Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

DPO and POPOP Carboxylate-Analogs Sensors by Sequential Palladium-Catalysed Direct Arylation of Oxazole-4-Carboxylates

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Contents

General Informations

Dioxane was distilled from benzophenone/Na and toluene was distilled from calcium hydride. Melting points are uncorrected. Column chromatography was performed using silica gel (mesh size 60-80 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz. Chemical shifts (δ) are given as ppm relative to the residual solvent peak. Microanalyses were carried out at the analytical laboratory of our Department (IRCOF). Commercially available halogenoaromatics, 2-(dicyclohexylphosphino)biphenyl (Cy-JohnPhos Buchwald's ligand), and 1,3-bis-(mesitylimidazolyl)carbene (IMes) were used without further purification.

UV-visible and fluorescence spectroscopy

UV-visible spectra were obtained on a Varian Cary 50 scan spectrophotometer, in a quartz Suprasil cell (Hellma, 100-QS, 10 x 10 mm, 3500 µl). A Cary Eclipse fluorescence spectrophotometer Varian was used to measure the absorption spectra. A 80 Hz xenon flash lamp was used as the excitation source and two Czerny-Turner monochromators; the slit width was 5 nm (10 nm band-pass). Its excitation and emission wavelength range is of 200-

900 nm. Scan rate was 120 nm/min. The excitation light was focused on the sample cell (Hellma, 104F-QS, 10 x 4 mm, 1400 µl).

All measurements were made at 25 °C temperature with peltier thermostated cell holder.

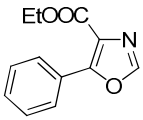
The fluorescence quantum yield of the analogs was measured relative to sodium fluorescein in 0.1 M NaOH and distilled water (ϕ_f = 0.90) at λ_{exc} = 450 nm, relative to harmane in a 0.1 M sulfuric acid and distilled water (ϕ_f = 0.83) at λ_{exc} = 360 nm, relative to Rhodamin 6G in distilled water (ϕ_f = 0.76) at λ_{exc} = 488 nm.

The reproductibility of fluorescence quantum yield was typically ± 10% as described in the literature.

General procedure A for synthesis of 5-aryl oxazole-4-carboxylates:

The 5-aryl oxazole-4-carboxylates were prepared following the Schröder's procedure:[1] A solution of ethyl isocyanoacetate (1.5 g, 13 mmol) in dry THF (8 ml) was added dropwise to a stirred ice-cooled solution of potassium *tert*-butoxyde (1.5 g, 13 mmol) in dry THF (15 ml) under argon. A solution of acyl chloride (13 mmol) in THF (6 ml) was then added dropwise by maintaining the temperature below 0 °C. The resulting mixture was stirred at room temperature during 1 h. An aqueous solution of acetic acid (0.4 ml, 6.5 mmol) was added and the mixture was extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$), concentrated in *vacuo* and the crude product was purified by flash chromatography to afford 5-aryloxazole-4-carboxylates **1a-e**.

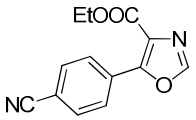
Ethyl 5-phenyloxazole-4-carboxylate (1a):



According to the general procedure A using benzoyl chloride (1.5 ml, 13 mmol). Standard workup followed by flash chromatography (EtOAc/PE 4/6, Rf = 0.35) afforded **1a** (82%) as a white solid (mp < 50 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.39 (t, 3H, J = 7.2 Hz), 4.41 (q, 2H, J = 7.2 Hz), 7.45-7.47 (m, 3H), 7.90 (s, 1H), 8.04-8.07 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 61.5, 126.7, 128.5, 128.6, 130.1, 130.6, 149.1, 155.6, 162.0; IR (KBr) ν 3109, 2977, 1719, 1583, 1495, 1370, 1226, 1189, 1066, 762, 686, 643 cm^{-1}; Anal. Calcd for $C_{12}H_{11}NO_3$ (217.2): C, 66.35; H, 5.10; N, 6.45. Found: C, 66.27; H, 5.04; N, 6.58. Spectral data were in agreement with those previously reported.[2]

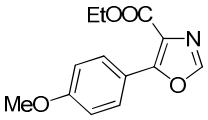
[1] R. Schröder, U. Schöllkopf, E. Blume, I. Hoppe, Liebigs Ann. Chem., 1975, 533-546.
[2] A. P. Kozikowski, A. Ames, *Tetrahedron*, 1985, **41**, 4821-4834.

Ethyl 5-(4-cyanophenyl)oxazole-4-carboxylate (1b):



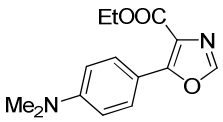
According to the general procedure A using 4-cyanobenzoyl chloride (2.1 g, 13 mmol). Standard workup followed by flash chromatography (EtOAc/PE 4/6, Rf = 0.23) afforded **1b** (80%) as a white solid (mp = 147-148 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.41 (t, 3H, J = 7.2 Hz), 4.43 (q, 2H, J = 7.2 Hz), 7.75 (d, 2H, J = 8.7 Hz), 7.98 (s, 1H), 8.25 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 62.0, 113.8, 118.3, 128.7, 128.9, 130.8, 132.3, 149.9, 153.2, 161.7; IR (KBr) ν 3136, 2987, 2226, 1719, 1591, 1500, 1076, 1027, 989, 842, 787, 643, 559 cm^{-1}; Anal. Calcd for $C_{13}H_{10}N_2O_3$ (242.2): C, 64.46; H, 4.16; N, 11.56. Found: C, 64.35; H, 4.26; N, 11.85. Spectral data were in agreement with those previously reported.[3]

Ethyl 5-(4-methoxyphenyl)oxazole-4-carboxylate (1c):



According to the general procedure A using *p*-anisoyl chloride (1.8 ml, 13 mmol). Standard workup followed by flash chromatography (EtOAc/PE 4/6, Rf = 0.31) afforded **1c** (71%) as a white solid (mp = 70-71 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.41 (t, 3H, J = 7.2 Hz), 3.86 (s, 3H), 4.41 (q, 2H, J = 7.2 Hz), 7.00 (d, 2H, J = 9.0 Hz), 7.85 (s, 1H), 8.07 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.4, 55.5, 61.4, 113.9, 119.3, 125.4, 130.3, 148.5, 155.9, 161.3, 162.3; IR (KBr) ν 3139, 2975, 1694, 1608, 1504, 1182, 1077, 847, 790, 643, 617, 547 cm^{-1}; Anal. Calcd for $C_{13}H_{13}NO_4$ (247.2): C, 63.15; H, 5.30; N, 5.67. Found: C, 62.84; H, 5.61; N, 6.02.

Ethyl 5-(4-(dimethylamino)phenyl)oxazole-4-carboxylate (1d):

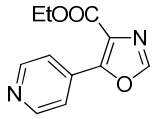


According to the general procedure A using 4-dimethylaminobenzoyl chloride (2.4 g, 13 mmol). Standard workup followed by flash chromatography (EtOAc/PE 4/6, Rf = 0.29) afforded **1d** (75%) as a white solid (mp = 83-84 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.41 (t, 3H, J = 7.2 Hz), 3.03 (s, 6H), 4.41 (q, 2H, J = 7.2 Hz), 6.74 (d, 2H, J = 9.0 Hz), 7.79 (s, 1H), 8.03 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 39.9, 60.9, 111.1, 113.8,

[3] M. Baumann, I. R. Baxendale, S. V. Ley, C. D. Smith, G. K. Tranmer, *Org. Lett.* 2006, **8**, 5231-5234.

123.6, 129.6, 147.6, 151.3, 156.7, 162.3; IR (KBr) ν 3125, 2899, 1705, 1608, 1516, 1371, 1181, 1070, 1029, 944, 785, 641 cm^{-1}; Anal. Calcd for $C_{14}H_{16}N_2O_3$ (260.3): C, 64.60; H, 6.20; N, 10.76. Found: C, 64.82; H, 6.34; N, 10.84.

Ethyl 5-(pyridin-4-yl)oxazole-4-carboxylate (1e)

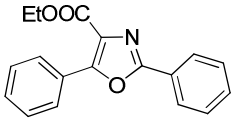


A solution of ethyl isocyanoacetate (6.7 ml, 61.7 mmol) and triethylamine (17.2 ml, 121.3 mmol) was added dropwise to a stirred ice-cooled solution of isonicotinoyl chloride hydrochloride (2.3 g, 13 mmol) in dry THF (40 ml) under argon and the resulting mixture was stirred for 1 h. The solution was refluxed for 24 h, and concentrated *in vacuo*. Then, water (50 ml) was added and the aqueous layer was further extracted with ethyl acetate (3 × 30 ml). The combined organic layers were dried over $MgSO_4$, filtered and solvent was evaporated. The crude product was purified on silica gel (EtOAc/PE 3/7, Rf = 0.22) afforded **1e** (66%) as a white solid (mp = 47-48 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.40 (t, 3H, *J* = 7.1 Hz), 4.42 (q, 2H, *J* = 7.1 Hz), 7.98-8.00 (m, 3H), 8.73 (d, 2H, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.2, 61.9, 121.7, 129.4, 133.8, 150.0, 150.4, 152.5, 161.5; IR (KBr) ν 3094, 2993, 1721, 1584, 1518, 1203, 1103, 824, 788, 693, 624, 515 cm^{-1}; Anal. Calcd for $C_{11}H_{10}N_2O_3$ (218.2): C, 60.55; H, 4.62; N, 12.84. Found: C, 60.31; H, 4.59; N, 12.64.

General procedure B for preparation of DPO and POPOP mono(di)carboxylate-analogs:

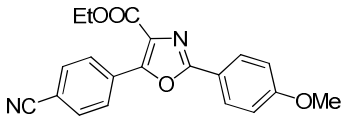
The direct (hetero)arylation reactions were carried out in a sealed tube at 110 °C for 18 h under argon. A solution of ethyl 5-aryl oxazole-4-carboxylate derivative **1** (0.35 mmol) was allowed to react with arylhalide (0.35-0.7 mmol) with palladium acetate (0.017-0.034 mmol), cesium carbonate (231 mg, 0.7 mmol) and ligand (0.035-0.07 mmol).in the appropriate solvent (1 mL). After filtration on Celite and concentration under *vacuo*, the crude product was purified by flash column chromatography on silica gel using a mixture of ethyl acetate (EtOAc) and petroleum Ether (PE) as eluent to give the DPO (**2-7**) and POPOP (**8**) mono(di)carboxylate-analogs. The following detailed procedures are given using optimized experimental conditions.

Ethyl 2,5-diphenyl-4-oxazolecarboxylate (2)



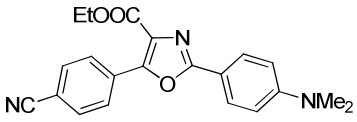
According to the general procedure B using **1a** (76 mg, 0.35 mmol) with 4-iodobenzene (40 μL, 0.35 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 2/8, Rf = 0.42) afforded **2** (100%) as a white solid (mp = 86-87 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.43 (t, 3H, J = 7.0 Hz), 4.47 (q, 2H, J = 7.0 Hz), 7.48-7.50 (m, 6H), 8.10-8.17 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 61.6, 126.4, 127.0, 127.2, 128.3, 128.5, 128.6, 128.9, 130.4, 131.2, 155.2, 159.9, 162.4; IR (KBr) ν 1585, 1716, 2926, 2950, 2975 cm^{-1}; Anal. Calcd for $C_{18}H_{15}NO_3$ (293.32): C, 73.71; H, 5.15; N, 4.78. Found: C, 73.85; H, 5.11; N, 4.52. Spectral data were in agreement with those previously reported.[4]

Ethyl [5-(4-cyanophenyl)-2-(4-methoxyphenyl)]oxazole-4-carboxylate (3a):



According to the general procedure B using **1b** (86 mg, 0.35 mmol) with 4-iodoanisole (82 mg, 0.35 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 4/6, Rf = 0.42) afforded **3a** (83%) as a white solid (mp = 193-194 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.41 (t, 3H, J = 7.2 Hz), 3.83 (s, 3H), 4.43 (q, 2H, J = 7.2 Hz), 6.95 (d, 2H, J = 8.7 Hz), 7.72 (d, 2H, J = 8.5 Hz), 8.03 (d, 2H, J = 8.7 Hz), 8.24 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.2, 55.4, 61.8, 113.0, 114.3, 118.4, 128.6, 128.8, 130.2, 131.2, 132.1, 151.9, 160.7, 162.0, 162.2; IR (KBr) ν 2222, 1708, 1610, 1500, 1370, 1096, 1025, 829, 740 cm^{-1}; Anal. Calcd for $C_{20}H_{16}N_2O_4$ (348.4): C, 68.96; H, 4.63; N, 8.04. Found: C, 69.11; H, 4.56; N, 8.19.

Ethyl [5- (4-cyanophenyl)-2-(4-dimethylaminophenyl)]oxazole-4-carboxylate (3b)

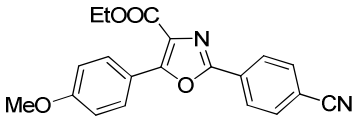


According to the general procedure B using **1b** (86 mg, 0.35 mmol) with 4-bromo-*N*,*N*-dimethylaniline (71 mg, 0.35 mmol), $Pd(OAc)_2$/Cy-JohnPhos (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 4/6,

[4] C. Verrier, T. Martin, C. Hoarau, F. Marsais, *J. Org. Chem*. 2008, **73**, 7383-7386.

