Supporting Information

Reactions of Arylaldehydes and *N*-Sulfonated Imines with Dimethyl Acetylenedicarboxylate Catalyzed by Nitrogen and Phosphine Lewis bases

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Experimental Procedures

General Methods. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA^{+} mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. Deuterated benzaldehyde $C_6H_5C(O)D$, phenylacetylene, methyl propiolate, and 3-butyn-2-one were purchased from Aldrich Co. Phenylpropynoic acid ethyl ester was prepared according to the literature.[1]

(1) Chan, K. S.; Yeung, M. L.; Chan, W. K.; Wang, R. J.; Thomas, C. W. M. *J. Org. Chem*. **1996**, *60*, 1741.

General Procedure for the Reactions of Dimethyl Acetylenedicarboxylate with Aldehydes or *N*-Sulfonated Imines.

Under argon atmosphere, aldehydes or *N*-sulfonated imines **1** (0.5 mmol) was dissolved in THF (3 mL), then dimethyl acetylenedicarboxylate (DMAD) (0.6 mmol) was added into the

solution. The reaction mixture was stirred for 5 minute at room temperature and then 20 mol% of pyridine or DMAP was added into the reaction mixture. The reaction mixture was stirred for 12 h at 60°C. The solvent was then removed under reduced pressure and the residue was purified by a silica gel column chromatography using hexane/ethyl acetate (80/20) as a eluent to give the product.

(*E*)-2-(4-Nitrobenzoyl)-but-2-enedioic acid dimethyl ester (1a):

This compound was obtained as a pale yellow solid, yield: 126 mg, 86%, mp: 114-116 °C. IR (KBr): ν 2595, 1735, 1687, 1608, 1528, 1437, 1281, 1206, 963 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.34 (d, *J* = 7.2 Hz, 2H, Ar), 8.06 (d, *J* = 7.2 Hz, 2H, Ar), 7.15 (s, 1H, =CH), 3.81 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 190.70, 164.14, 162.92, 150.58, 144.37, 139.79, 131.34, 129.52, 124.04, 53.45, 52.75; MS (EI) m/z: 293 (M^+, 27.0), 278 [$(M-15)^+$, 12.0], 150 [$(M-143)^+$, 100.0], 104 [$(M-189)^+$, 19.6]; Anal. Calcd. for $C_{13}H_{11}NO_7$: C, 53.25; H, 3.78; N, 4.78; found: C, 53.12; H, 3.89; N, 4.64%.

(*E*)-2-(3-Nitrobenzoyl)-but-2-enedioic acid dimethyl ester (1b):

This compound was obtained as a pale yellow solid, yield: 130 mg, 89%, mp: 97-99 °C. IR (KBr): ν 2960, 1735, 1680, 1608, 1528, 1437, 1279, 1082, 1012, 856 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.64 (s, 1H, Ar), 8.47 (d, *J* = 7.8 Hz, 1H, Ar), 8.25 (d, *J* = 7.8 Hz, 1H, Ar), 7.72 (dd, *J* = 7.8, 7.8 Hz, 1H, Ar), 7.17 (s, 1H, =CH), 3.82 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 190.25, 164.13, 162.87, 148.44, 144.12, 136.76, 133.88, 131.42, 130.10, 127.93, 123.31, 53.44, 52.72; MS (EI) m/z: 293 (M^+, 19.5), 278 [$(M-15)^+$, 10.5], 150 [$(M-143)^+$, 100.0], 104 [$(M-189)^+$, 24.4]; Anal. Calcd. for $C_{13}H_{11}NO_7$: C, 53.25; H, 3.78; N, 4.78; found: C, 53.06; H, 3.72; N, 4.66%.

(*E*)-2-(2-Nitrobenzoyl)-but-2-enedioic acid dimethyl ester (1c):

This compound was obtained as a pale yellow solid, yield: 125 mg, 85%, mp: 116-118 °C. IR (KBr): ν 2955, 1764, 1703, 1651, 1352, 1178, 998, 764, 749 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.99 (d, *J* = 8.1 Hz, 1H, Ar), 7.63 (dd, *J* = 7.5, 7.5 Hz, 1H, Ar), 7.55 (dd, *J* = 7.5, 7.5 Hz, 1H, Ar), 7.28 (d, *J* = 7.8 Hz, 1H, Ar), 6.97 (s, 1H, =CH), 4.32 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 190.70, 166.14, 160.88, 148.46, 142.24, 133.37, 130.22., 129.57, 127.69, 125.07, 121.78, 60.32, 52.40; MS (EI) m/z: 294 [$(M+1)^+$, 0.6], 262 [$(M-31)^+$, 11.8], 150 [$(M-143)^+$, 100.0], 104 [$(M-189)^+$, 64.9]; HRMS (EI) Calcd. for $C_{12}H_8NO_6$ (M^+-CH_3O): 262.0360, found: 262.0364.

(*E*)-2-(4-Bromobenzoyl)-but-2-enedioic acid dimethyl ester (1d):

This compound was obtained as a crystalline colorless solid, yield: 117 mg, 72%, mp: 88-90 °C. IR (KBr): ν 2956, 1716, 1673, 1646, 1583, 1439, 1276, 1176, 973 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.74 (d, *J* = 8.4 Hz, 2H, Ar), 7.62 (d, *J* = 8.4 Hz, 2H, Ar), 7.09 (s, 1H, =CH), 3.78 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 191.22, 164.10, 163.27, 144.73, 134.25, 132.19, 130.72, 130.02, 129.19, 53.33, 52.57; MS (EI) m/z: 326 (M^+, 14.0), 297 [$(M-29)^+$, 6.0], 183 [$(M-143)^+$, 100.0], 155 [$(M-171)^+$, 25.5]; Anal. Calcd. for $C_{13}H_{11}BrO_5$: C, 47.73; H, 3.39; found: C, 47.74; H, 3.49%.

