 (dt, J = 7.6 Hz, 1.6 Hz, 1 H), 7.59 (t, J = 7.6 Hz, 1 H), 7.50 ppm (s, 2 H); ^{13}C NMR (100 MHz, acetone-d_6): δ 193.4, 140.8, 136.9, 136.3, 131.8, 129.1 ppm. (*The boron-bound carbon was not observed due to quadrupolar relaxation.*)



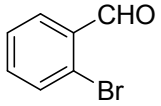
Benzaldehyde (2l): *Following the general procedure*, **2l** was isolated as a yellow oil (23.9mg, 90%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}HNMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1 H), 7.90-7.87 (m, 2 H), 7.66-7.61 (m, 1 H), 7.55-7.52 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 136.3, 134.4, 129.7, 129.0 ppm.



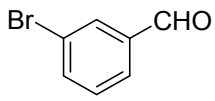
4-Fluorobenzaldehyde (2m): *Following the general procedure*, **2m** was isolated as a yellow oil (25.4mg, 82%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1 H), 7.93-7.88 (m, 2 H), 7.23-7.18 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 166.5 (d, J = 255.1 Hz), 132.9 (d, J = 2.8 Hz), 132.2 (d, J = 9.6 Hz), 116.3 (d, J = 22.1 Hz) ppm.



4-Chlorobenzaldehyde (2n): *Following the general procedure*, **2n** was isolated as a yellow oil (30.5mg, 87%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1 H), 7.82 (d, J = 8.4 Hz, 2 H), 7.51 ppm (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 140.9, 134.7, 130.9, 129.4 ppm.

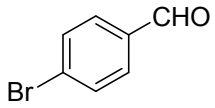


2-Bromobenzaldehyde (2o): *Following the general procedure*, **2o** was isolated as a yellow oil (39.5mg, 86%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 1 H), 7.92-7.90 (m, 1 H), 7.66-7.63 (m, 1 H), 7.46-7.40 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 135.4, 133.9, 133.4, 129.8, 127.9, 127.1 ppm.

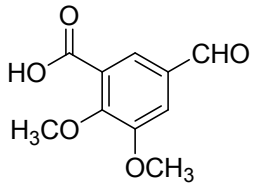


3-Bromobenzaldehyde (2p): *Following the general procedure*, **2p** was isolated as a yellow oil (37.7mg, 82%), known compound. The NMR spectroscopic data agree with those described in ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1 H), 8.02 (t, J = 1.8 Hz, 1 H), 7.83-7.80 (

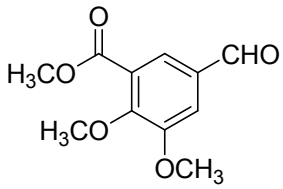
m, 1 H), 7.78-7.75 (m, 1 H), 8.02 ppm (t, J = 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 138.0, 137.3, 132.4, 130.6, 128.4, 123.4 ppm.



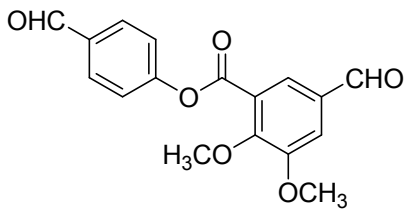
4-Bromobenzaldehyde (2q): *Following the general procedure*, **2q** was isolated as a white soli d (40.0mg, 87%), known compound. The NMR spectroscopic data agree with those described i n ref.[S1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1 H), 7.77-7.74 (m, 2 H), 7.70-7.67 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 135.0, 132.4, 131.0, 129.9 ppm. Mp: 51.8-53.2 ^{o}C.



5-Formyl-2,3-dimethoxybenzoic acid (2r): *Following the general procedure*, **2r** was isolated a s a white solid (34.1mg, 65%), known compound. (CAS: 27203-73-2). ^{1}H NMR (400 MHz, C DCl_3): δ 9.95 (s, 1 H), 8.20 (d, J = 2.0 Hz, 1 H), 7.66 (d, J = 2.0 Hz, 1 H), 4.17 (s, 3 H), 3.99 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 165.1, 153.3, 153.1, 132.6, 128.7, 122.8, 113.7, 62.6, 56.4 ppm. Mp: 141.5-143.2 ^{o}C.

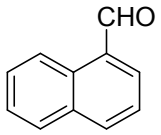


Methyl 5-formyl-2,3-dimethoxybenzoate (2s):*Following the general procedure*, **2s** was isolated as a white solid (39.8mg, 71%), known compound. (CAS: 38209-57-3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1 H), 7.84 (d, J = 2.0 Hz, 1 H), 7.56 (d, J = 2.0 Hz, 1 H), 3.98 (s, 3 H), 3.94 (s, 3 H), 3.93 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 165.6, 154.4, 154. 2, 131.9, 127.1, 126.0, 112.7, 61.7, 56.2, 52.5 ppm. Mp: 62.1-64.0 ^{o}C.

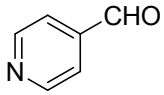


4-Formylphenyl 5-formyl-2,3-dimethoxybenzoate (2t):*Following the general procedure*, **2t** was isolated as a white solid (47.1 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1 H), 9.9

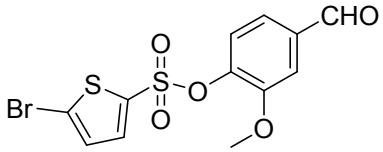
7 (s, 1 H), 8.05 (d, *J* =1.6 Hz, 1 H), 7.99 (d, *J* =8.4 Hz, 2 H), 7.66 (d, *J* =2.0 Hz, 1 H), 7. 44 (d, *J* =8.4 Hz, 2 H), 4.06 (s, 3 H), 3.99 ppm (s 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 1 90.9, 190.2, 162.7, 155.2, 155.2, 154.4, 134.2, 132.0, 131.3, 127.1, 124.6, 122.5, 113.7, 61.9, 5 6.3 ppm; HRMS (ESI) calcd. for $C_{17}H_{14}O_6H^+$ [M + H^+] m/z 315.08631, found 315.08624; IR (KBr, cm^{-1}): ν_{max} 1751, 1697, 1595, 1503, 1487, 1465, 1339, 1289, 1209, 1155, 1040, 863, 789, 507. Mp: 118.5-119.5 °C.



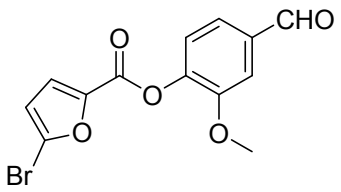
1-Naphthaldehyde (2u): *Following the general procedure*, **2u** was isolated as a yellow oil (25.7 mg, 66%), known compound. The NMR spectroscopic data agree with those described in ref.[S 1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.40 (s, 1 H), 9.26 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* =8.0 Hz, 1 H), 7.98 (dd, *J* =6.8 Hz, 1.2 Hz, 1 H), 7.92 (d, *J* =8.4 Hz, 1 H), 7.72-7.68 (m, 1 H), 7.64-7.58 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 136.7, 135.3, 133.7, 131.3, 1 30.5, 129.0, 128.4, 126.9, 124.8 ppm.



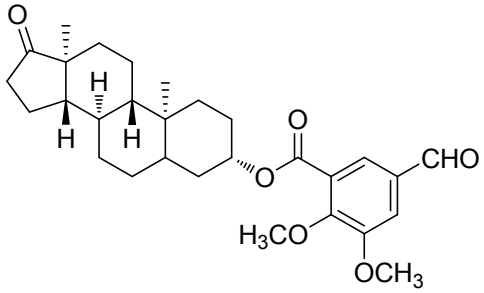
Isonicotinaldehyde (2v): *Following the general procedure*, **2v** was isolated as a yellow oil (2 3.4 mg, 87%), known compound. The NMR spectroscopic data agree with those described in ref.[S6]. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.15 (s, 1 H), 8.89 (d, *J* = 6.0 Hz, 2 H), 7.80 ppm (d, *J* = 6.0 Hz, 2 H); ^{13}C NMR (100 MHz, acetone-d_6): δ 193.1, 152.0, 142.5, 122.8 pp m.



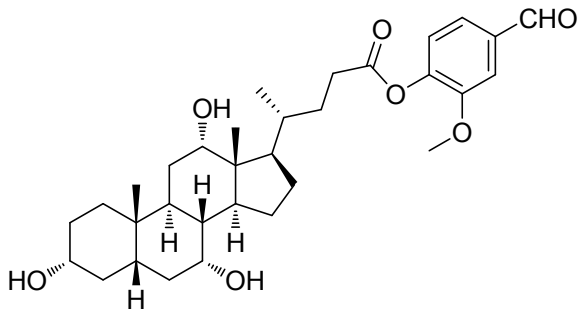
4-Formyl-2-methoxyphenyl 5-bromothiophene-2-sulfonate (2w): *Following the general procedu re except that the oxidant is oxygen*, **2w** was isolated as a white solid (70.5mg, 75%). ^{1}H NM R (400 MHz, $CDCl_3$): δ 9.95 (s, 1 H), 7.48-7.46 (m, 1 H), 7.42-7.40 (m, 2 H), 7.39 (d, *J* = 4.0 Hz, 1 H), 7.10 (d, *J* =4.0 Hz, 1 H), 3.74 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 152.5, 142.5, 136.1, 135.7, 135.6, 130.4, 124.7, 124.4, 123.2, 111.0, 55.9 ppm; HRM S (ESI) calcd. for $C_{12}H_9BrO_5S_2H^+$ [M + H^+] m/z 376.91475, found 376.91434; IR (KBr, cm^{-1}): ν_{max} 1698, 1599, 1497, 1464, 1385, 1273, 1191, 1172, 1145, 1114, 1024, 971, 851, 710, 672, 602, 537. Mp: 91.5-92.6 °C.



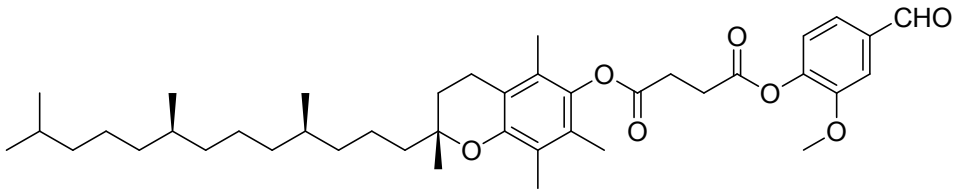
4-Formyl-2-methoxyphenyl 5-bromofuran-2-carboxylate (2x): *Following the general procedure*, **2x** was isolated as a yellow solid (55.1mg, 68%), known compound. (CAS: 875886-01-4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1 H), 7.53-7.50 (m, 2 H), 7.36 (d, *J* =3.6 Hz, 1 H), 7. 33 (d, *J* =8.0 Hz, 1 H), 6.57 (d, *J* =3.6 Hz, 1 H), 3.89 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 154.6, 151.9, 144.8, 143.9, 135.4, 129.0, 124.7, 123.4,122.2, 114.4, 110.8, 5 6.1 ppm. Mp: 108.2-110.0 ^{o}C.



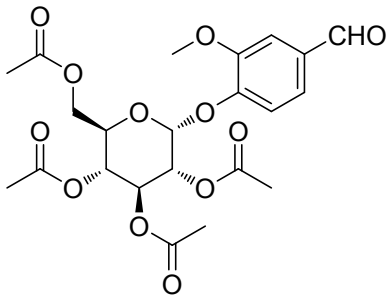
(3S,8R,9S,10S,13S,14S)-10,13-Dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 5-formyl-2,3-dimethoxybenzoate (4a): *Following the general procedure*, **4a** was isolated as a white solid (82.0mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1 H), 7.79 (d, *J* =2.0 Hz, 1 H), 7.54 (d, *J* =2.0 Hz, 1 H), 5.01-4.93 (m, 1 H), 3.98 (s, 3 H), 3.94 (s, 3 H), 2.47-2.40 (m, 1 H), 2.12-1.90 (m, 4 H), 1.82-1.78 (m, 5 H), 1.71-1.45 (m, 7 H), 1.35-1.24 (m, 5 H), 0. 89 (s, 3 H), 0.86 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.3, 190.5, 164.9, 154.2, 154.1, 131.9, 127.0, 126.8, 112.4, 74.9, 61.7, 56.2, 54.2, 51.3, 47.8, 44.7, 36.7, 35.9, 35.7, 35. 0, 33.9, 31.5, 30.8, 28.2, 27.4, 21.8, 20.4, 13.8, 12.2 ppm; HRMS (ESI) calcd. for $C_{29}H_{38}O_6H^+$ [M + H^+] m/z 483.27412, found 483.27423; IR (KBr, cm^{-1}): ν_{max} 2937, 2854, 1737, 1697, 158 2, 1507, 1486, 1456, 1425, 1387, 1339, 1263, 1198, 1140, 1059, 1011, 870, 804, 764, 634, 59 2.



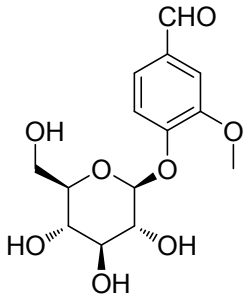
(*R*)-4-Formyl-2-methoxyphenyl 4-((3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-3,7,12-trihydroxy-10, 13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (4b): *Following the general procedure*, **4b** was isolated as a white solid (105.7mg, 78%). ^{1}H NMR (400 MHz, CD Cl_3): δ 9.93 (s, 1 H), 7.47-7.45 (m, 2 H), 7.19 (d, *J* =7.6 Hz, 1 H), 3.98 (brs, 1 H), 3.88 (s, 3 H), 3.84 (brs, 1 H), 3.46 (brs, 4 H), 2.70-2.51 (m, 2 H), 2.28-2.16 (m, 2 H), 1.93-1.31 (m, 20 H), 1.04 (d, *J* =5.2 Hz, 3 H), 0.87 (s, 3 H), 0.68 ppm (s, 3 H); ^{13}C NMR (100 MHz, C DCl_3): δ 191.1, 171.7, 151.9, 145.0, 135.0, 124.8, 123.4, 110.7, 73.1, 72.0, 68.5, 56.0, 47.0, 4 6.4, 41.6, 41.4, 39.4, 39.3, 35.2, 34.7, 34.6, 31.0, 30.8, 30.2, 28.1, 27.5, 26.3, 23.2, 22.4, 17.3, 12.5 ppm; HRMS (ESI) calcd. for $C_{32}H_{46}O_7H^+$ [M + H^+] m/z 543.33163, found 543.33160; I R (KBr, cm^{-1}): ν_{max} 3397, 2936, 2867, 1766, 1699, 1600, 1503, 1464, 1422, 1378, 1272, 1199, 1147, 1118, 1033, 981, 914, 780, 734, 612.



4-Formyl-2-methoxyphenyl ((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroma n-6-yl) succinate (4c): *Following the general procedure*, **4c** was isolated as a yellow oil (136. 2mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1 H), 7.50 (d, *J* =1.2 Hz, 1 H), 7.48 (d d, *J* =8.0 Hz, 1.6 Hz, 1 H), 7.23 (d, *J* =8.0 Hz, 1 H), 3.88 (s, 3 H), 3.10-3.04 (m, 4 H), 2.5 8 (t, *J* =6.8 Hz, 2 H), 2.08 (s, 3 H), 2.01 (s, 3 H), 1.97 (s, 3 H), 1.85-1.74 (m, 2 H), 1.57-1.4 9 (m, 2 H), 1.42-1.20 (m, 16 H), 1.16-1.03 (m, 6 H), 0.87-0.83 ppm (m, 12 H); ^{13}C NMR (1 00 MHz, $CDCl_3$): δ 191.1, 170.7, 169.8, 151.9, 149.5, 144.8, 140.4, 135.2, 126.6, 124.9, 124.8, 123.4, 123.1, 117.4, 110.7, 75.1, 56.1, 39.3, 37.4, 37.3, 32.8, 32.7, 28.9, 28.7, 28.0, 24.8, 24.4, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 13.0, 12.1, 11.8 ppm; HRMS (ESI) calcd. for $C_{41}H_{60}O_7H^+$ [M + H^+] m/z 665.44118, found 665.44153; IR (KBr, cm^{-1}): ν_{max} 2927, 2867, 1759, 1703, 1601, 1503, 1463, 1422, 1378, 1272, 1125, 1032, 780, 734.



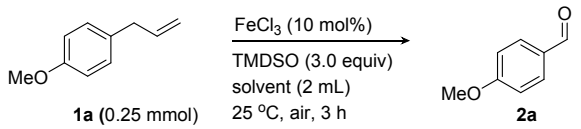
(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(4-formyl-2-methoxyphenoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (4d): *Following the general procedure*, **4d** was isolated as a white solid (98.8 mg, 82%), known compound. The NMR spectroscopic data agree with those described in ref.[S7]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1 H), 7.42-7.40 (m, 2 H), 7.20 (d, *J* =8.0 Hz, 1 H), 5.31-5.27 (m, 2 H), 5.19-5.15 (m, 1 H), 5.10-5.08 (m, 1 H), 4.29-4.25 (m, 1 H), 4.19-4.16 (m, 1 H), 3.88 (s, 3 H), 3.87-3.82 (m, 1 H), 2.07 (d, *J* =2.4 Hz, 6 H), 2.04 ppm (d, *J* =2.4 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 170.5, 170.2, 169.4, 169.2, 151.0, 150.9, 132.7, 125.4, 118.0, 110.6, 99.6, 72.3, 72.2, 70.9, 68.1, 61.8, 56.0, 20.7, 20.6, 20.6, 20.6 ppm.



Glucovanillin (4e) *Following the general procedure*, **4e** was isolated as a white solid (68.3 mg, 87%), known compound. The NMR spectroscopic data agree with those described in ref.[S8]. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.86 (s, 1 H), 7.52 (dd, *J* = 8.4 Hz, 1.6Hz, 1 H), 7.43 (d, *J* = 1.6 Hz, 1 H), 7.28 (d, *J* = 8.4 Hz, 1 H), 5.38 (d, *J* = 4.8 Hz, 1 H), 5.15 (d, *J* = 4.0 Hz, 1 H), 5.11-5.08 (m, 2 H), 4.59 (t, *J* = 5.6 Hz, 1 H), 3.84 (s, 3 H), 3.68-3.65 (m, 1 H), 3.50-3.47 (m, 1 H), 3.38-3.37 (m, 1 H), 3.30-3.28 (m, 2 H), 3.20-3.14 (m, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.6, 151.7, 149.3, 130.5, 125.4, 114.5, 110.4, 99.3, 77.1, 76.8, 73.1, 69.5, 60.5, 55.6 ppm. Mp: 184.7-185.3 °C.

3. Conditional Optimization

Table S1. Optimization for iron-catalyzed aerobic oxidative C–C bond cleavage of **1a** at ambient conditions.