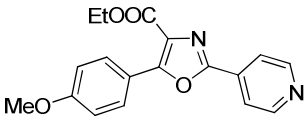
Rf = 0.35) afforded **3b** (92%) as a yellow solid (mp = 191-192 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.42 (t, 3H, J = 7.2 Hz), 3.02 (s, 6H), 4.44 (q, 2H, J = 7.2 Hz), 6.71 (d, 2H, J = 8.7 Hz), 7.71 (d, 2H, J = 8.2 Hz), 7.95 (d, 2H, J = 8.7 Hz), 8.25 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 40.2, 61.8, 111.6, 112.6, 113.3, 128.4, 128.5, 130.2, 131.5, 132.0, 151.2, 152.0, 161.7, 162.3; IR (KBr) ν 2903, 2223, 1711, 1614, 1604, 1509, 1432, 1347, 1317, 1219, 1191, 1099 cm^{-1}; Anal. Calcd for $C_{21}H_{19}N_3O_3$ (361.4): C, 69.79; H, 5.30; N, 11.63. Found: C, 69.87; H, 5.26; N, 11.97.

Ethyl [2-(4-cyanophenyl)-5-(4-methoxyphenyl)]oxazole-4-carboxylate (4a):



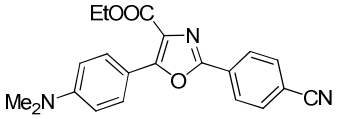
According to the general procedure B using **1c** (85 mg, 0.35 mmol) with 4-iodoanisole (82 mg, 0.35 mmol), $Pd(OAc)_2$/P(*o*-tol)$_3$ (4:11 mg, 0.017:0.035 mmol) and toluene solvent. Standard workup followed by flash chromatography (EtOAc/PE 3/7, Rf = 0.43) afforded **4a** (94%) as a white solid (mp = 192-193 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ =1.41 (t, 3H, J = 6.9 Hz), 3.87 (s, 3H), 4.43 (q, 2H, J = 6.9 Hz), 8.64 (d, 2H, J = 8.6 Hz), 7.76 (d, 2H, J = 8.1 Hz), 8.10 (d, 2H, J = 8.6 Hz), 8.23 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.4, 55.5, 61.6, 114.0, 114.1, 118.3, 119.1, 127.1, 127.6, 130.3, 130.4, 132.7, 156.4, 157.1, 161.5, 162.1; IR (KBr) ν 2994, 2947, 2837, 2227, 1709, 1610, 1578, 1507 cm^{-1}; Anal. Calcd for $C_{20}H_{16}N_2O_4$ (348.4): C, 68.96; H, 4.63; N, 8.04. Found: C, 69.06; H, 4.85; N, 8.21. Spectral data were in agreement with those previously reported.[3]

Ethyl [5-(4-methoxyphenyl)-2-(pyridin-4-yl)]oxazole-4-carboxylate (4b):



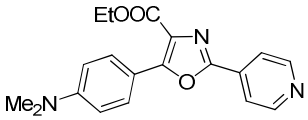
According to the general procedure B using **1c** (88 mg, 0.35 mmol) with 4-bromopyridine.HCl (69 mg, 0.35 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 7/3, Rf = 0.19) afforded **4b** (79%) as a white solid (mp = 145-146 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.39 (t, 3H, J = 7.2 Hz), 3.83 (s, 3H), 4.42 (q, 2H, J = 7.2 Hz), 6.97 (d, 2H, J = 9.0 Hz), 7.93 (d, 2H, J = 5.8 Hz), 8.06 (d, 2H, J = 9.0 Hz), 8.72 (d, 2H, J = 5.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 55.4, 61.6, 114.0, 119.0, 120.2, 127.5, 130.4, 133.4, 150.6, 156.4, 156.7, 161.5, 162.0; IR (KBr) ν 3535, 1709, 1608, 1507, 1263, 1233, 1181, 1099, 1032, 835, 709 cm^{-1}; Anal. Calcd for $C_{18}H_{16}N_2O_4$ (324.3): C, 66.66; H, 4.97; N, 8.64. Found: C, 66.48; H, 5.05; N, 8.79.

Ethyl [2-(4-cyanophenyl)-5-(4-(dimethylamino)phenyl)]oxazole-4-carboxylate (5a):



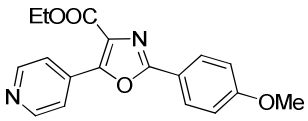
According to the general procedure B using **1d** (92 mg, 0.35 mmol) with 4-iodobenzonitrile (81 mg, 0.35 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 4/6, Rf = 0.39) afforded **5a** (61%) as a yellow solid (mp = 149-150 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.42 (t, 3H, J = 7.1 Hz), 3.04 (s, 6H), 4.44 (q, 2H, J = 7.1 Hz), 6.74 (d, 2H, J = 8.8 Hz), 7.73 (d, 2H, J = 8.2 Hz), 8.05 (d, 2H, J = 8.8 Hz), 8.20 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.4, 40.2, 61.4, 111.3, 113.7, 113.8, 118.4, 126.1, 127.0, 130.0, 130.5, 132.6, 151.6, 156.3, 157.5, 162.4; IR (KBr) ν 2229, 1709, 1610, 1513, 1369, 1218, 1197, 1093, 847, 816 cm^{-1}; Anal. Calcd for $C_{21}H_{19}N_3O_3$ (361.4): C, 69.79; H, 5.30; N, 11.63. Found: C, 69.99; H, 5.13; N, 11.58.

Ethyl [5-(4-(dimethylamino)phenyl)-2-(pyridin-4-yl)]oxazole-4-carboxylate (5b):



According to the general procedure B using **1d** (92 mg, 0.35 mmol) with 4-bromopyridine.HCl (69 mg, 0.35 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 7/3, Rf = 0.15) afforded **5b** (57%) as a yellow solid (mp = 156-157 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.42 (t, 3H, J = 7.1 Hz), 3.02 (s, 6H), 4.44 (q, 2H, J = 7.1 Hz), 6.72 (d, 2H, J = 9.0 Hz), 7.94 (d, 2H, J = 5.8 Hz), 8.05 (d, 2H, J = 9.0 Hz), 8.72 (d, 2H, J = 5.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.4, 40.0, 61.3, 111.2, 113.6, 120.1, 126.0, 130.0, 133.7, 150.5, 151.7, 155.8, 157.6, 162.3; IR (KBr) ν 3502, 1709, 1608, 1519, 1229, 1196, 1091, 1027, 816, 788, 706 cm^{-1}; Anal. Calcd for $C_{19}H_{19}N_3O_3$ (337.4): C, 67.64; H, 5.68; N, 12.46. Found: C, 67.59; H, 5.72; N, 12.53.

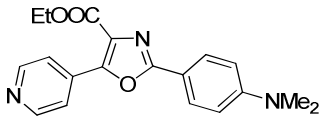
Ethyl [2-(4-methoxyphenyl)-5-(pyridin-4-yl)]oxazole-4-carboxylate (6a):



According to the general procedure B using **1e** (78 mg, 0.35 mmol) with 4-iodoanisole (83 mg, 0.35 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 7/3, Rf = 0.21) afforded **6a** (82%) as a white solid (mp = 88-89 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.39 (t, 3H, J = 7.2

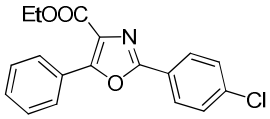
Hz), 3.80 (s, 3H), 4.43 (q, 2H, *J* = 7.2 Hz), 6.93 (d, 2H, *J* = 9.0 Hz), 7.98-8.04 (m, 4H), 8.70 (d, 2H, *J* = 5.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.2, 55.4, 61.8, 118.4, 121.5, 128.8, 130.9, 134.2, 150.2, 151.2, 160.9, 161.9, 162.3; IR (KBr) ν 3514, 1719, 1614, 1500, 1257, 1107, 840, 743, 702 cm^{-1}; Anal. Calcd for $C_{18}H_{16}N_2O_4$ (324.3): C, 66.66; H, 4.97; N, 8.64. Found: C, 66.84; H, 4.73; N, 9.06.

Ethyl [2-(4-(dimethylamino)phenyl)-5-(pyridin-4-yl)]oxazole-4-carboxylate (6b):



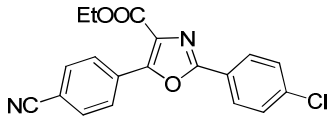
According to the general procedure B using **1e** (78 mg, 0.35 mmol) with 4-bromo-*N*,*N*-dimethylaniline (71 mg, 0.35 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 6/4, Rf = 0.19) afforded **6b** (45%) as a orange solid (mp = 179-180 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.43 (t, 3H, *J* = 7.1 Hz), 3.03 (s, 6H), 4.46 (q, 2H, *J* = 7.1 Hz), 6.70 (d, 2H, *J* = 9.0 Hz), 7.98 (d, 2H, *J* = 9.0 Hz), 8.04 (d, 2H, *J* = 6.0 Hz), 8.72 (d, 2H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 40.1, 61.8, 111.4, 113.0, 121.5, 128.6, 131.0, 134.6, 150.2, 150.5, 152.3, 162.0, 162.3; IR (KBr) ν 2972, 2930, 1711, 1611, 1512, 1189, 1104, 819, 741 cm^{-1}; Anal. Calcd for $C_{19}H_{19}N_3O_3$ (337.4): C, 67.64; H, 5.68; N, 12.46. Found: C, 67.84; H, 5.77; N, 12.40.

Ethyl [2-(4-chlorophenyl)-5-phenyl]oxazole-4-carboxylate (7a):



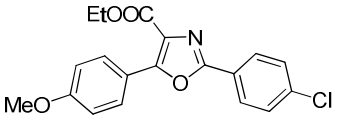
According to the general procedure B using **1a** (77 mg, 0.35 mmol) with 1-chloro-4-iodobenzene (169 mg, 0.70 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 2/8, Rf = 0.37) afforded **7a** (87%) as a white solid (mp = 95-96 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.41 (t, 3H, *J* = 7.1 Hz), 4.45 (q, 2H, *J* = 7.1 Hz), 7.44-7.51 (m, 5H), 8.07-8.10 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.4, 61.7, 124.9, 127.0, 128.2, 128.4, 128.5, 128.6, 129.2, 130.5, 137.3, 155.4, 158.9, 162.2; IR (KBr) ν 3515.1, 2925.4, 1721.3, 1606.6, 1484.5 cm^{-1}; Anal. Calcd for $C_{18}H_{14}ClNO_3$ (327.8): C, 65.96; H, 4.31; Cl, 10.82; N, 4.27. Found: C, 65.71; H, 4.56; Cl, 10.95; N, 4.15.

Ethyl [2-(4-chlorophenyl)-5-(4-cyanophenyl)]oxazole-4-carboxylate (7b):



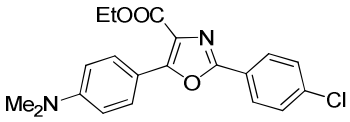
According to the general procedure B using **1b** (86 mg, 0.35 mmol) with 1-chloro-4-iodobenzene (169 mg, 0.70 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 2/8, Rf = 0.26) afforded **7b** (66%) as a white powder (mp = 166-167 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.42 (t, 3H, J = 6.9 Hz), 4.45 (q, 2H, J = 6.9 Hz), 7.44 (d, 2H, J = 8.4 Hz), 7.75 (d, 2H, J = 8.4 Hz), 8.05 (d, 2H, J = 8.4 Hz), 8.26 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 62.0, 113.5, 118.3, 124.3, 128.3, 128.8, 129.3, 130.4, 130.9, 132.2, 137.9, 152.7, 159.7, 161.8; IR (KBr) ν 3514, 2928, 2230, 1719, 1603, 1483, 1239, 1094, 835, 737, 547 cm^{-1}; Anal. Calcd for $C_{19}H_{13}ClN_2O_3$ (352.8): C, 64.69; H, 3.71; Cl, 10.05; N, 7.94. Found: C, 64.59; H, 3.54; Cl, 9.87; N, 8.08.

Ethyl [2-(4-chlorophenyl)-5-(4-methoxyphenyl)]oxazole-4-carboxylate (7c):



According to the general procedure B using **1c** (88 mg, 0.35 mmol) with 1-chloro-4-iodobenzene (169 mg, 0.70 mmol), $Pd(OAc)_2$/IMes (8:24 mg, 0.034:0.07 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 3/7, Rf = 0.40) afforded **7c** (91%) as a white solid (mp = 145-146 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.43 (t, 3H, J = 7.1 Hz), 3.88 (s, 3H), 4.45 (q, 2H, J = 7.1 Hz), 7.01 (d, 2H, J = 9.0 Hz), 7.46 (d, 2H, J = 8.7 Hz), 8.06-8.11 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.5, 55.6, 61.6, 114.0, 119.5, 125.1, 127.2, 128.2, 129.3, 130.4, 137.2, 155.7, 158.4, 161.4, 162.5; IR (KBr) ν 3504, 2977, 1714, 1610, 1507, 1226, 1170, 1000, 834, 734 cm^{-1}; Anal. Calcd for $C_{19}H_{16}ClNO_4$ (357.8): C, 63.78; H, 4.51; Cl, 9.91; N, 3.91. Found: C, 63.80; H, 4.58; Cl, 9.84; N, 4.08.

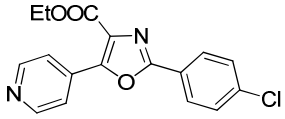
Ethyl [2-(4-chlorophenyl)-5-(4-(dimethylamino)phenyl)]oxazole-4-carboxylate (7d):



According to the general procedure B using **1d** (92 mg, 0.35 mmol) with 1-chloro-4-iodobenzene (169 mg, 0.70 mmol), $Pd(OAc)_2$/IMes (8:24 mg, 0.034:0.07 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 3/7, Rf = 0.40) afforded **7d** (90%) as a white solid (mp > 260 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.43 (t, 3H, J = 7.2 Hz), 3.04 (s, 6H), 4.45 (q, 2H, J = 7.2 Hz), 6.75 (d, 2H, J = 8.7 Hz), 7.44 (d, 2H, J

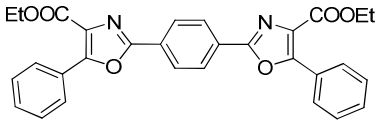
= 8.1Hz), 8.04-8.07 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.5, 40.2, 61.3, 111.3, 114.2, 125.3, 125.7, 128.0, 129.1, 129.9, 136.8, 151.6, 156.8, 157.5, 162.7; IR (KBr) ν 1711, 1614, 1515, 1197, 1086, 817, 731 cm^{-1}; Anal. Calcd for $C_{20}H_{19}ClN_2O_3$ (370.8): C, 64.78; H, 5.16; Cl, 9.56; N, 7.55. Found: C, 64.93; H, 5.31; Cl, 9.44; N, 7.83.