(*E*)-2-(4-Chlorobenzoyl)-but-2-enedioic acid dimethyl ester (1e):

This compound was obtained as a crystalline colorless solid, yield: 90 mg, 64%, mp: 75-77 °C. IR (KBr): ν 2957, 1713, 1674, 1647, 1586, 1440, 1275, 1208, 974 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 7.8 Hz, 2H, Ar), 7.46 (d, *J* = 7.8 Hz, 2H, Ar), 7.09 (s, 1H, =CH), 3.78 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 190.99, 164.09, 163.30, 144.76, 140.36, 133.86, 130.67, 129.94, 129.18, 53.31, 52.54; MS (EI) m/z: 282 (M^+, 14.8), 267 [$(M-15)^+$, 1.8], 139 [$(M-143)^+$, 100.0], 111 [$(M-171)^+$, 30.5]; Anal. Calcd. for $C_{13}H_{11}ClO_5$: C, 55.23; H, 3.89; found: C, 55.10; H, 3.92%.

(*E*)-2-(3-Chlorobenzoyl)-but-2-enedioic acid dimethyl ester (1f):

This compound was obtained as a crystalline colorless solid, yield: 100 mg, 71%, mp: 72-74 °C. IR (KBr): ν 2955, 1726, 1686, 1573, 1436, 1255, 1081, 783 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.85 (s, 1H, Ar), 7.73 (d, *J* = 7.8 Hz, 1H, Ar), 7.56 (d, *J* = 7.8 Hz, 1H, Ar), 7.42 (dd, *J* = 7.8, 7.8 Hz, 1H, Ar), 7.10 (s, 1H, =CH), 3.78 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 190.87, 164.03, 163.14, 144.59, 136.96, 135.07, 133.72, 130.81, 130.10, 128.37, 126.71, 53.28, 52.53; MS (EI) m/z: 282 (M^+, 16.0), 251 [$(M-31)^+$, 7.1], 139 [$(M-143)^+$, 100.0), 111 [$(M-171)^+$, 10.0], 75 [$(M-207)^+$, 19.1]; HRMS (EI) Calcd. for $C_{13}H_{11}ClO_5$: 282.0295, found: 282.0266.

(*E*)-2-(2,4-Dichlorobenzoyl)-but-2-enedioic acid dimethyl ester (1g):

This compound was obtained as a crystalline colorless solid, yield: 132 mg, 83%, mp: 60-62 °C. IR (KBr): ν 2955, 1752, 1680, 1625, 1582, 1437, 1252, 974 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.85 (d, *J* = 8.4 Hz, 1H, Ar), 7.37 (s, 1H, Ar), 7.29 (d, *J* = 8.4 Hz, 1H, Ar), 6.89 (s, 1H, =CH), 3.73 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 189.35, 164.39, 163.16, 146.23, 139.66, 134.57, 132.93, 132.71, 131.02, 129.20, 127.53, 53.26, 52.56; MS (EI) m/z: 317 (M^+, 1.8), 281 [$(M-36)^+$, 37.3), 173 [$(M-144)^+$, 100.0], 145 [$(M-172)^+$, 15.0]; HRMS (EI) Calcd. for $C_{13}H_{10}C_{l2}O_5$: 315.9905, found: 315.9916.

(*E*)-2-(4-Methylbenzoyl)-but-2-enedioic acid dimethyl ester (1h):

This compound was obtained as a crystalline colorless solid, yield: 66 mg, 50%, mp: 86-88 °C. IR (KBr): ν 2955, 1731, 1678, 1604, 1437, 1268, 1174, 1013 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.77 (d, *J* = 8.1 Hz, 2H, Ar), 7.27 (d, *J* = 8.1 Hz, 2H, Ar), 7.09 (s, 1H, =CH), 3.78 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 191.75, 164.17, 163.66, 145.30, 144.93, 133.11, 130.21, 129.53, 128.77, 53.21, 52.41, 21.78;

MS (EI) m/z: 262 (M^+, 13.6), 231 [$(M-31)^+$, 4.8], 119 [$(M-143)^+$, 100.0], 91 [$(M-171)^+$, 31.3]; HRMS (EI) Calcd. for $C_{14}H_{14}O_5$: 262.0841, found: 242.0853.

(*E*)-2-Benzoyl-but-2-enedioic acid dimethyl ester (1i):

This compound was obtained as a colorless crystalline solid, yield: 53 mg, 43%, mp: 79-81°C. IR (KBr): ν 2957, 1729, 1675, 1596, 1436, 1271, 1207, 1014 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 7.87 (d, *J* = 7.8 Hz, 2H, Ar), 7.58 (dd, *J* = 7.8, 7.8 Hz, 1H, Ar), 7.48 (dd, *J* = 7.8, 7.8 Hz, 2H, Ar), 7.10 (s, 1H, =CH), 3.78 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 192.11, 164.11, 163.51, 145.15, 135.43, 133.84, 130.39, 128.76, 128.60, 53.22, 52.40; MS (EI) m/z: 248 (M^+, 16.2), 217 [$(M-31)^+$, 11.7], 105 [$(M-143)^+$, 100.0], 77 [$(M-171)^+$, 16.3]; HRMS (EI) Calcd. for $C_{13}H_{12}O_5$: 248.0685, found: 248.0719.