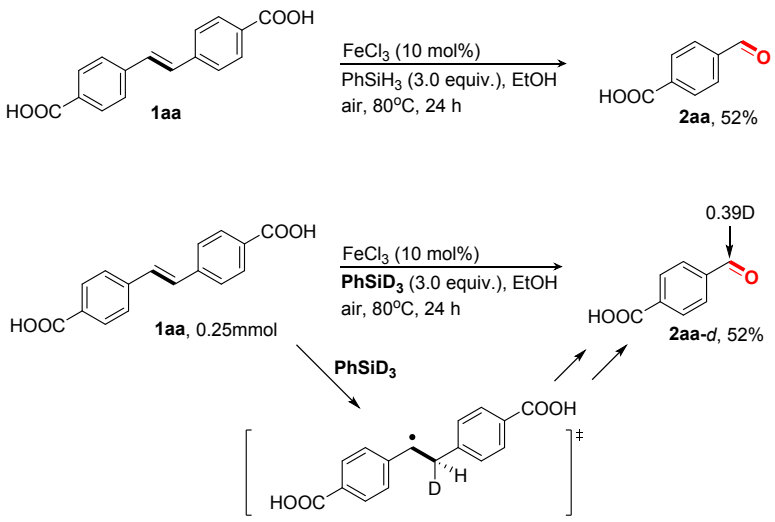


Entry	Solvent	Yield of **2a** (%)
1	EtOH	88(80)[a](87)[b]
2	*i*PrOH	64
3	*t*BuOH	18
4	THF	36
5	1,4-Dioxane	76
6	DCM	0
7	DMF	15
8	CH_3CN	8
9	DMSO	11

[a] TMDSO (2.0 equiv). [b] TMDSO (4.0 equiv). Yields of the isolated products are given

4. Preliminary Mechanistic Studies

(1) The effect of $PhSiD_3$ as hydrosilane



Following the *general procedure A*, a reaction of $FeCl_3$ (0.025 mmol, 4.1 mg), **1aa** (0.25 mmol, 69.9 mg), and **$PhSiD_3$** (98% deuterium incorporation) (0.75 mmol, 92 μL) in EtOH (2.0 mL) was carried out in air atmosphere at 80 °C for 24 h. Then, the volatiles were removed and the analytically pure product was obtained by flash chromatography. Subjecting olefin **1aa** to the reaction conditions using **$PhSiD_3$** as the solvent led to the isolation of the desired ketone **2aa-*d*** (52%

yield) with bearing a deuterium atom (39% atom D), indicating the H that adds across the olefin stems from hydrosilane. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.10 (s, J = 8.8 Hz, 0.61 H), 8.12 (d, J = 8.0 Hz, 2 H), 8.01 ppm (d, J = 8.0 Hz, 2 H).

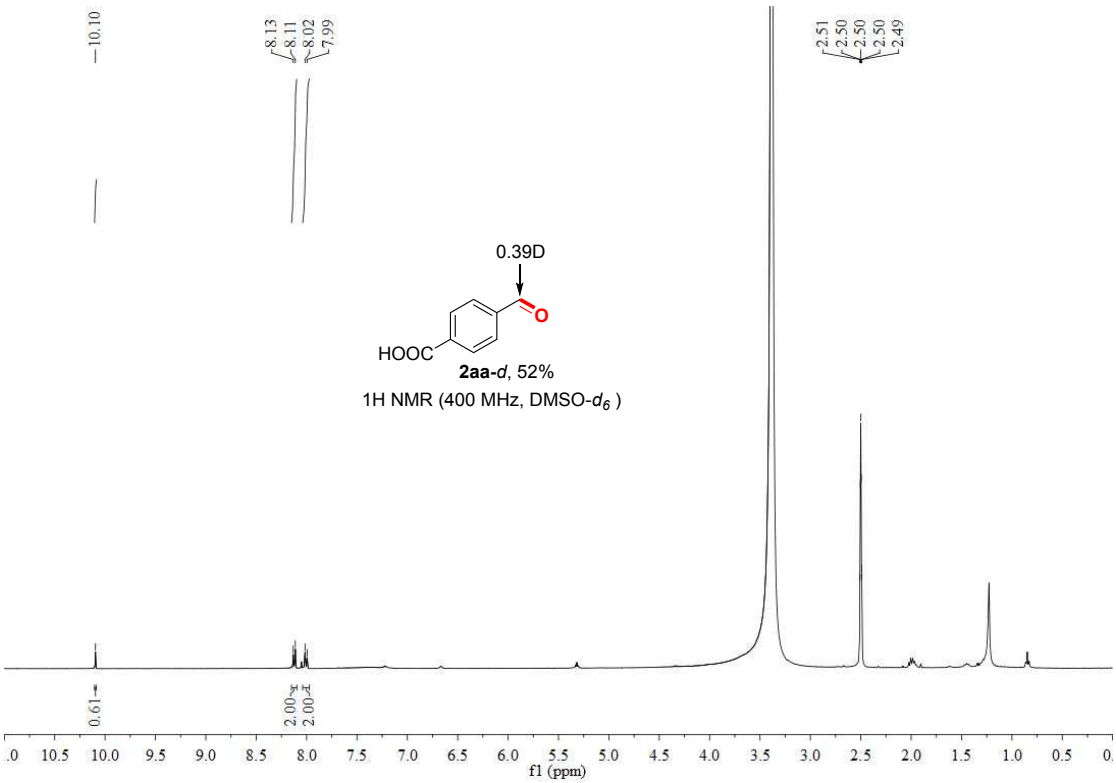
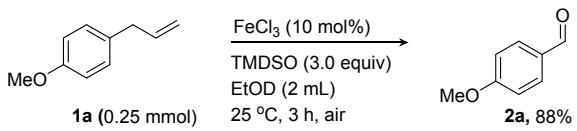


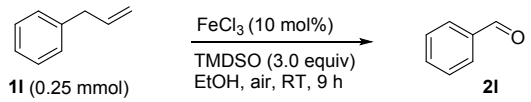
Figure S1. Spectra for the deuterium labeling study

(2) The effect of EtOD as solvent



Following the *general procedure A*, a reaction of $FeCl_3$ (0.025 mmol, 4.1 mg), **1a** (0.25 mmol, 40 μL), and TMDSO (0.75 mmol, 135 μL) in **EtOD** (2.0 mL) was carried out in air atmosphere at 25 °C for 3 h. Then, the volatiles were removed and the analytically pure product was obtained by flash chromatography. Subjecting olefin **1a** to the reaction conditions using EtOD as the solvent led to the isolation of the desired ketone without bearing a deuterium atom, implying the H that adds across the olefin doesn't originate from solvent EtOH.

(3) Effect of radical scavengers

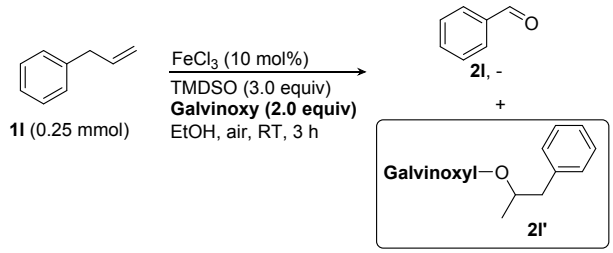


No scavenger	90%
TEMPO (1.0 equiv)	0
DDQ (1.0 equiv)	0

Scheme S1. Effect of radical scavengers.

As per the *general procedure A*, two reactions of $FeCl_3$ (0.025 mmol, 4.1 mg), **1l** (0.25 mmol, 34 µL), and TMDSO (0.75 mmol, 135 µL) in EtOH (2.0 mL) was carried out, one as a control. A radical scavenger [TEMPO (39.9 mg, 0.25 mmol), or DDQ (57.9 mg, 0.25 mmol)] was introduced to the reactions. All reaction mixtures were stirred at 80 °C and ambient pressure for 2 h.

(4) Interception of radical intermediate



Following the *general procedure A*, a reaction of $FeCl_3$ (0.025 mmol, 4.1 mg), galvinoxyl (0.5 mmol, 215.1 mg), **1l** (0.25 mmol, 34 µL), and TMDSO (0.75 mmol, 135 µL) in EtOH (2.0 mL) was carried out in air atmosphere at 25 °C for 3 h. Consequently, the oxidation process is completely inhibited and a radical intermediate is intercepted by the galvinoxyl to generate 2**l'** that is detected according to HRMS (ESI) analysis (Figure S2). This result supports formation of carbon radical intermediate.

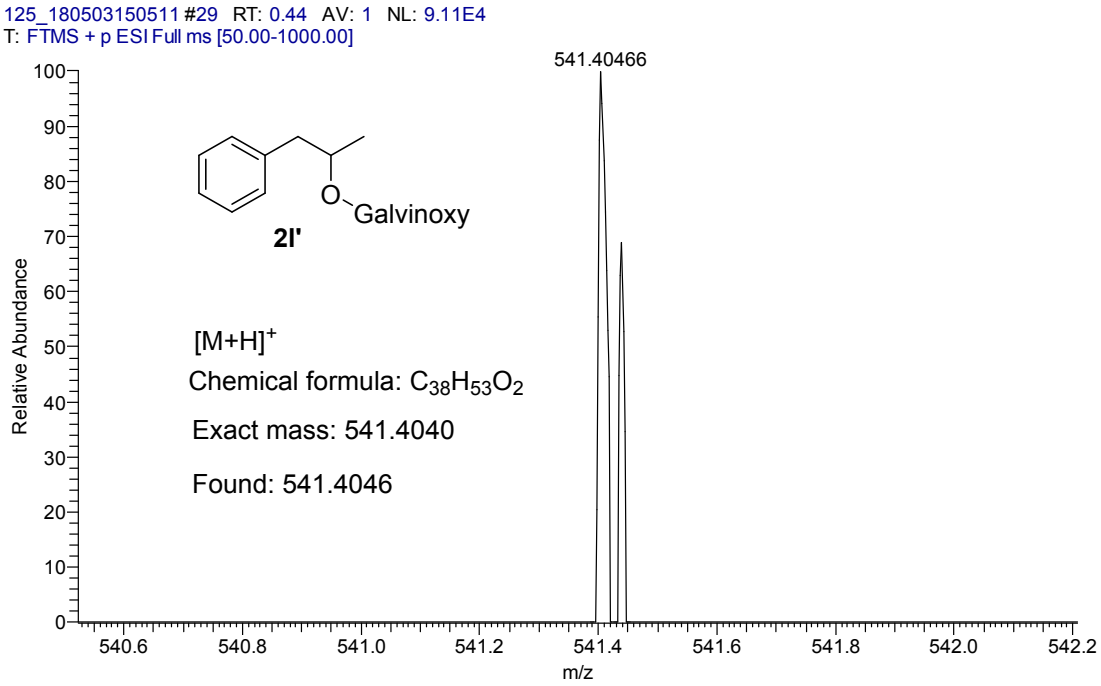
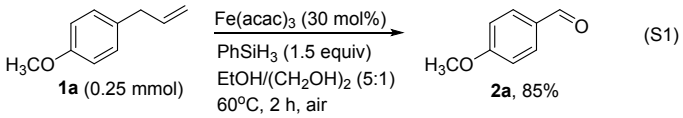


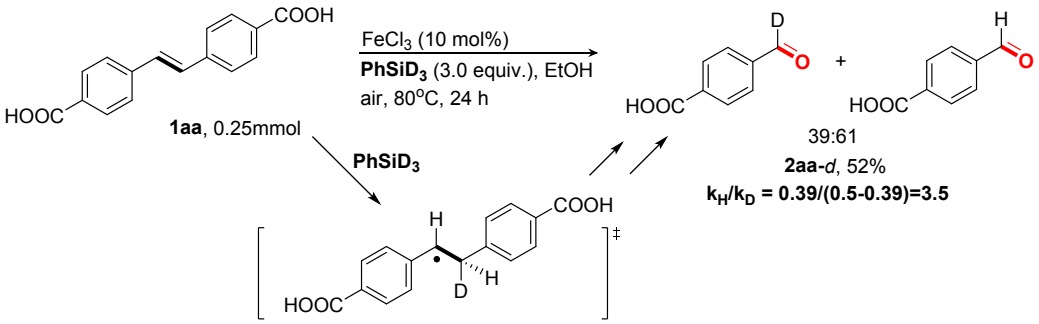
Figure S2. HRMS of **2l'**

(5) An experiment under Baran's conditions



Recently, Baran and co-workers reported an iron-catalyzed reductive olefin coupling via a hydrogen radical transfer process (J. C. Lo, Y. Yabe, P. S. Baran, *J. Am. Chem. Soc.* **2014**, *136*, 1304−1307). According to the Baran's procedure, the reaction of **1a (**0.25 mmol, 40 μL) provided the desired 4-methoxybenzaldehyde (**2a**) in 85% yield under the conditions of $Fe(acac)_3$ (0.075 mmol, 26.8 mg), $PhSiH_3$ (0.375 mmol, 48 μL), $EtOH/(CH_2OH)_2$ (5:1, 1.2 mL), 60 °C, 2 h, and air atmosphere [eqn(S1)]. This result suggests that hydrogen radical transfer process may be involved in the present transformation.

(6) Kinetic isotope effect



Following *general procedure A*, a reaction of $FeCl_3$ (0.025 mmol, 4.1 mg), **1aa** (0.25 mmol, 69.9 mg), and **$PhSiD_3$** (98% deuterium incorporation) (0.75 mmol, 92 μL) in EtOH (2.0 mL) was carried out in air atmosphere at 80 °C for 24 h. Then, the volatiles were removed and the analytically pure product was obtained by flash chromatography. A primary kinetic isotope effect k_H/k_D of 3.5 for the formation of the aldehyde was measured via ^{1}H NMR, indicating that deprotonation is the overall turnover-limiting step. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.10 (s, J = 8.8 Hz, 0.61 H), 8.12 (d, J = 8.0 Hz, 2 H), 8.01 ppm (d, J = 8.0 Hz, 2 H).

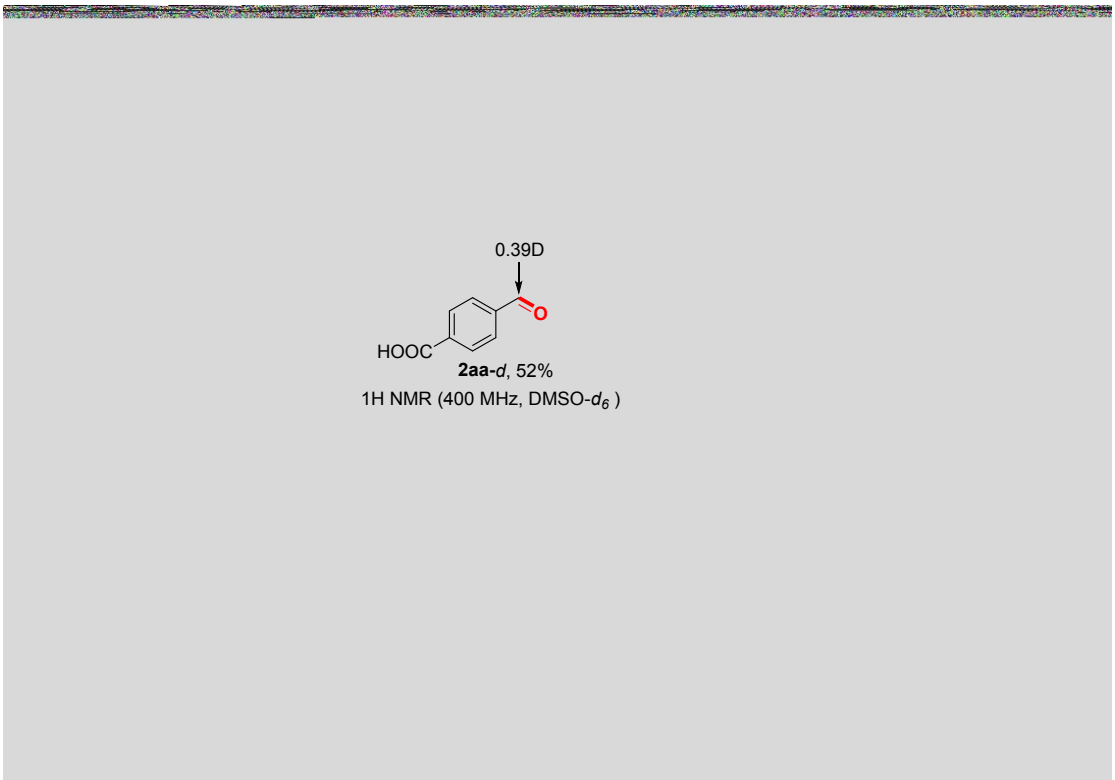
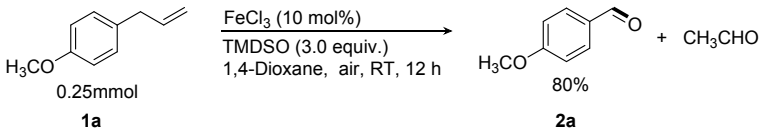


Figure S3. Spectra for the deuterium labeling study

(7) GC analysis of acetaldehyde in reaction mixture



Following *general procedure A*, a 25mL flask was charge with $FeCl_3$ (0.025 mmol, 4.1 mg), **1a** (0.25 mmol, 40 μL), and TMDSO (0.75 mmol, 135 μL) in 1,4-dioxane (To exclude the interference of EtOH generating acetaldehyde, 1,4-dioxane was chosen as the solvent.) (2.0 mL), and sealed with a rubber stopper. The reaction was stirred at room temperature for 12 h. Head space sampling was taken from the reaction flask and analyzed by GC (gas chromatography) (Figure S3, black trace). In the spectrum, two higher peaks are corresponding to 1,4-dioxane and TMDSO that were identified by their GC (Figure S3, light green trace and orange trace) under the same conditions. The rest peak is identical to the GC of the acetaldehyde standard sample (Figure S3, blue trace), indicating that acetaldehyde is generated in the reaction. (GC analysis was performed on an HP-5 (Agilent 19091J-413, 30 m × 320 μm × 0.25 μm) capillary column. GC conditions were 60 °C held for 2.0 min, ramped at 5°C/min to 200°C, with a carrier gas flow rate of 4.0 mL/min.)

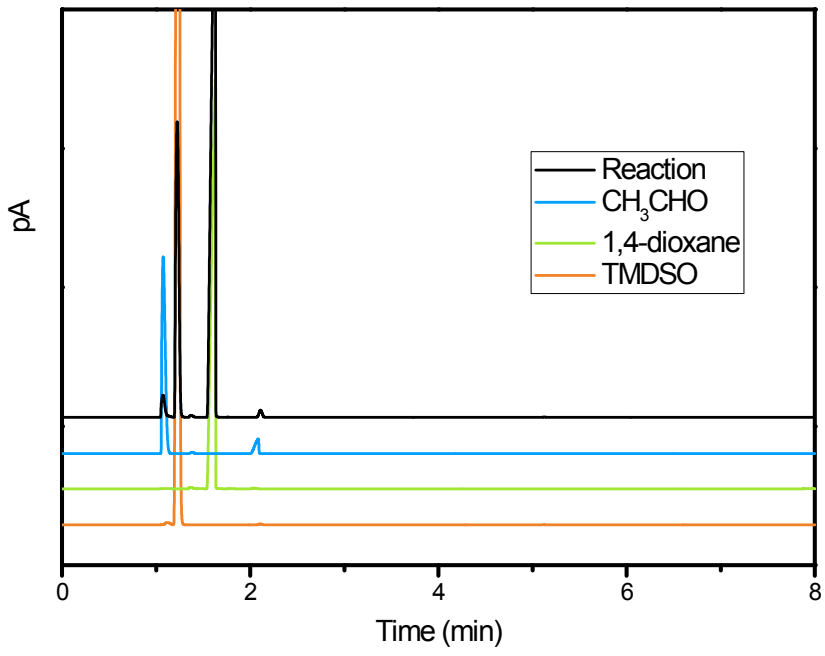
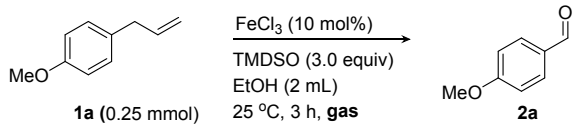


Figure S4. GC analysis of acetaldehyde in the reaction mixture

(8) The effect of gases

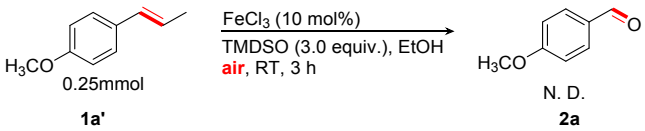
Table S2. The effect of gases.