Ethyl [2-(4-chlorophenyl)-5-(pyridin-4-yl)]oxazole-4-carboxylate (7e):



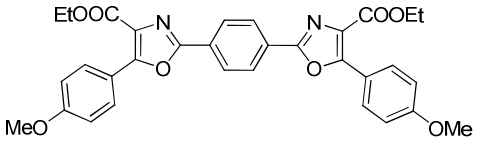
According to the general procedure B using **1e** (78 mg, 0.35 mmol) with 1-chloro-4-iodobenzene (169 mg, 0.70 mmol), $Pd(OAc)_2$/IMes (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 6/4, Rf = 0.32) afforded **7e** (78%) as a white solid (mp = 87-88 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.43 (t, 3H, *J* = 7.1 Hz), 4.47 (q, 2H, *J* = 7.1 Hz), 7.46 (d, 2H, *J*= 8.4 Hz), 8.03 (d, 2H, *J* = 6.0 Hz), 8.07 (d, 2H, *J* = 8.4 Hz), 8.75 (d, 2H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.4, 62.1, 121.7, 124.4, 128.4, 129.4, 131.2, 134.0, 138.0, 150.4, 152.1, 160.0, 161.8; IR (KBr) ν 1720, 1602, 1583, 1482, 1091, 835, 735, 694, 495 cm^{-1}; Anal. Calcd for $C_{17}H_{13}ClN_2O_3$ (328.7): C, 62.11; H, 3.99; Cl, 10.78; N, 8.52. Found: C, 62.04; H, 4.22; Cl, 10.86; N, 8.64.

POPOP dicarboxyalte-analog 8a:



According to the general procedure B using **1a** (77 mg, 0.35 mmol) with **7a** (232 mg, 0.70 mmol), $Pd(OAc)_2$/Cy-JohnPhos Buchwald's ligand (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 4/6, Rf = 0.35) afforded **8a** (22%) as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.43 (t, 3H, *J* = 7.2 Hz), 4.47 (q, 4H, *J* = 7.2 Hz), 7.50-7.52 (m, 6H), 8.12-8.14 (m, 4H), 8.29 (s, 4H).

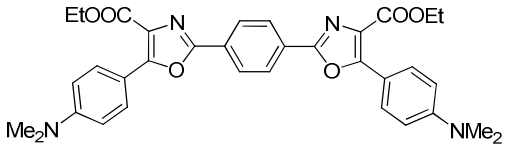
POPOP dicarboxyalte-analog 8b:



According to the general procedure B using **1c** (88 mg, 0.35 mmol) with **7c** (254 mg, 0.70 mmol), $Pd(OAc)_2$/Cy-JohnPhos Buchwald's ligand (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 4/6, Rf = 0.24)

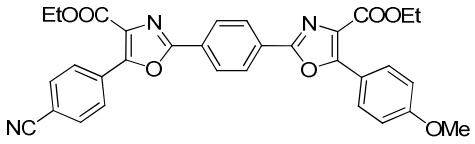
afforded **8b** (98%) as a white solid (mp > 260 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.44 (t, 6H, J = 7.1 Hz), 3.89 (s, 6H), 4.47 (q, 4H, J = 7.1 Hz), 7.03 (d, 4H, J = 8.7 Hz), 8.13 (d, 4H, J = 8.7 Hz), 8.25 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.4, 55.5, 61.6, 114.0, 119.5, 127.2, 127.4, 128.4, 130.4, 155.9, 158.4, 161.4, 162.4; IR (KBr) ν 2971, 2841, 1713, 1609, 1578, 1504, 1220, 1178, 1033, 833, 787, 711, 648 cm^{-1}; Anal. Calcd for $C_{32}H_{28}N_2O_8$ (568.6): C, 67.60; H, 4.96; N, 4.93. Found: C, 67.48; H, 5.24; N, 5.11.

POPOP dicarboxyalte-analog 8c:



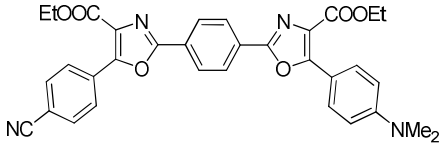
According to the general procedure B using **1d** (92 mg, 0.35 mmol) with **7d** (263 mg, 0.70 mmol), $Pd(OAc)_2$/Cy-JohnPhos Buchwald's ligand (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 6/4, Rf = 0.32) afforded **8c** (99%) as a yellow solid (decomposition 180 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.45 (t, 6H, J = 7.1 Hz), 3.06 (s, 12H), 4.47 (q, 4H, J = 7.1 Hz), 6.77 (d, 4H, J = 8.7 Hz), 8.10 (d, 4H, J = 8.7 Hz), 8.23 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.5, 40.2, 61.4, 111.4, 114.3, 126.0, 127.0, 128.4, 130.0, 151.7, 157.1, 157.7, 162.8; IR (KBr) ν 2929, 1717, 1610, 1560, 1513 cm^{-1}; Anal. Calcd for $C_{34}H_{34}N_4O_6$ (594.7): C, 68.67; H, 5.76; N, 9.42. Found: C, 68.59; H, 5.66; N, 9.58.

POPOP dicarboxyalte-analog 8d:



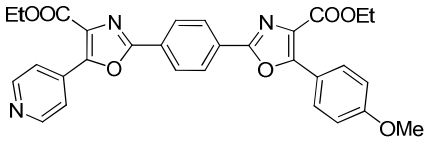
According to the general procedure B using **1b** (86 mg, 0.35 mmol) with **7c** (254 mg, 0.70 mmol), $Pd(OAc)_2$/Cy-JohnPhos Buchwald's ligand (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 5/5, Rf = 0.38) afforded **8d** (86%) as a yellow solid (mp = 241-242 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.39-1.45 (m, 6H), 3.84 (s, 3H), 4.39-4.49 (m, 4H), 6.97 (d, 2H, J = 9.0 Hz), 7.75 (d, 2H, J = 8.4 Hz), 8.07 (d, 2H, J = 9.0 Hz), 8.18 (s, 4H), 8.27 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 14.4, 55.4, 61.5, 62.1, 113.5, 113.9, 118.3, 119.2, 127.1, 127.3, 127.4, 127.5, 128.9, 130.3, 130.6, 130.8, 132.2, 152.9, 155.9, 157.9, 159.7, 161.4, 161.8, 162.2; IR (KBr) ν 2984, 2840, 2227, 1715, 1608, 1578, 1560, 1506 cm^{-1}; Anal. Calcd for $C_{32}H_{25}N_3O_7$ (563.6): C, 68.20; H, 4.47; N, 7.46. Found: C, 68.14; H, 4.58; N, 7.49.

POPOP dicarboxyalte-analog 8e:



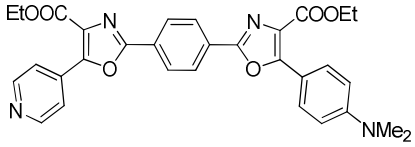
According to the general procedure B using **1b** (86 mg, 0.35 mmol) with **7d** (263 mg, 0.70 mmol), $Pd(OAc)_2$/Cy-JohnPhos Buchwald's ligand (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 5/5, Rf = 0.33) afforded **8e** (95%) as a yellow solid (mp = 244-245 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.43 (m, 6H), 3.01 (s, 6H), 4.45 (m, 4H), 6.70 (d, 2H, J = 8.5 Hz), 7.74 (d, 2H, J = 8.1 Hz), 8.04 (d, 2H, J = 8.5 Hz), 8.16 (s, 4H), 8.27 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 14.4, 40.1, 61.3, 62.0, 111.2, 113.4, 113.9, 118.3, 125.8, 126.9, 127.1, 127.2, 128.8, 129.1, 129.8, 130.5, 130.8, 132.2, 151.4, 152.8, 157.0, 159.7, 161.8, 162.5; IR (KBr) ν 2980, 2926, 2226, 1715, 1608, 1512 cm^{-1}; Anal. Calcd for $C_{33}H_{28}N_4O_6$ (576.6): C, 68.74; H, 4.89; N, 9.72. Found: C, 68.63; H, 5.02; N, 9.91.

POPOP dicarboxyalte-analog 8f:

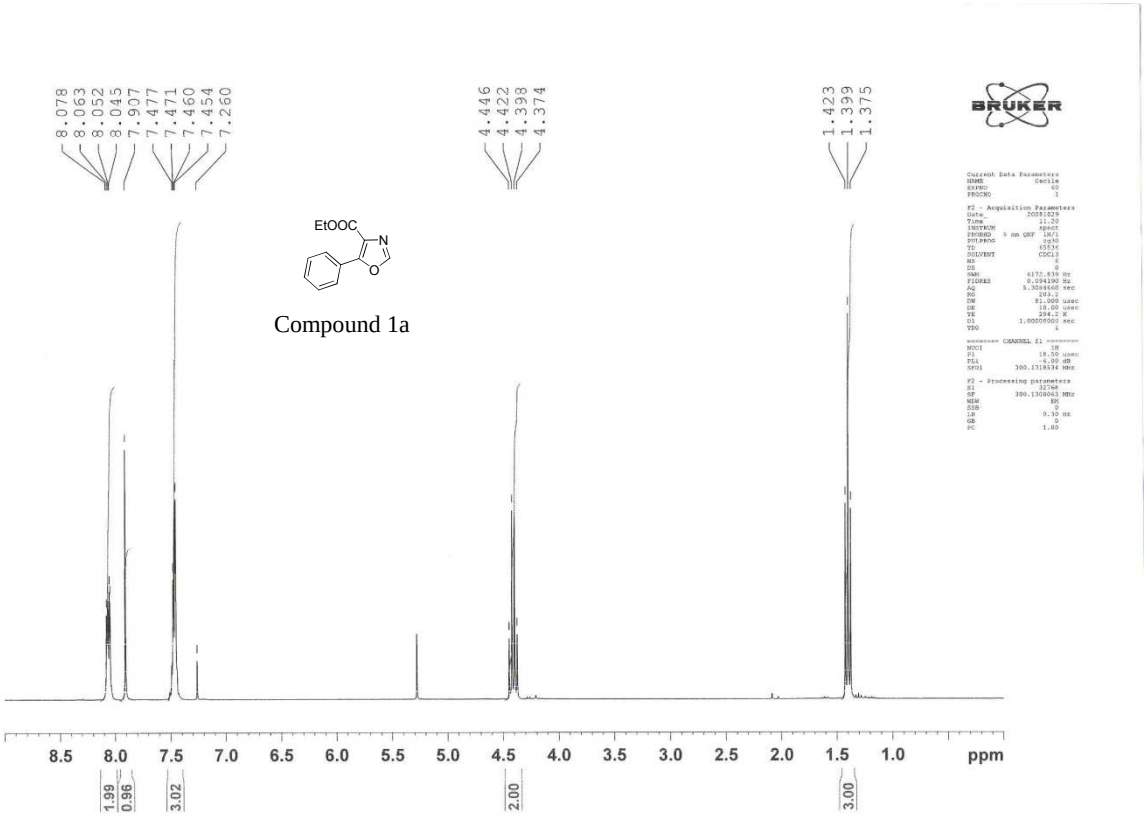


According to the general procedure B using **1e** (78 mg, 0.35 mmol) with **7c** (254 mg, 0.70 mmol), $Pd(OAc)_2$/Cy-JohnPhos Buchwald's ligand (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 7/3, Rf = 0.19) afforded **8f** (92%) as a yellow powder (mp = 225-226 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 139-1.47 (m, 6H), 3.86 (s, 3H), 4.41-4.52 (m, 4H), 6.99 (d, 2H, J = 9.0 Hz), 8.06-8.11 (m, 4H), 8.23 (s, 4H), 8.78 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.3, 14.4, 55.5, 61.6, 62.2, 113.9, 119.3, 121.9, 127.2, 127.4, 127.6, 129.1, 130.4, 131.4, 134.1, 150.3, 152.2, 156.0, 158.0, 160.1, 161.4, 161.7, 162.3; IR (KBr) ν 2977, 1715, 1609, 1578, 1542, 1505 cm^{-1}; Anal. Calcd for $C_{30}H_{25}N_3O_7$ (539.5): C, 66.78; H, 4.67; N, 7.79. Found: C, 66.84; H, 4.87; N, 7.62.