(*E*)-2-[(3-Nitrophenyl)-(toluene-4-sulfonylimino)methyl]-but-enedioic acid dimethyl ester (2a):

This compound was obtained as a crystalline colorless solid, yield: 185 mg, 83%, mp: 138-140 °C. IR (KBr): ν 2955, 1725, 1582, 1526, 1347, 1266, 1161, 1090, 1016, 854 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 8.65 (s, 1H, Ar), 8.39 (d, *J* = 8.1 Hz, 1H, Ar), 8.14 (d, *J* = 8.1 Hz, 1H, Ar), 7.85 (d, *J* = 8.4 Hz, 2H, Ar), 7.61 (dd, *J* = 8.1, 8.1 Hz, 1H, Ar), 7.36 (d, *J* = 8.4 Hz, 2H, Ar), 7.24 (s, 1H, =CH), 3.86 (s, 3H, OCH_3), 3.64 (s, 1H, OCH_3), 2.44 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 170.69, 163.74, 162.28, 148.35, 144.63, 141.40, 136.66, 136.00, 134.42, 134.13, 129.89, 129.61, 127.58, 126.25, 123.28, 53.51, 52.61, 21.56; MS (EI) m/z: 446 (M^+, 2.9), 415 [$(M-31)^+$, 1.6], 387 [$(M-59)^+$, 9.0], 291 [$(M-155)^+$, 19.3], 155 [$(M-291)^+$, 43.8], 91 [$(M-355)^+$, 100]; HRMS (EI) Calcd. for $C_{20}H_{18}N_2O_8S$: 446.0784, found: 446.0744.

(*E*)-2-[(4-Nitrophenyl)-(toluene-4-sulfonylimino)methyl]-but-enedioic acid dimethyl ester (2b):

This compound was obtained as a crystalline colorless solid, yield: 190 mg, 85%, mp: 124-126 °C. IR (KBr): ν 2955, 1732, 1645, 1526, 1347, 1161, 1090, 854, 774 cm^{-1}; ^1H NMR (300 MHz,

$CDCl_3$, TMS) δ 8.21 (d, *J* = 9.0 Hz, 2H, Ar), 7.97 (d, *J* = 9.0 Hz, 2H, Ar), 7.83 (d, *J* = 8.4 Hz, 2H, Ar), 7.32 (d, *J* = 8.4Hz, 2H, Ar), 7.20 (s, 1H, =CH), 3.84 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 170.71, 163.73, 162.26, 150.28, 144.60, 141.62, 140.30, 136.04, 131.28, 129.60, 129.58, 127.70, 123.70, 53.49, 52.62, 21.58; MS (EI) m/z: 446 (M^+, 4.9), 415 [$(M-31)^+$, 3.1], 387 [$(M-59)^+$, 11.5], 291 [$(M-155)^+$, 31.3], 155 [$(M-291)^+$, 57.9], 91 [$(M-355)^+$, 100]; HRMS (EI) Calcd. for $C_{20}H_{18}N_2O_8S$: 446.0784, found: 446.0765.

(*E*)-2-[(4-Bromophenyl)-(toluene-4-sulfonylimino)methyl]-but-enedioic acid dimethyl ester (2c):

This compound was obtained as a crystalline colorless solid, yield: 206 mg, 86%, mp: 135-137 °C. IR (KBr): ν 2952, 1721, 1646, 1578, 1323, 1154, 1087, 1009, 779 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.84 (d, *J* = 7.8 Hz, 2H, Ar), 7.69 (d, *J* = 6.9 Hz, 2H, Ar), 7.52 (d, *J* = 6.9 Hz, 2H, Ar), 7.31 (d, *J* = 7.8Hz, 2H, Ar), 7.18(s, 1H, =CH), 3.82 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 171.78, 163.67, 162.53, 144.18, 141.93, 136.58, 133.88, 132.03, 130.81, 130.11, 129.47, 128.96, 127.60, 53.37, 52.45, 21.56; MS (EI) m/z: 401 [$(M-79)^+$, 6.7], 342 [$(M-138)^+$, 17.6], 246 [$(M-234)^+$, 35.3], 186 [$(M-294)^+$, 22.2], 155 [$(M-325)^+$, 31.5], 91 [$(M-389)^+$, 100]; HRMS (EI) Calcd. for $C_{20}H_{18}BrNO_6S$: 479.0038, found: 479.0005.

(*E*)-2-[(4-Chlorophenyl)-(toluene-4-sulfonylimino)methyl]-but-enedioic acid dimethyl ester (2d):

This compound was obtained as a crystalline colorless solid, yield: 172 mg, 79%, mp: 120-122 °C. IR (KBr): ν 2953, 1721, 1647, 1437, 1325, 1272, 1155, 1010, 779 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.85 (d, *J* = 7.5 Hz, 2H, Ar), 7.78 (d, *J* = 7.8 Hz, 2H, Ar), 7.37 (d, *J* = 7.8 Hz, 2H, Ar), 7.32 (d, *J* = 7.5 Hz, 2H, Ar), 7.19 (s, 1H, =CH), 3.84 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 171.56, 163.61, 162.49, 144.13,

141.93, 140.10, 136.56, 133.36, 130.73, 130.00, 129.43, 129.01, 127.54, 53.33, 52.40, 21.51; MS (EI) m/z: 435 (M^+, 9.1), 280 [$(M-155)^+$, 25.8], 155 [$(M-280)^+$, 41.1] , 91 [$(M-344)^+$, 100]; Anal. Calcd. for $C_{20}H_{18}ClNO_6S$: C, 55.11; H, 4.13; N, 3.21; found: C, 55.21; H, 4.33; N, 3.09%.