Entry	Gas (1 atm)	Time (h)	Yield of **2a** (%)
1	N_2	3	0
3	air	3	88
4	O_2	2	91

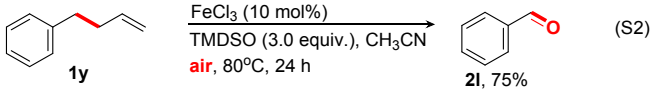
As per *general procedure A*, four reactions of $FeCl_3$ (0.025 mmol, 4.1 mg), **1a** (0.25 mmol, 40 μL), and TMDSO (0.75 mmol, 135 μL) in EtOH (2.0 mL) were carried out in different atmosphere [N_2, air, or O_2], one as a control. All reaction mixtures were stirred at 25 °C and ambient pressure for the indicated time. As shown in the Table S2, the concentration of molecular oxygen evidently affects the reaction rate. When molecular oxygen is absent, the reaction will not proceed. These results suggest that the oxygen atom in the product should stem from molecular oxygen.

(9) Examination on the process of tandem allylbenzene isomerization-oxidation cleavage

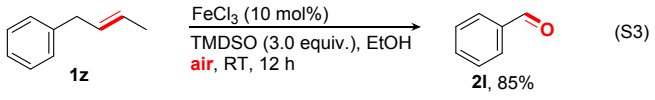


Following the *general procedure A*, a reaction of $FeCl_3$ (0.025 mmol, 4.1 mg), **1a'** (0.25 mmol, 38 μL), and TMDSO (0.75 mmol, 135 μL) in EtOH (2.0 mL) was carried out in air atmosphere at 25°C for 3 h. When *trans*-anethole (**1a'**) took the place of olefin **1a** under otherwise identical conditions, no product was produced. This result suggests that the process of tandem allylbenzene isomerization-oxidation cleavage can be ruled out.

5. Reactions of Homoallylbenzene, Internal Olefin, and Eugenol



(S2)



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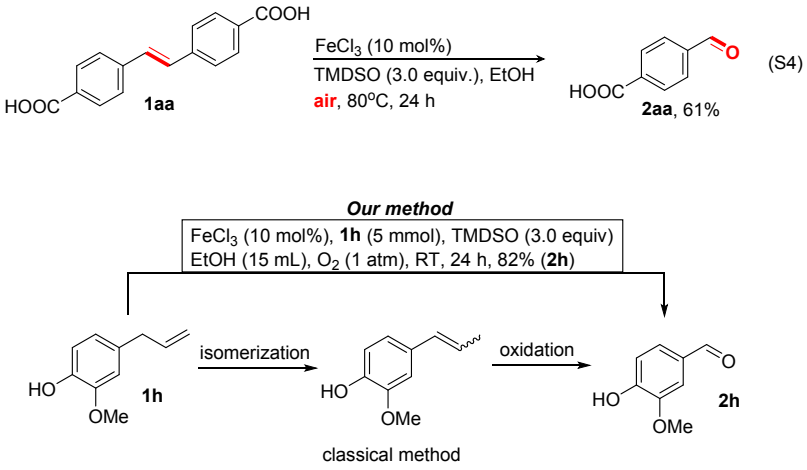

Scheme S2. Synthesis of Vanillin (**2h**).

6. References

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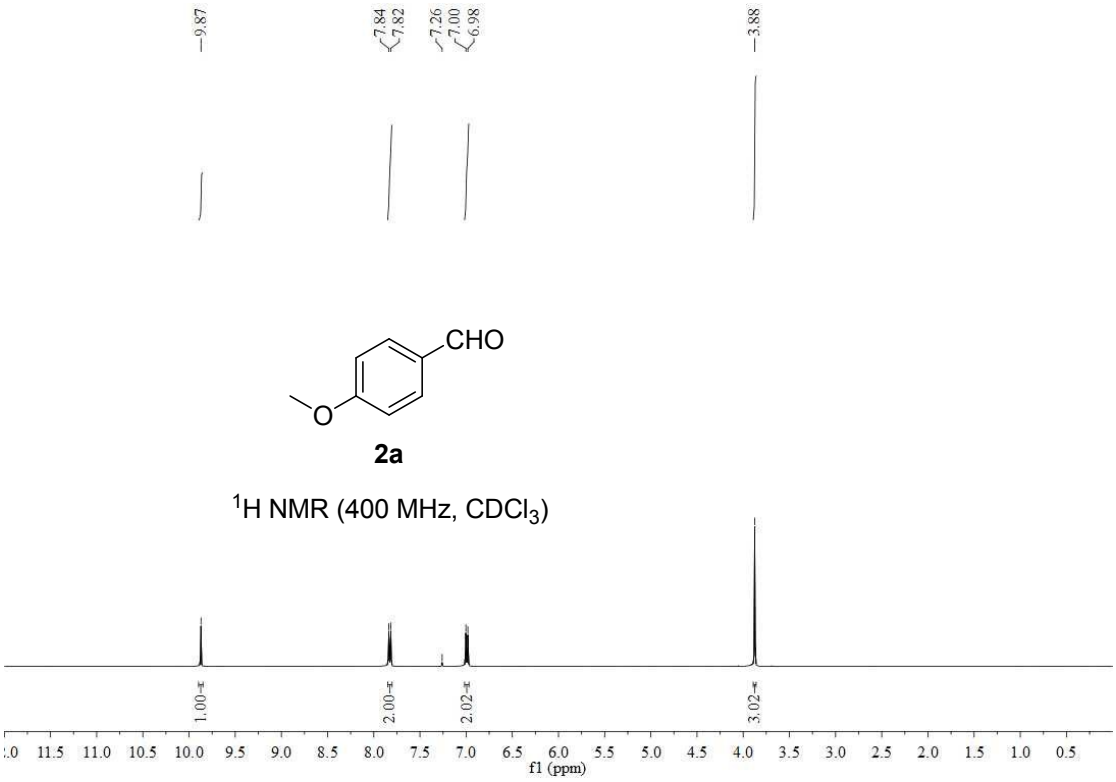
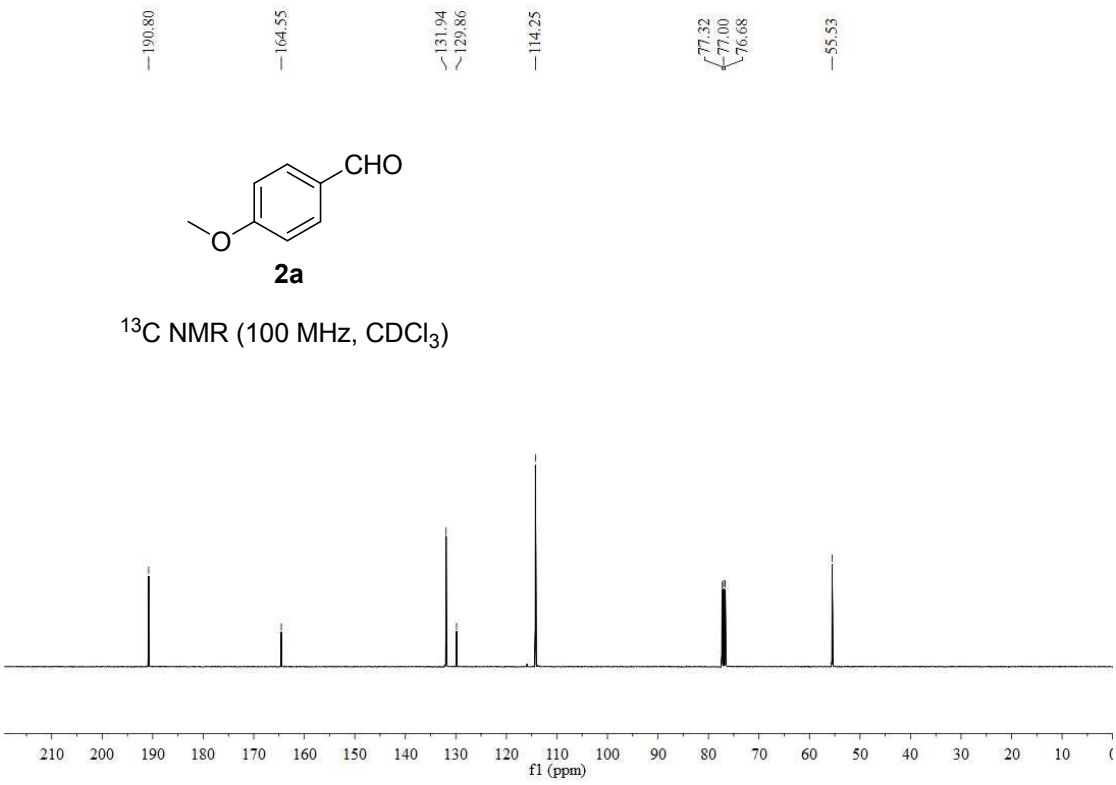
7. Copies of NMR Spectra



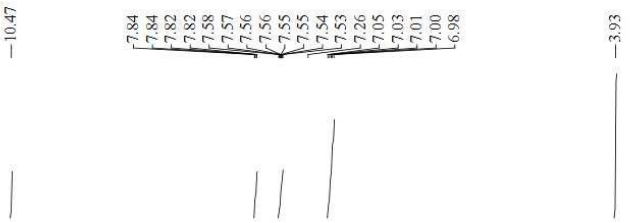
2a

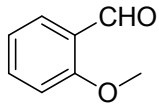
^{1}H NMR (400 MHz, $CDCl_3$)



2a

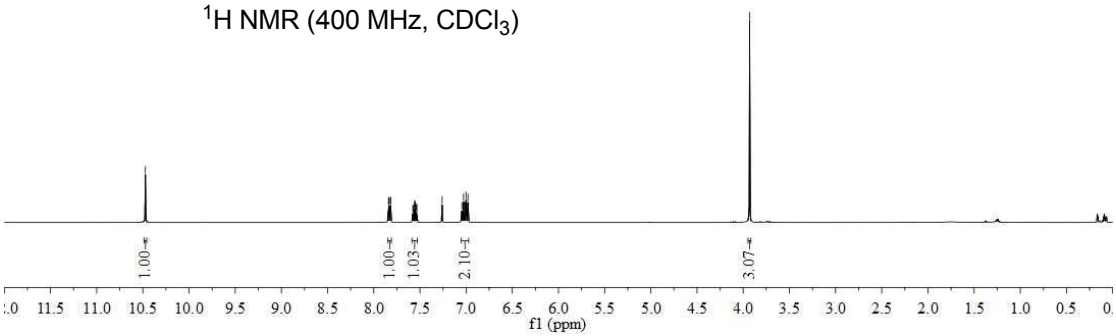
^{13}C NMR (100 MHz, $CDCl_3$)

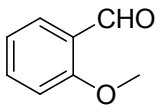




2b

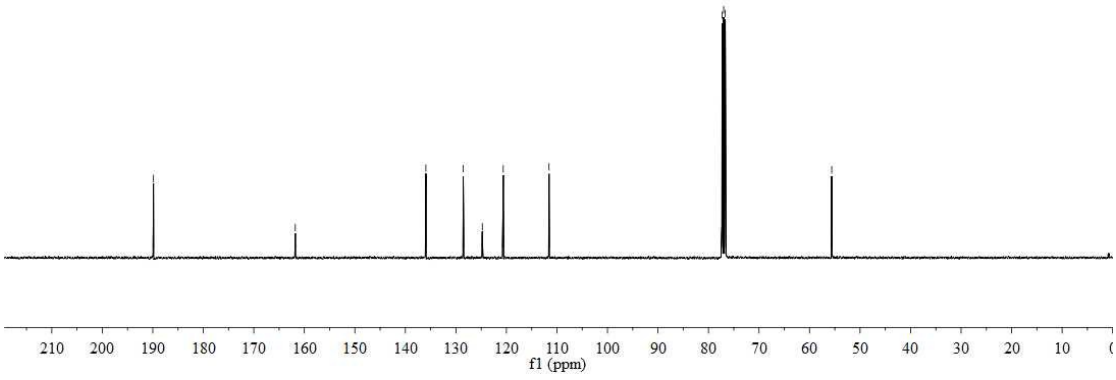
^{1}H NMR (400 MHz, $CDCl_3$)

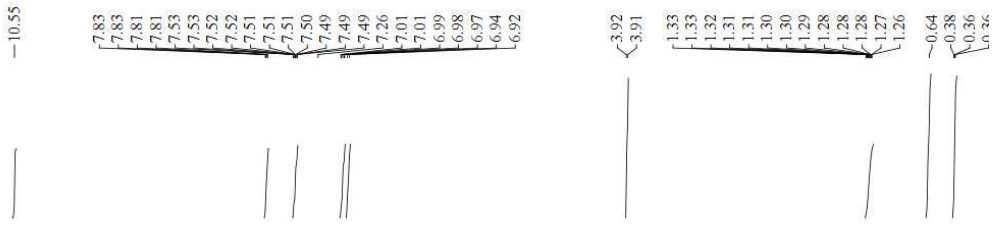


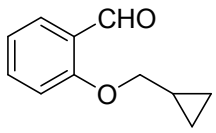


2b

^{13}C NMR (100 MHz, $CDCl_3$)







2c

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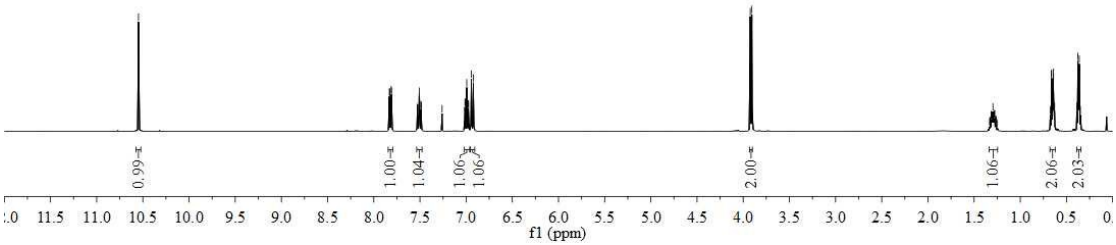
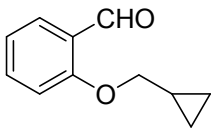
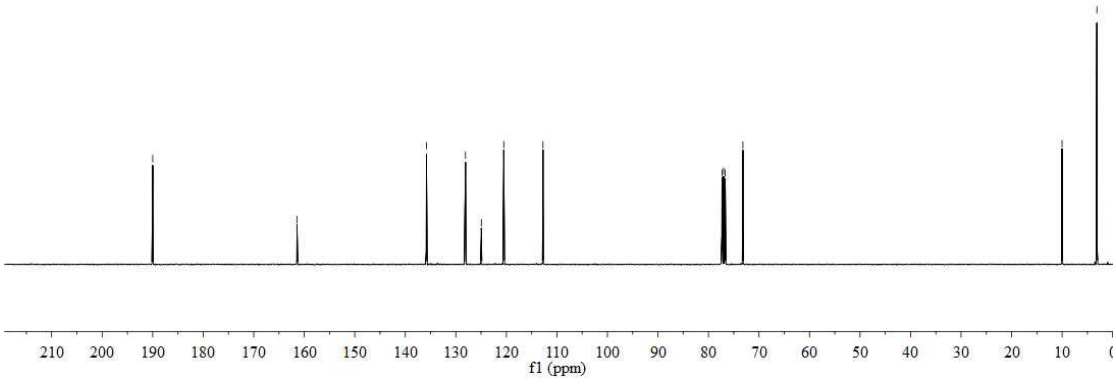
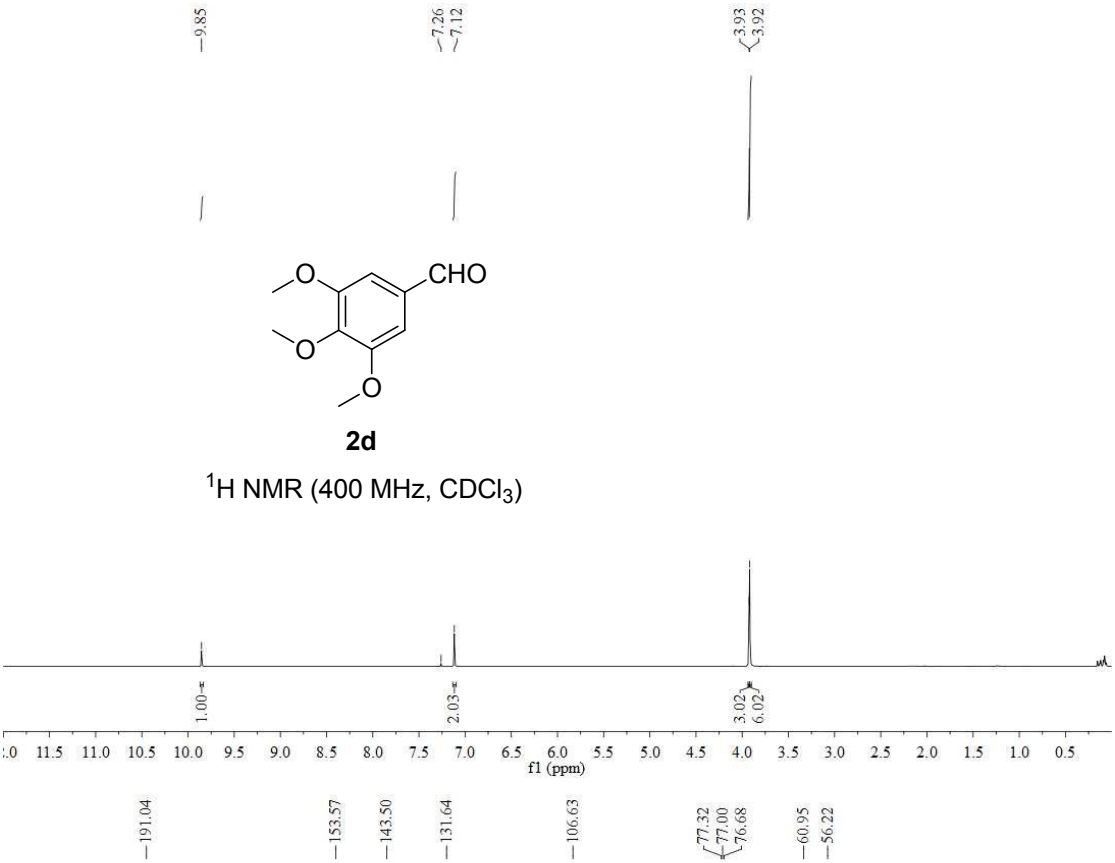




2c

^{13}C NMR (100 MHz, $CDCl_3$)