POPOP dicarboxyalte-analog (8g)



According to the general procedure B using **1e** (78 mg, 0.35 mmol) with **7d** (263 mg, 0.70 mmol), $Pd(OAc)_2$/Cy-JohnPhos Buchwald's ligand (4:12 mg, 0.017:0.035 mmol) and dioxane solvent. Standard workup followed by flash chromatography (EtOAc/PE 7/3, Rf = 0.16) afforded **8g** (98%) as a yellow powder (mp = 180-181 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.41-1.48 (m, 6H), 3.04 (s, 6H), 4.42-4.51 (m, 4H), 6.75 (d, 2H, J = 9 Hz), 8.06 (m, 4H), 8.24 (s, 4H), 8.78 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.4, 14.5, 40.2, 61.4, 62.2, 111.3, 114.0, 121.8, 126.0, 127.1, 127.3, 127.4, 129.4, 129.9, 131.4, 134.1, 150.4, 151.7, 152.3, 157.2, 160.2, 161.8, 162.6; IR (KBr) ν 2928, 1719, 1609, 1511 cm^{-1}; Anal. Calcd for $C_{31}H_{28}N_4O_6$ (552.6): C, 67.38; H, 5.11; N, 10.14. Found: C, 67.48; H, 4.86; N, 10.27.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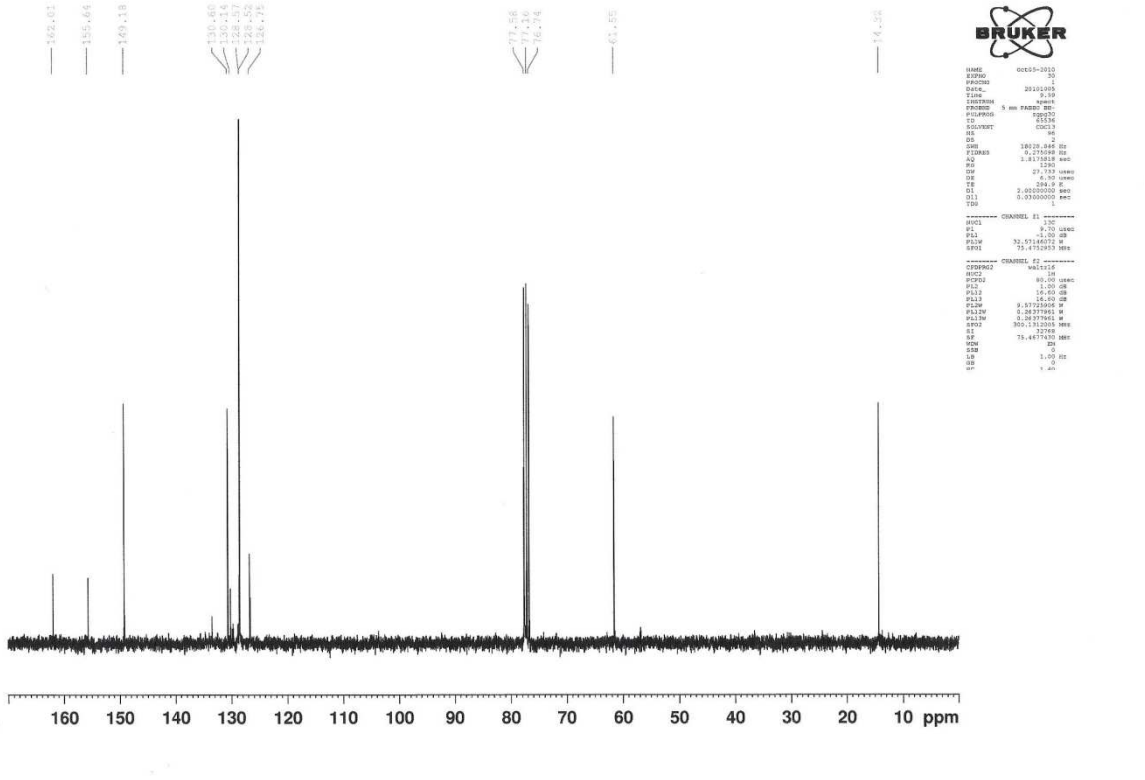
Compound 1a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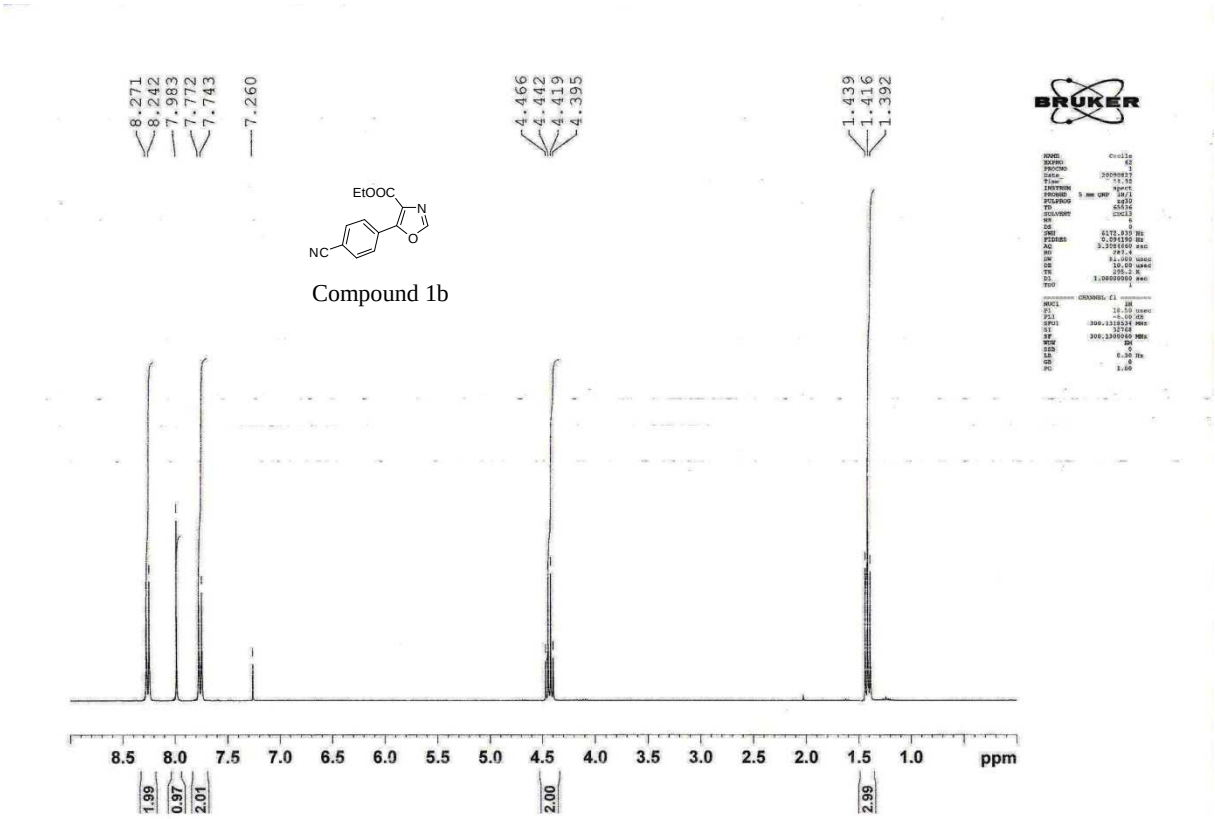
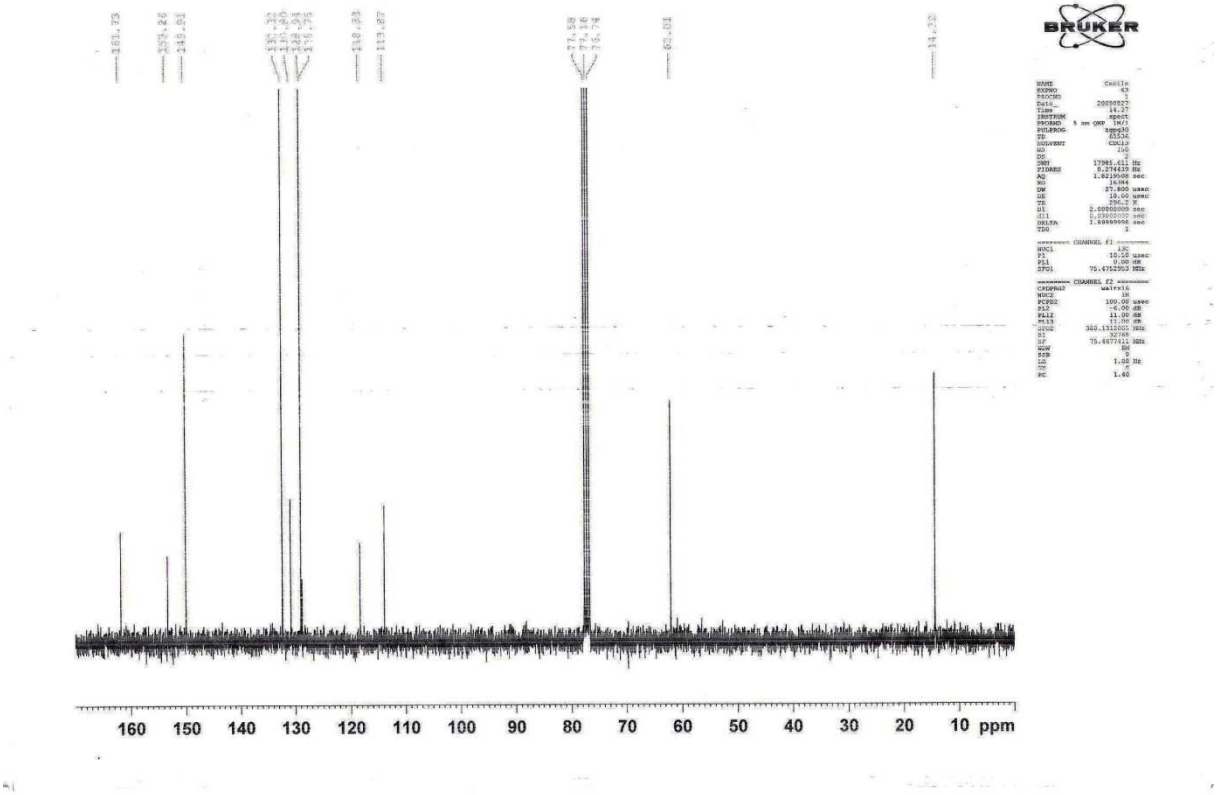
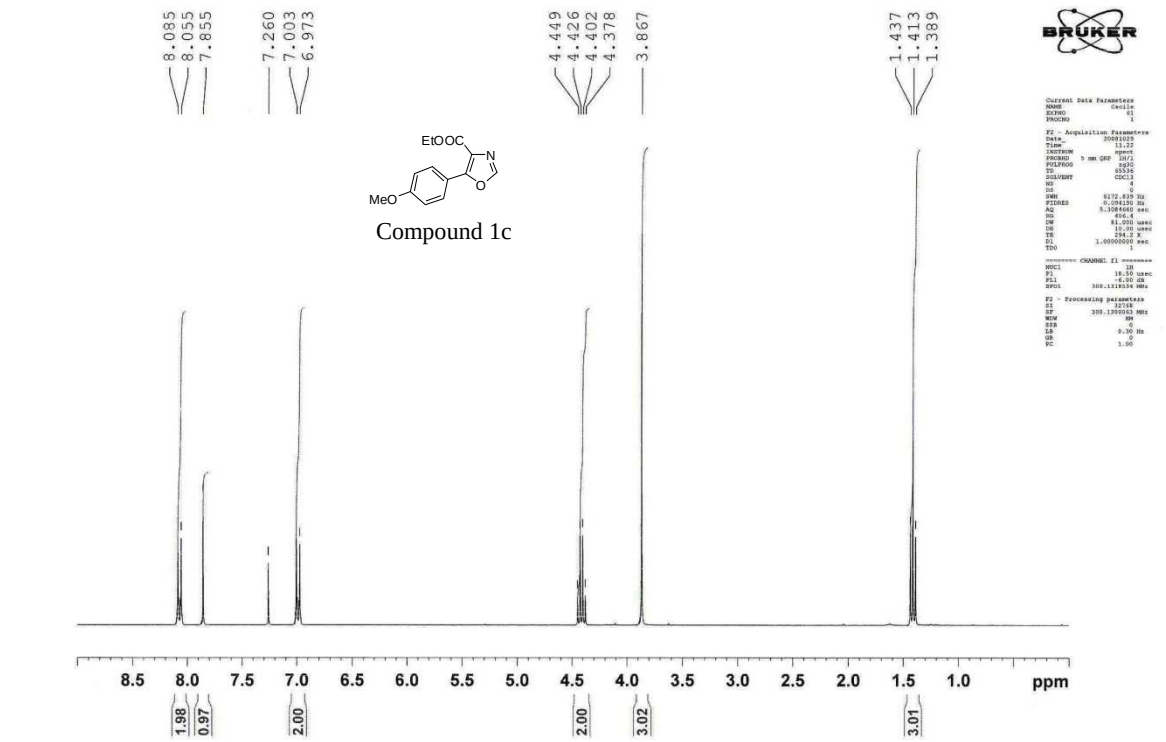
130.60
130.14
128.57
128.02
126.78
77.58
77.16
76.74
61.55
14.56
BRUKER
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

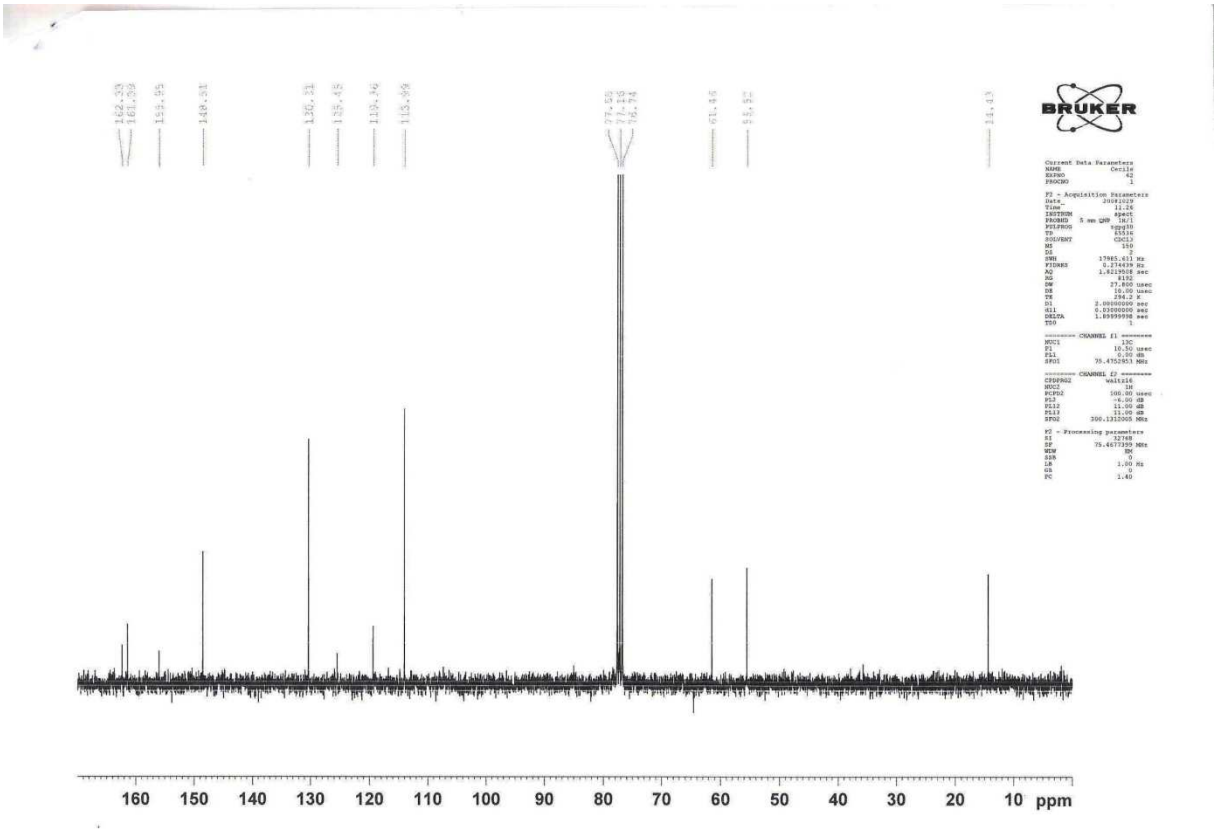

8.271
8.242
7.983
7.772
7.743
7.260
4.466
4.442
4.419
4.395
1.439
1.416
1.392
EtOOC
N
O
NC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.99
0.97
2.01
2.00
2.99