(*E*)-2-[(3-Chlorophenyl)-(toluene-4-sulfonylimino)methyl]-but-enedioic acid dimethyl ester (2e):

This compound was obtained as a crystalline colorless solid, yield: 165 mg, 76%, mp: 113-115 °C. IR (KBr): ν 2954, 1736, 1724, 1597, 1332, 1261, 1161, 1092, 1016, 833 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 7.86 (d, *J* = 6.9 Hz, 1H, Ar), 7.84 (s, 1H, Ar), 7.65 (d, *J* = 7.8 Hz, 1H, Ar), 7.50 (d, *J* = 7.8 Hz, 1H, Ar), 7.35 (dd, *J* = 7.8, 7.8 Hz, 2H, Ar), 7.31 (d, *J* = 6.9 Hz, 2H, Ar), 7.20 (s, 1H, =CH), 3.84 (s, 3H, OCH_3), 3.64 (s, 1H, OCH_3), 2.43 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 171.43, 163.66, 162.48, 144.28, 141.83, 136.61, 136.45, 134.96, 133.49, 130.95, 129.93, 129.50, 128.33, 127.63, 127.00, 53.40, 52.48, 21.56; MS (EI) m/z: 435 (M^+, 3.0), 404 [$(M-31)^+$, 2.2], 376 [$(M-59)^+$, 14.3], 280 [$(M-155)^+$, 19.2], 155 [$(M-280)^+$, 44.3] , 91 [$(M-344)^+$, 100]; HRMS (EI) Calcd. for $C_{20}H_{18}NClO_6S$: 435.0543, found: 435.0578.

(*E*)-2-[(3-Fluorophenyl)-(toluene-4-sulfonylimino)methyl]-but-enedioic acid dimethyl ester (2f):

This compound was obtained as a crystalline colorless solid, yield: 172 mg, 82%, mp: 126-128 °C. IR (KBr): ν 2950, 1747, 1719, 1564, 1321, 1248, 1164, 1016, 764 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 7.88 (d, 1H, *J* = 8.4 Hz, Ar),7.84 (d, *J* = 8.1 Hz, 2H, Ar), 7.31 (d, *J* = 8.1 Hz, 2H, Ar), 7.18 (s, 1H, =CH), 7.17-7.0 (m, 3H, Ar), 3.83 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 171.40, 166.11 (d, *J* = 255.4 Hz), 163.70, 162.63, 144.10, 144.09, 142.13, 136.81, 131.44, 131.40 (d, *J* = 9.5 Hz), 130.70, 130.58, 129.49, 127.59, 116.23 (d, *J* = 22.1 Hz), 53.36, 52.40, 21.55; MS (EI) m/z: 419 (M^+, 4.6), 264 [$(M-155)^+$, 22.6], 155 [$(M-264)^+$, 36.5] , 91 [$(M-329)^+$, 100]; Anal. Calcd. for $C_{20}H_{18}NFO_6S$: C, 57.27; H, 4.33; N, 3.34; found: C, 57.02; H, 4.41; N, 3.32%.

(*E*)-2-[(4-Methoxyphenyl)-(toluene-4-sulfonylimino)methyl]-but-enedioic acid dimethyl ester (2g):

This compound was obtained as a crystalline colorless solid, yield: 151 mg, 70%, mp: 110-112 °C. IR (KBr): ν 2955, 1727, 1582, 1549, 1319, 1156, 1088, 846, 770 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 7.86 (d, *J* = 7.8 Hz, 2H, Ar), 7.80 (d, *J* = 8.4 Hz, 2H, Ar), 7.29 (d, *J* = 8.4 Hz, 2H, Ar), 7.17 (s, 1H, =CH), 6.86 (d, *J* = 7.8 Hz, 2H, Ar), 3.83 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 171.73, 164.30, 163.59, 162.89, 143.69, 142.44, 138.73, 131.21, 130.27, 129.34, 127.52, 127.48, 114.17, 55.51, 53.29, 52.28, 13.22; MS (EI) m/z: 431 (M^+, 47.4), 276 [$(M-155)^+$, 62.2], 155 [$(M-276)^+$, 30.4], 91 [$(M-340)^+$, 100]; Anal. Calcd. for $C_{21}H_{21}NO_7S$: C, 58.46; H, 4.91; N, 3.25; found: C, 58.42; H, 4.74; N, 3.07%.