2d

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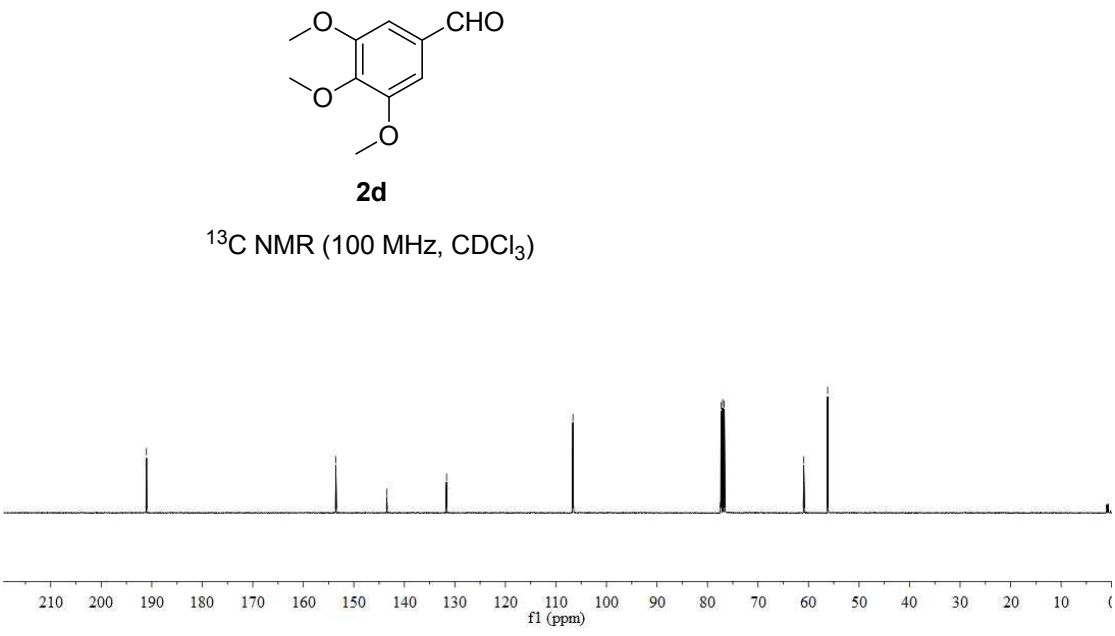

2d

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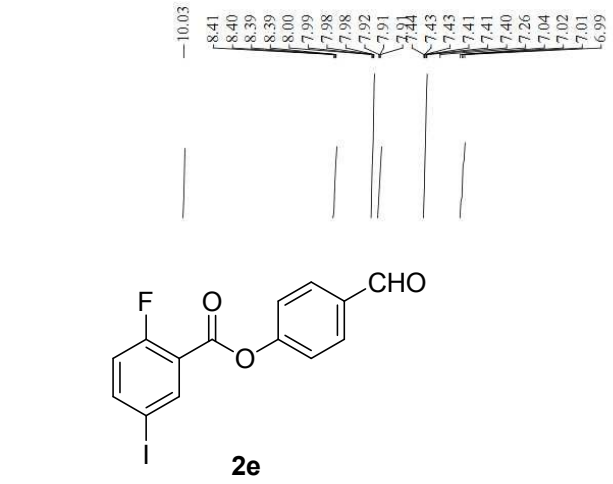

2e

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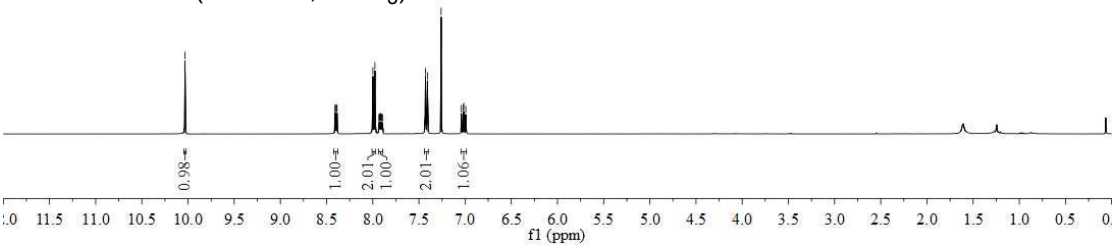

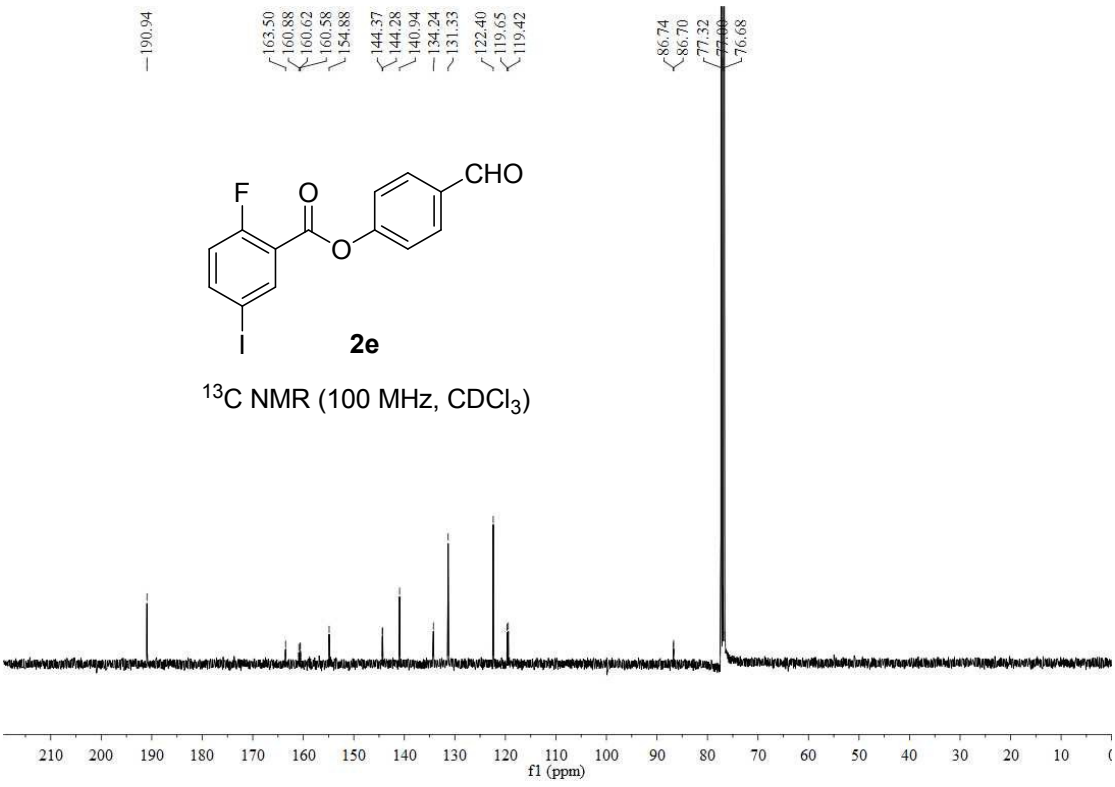

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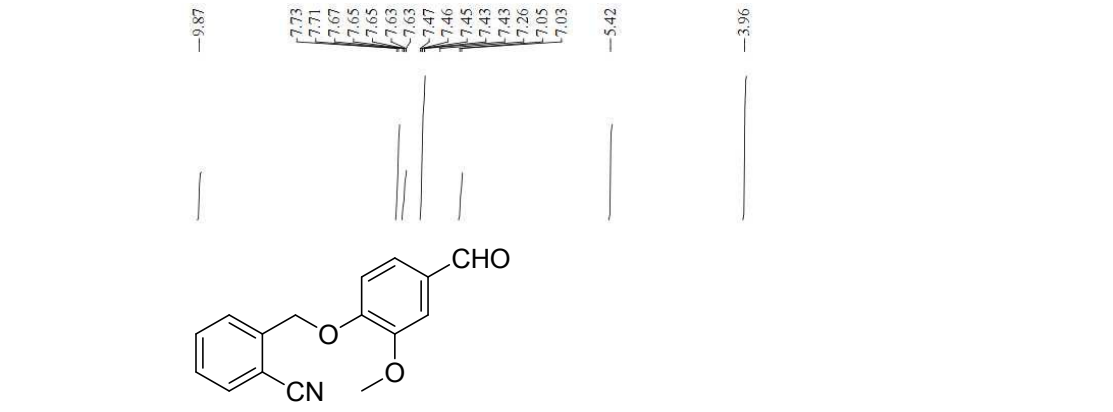

2f

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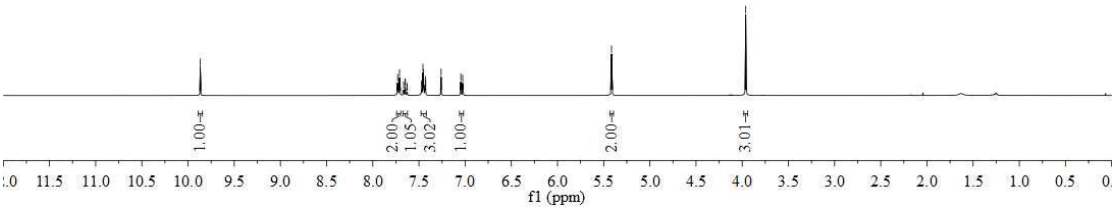

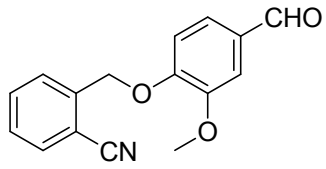

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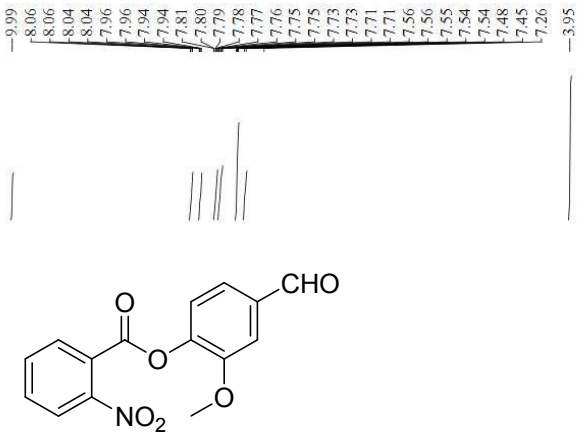

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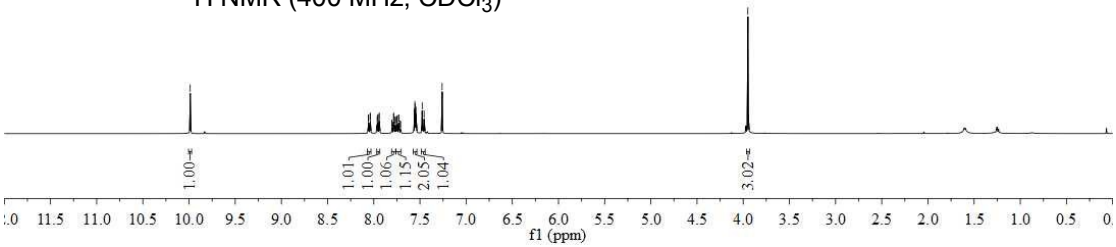

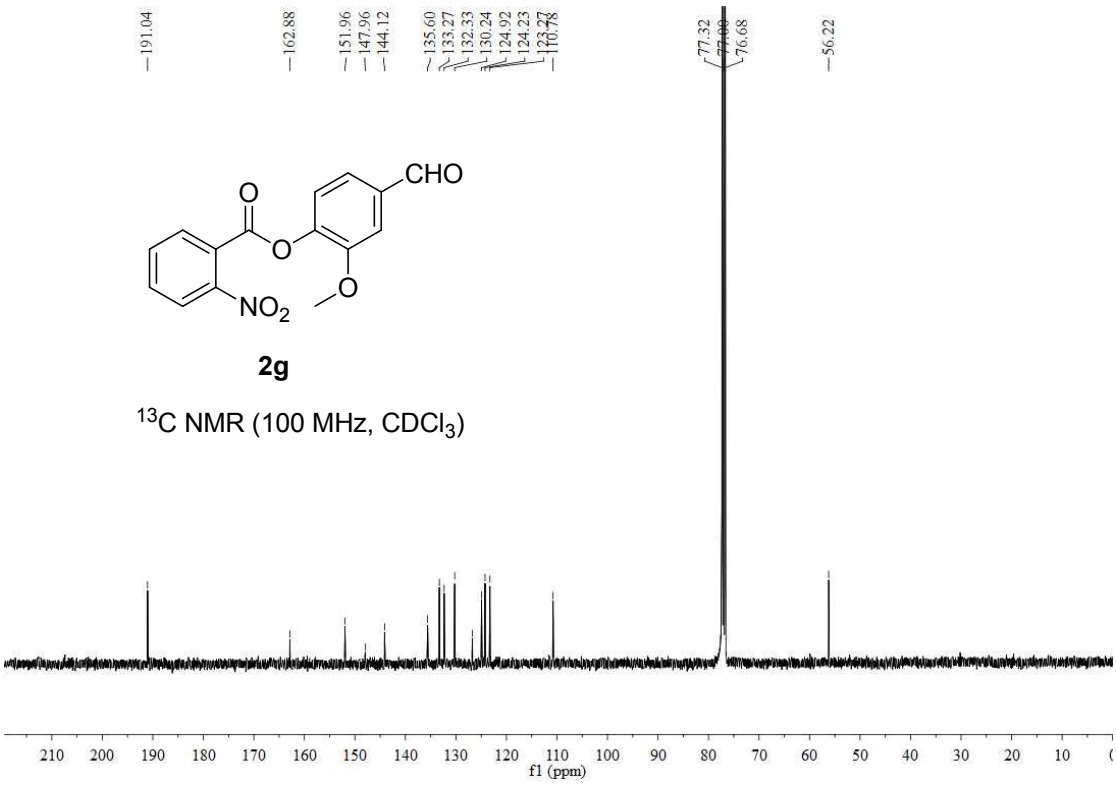

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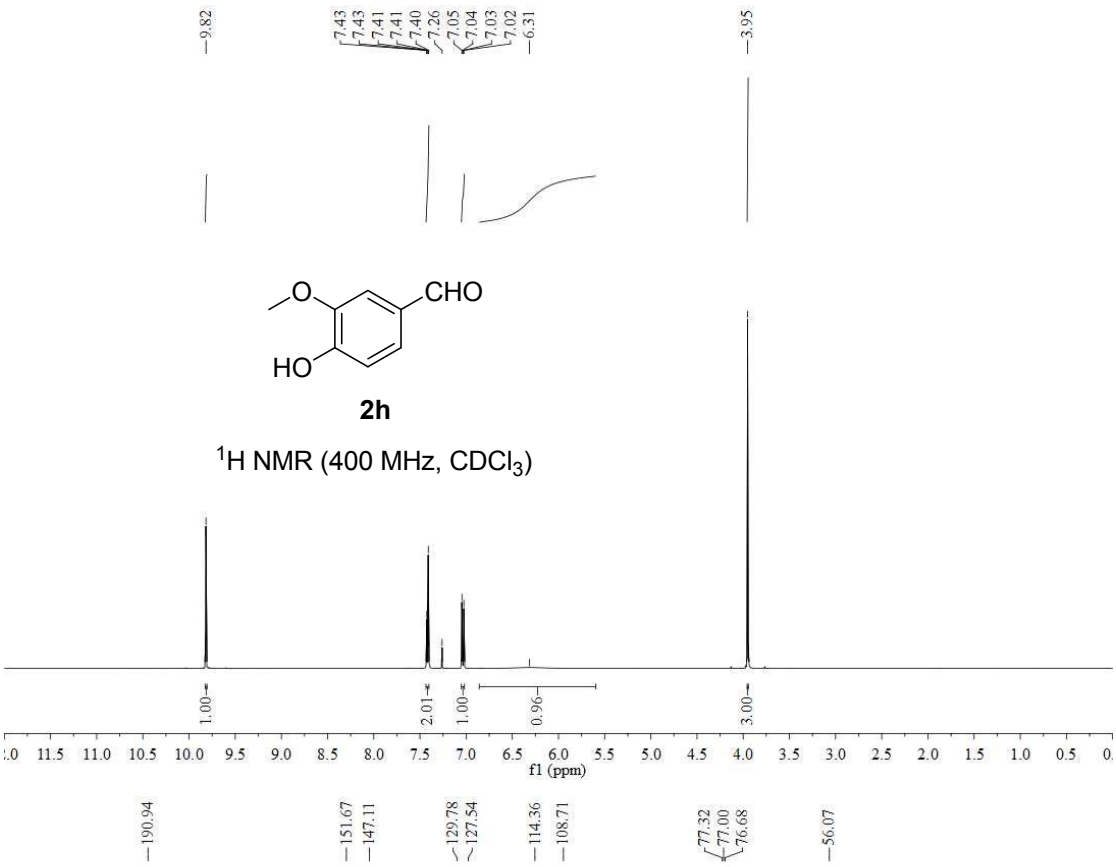

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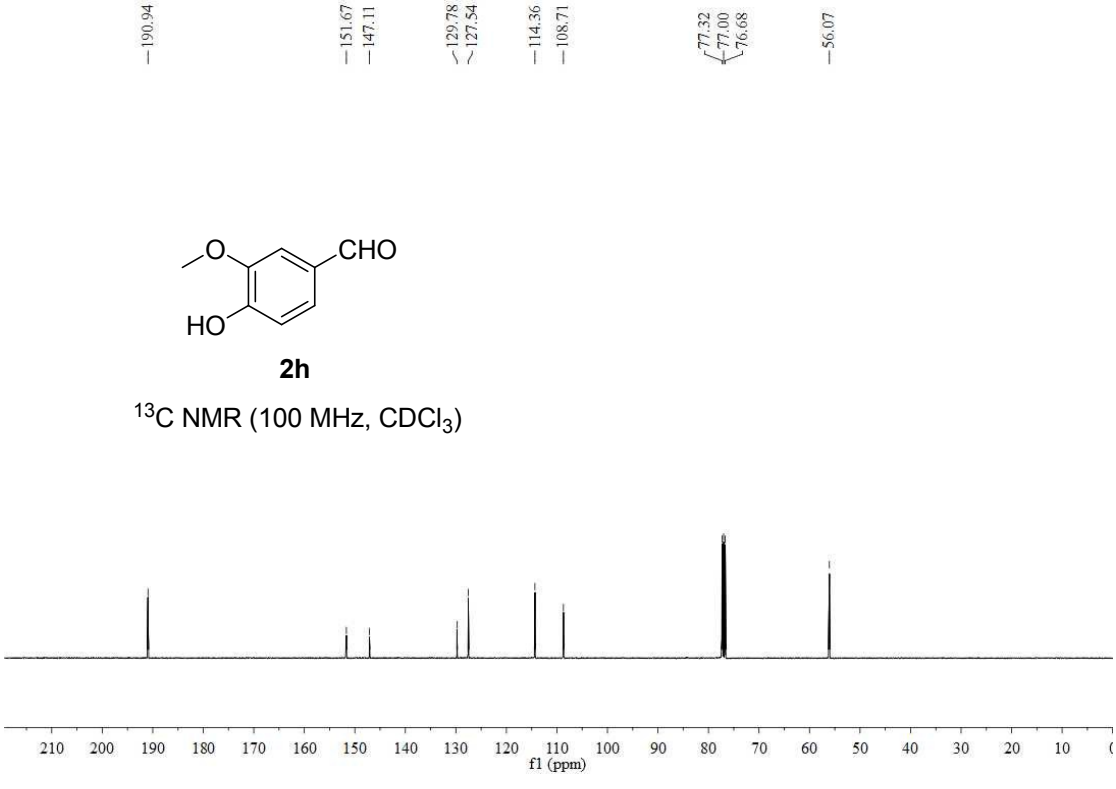