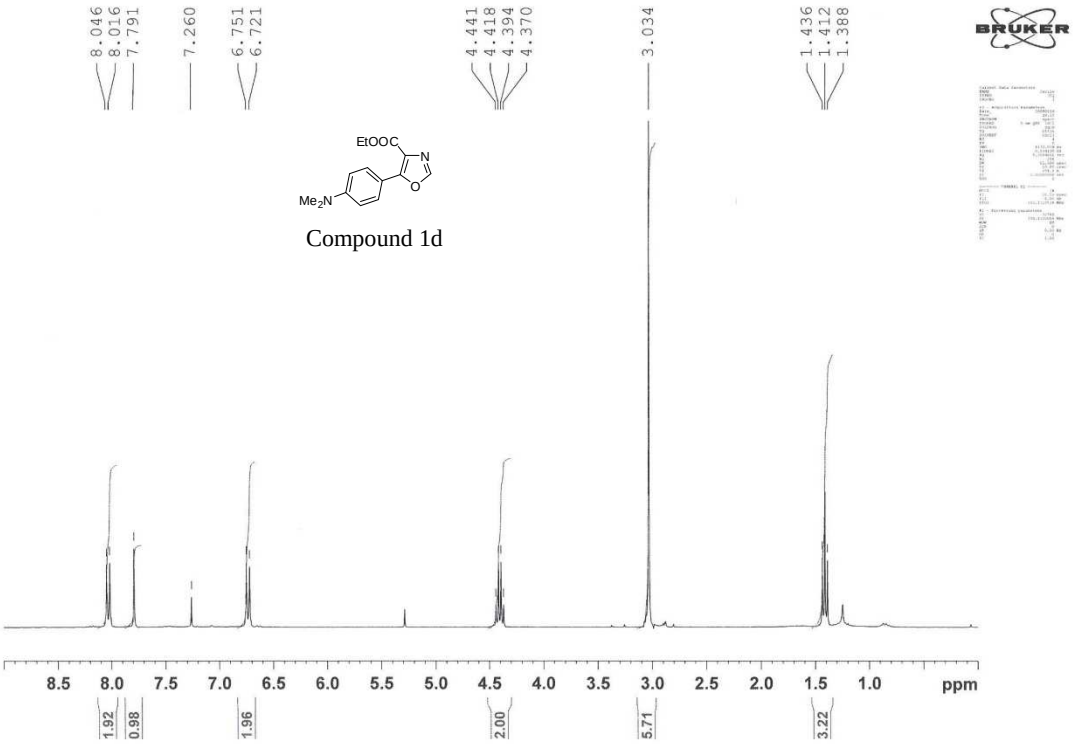
Compound 1b


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

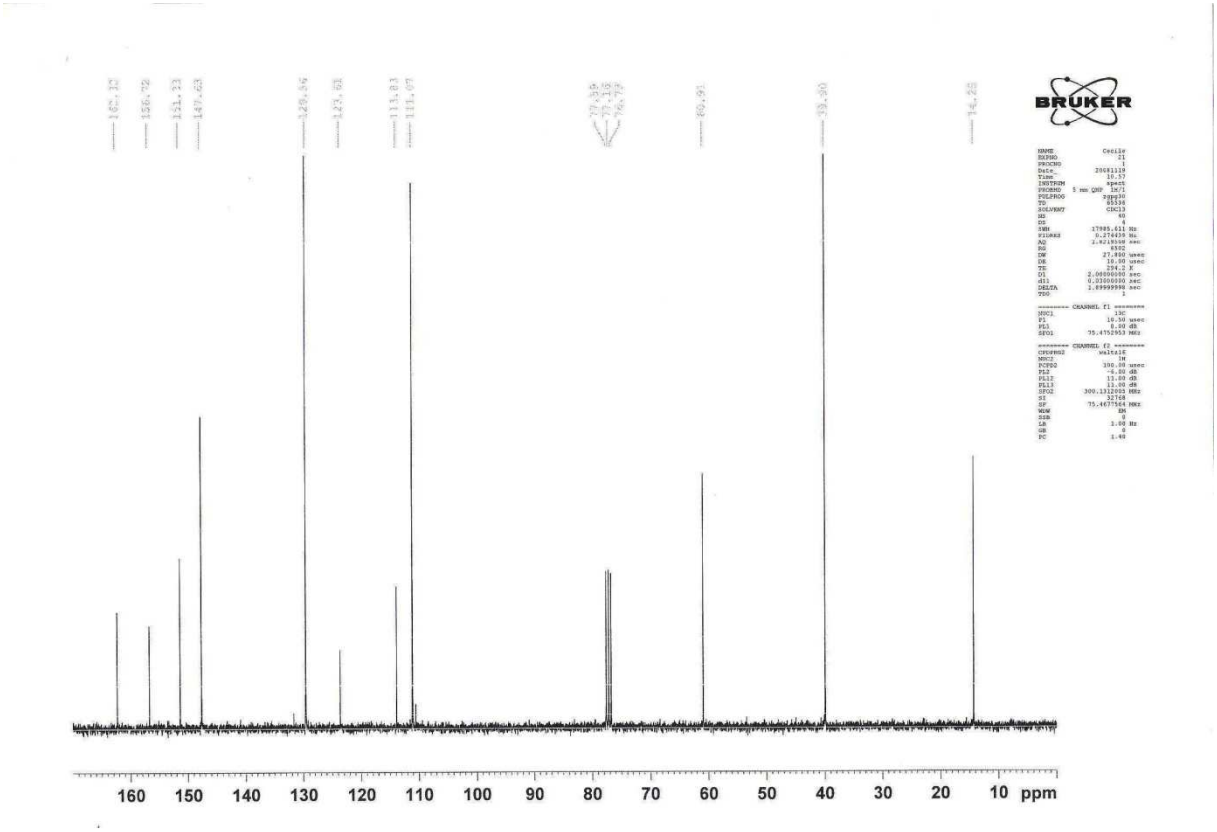

8.085
8.055
7.855
7.260
7.003
6.973
4.449
4.426
4.402
4.378
3.867
1.437
1.413
1.389
EtOOC
N
O
MeO
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.98
0.97
2.00
2.00
3.02
3.01

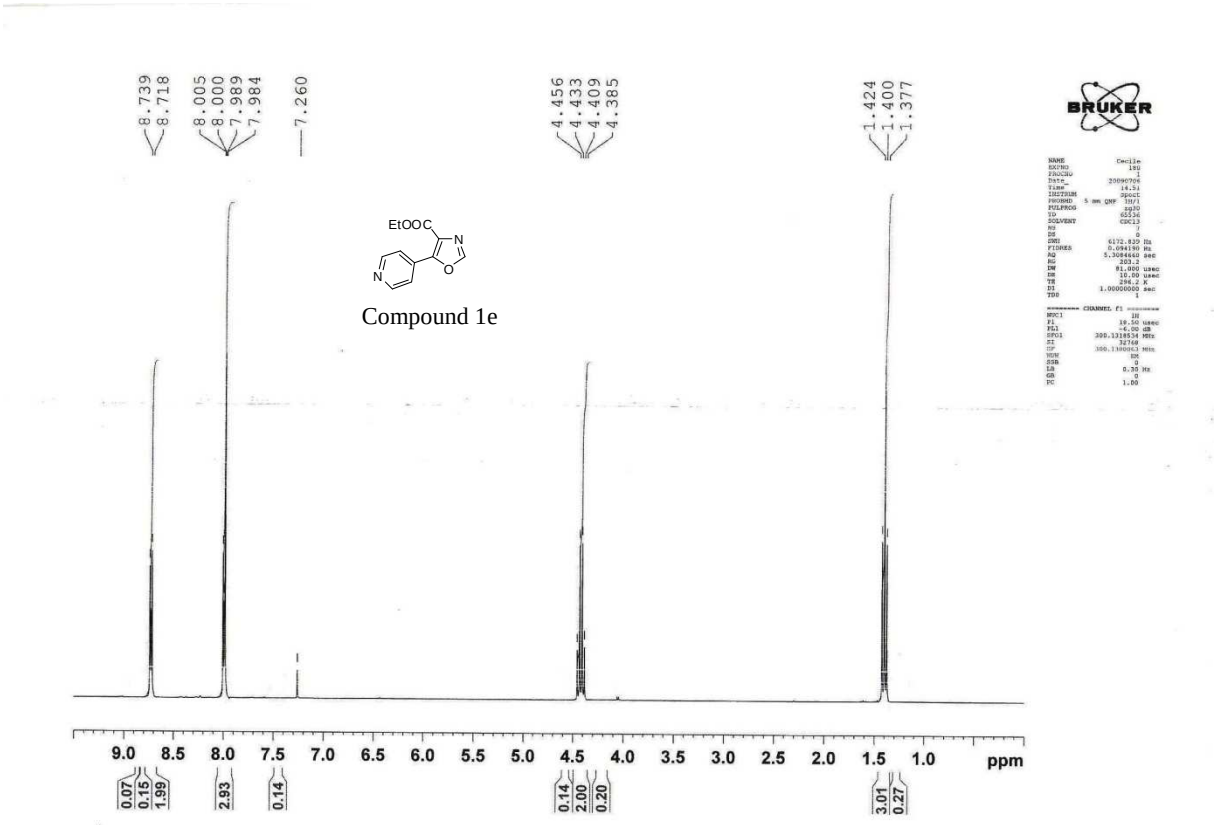
Compound 1c


162.39
161.59
153.95
140.31
130.31
125.45
110.46
105.69
77.55
77.15
76.74
61.46
55.57
14.13
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

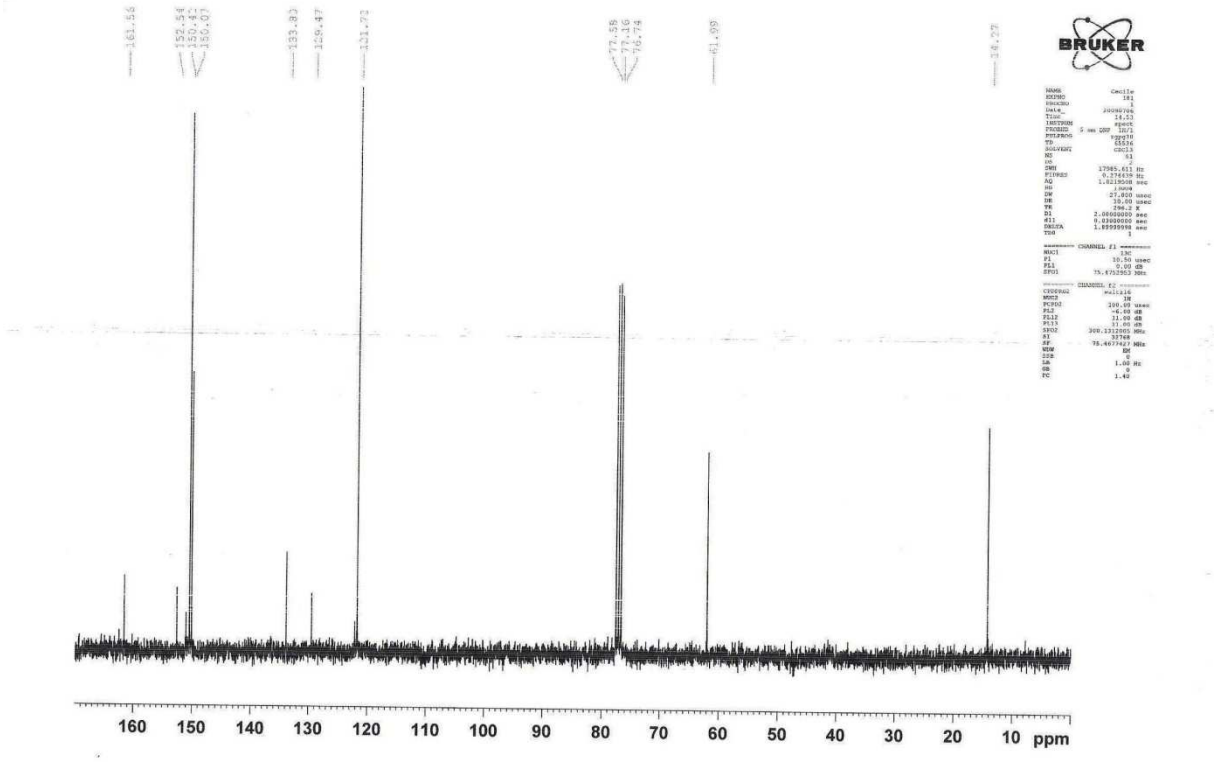

8.046
8.016
7.791
7.260
6.751
6.721
4.441
4.418
4.394
4.370
3.034
1.436
1.412
1.388
EtOOC
N
O
Me2N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.92
0.98
1.96
2.00
5.71
3.22