(*E*)-2-Phenyl-(toluene-4-sulfonylimino)methyl]-but-enedioic acid dimethyl ester (2h):

This compound was obtained as a crystalline colorless solid, yield: 140 mg, 70%, mp: 140-142 °C. IR (KBr): ν 2956, 1747, 1720, 1557, 1319, 1160, 1013, 774 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 7.88 (d, *J* = 8.1 Hz, 2H, Ar), 7.83 (d, *J* = 7.8 Hz, 2H, Ar), 7.54 (dd, *J* = 7.2, 7.2 Hz, 1H, Ar), 7.40 (dd, *J* = 7.8, 7.8 Hz, 2H, Ar), 7.32 (d, *J* = 8.1 Hz, 2H, Ar), 7.20 (s, 1H, =CH), 3.84 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 172.69, 163.71, 162.76, 143.99, 142.35, 136.92, 134.97, 133.68, 130.62, 129.44, 128.84, 128.71, 127.62, 53.32, 52.35, 21.58; MS (EI) m/z: 401 (M^+, 6.1), 246 [$(M-155)^+$, 41.2], 155 [$(M-246)^+$, 38.0] , 91 [$(M-310)^+$, 100]; Anal. Calcd. for $C_{20}H_{19}NO_6S$: C, 59.84; H, 4.77; N, 3.49; found: C, 59.71; H, 4.91; N, 3.34%.

4-Methoxy-5-oxo-2-(4-nitrophenyl)-2,5-dihydrofuran-3-carboxylic acid methyl ester (3a):

This compound was obtained as a crystalline colorless solid , yield: 79 mg, 54%, mp: 100-102

°C. IR (KBr): ν 2956, 1801, 1724, 1659, 1610, 1525, 1347, 1156, 850, 706 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.26 (d, *J* = 8.4Hz, 2H, Ar), 7.53 (d, *J* = 8.4 Hz, 2H, Ar), 6.10 (s, 1H, CH), 4.37 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 165.94, 161.08, 148.49, 148.26, 141.68, 128.32, 123.96, 121.57, 78.23, 60.30, 52.36; MS (EI) m/z: 293 (M^+, 9.9), 264 [$(M-29)^+$, 20.8], 143 [$(M-150)^+$, 100.0],; Anal Calcd. for $C_{13}H_{11}NO_7$: C, 53.25; H, 3.78; N, 4.78; found: C, 52.96; H, 3.80; N, 4.72%.

4-Methoxy-5-oxo-2-(3-nitrophenyl)-2,5-dihydrofuran-3-carboxylic acid methyl ester (3b):

This compound was obtained as a crystalline colorless solid , yield: 64 mg, 44%, mp: 96-98 °C. IR (KBr): ν 2954, 1776, 1712, 1652, 1534, 1394, 1342, 1243, 1107, 740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.26 (d, *J* = 7.8Hz, 1H, Ar), 8.18 (s, 1H, Ar), 7.68 (d, *J* = 7.8 Hz, 1H, Ar), 7.61 (dd, *J* = 7.8, 7.8 Hz, 1H, Ar), 6.10 (s, 1H, CH), 4.36 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 165.86, 161.04, 148.37, 148.26, 137.01, 133.31, 129.83, 124.41, 122.39, 121.32, 78.28, 60.30, 52.29; MS (EI) m/z: 293 (M^+, 7.1), 264 [$(M-29)^+$, 17.3], 143 [$(M-150)^+$, 100.0]; HRMS (EI) Calcd. for $C_{13}H_{10}NO$ [$(M-17)^+$]: 276.0500, found: 276.0502.

(*E*)-2-(4-Nitrobenzoyl)-but-2-enedioic acid diethyl ester (4):

This compound was obtained as a crystalline colorless solid, yield: 125 mg,78%, mp: 64-66 °C. IR (KBr): ν 2985, 1722, 1690, 1606, 1529, 1344, 1259, 1197, 1080, 958, 854 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.30 (d, *J* = 8.7 Hz, 2H, Ar), 8.02 (d, *J* = 8.7 Hz, 2H, Ar), 7.09 (s, 1H, =CH), 4.24 (q, *J* = 6.9Hz, 2H, CH_2), 4.07 (q, *J* = 7.5 Hz, 2H, CH_2), 1.19 (t, *J* = 7.5 Hz, 3H, CH_3), 1.11 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 190.78, 163.59, 162.42, 150.39, 144.23, 139.89, 131.40, 129.42, 123.88, 62.63, 61.93, 13.74, 13.60; MS (EI) m/z: 321 (M^+, 5.7), 292 [$(M-31)^+$, 23.7], 276 [$(M-45)^+$, 10.6], 150 [$(M-171)^+$, 100], 104

[(M-217)$^+$, 22.4]; HRMS (EI) Calcd. for $C_{15}H_{15}NO_7$: 321.0849, found: 321.0876.

(*E*)-2-[(4-Chlorophenyl)-(toluene-4-sulfonylimino)-methyl]-but-enedioic acid diethyl ester (5):

This compound was obtained as a crystalline colorless solid, yield: 185 mg, 80%, mp: 84-86 °C; IR (KBr): ν 2983, 1721, 1647, 1583, 1437, 1325, 1155, 1090, 1010, 779, 737 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.83 (d, *J* = 8.4 Hz, 2H, Ar), 7.76 (d, *J* = 8.7 Hz, 2H, Ar), 7.35 (d, *J* = 8.4 Hz, 2H, Ar), 7.30 (d, *J* = 8.7 Hz, 2H, Ar), 7.16 (s, 1H, =CH), 4.29 (q, *J* = 6.9Hz, 2H, CH_3), 3.97 (q, *J* = 6.9 Hz, 2H, CH_2), 2.40 (s, 1H, CH_2), 1.24 (t, *J* = 6.9 Hz, 3H, CH_3), 1.07 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 171.72, 163.27, 162.11, 144.16, 142.06, 140.03, 136.78, 133.68, 130.97, 130.10, 129.48, 129.01, 127.62, 62.66, 61.75, 21.57, 13.88, 13.63; MS (EI) m/z: 463 (M$^+$, 4.8), 418 [(M-45)$^+$, 2.0], 390 [(M-73)$^+$, 18.1], 308 [(M-155)$^+$, 29.7], 155 [(M-308)$^+$, 33.9] , 91 [(M-372)$^+$, 100]; HRMS (EI) Calcd. for $C_{22}H_{22}ClNO_7S$: 463.0856, found: 463.0807.