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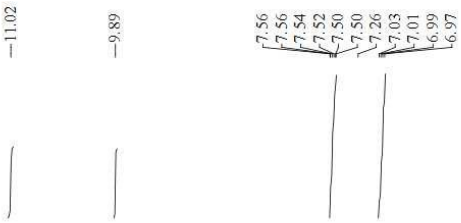

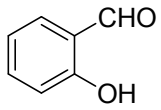

2i

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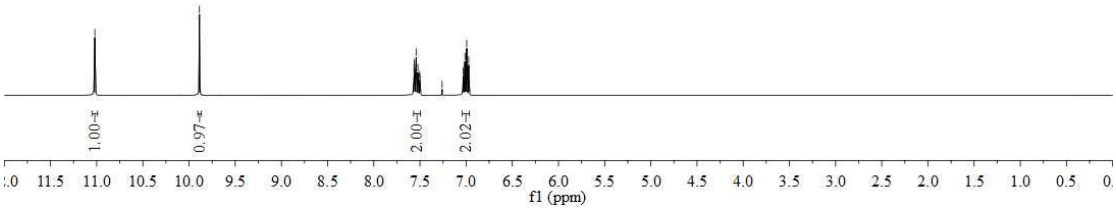

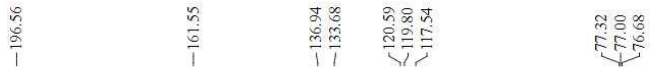

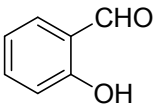

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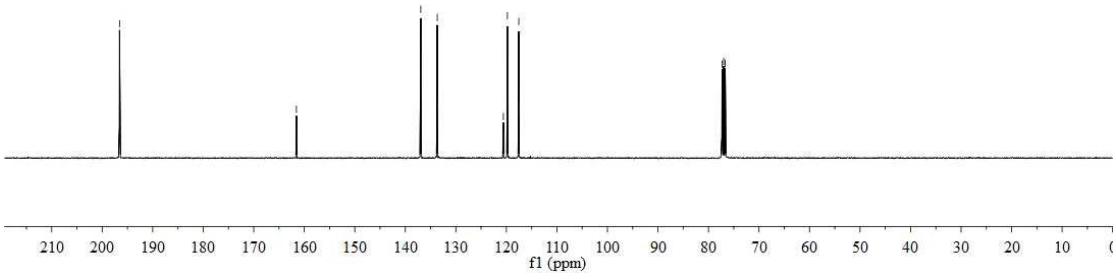

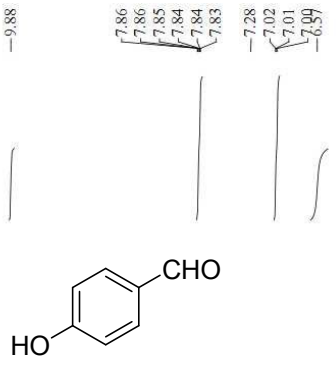

2j

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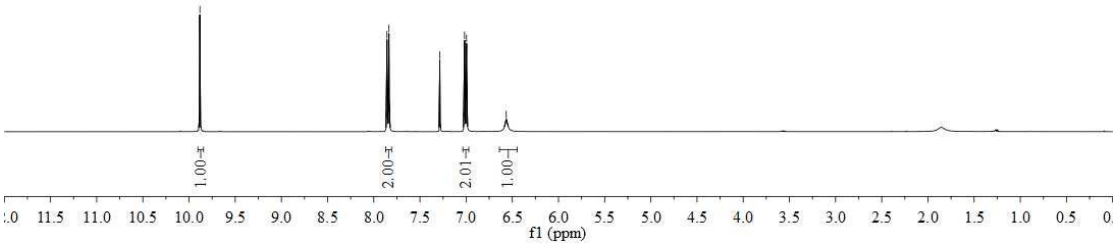

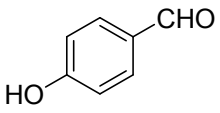

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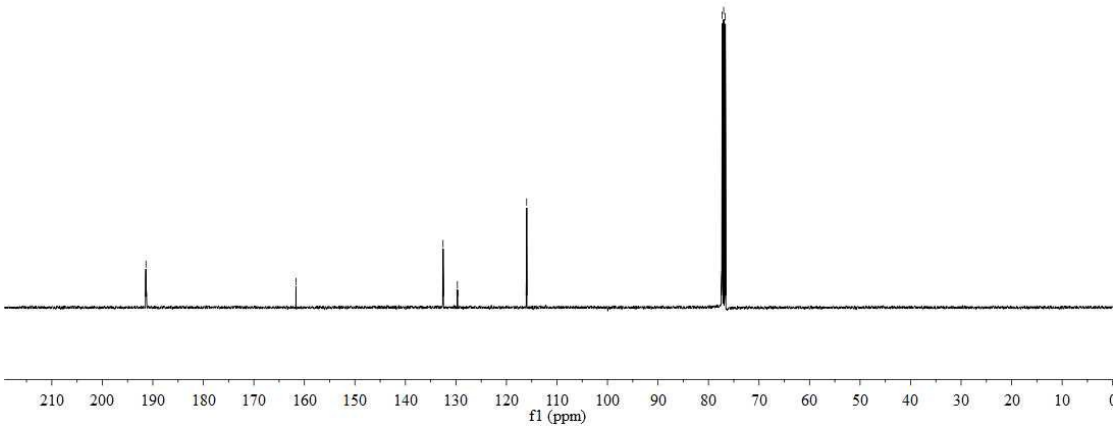
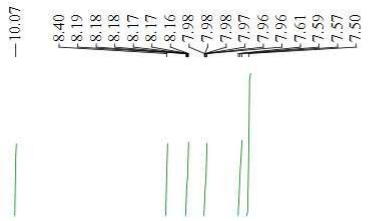
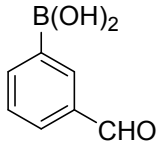
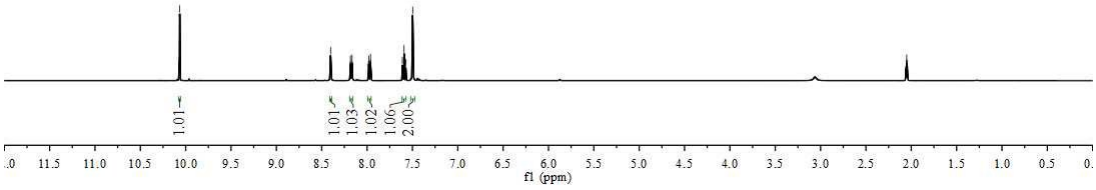


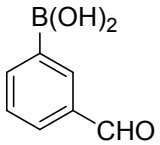




2k

^{1}H NMR (400 MHz, acetone-d_6)





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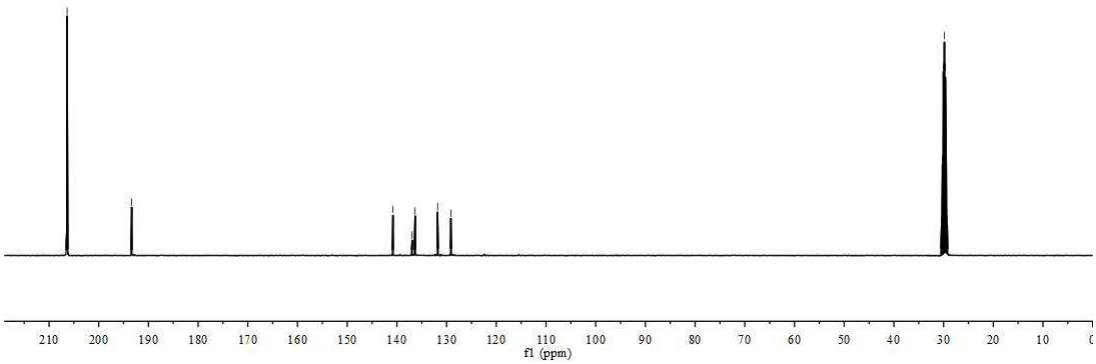

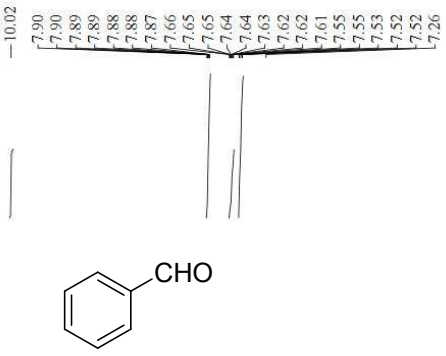

2l

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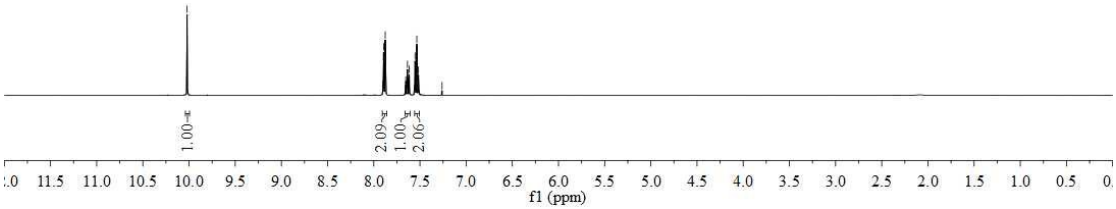

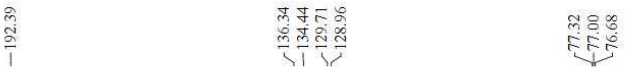

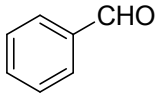

2l

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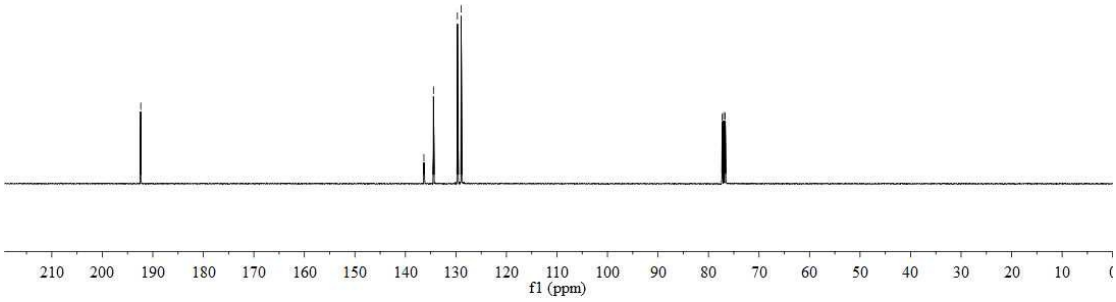

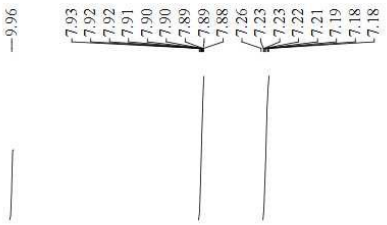

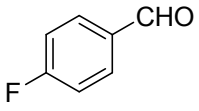

2m

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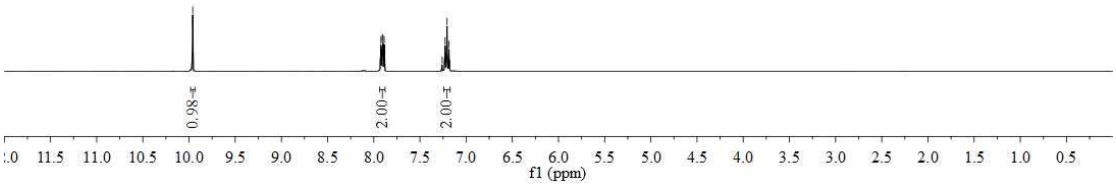
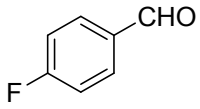
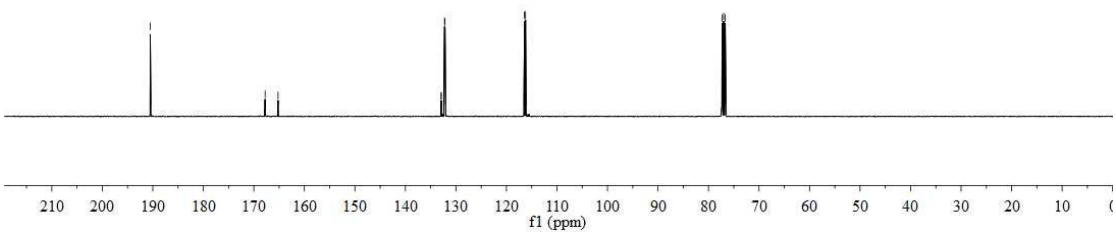
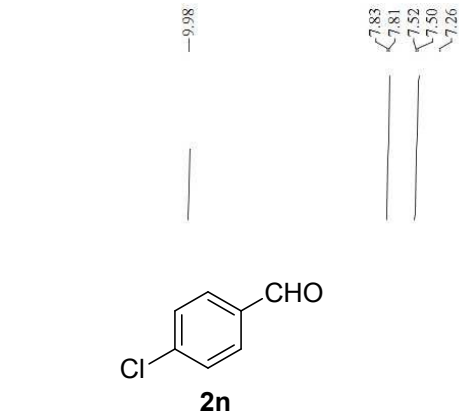




2m

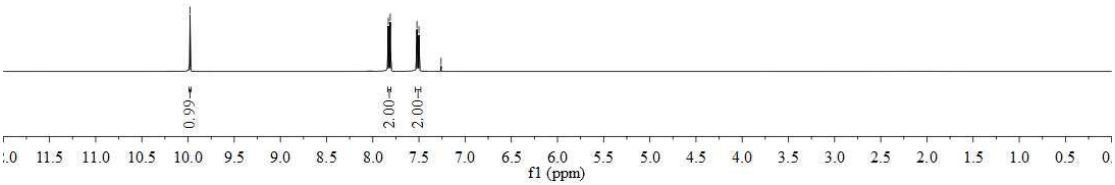
^{13}C NMR (100 MHz, $CDCl_3$)

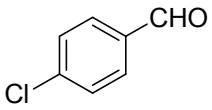




2n

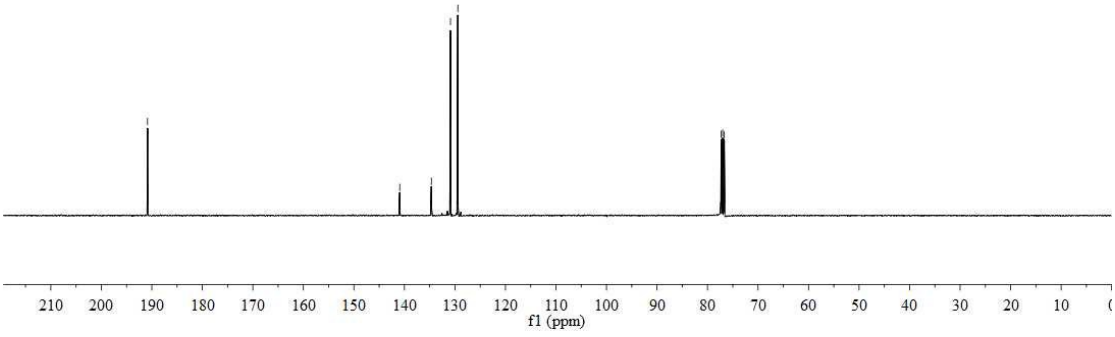
^{1}H NMR (400 MHz, $CDCl_3$)

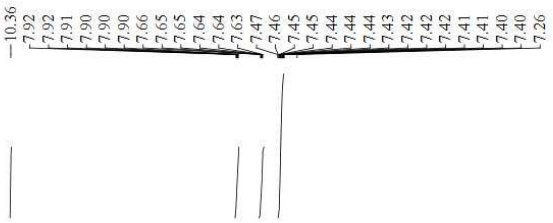


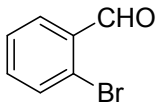


2n

^{13}C NMR (100 MHz, $CDCl_3$)

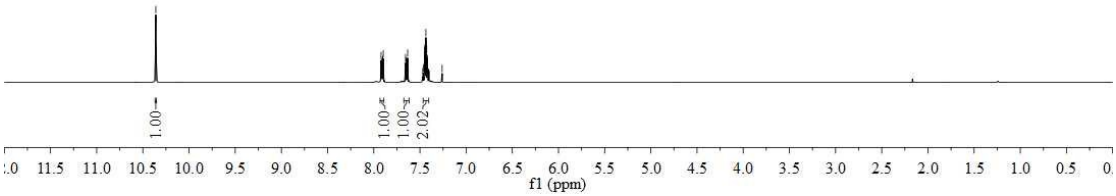


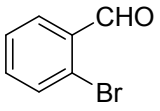




2o

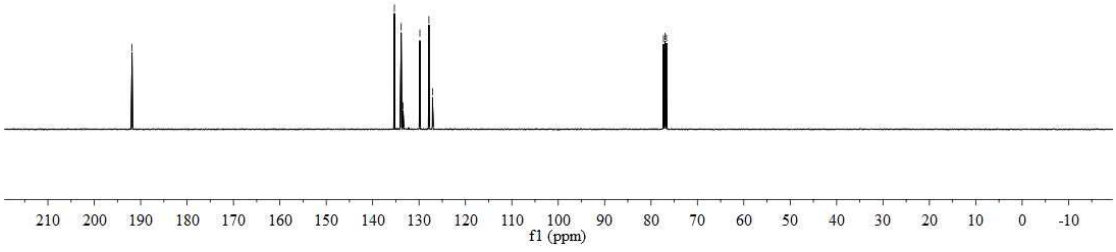
^{1}H NMR (400 MHz, $CDCl_3$)

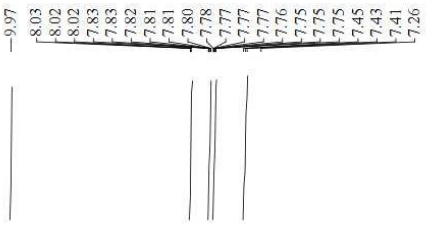


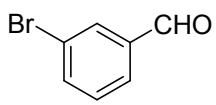


2o

^{13}C NMR (100 MHz, $CDCl_3$)