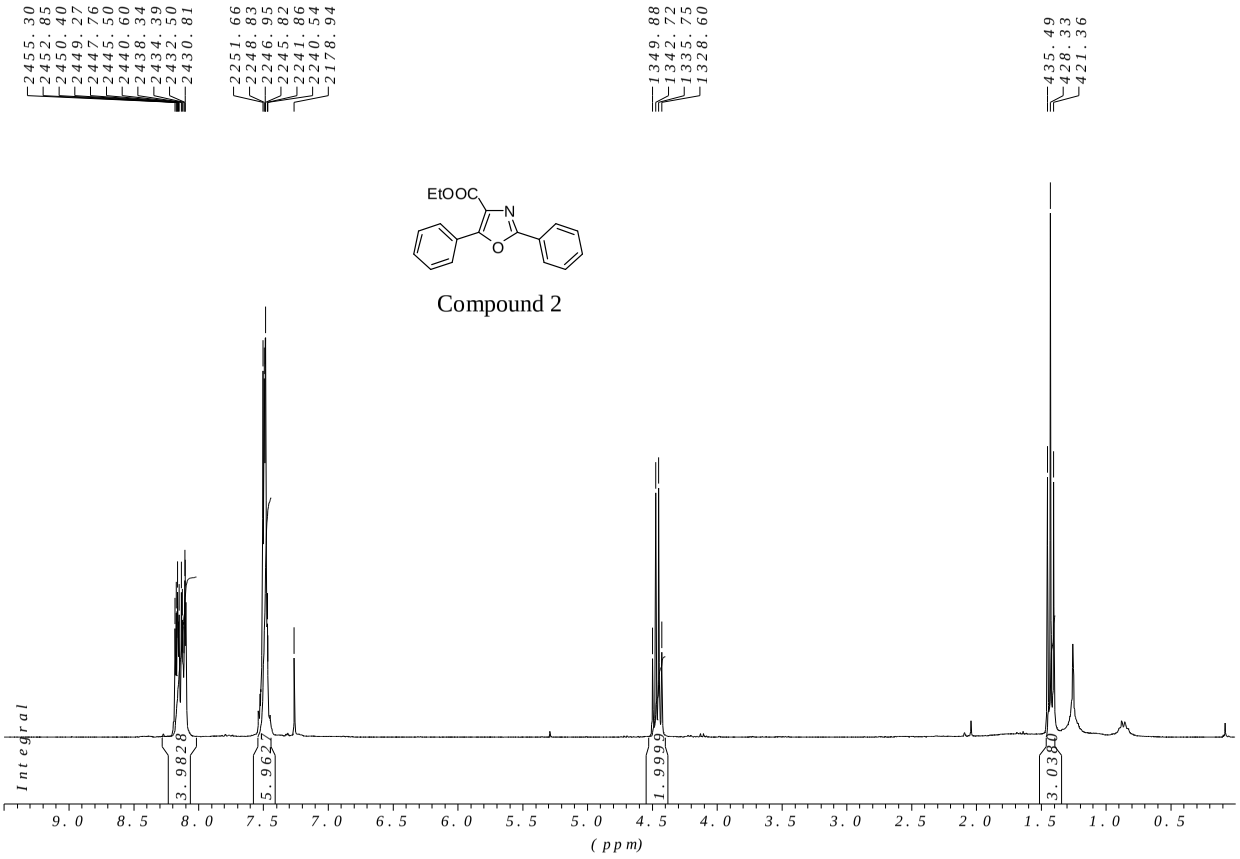
Compound 1d


160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

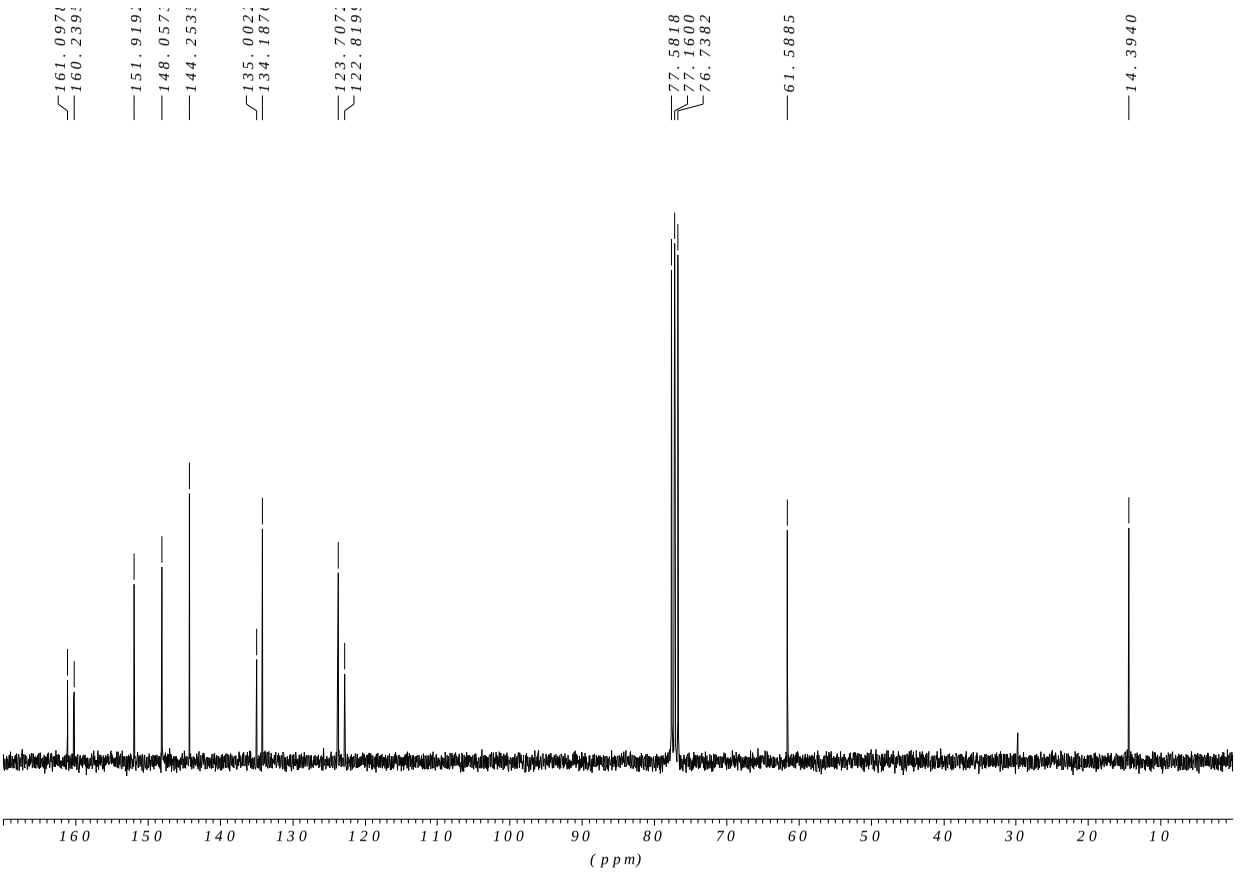

8.739
8.718
8.005
8.000
7.989
7.984
7.260
4.456
4.433
4.409
4.385
1.424
1.400
1.377
BRUKER
EtOOC
N
N
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.07
0.15
1.99
2.93
0.14
0.14
2.00
0.20
3.01
0.27

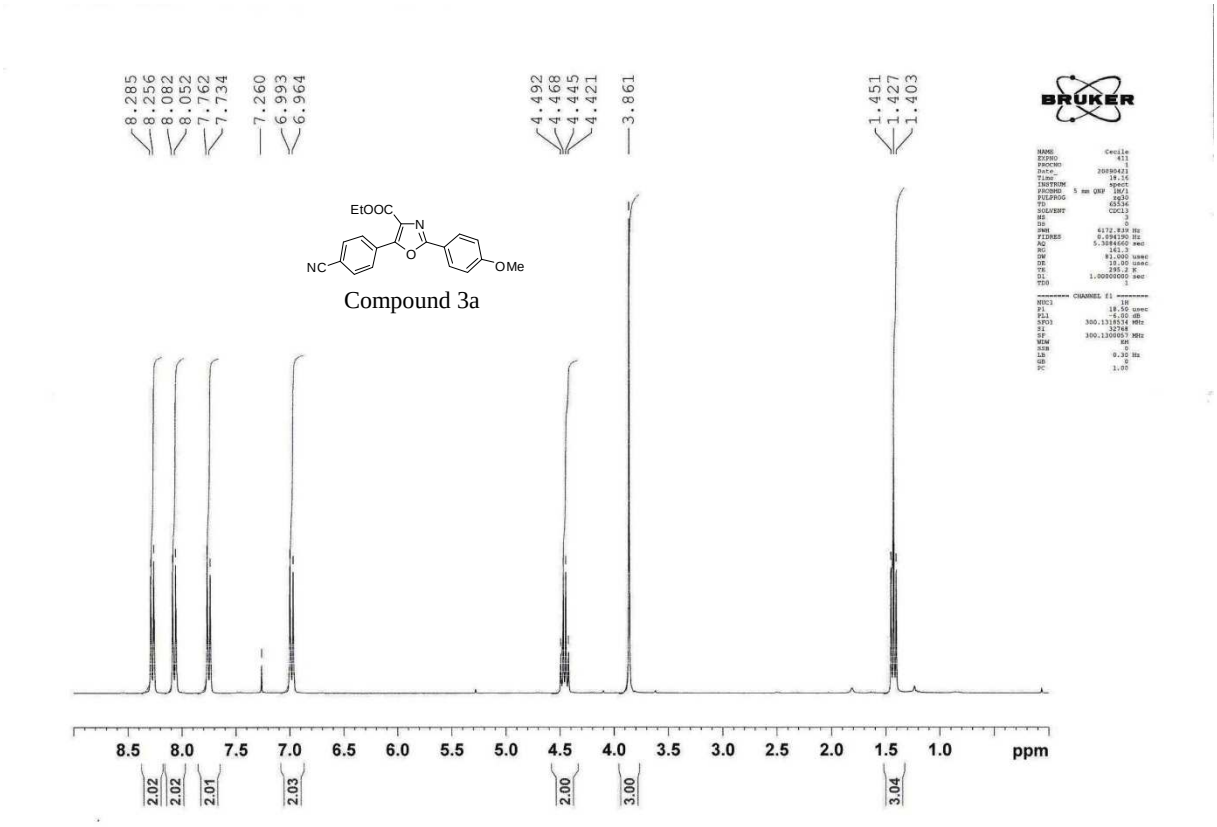
Compound 1e


161.56
152.54
150.46
150.07
133.83
129.47
121.72
77.58
77.16
76.74
61.99
14.27
BRUKER
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