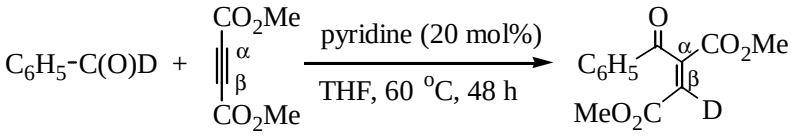
Synthesis of Phenylpropynoic acid ethyl ester.

$$C_6H_5{-}C{\equiv}CH \xrightarrow[THF,\ 60\ ^oC]{BuLi,\ ClCO_2Et} C_6H_5{-}C{\equiv}C{-}CO_2Et$$

This compound was prepared as the Scheme shown above according to the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.60-7.56 (m, 2H, Ar), 7.44-7.34 (m, 3H, Ar), 4.31 (q, *J* = 7.2 Hz, 2H, CH_2), 1.33 (t, *J* = 7.2 Hz, 3H, CH_3).

Scheme. The reaction of deuterated benzaldehyde [$C_6H_5C(O)D$] (0.5 mmol) with DMAD (0.6 mmol) in the presence of pyridine (20 mol%) which supports the mechanism shown in Scheme 5.



1i-*d*, 27%
D content 50%

Figure SI-1. The X-ray crystal structure of **2h**.