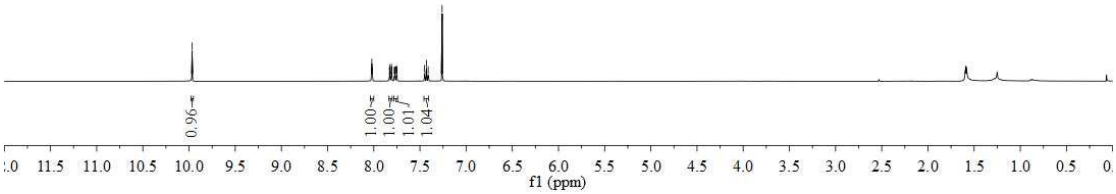


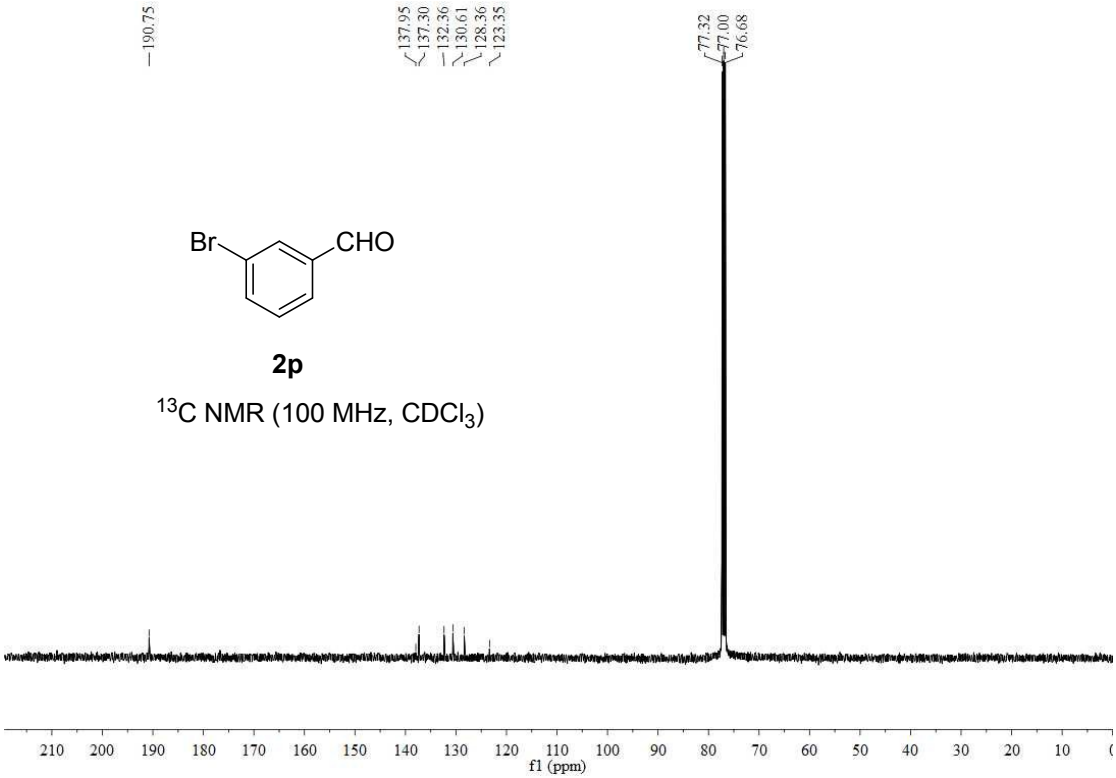




2p

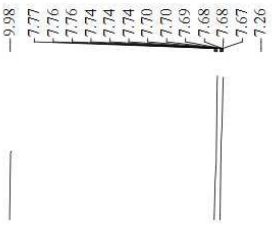
^{1}H NMR (400 MHz, $CDCl_3$)





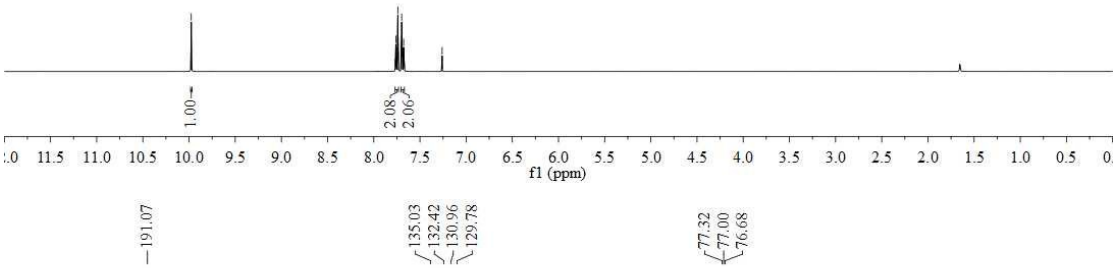
2p

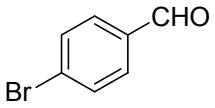
^{13}C NMR (100 MHz, $CDCl_3$)



2q

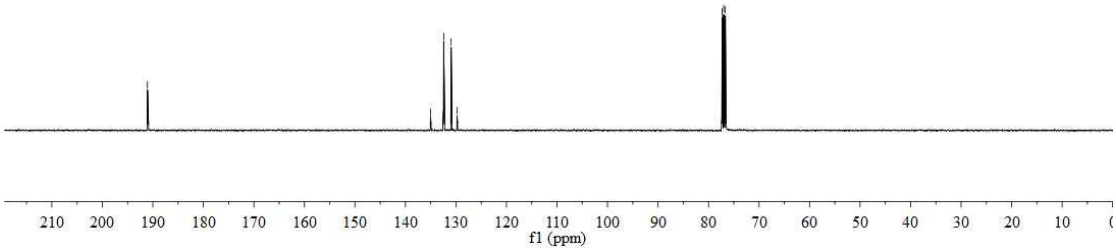
^{1}H NMR (400 MHz, $CDCl_3$)

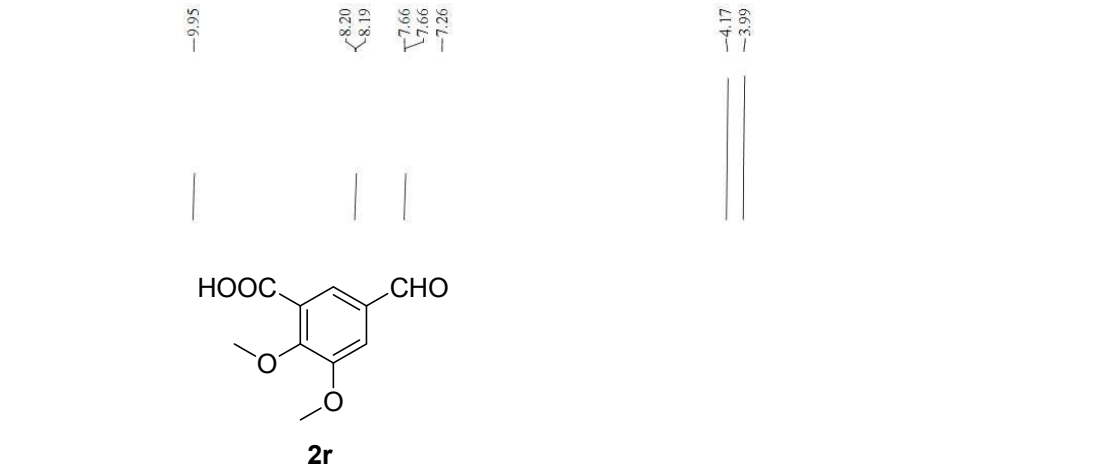




2q

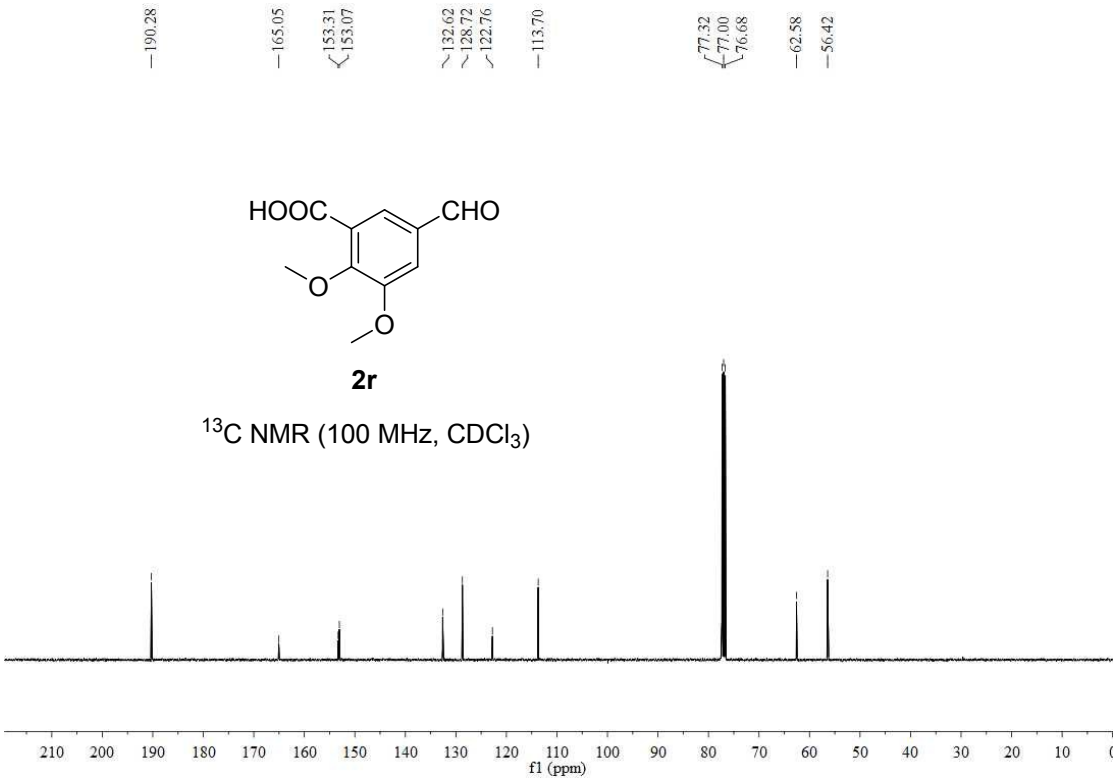
^{13}C NMR (100 MHz, $CDCl_3$)





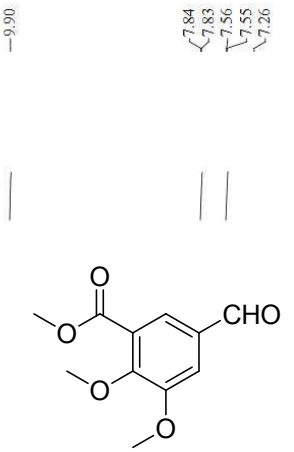
2r

^{1}H NMR (400 MHz, $CDCl_3$)



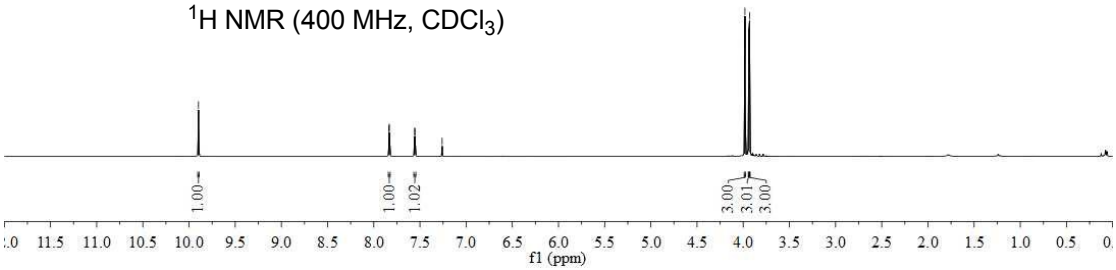
2r

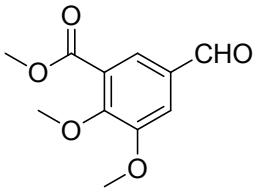
^{13}C NMR (100 MHz, $CDCl_3$)



2s

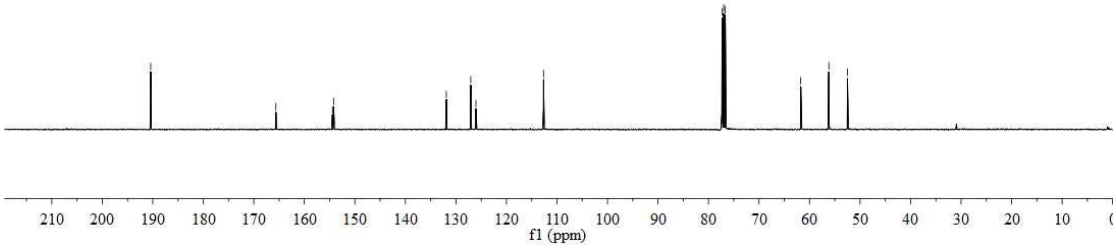
^{1}H NMR (400 MHz, $CDCl_3$)

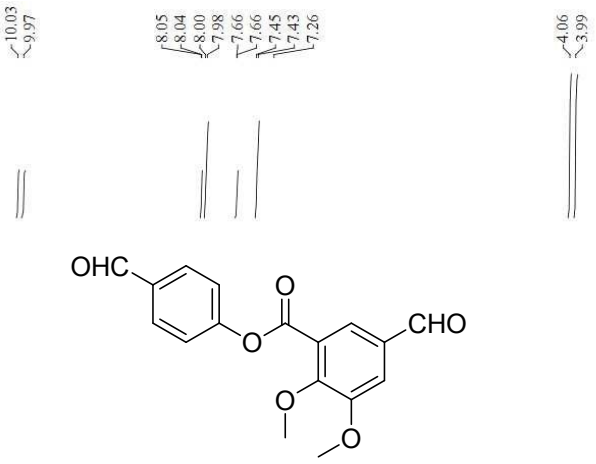




2s

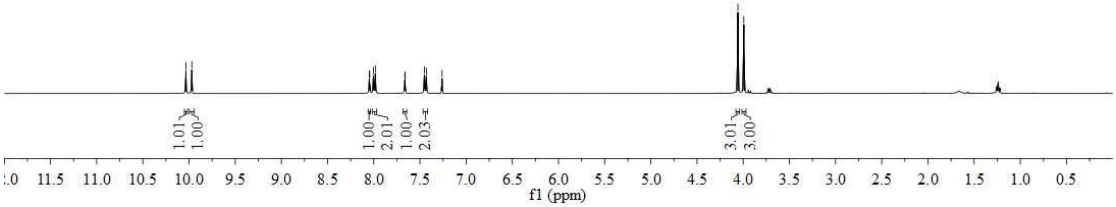
^{13}C NMR (100 MHz, $CDCl_3$)

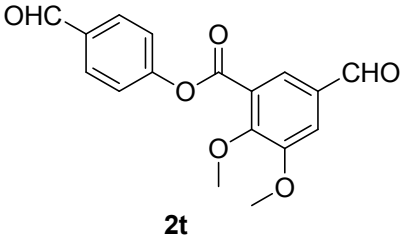




2t

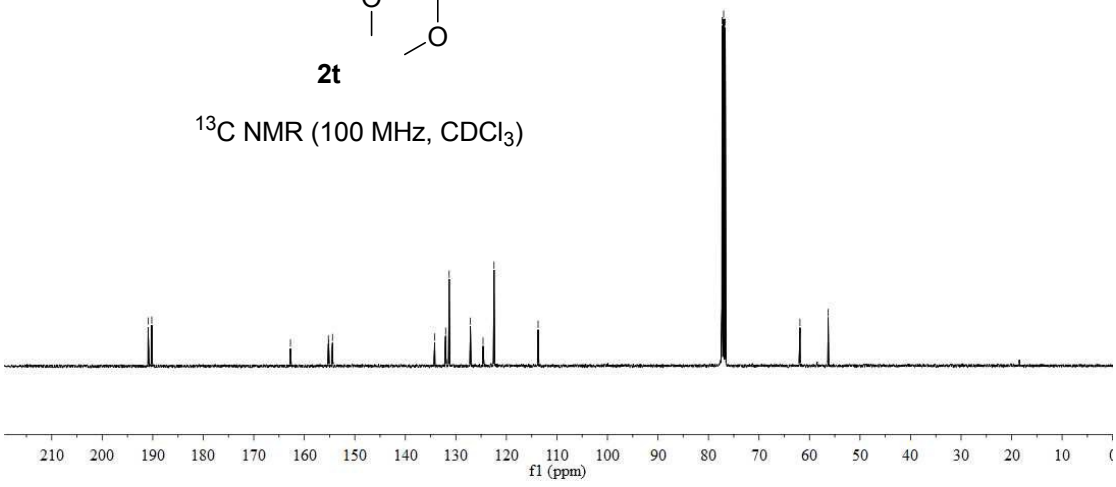
^{1}H NMR (400 MHz, $CDCl_3$)

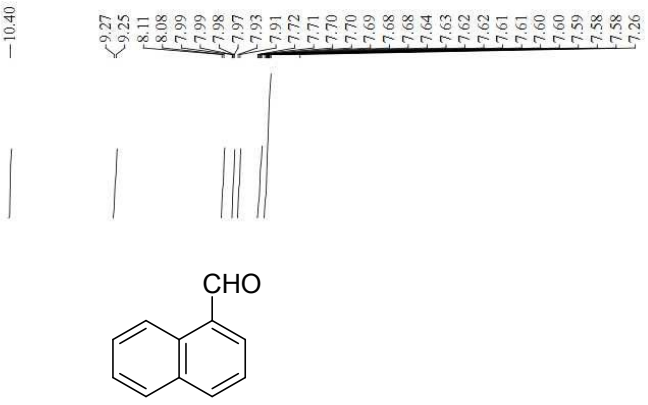




2t

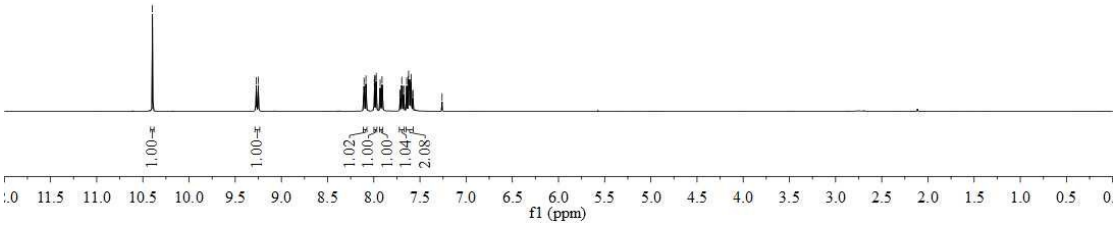
^{13}C NMR (100 MHz, $CDCl_3$)

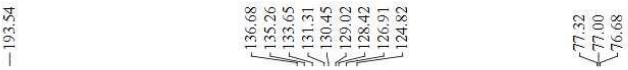


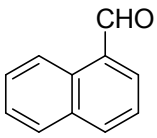


2u

^{1}H NMR (400 MHz, $CDCl_3$)