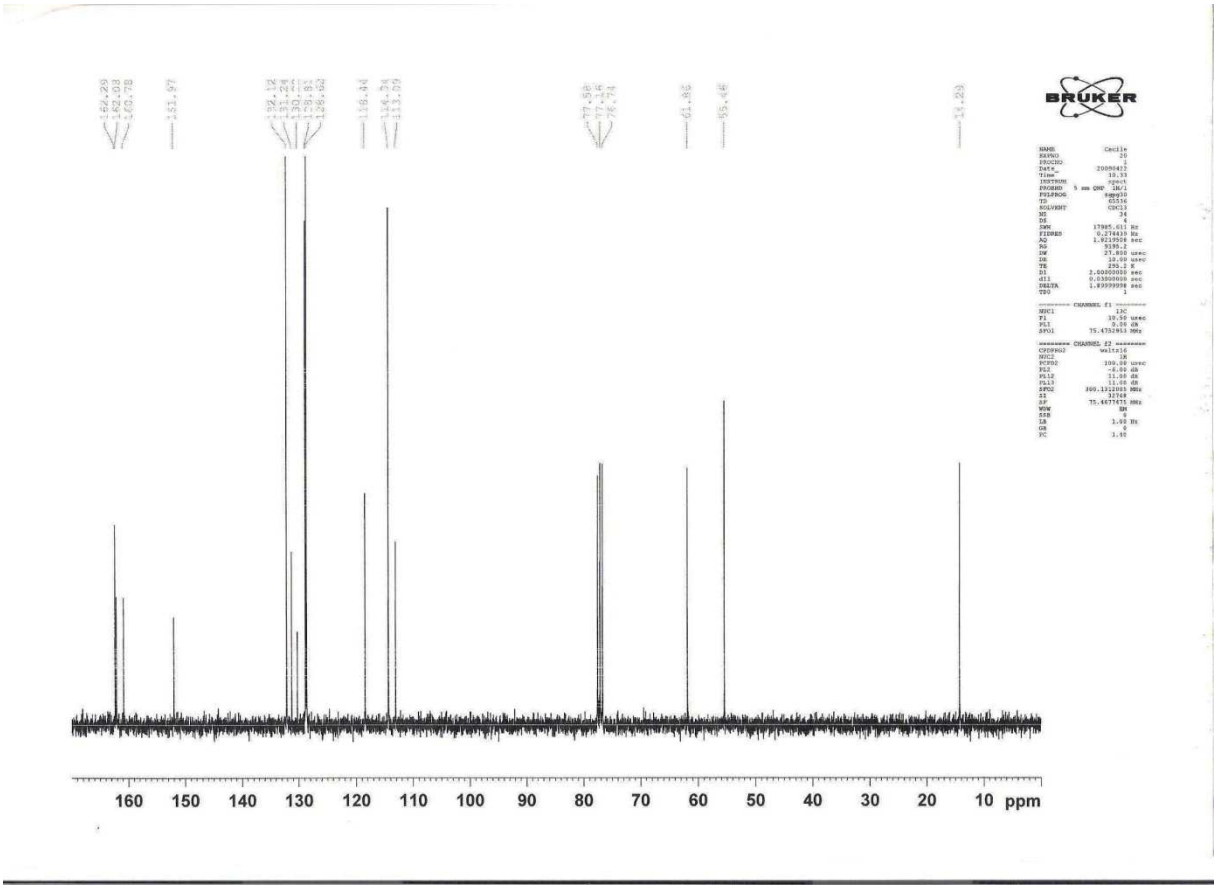


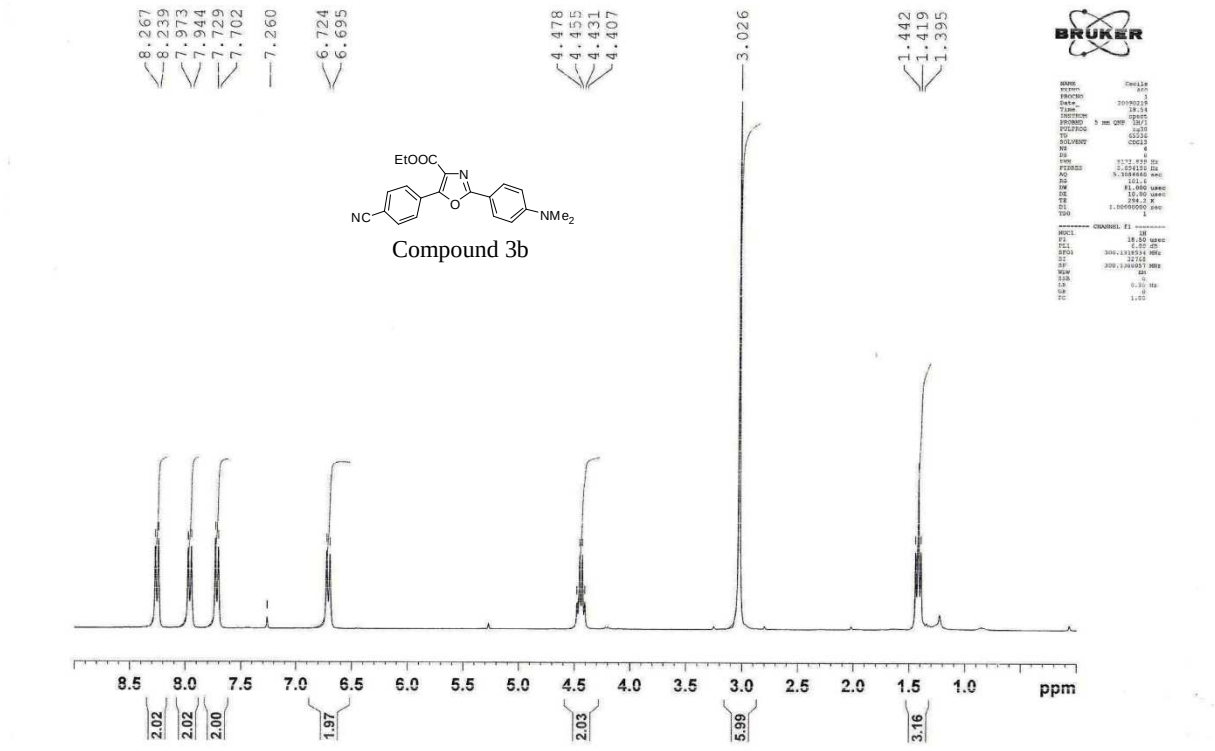
Compound 2



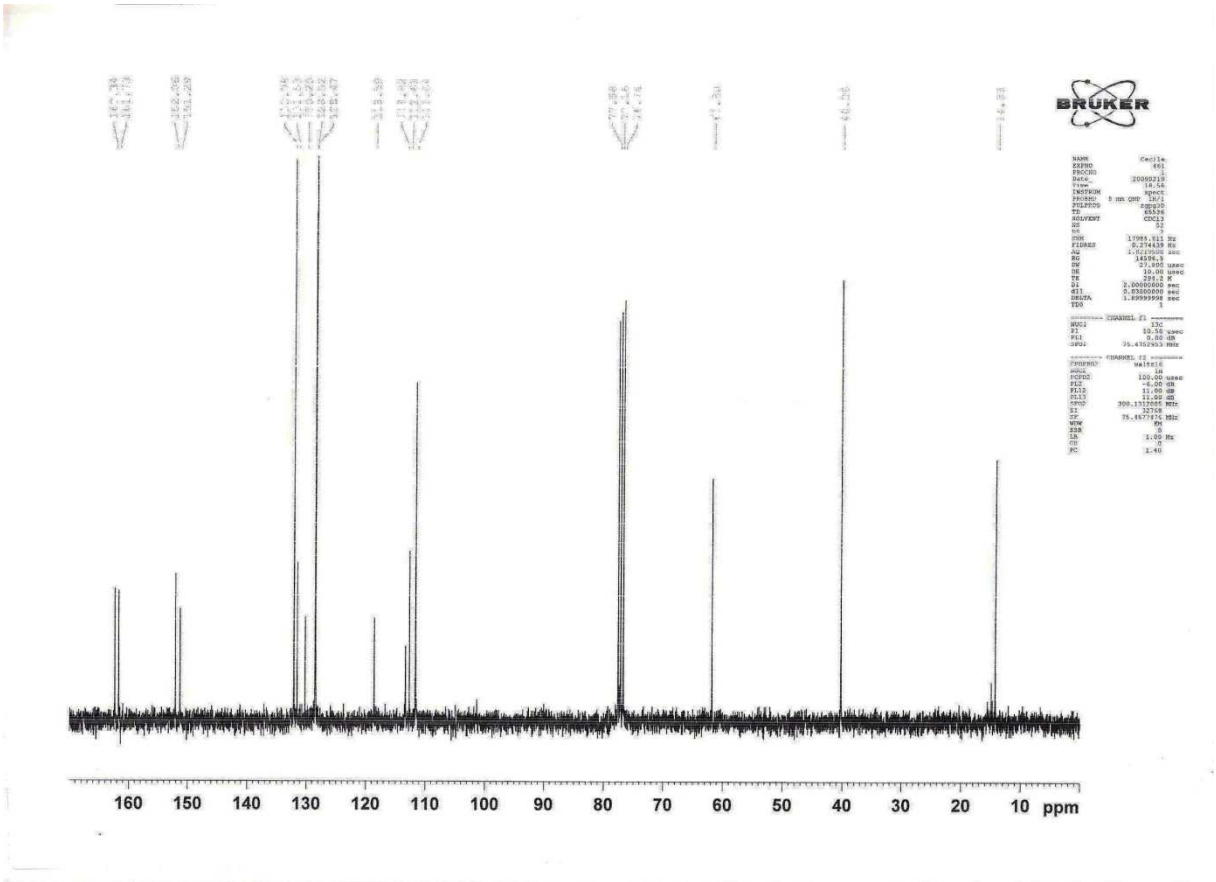

8.285
8.256
8.082
8.052
7.762
7.734
7.260
6.993
6.964
4.492
4.468
4.445
4.421
3.861
1.451
1.427
1.403
EtOOC
N
O
NC
OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.02
2.02
2.01
2.03
2.00
3.00
3.04

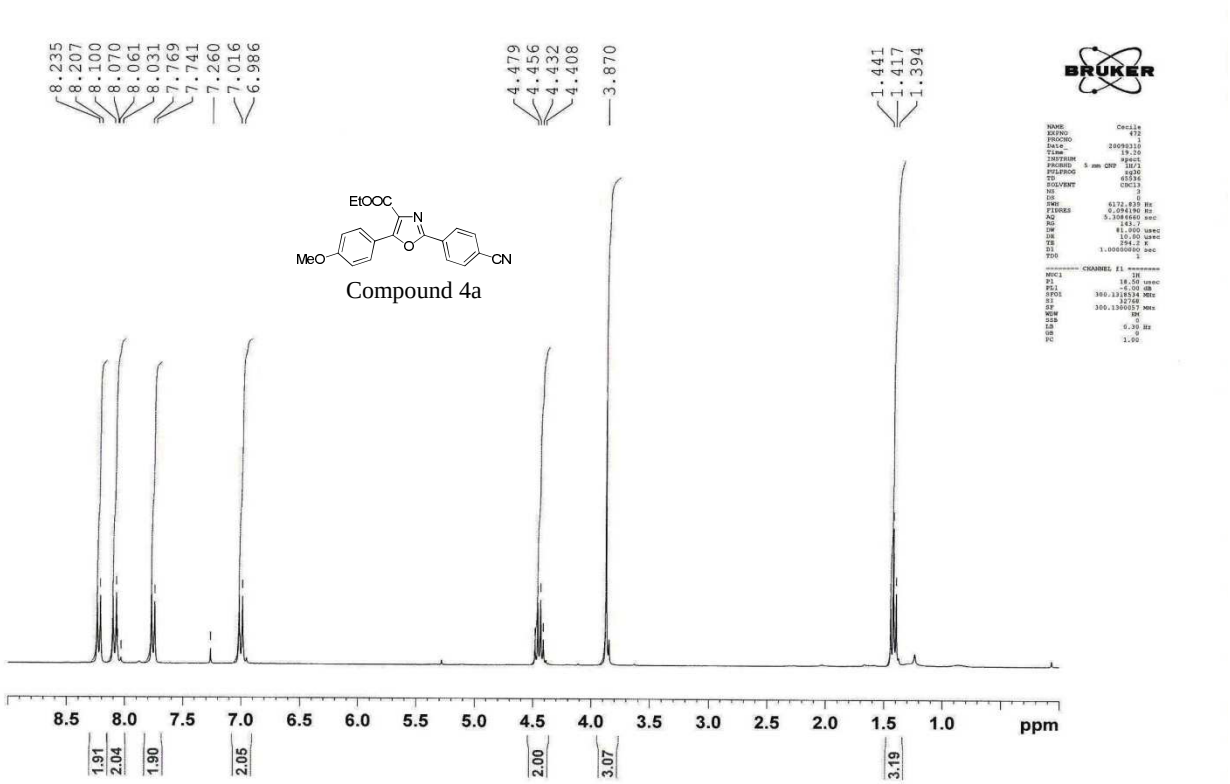
Compound 3a


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

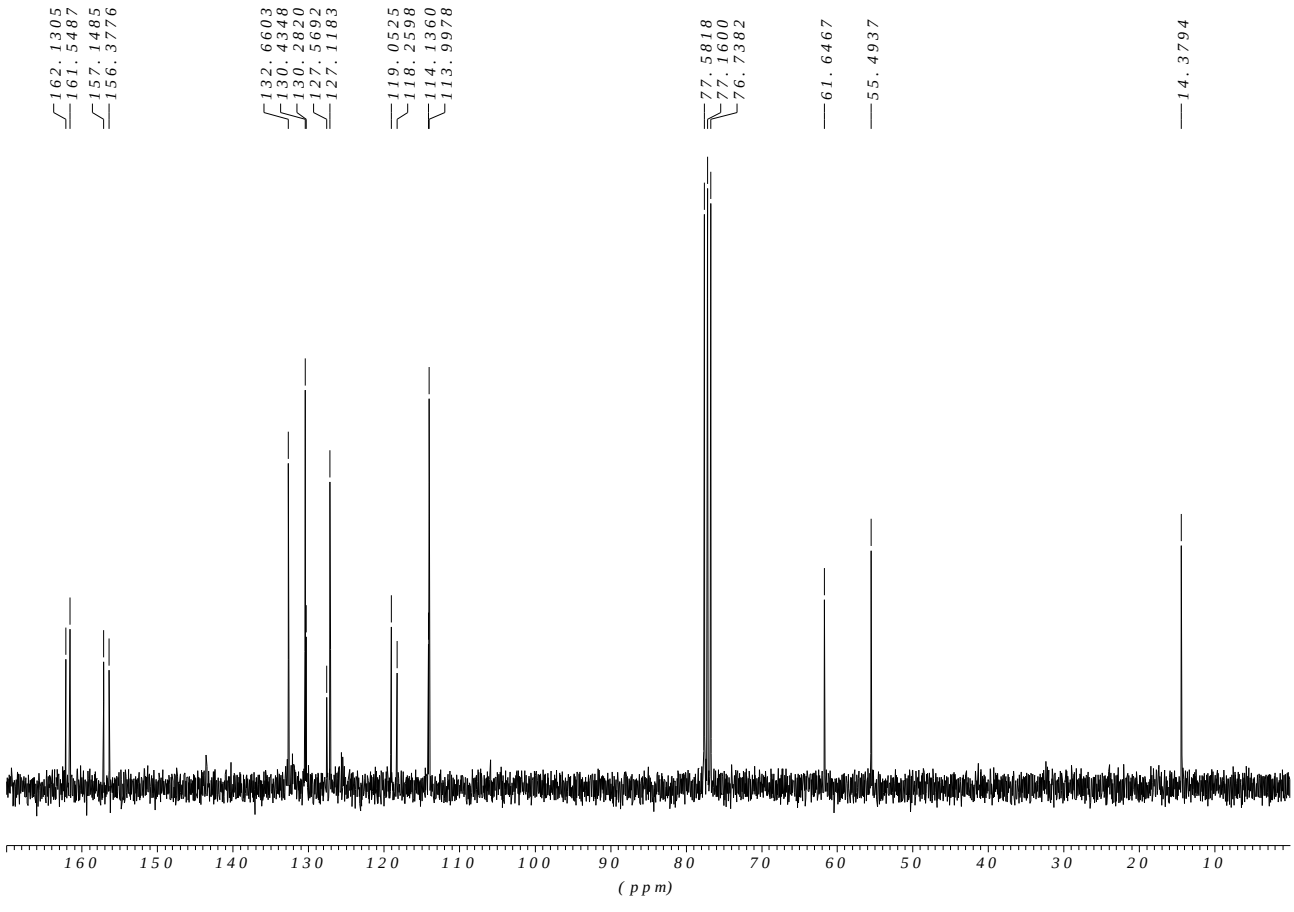

8.267
8.239
7.973
7.944
7.729
7.702
7.260
6.724
6.695
4.478
4.455
4.431
4.407
3.026
1.442
1.419
1.395
EtOOC
N
O
NC
NMe2
BRUKER
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.02
2.02
2.00
1.97
2.03
5.99
3.16