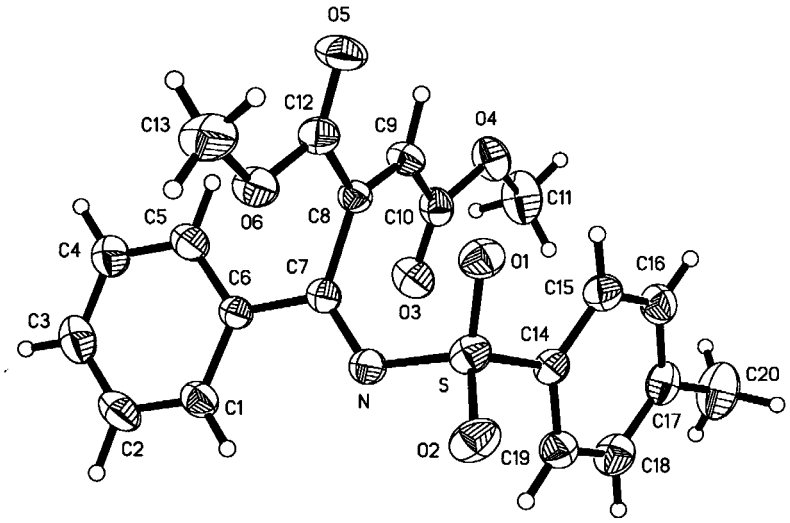
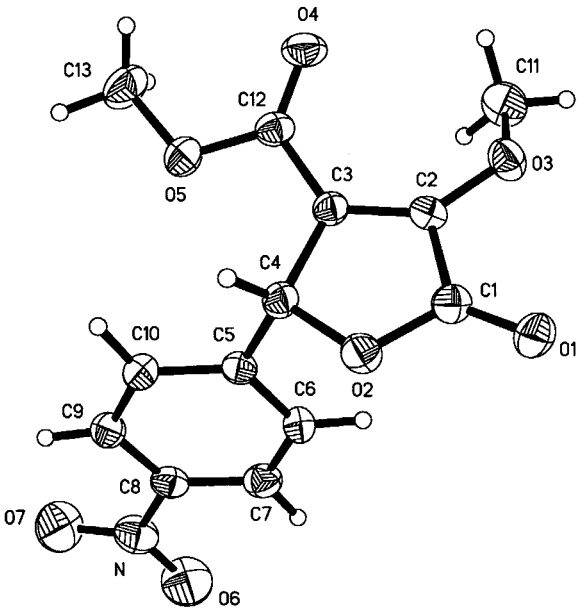
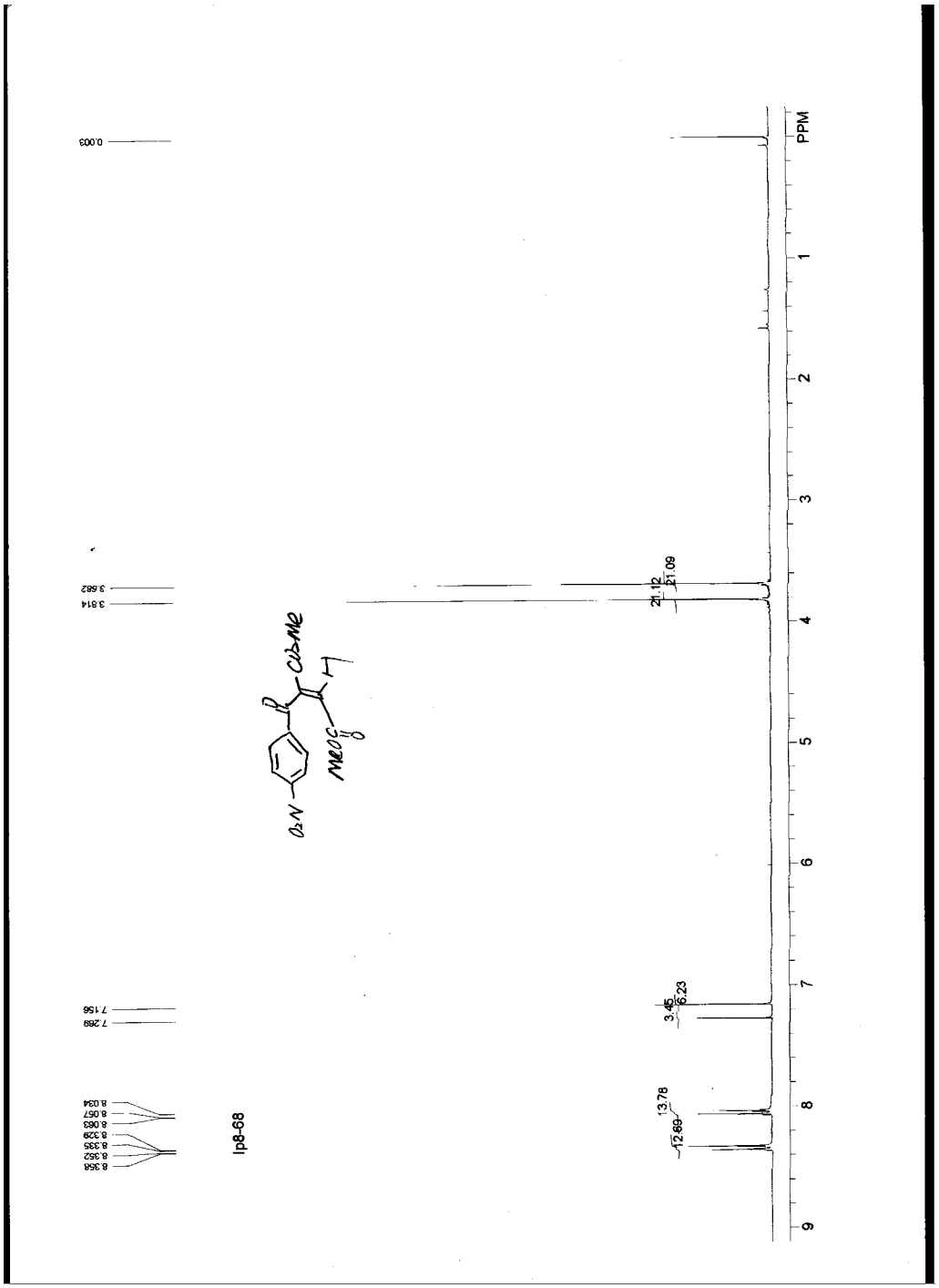
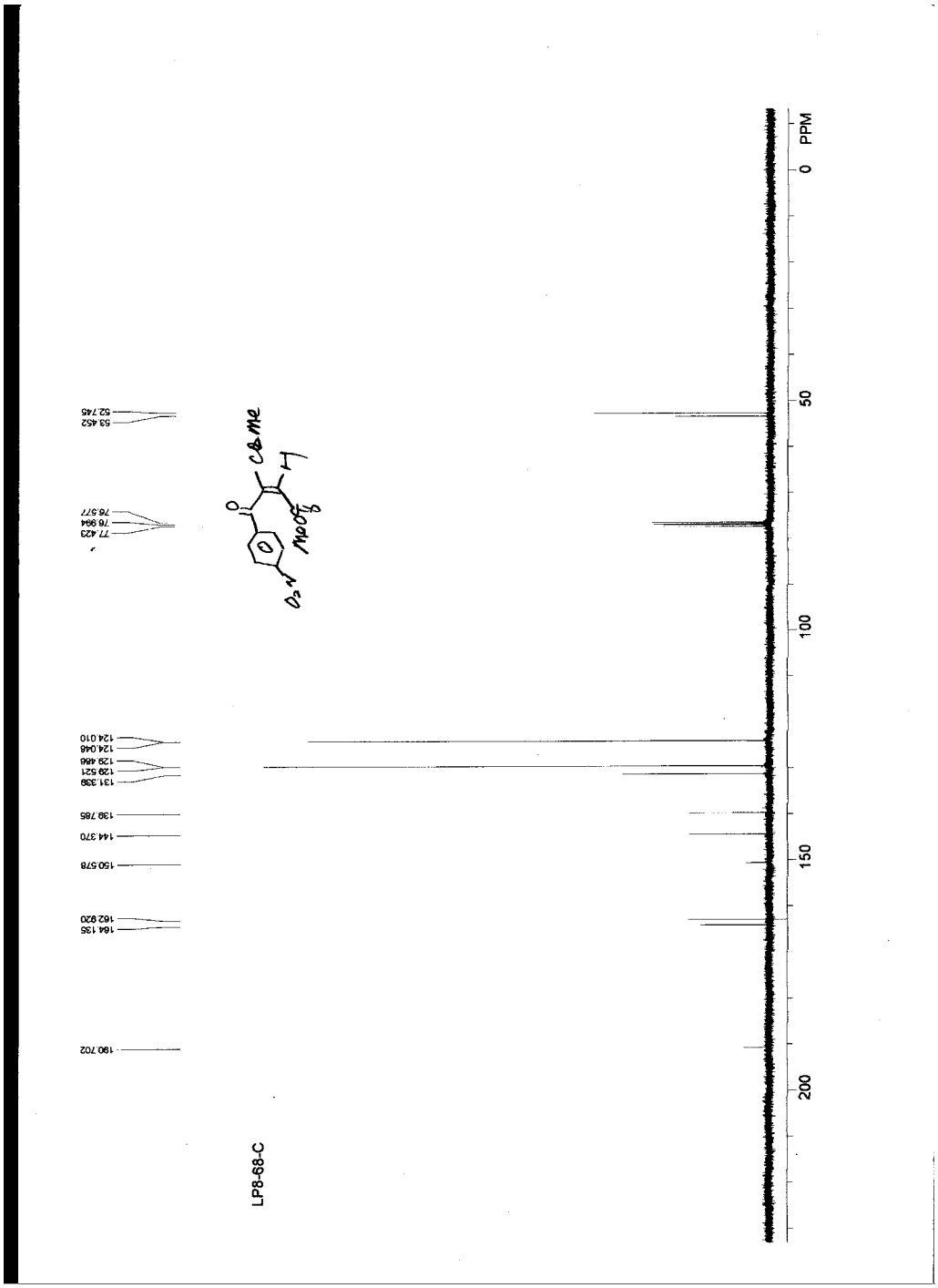