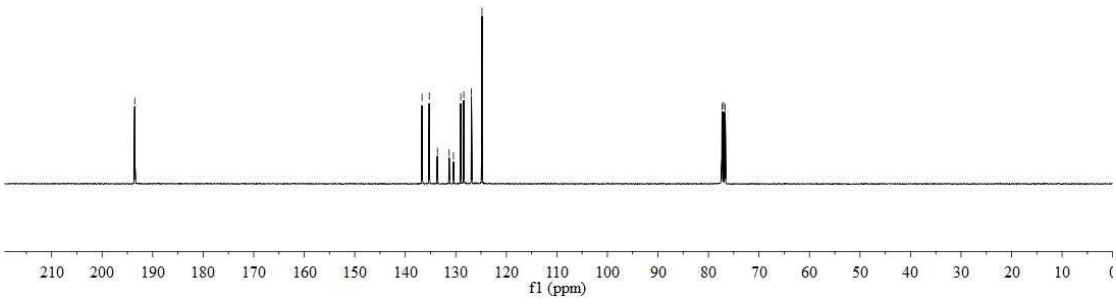


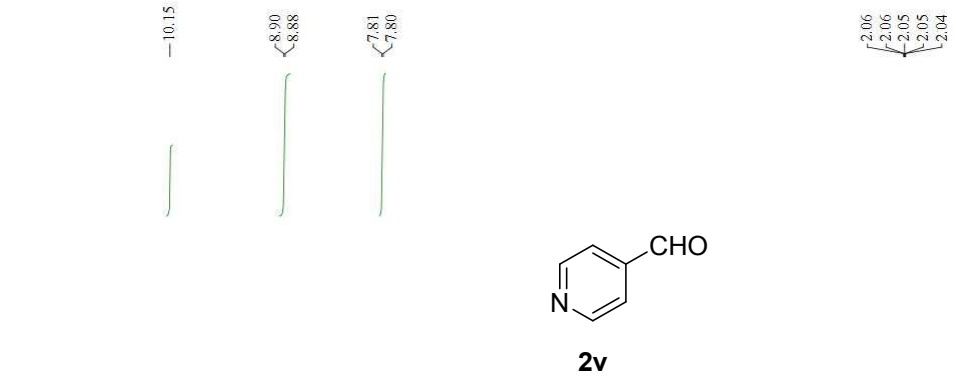




2u

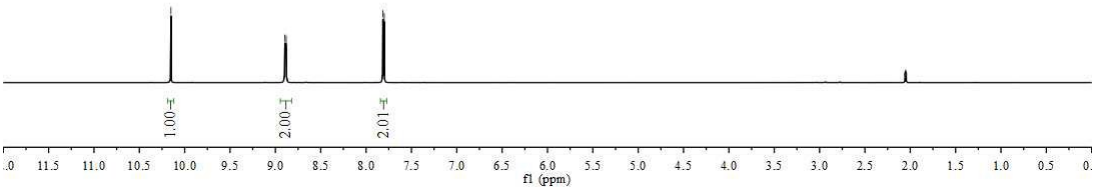
^{13}C NMR (100 MHz, $CDCl_3$)

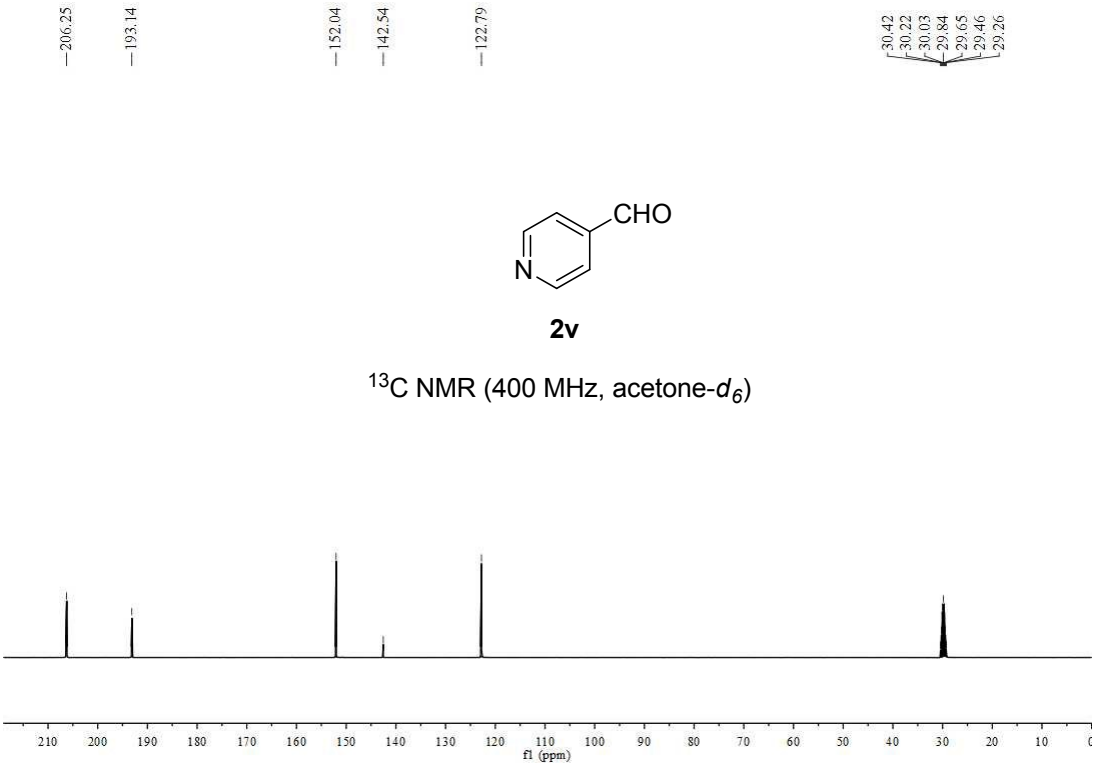




2v

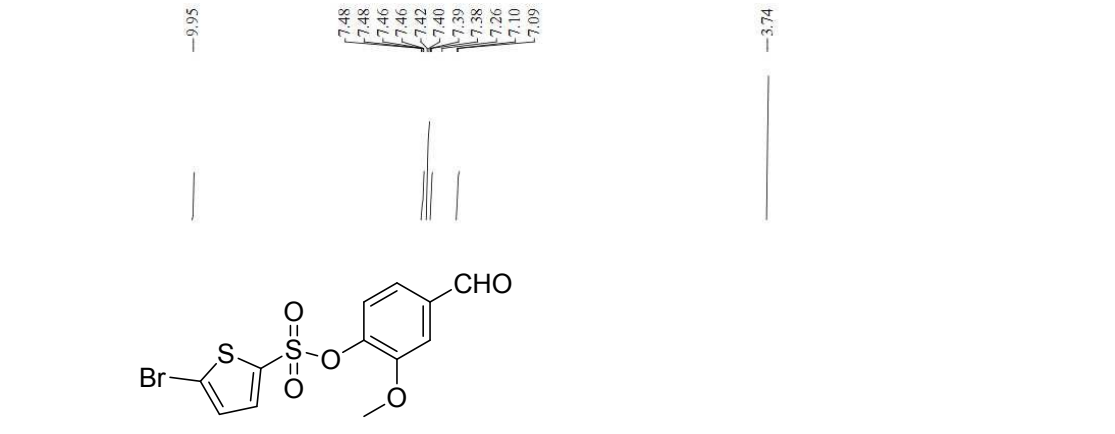
^{1}H NMR (400 MHz, acetone-d_6)





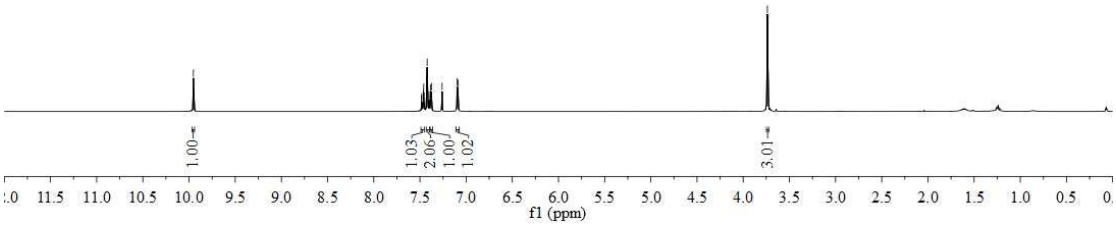
2v

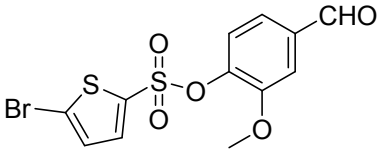
^{13}C NMR (400 MHz, acetone-d_6)



2w

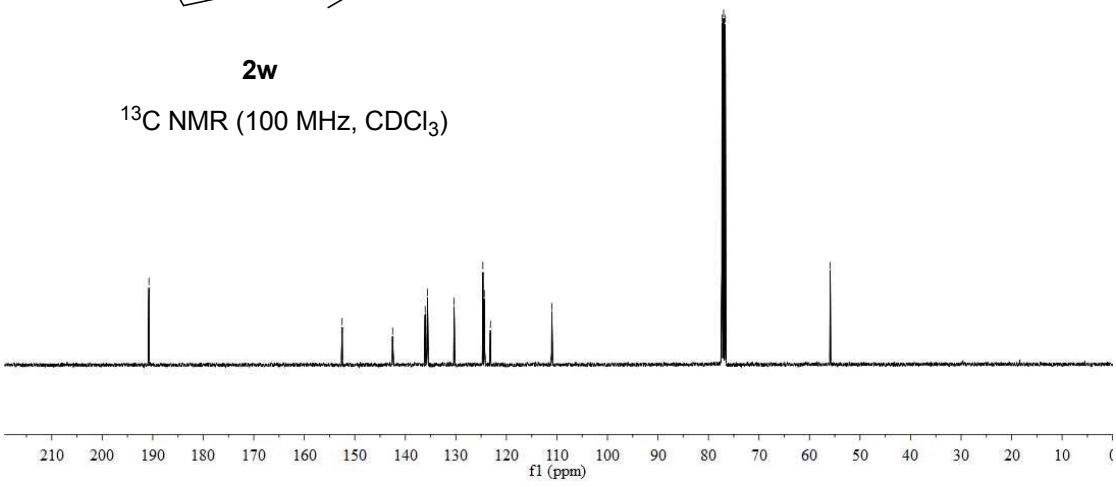
^{1}H NMR (400 MHz, $CDCl_3$)

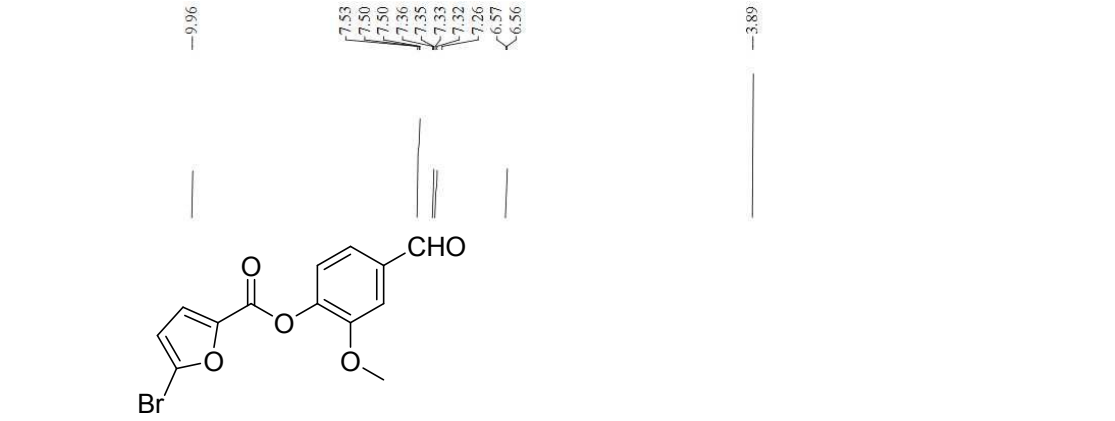




2w

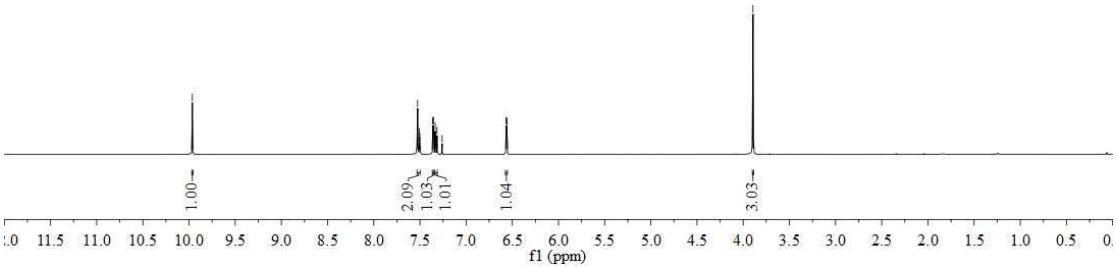
^{13}C NMR (100 MHz, $CDCl_3$)

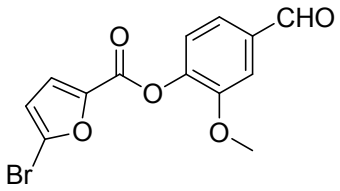




2x

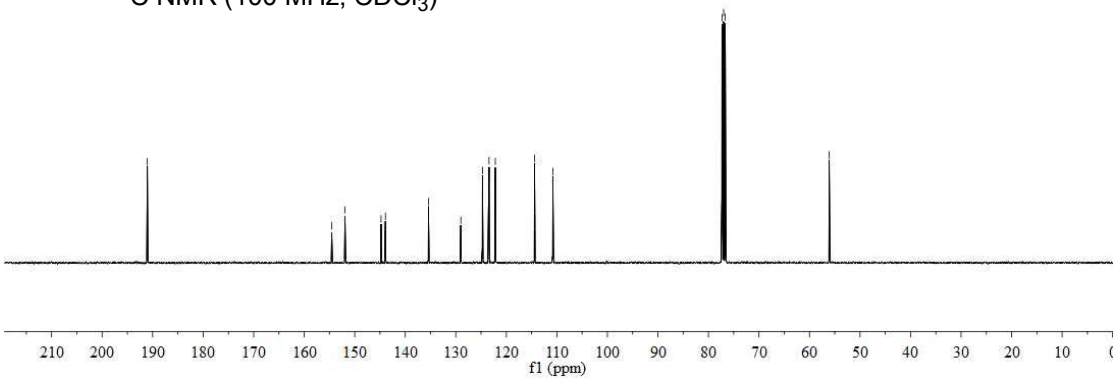
^{1}H NMR (400 MHz, $CDCl_3$)

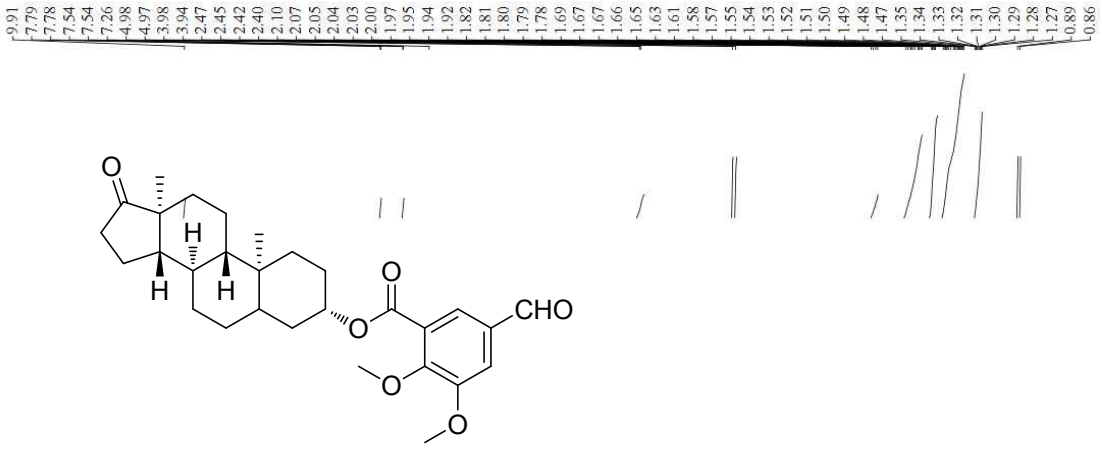




2x

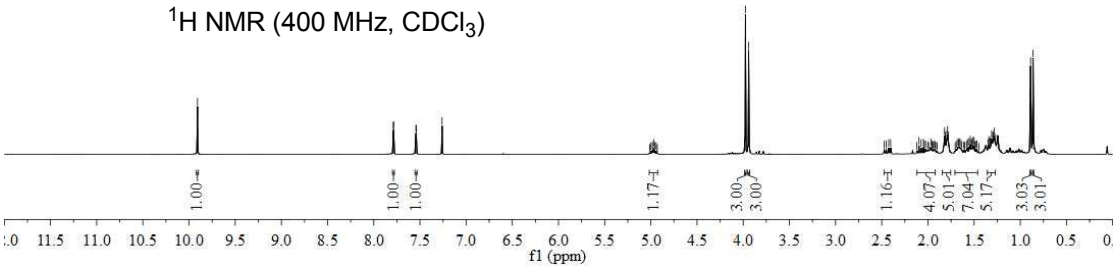
^{13}C NMR (100 MHz, $CDCl_3$)

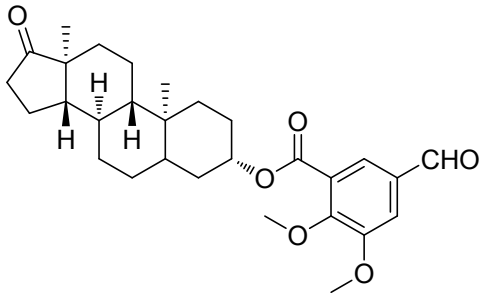




4a

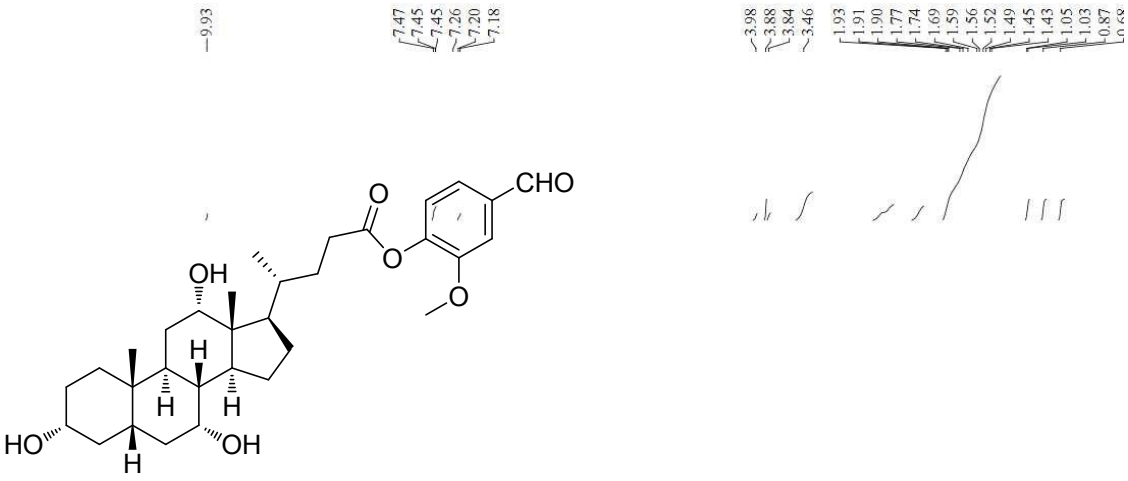
^{1}H NMR (400 MHz, $CDCl_3$)