Figure SI-2. The X-ray crystal structure of **3a**.

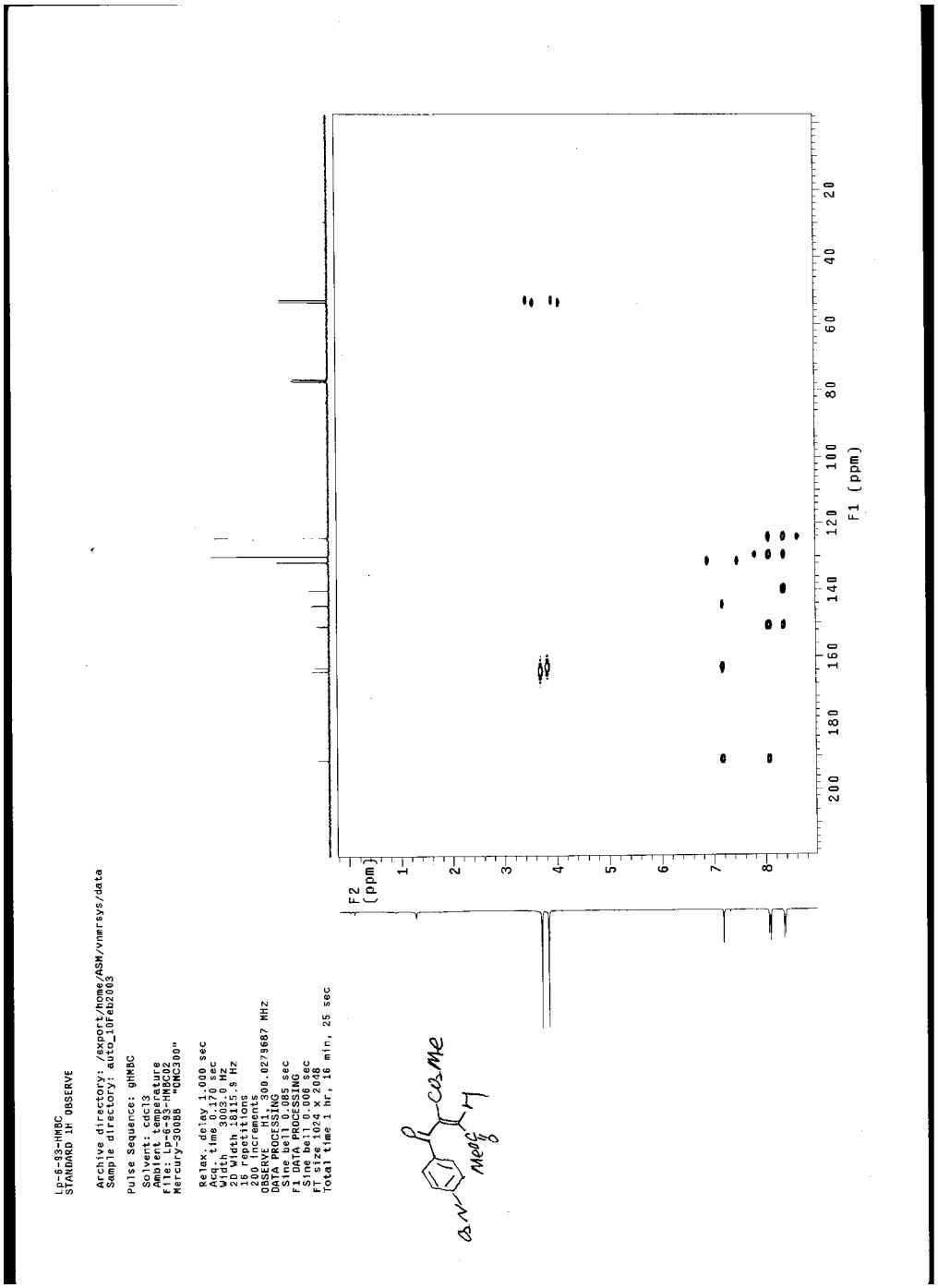

O4
C13
C12
C11
O5
C3
C2
O3
C4
C1
O1
C10
C5
O2
C6
C9
C8
C7
O7
N
O6



^{1}H NMR spectrum of **1a**.



^{13}C NMR spectrum of **1a**.



HMBC spectrum of **1a**.

No long range coupling of olefinic proton with aromatic proton.