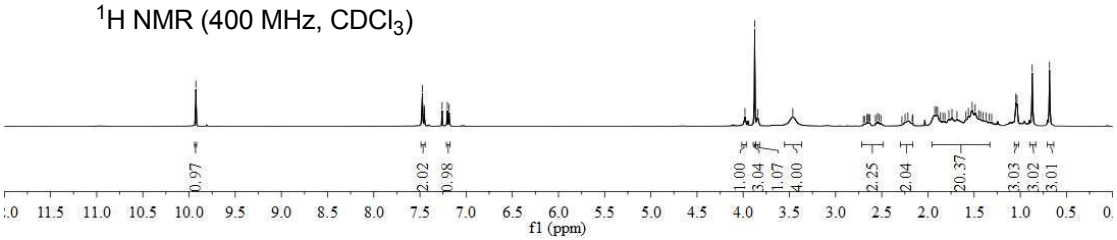
4a

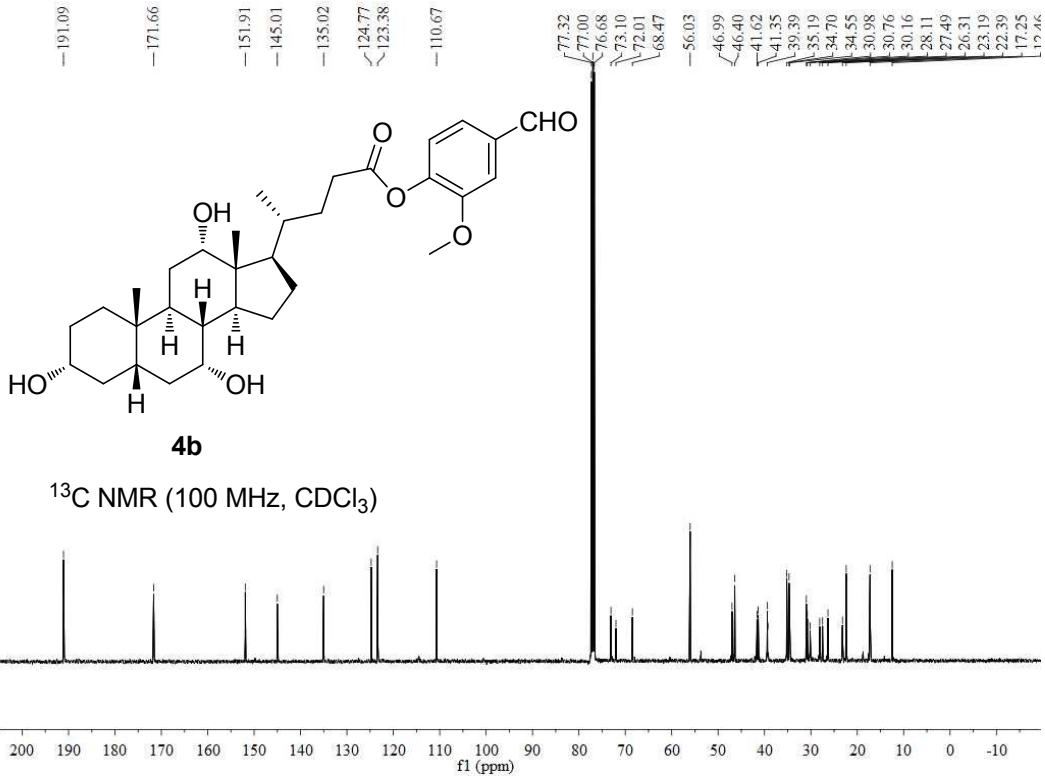
^{13}C NMR (100 MHz, $CDCl_3$)



4b

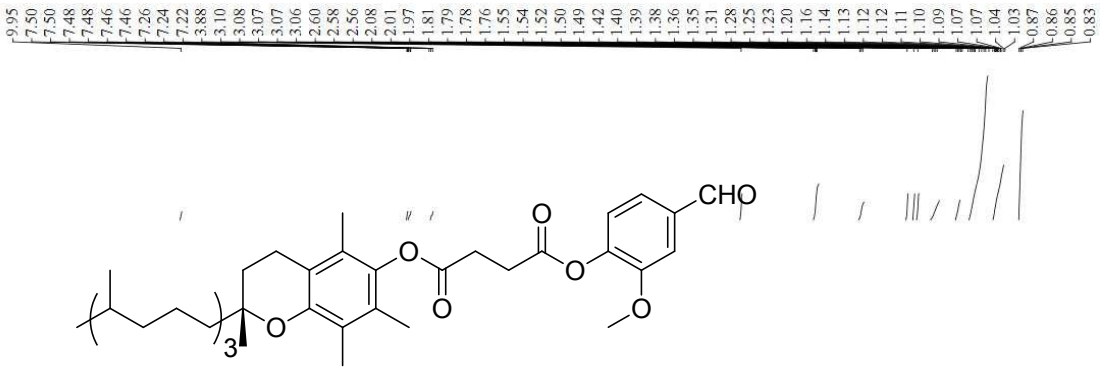
^{1}H NMR (400 MHz, $CDCl_3$)





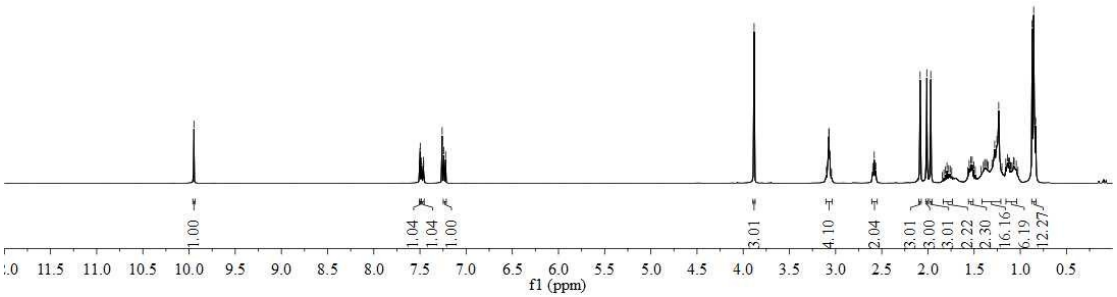
4b

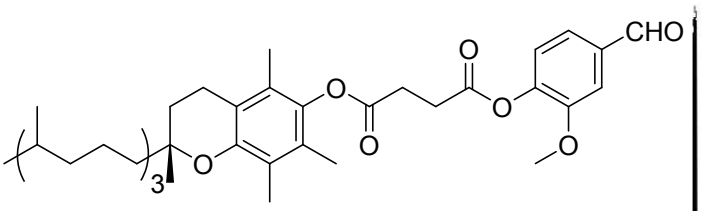
^{13}C NMR (100 MHz, $CDCl_3$)



4c

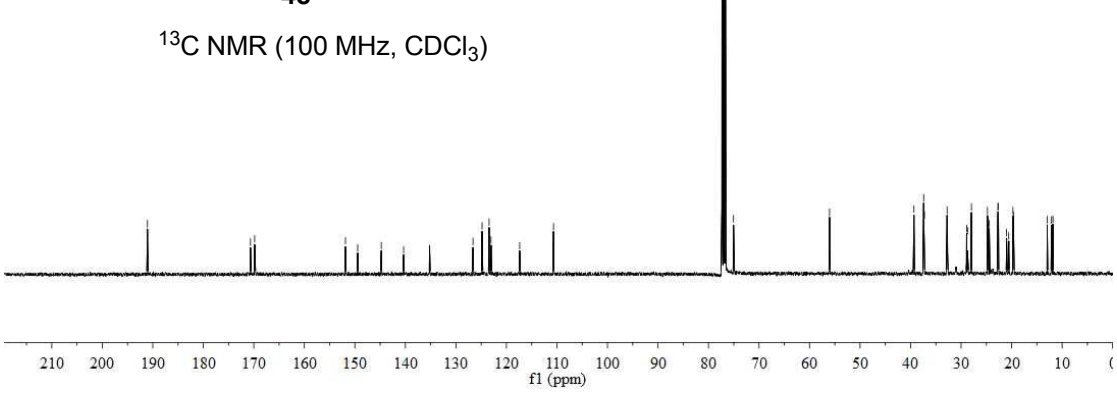
^{1}H NMR (400 MHz, $CDCl_3$)

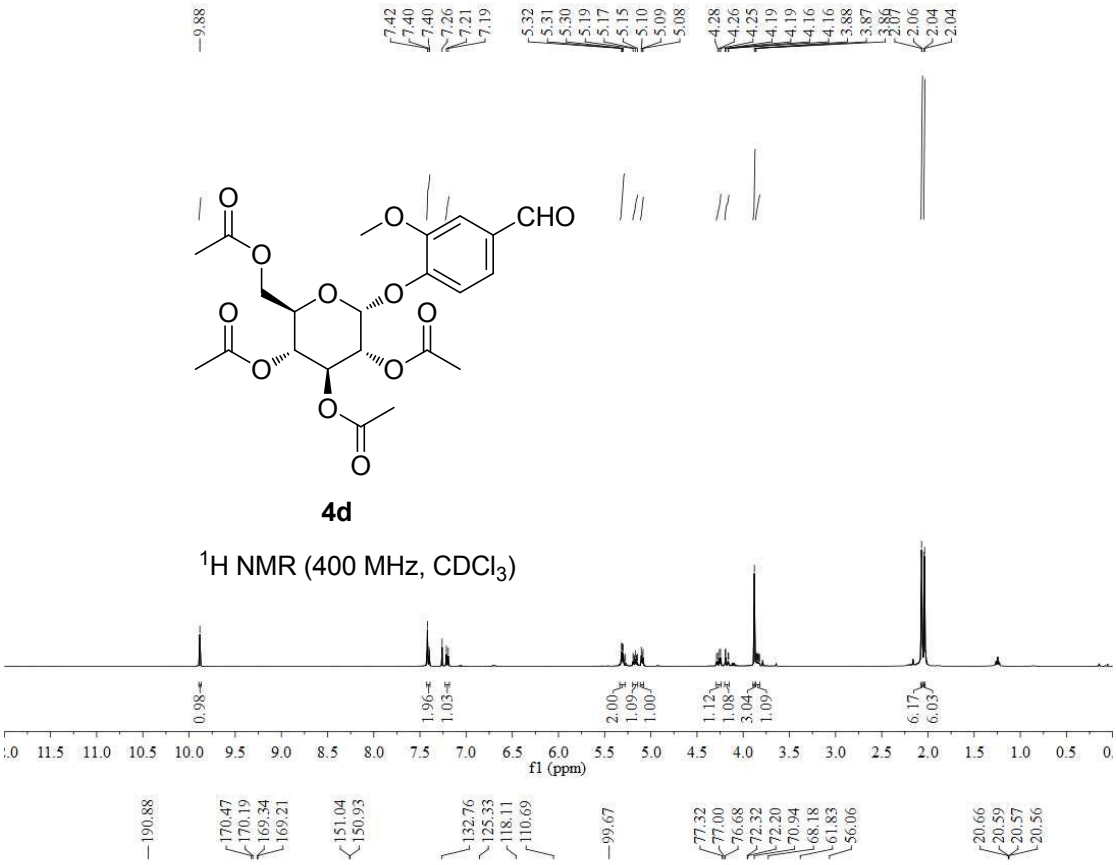




4c

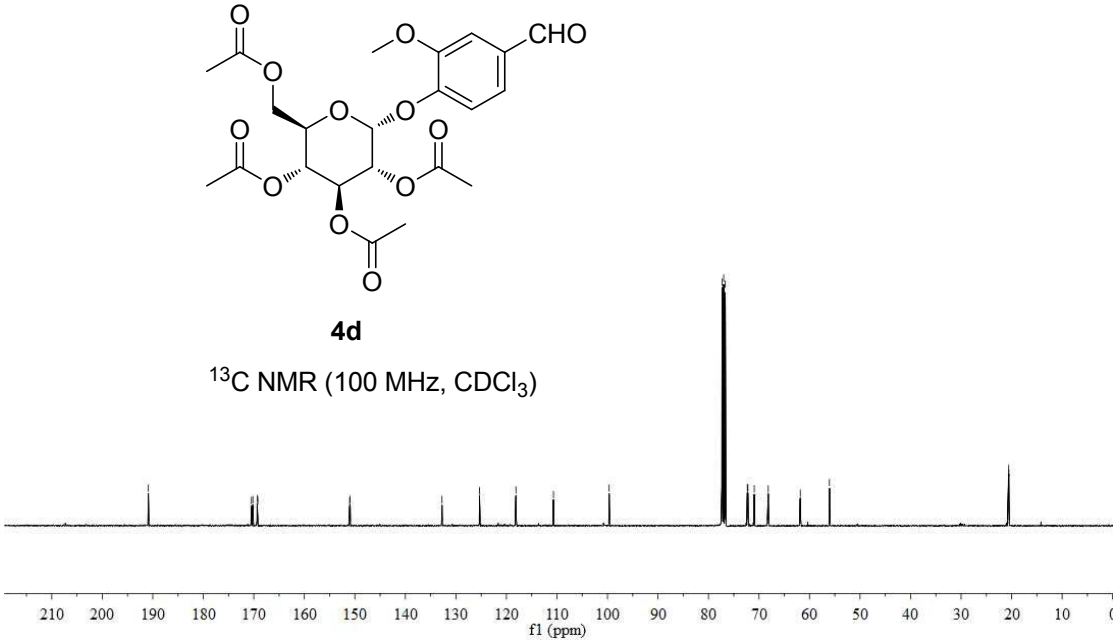
^{13}C NMR (100 MHz, $CDCl_3$)





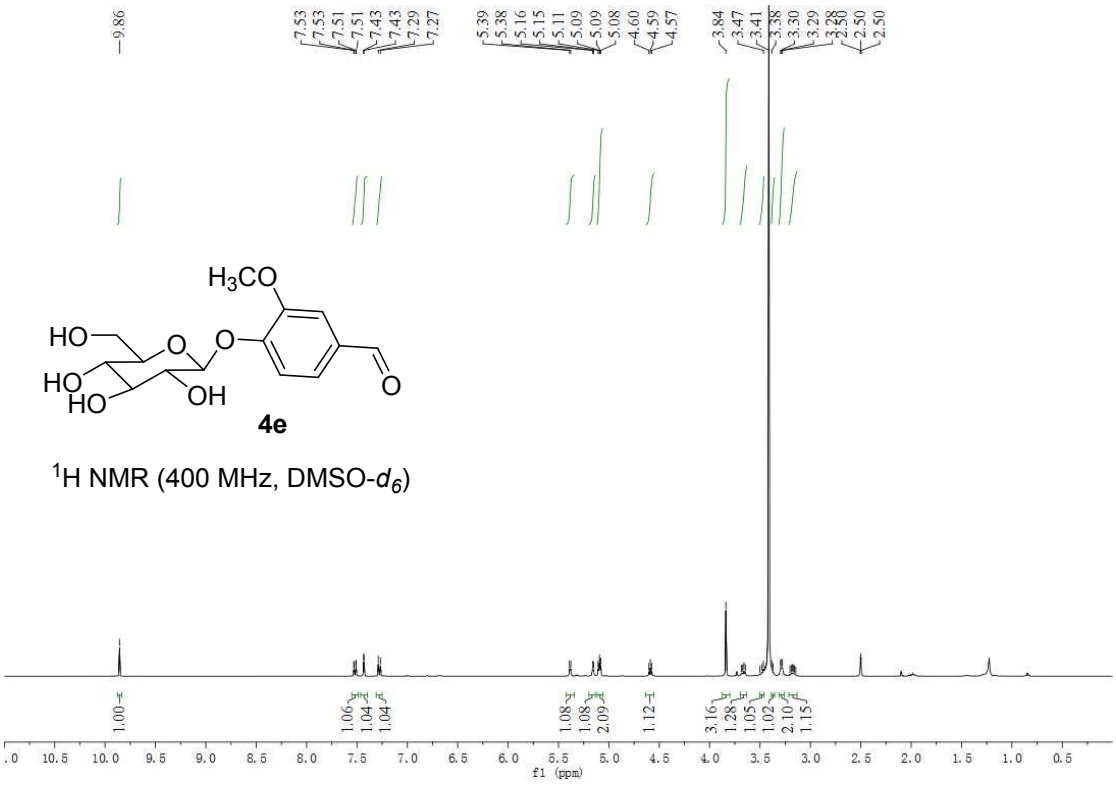
4d

^{1}H NMR (400 MHz, $CDCl_3$)



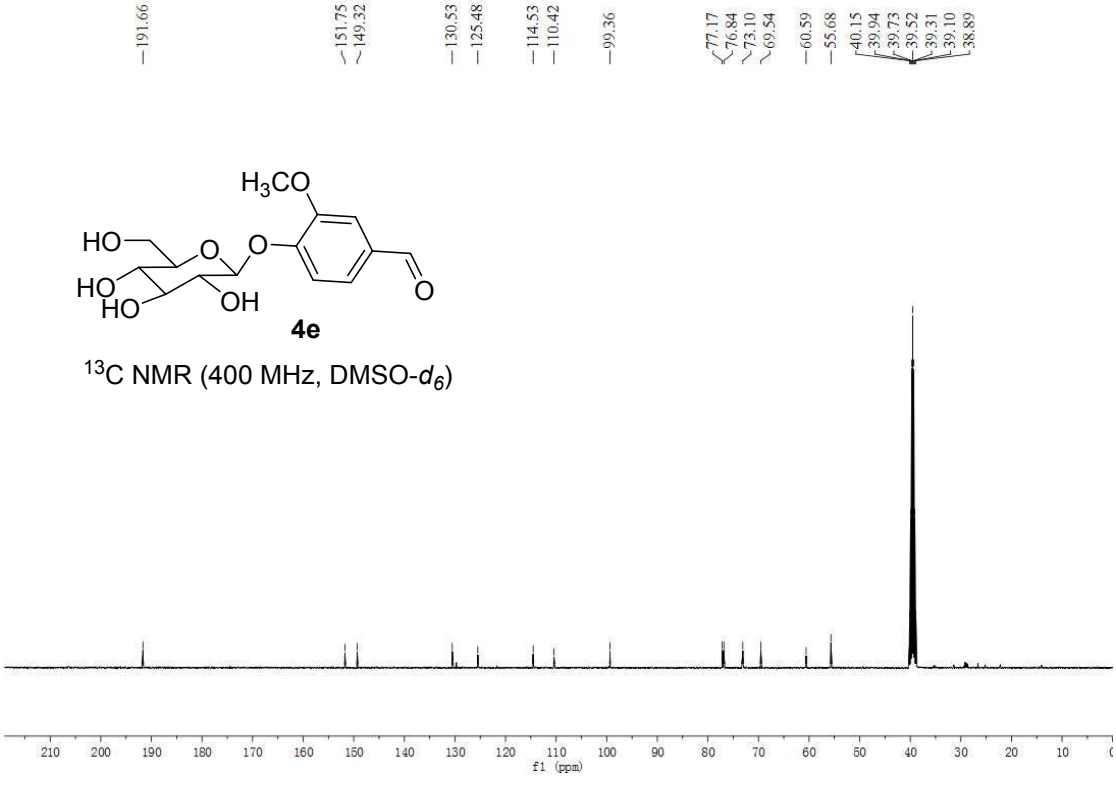
4d

^{13}C NMR (100 MHz, $CDCl_3$)



4e

^{1}H NMR (400 MHz, DMSO-d_6)



4e

^{13}C NMR (400 MHz, DMSO-d_6)