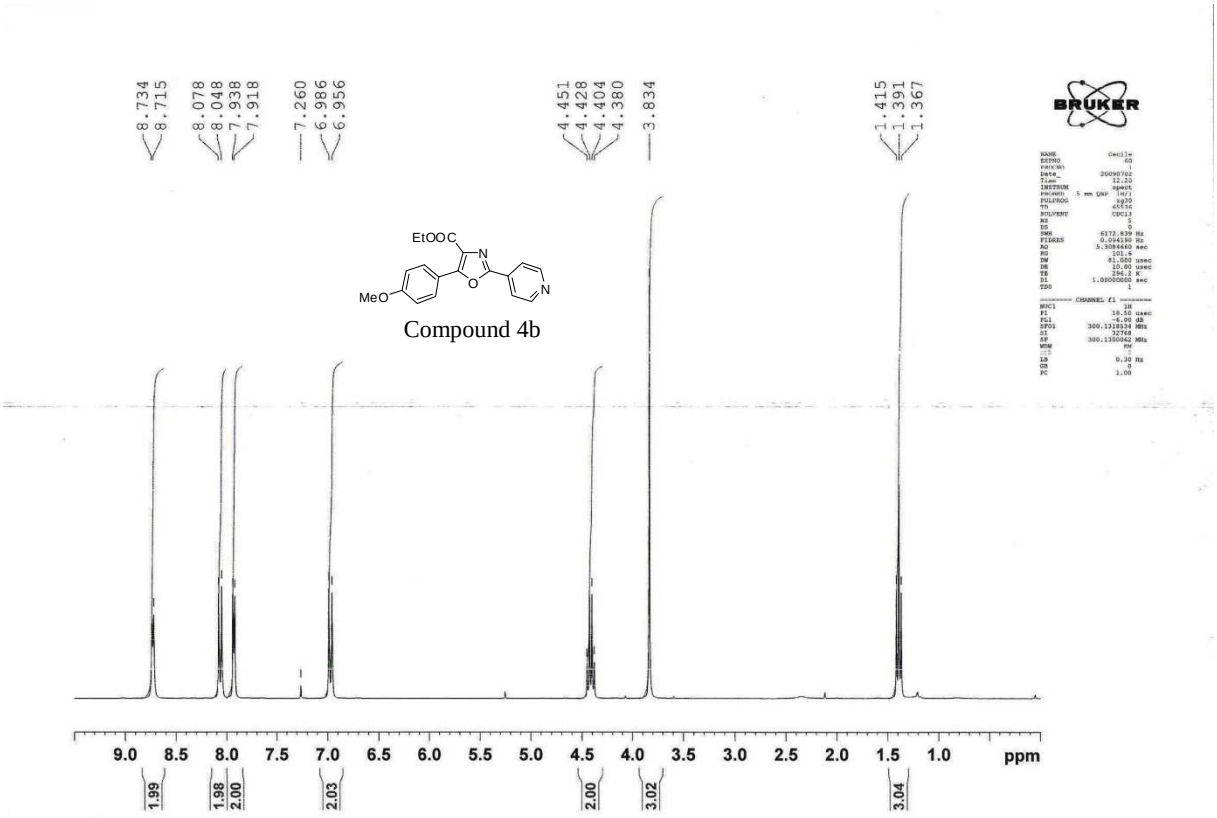
Compound 3b


BRUKER
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

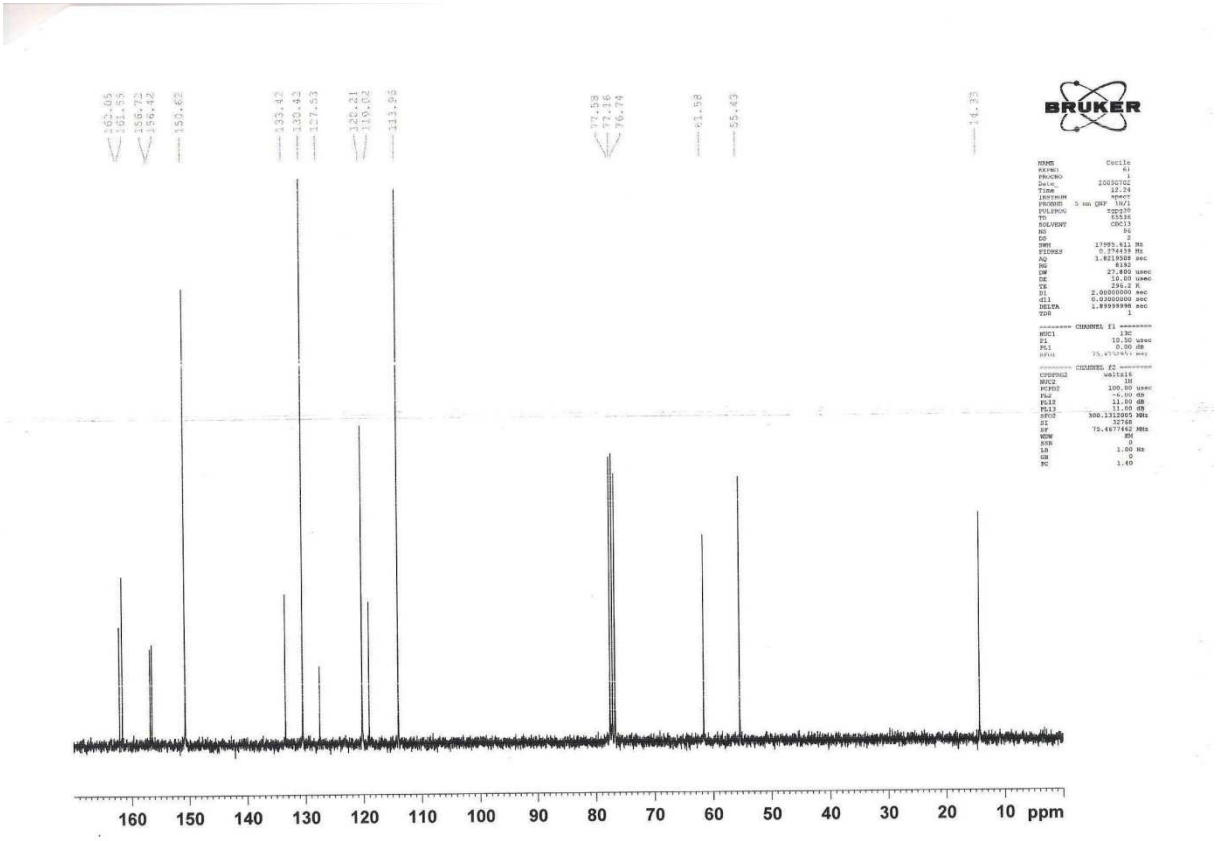

8.235
8.207
8.100
8.070
8.061
8.031
7.769
7.741
7.260
7.016
6.986
4.479
4.456
4.432
4.408
3.870
1.441
1.417
1.394
BRUKER
EtOOC
N
O
MeO
CN
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.91
2.04
1.90
2.05
2.00
3.07
3.19

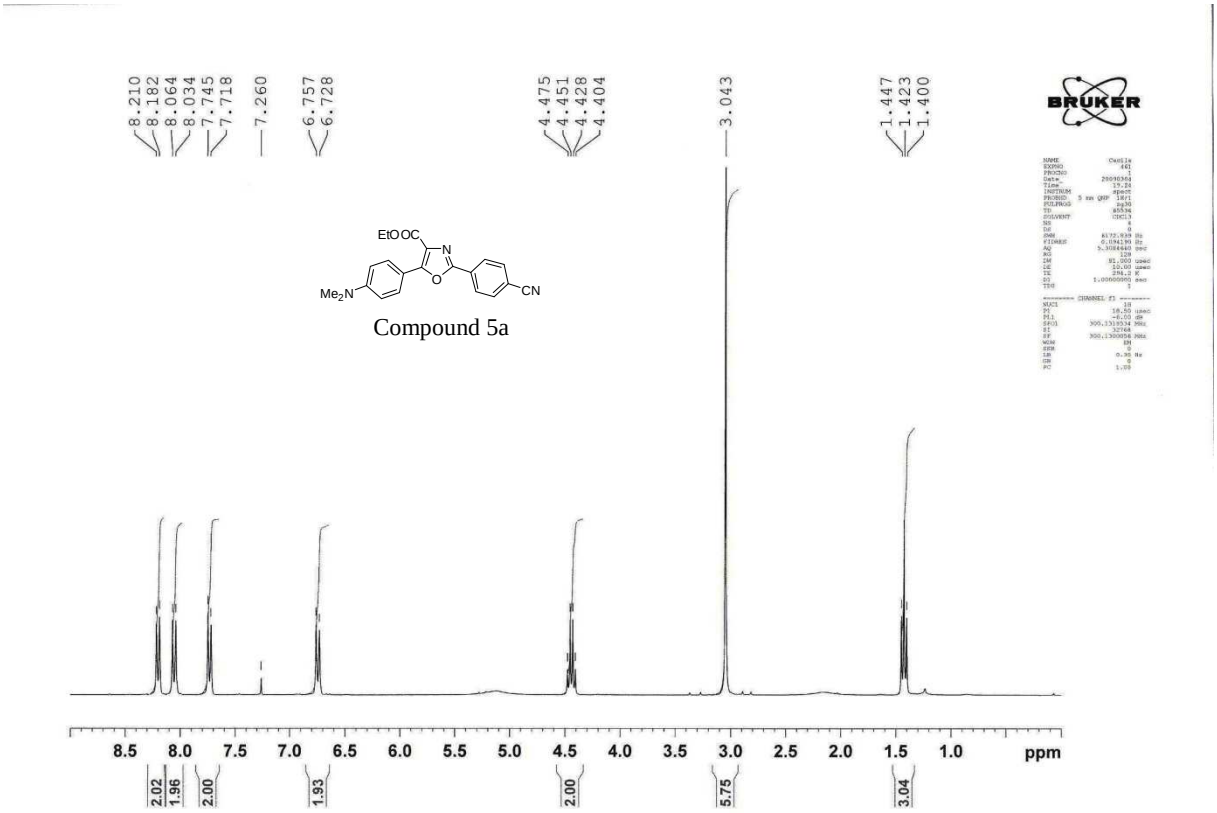
Compound 4a


162.1305
161.5487
157.1485
156.3776
132.6603
130.4348
130.2820
127.5692
127.1183
119.0525
118.2598
114.1360
113.9978
77.5818
77.1600
76.7382
61.6467
55.4937
14.3794
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

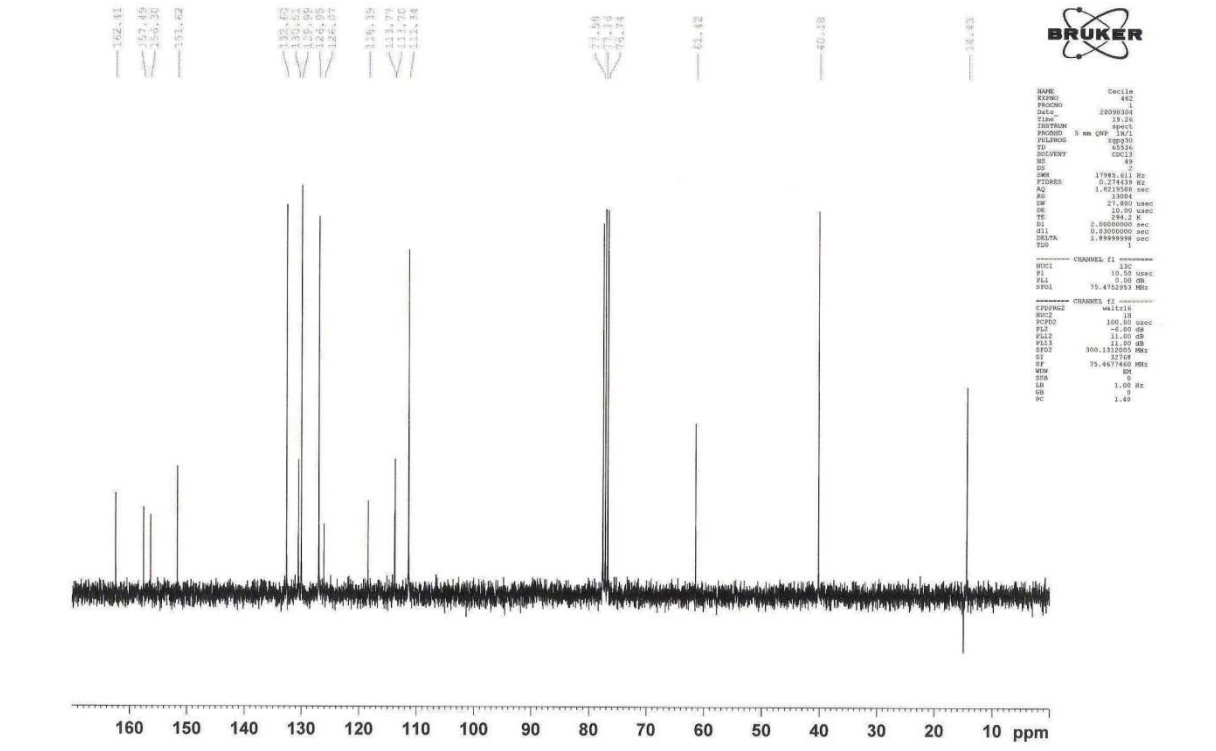

8.734
8.715
8.078
8.048
7.938
7.918
7.260
6.986
6.956
4.451
4.428
4.404
4.380
3.834
1.415
1.391
1.367
EtOOC
N
O
MeO
N
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.99
1.98
2.00
2.03
2.00
3.02
3.04

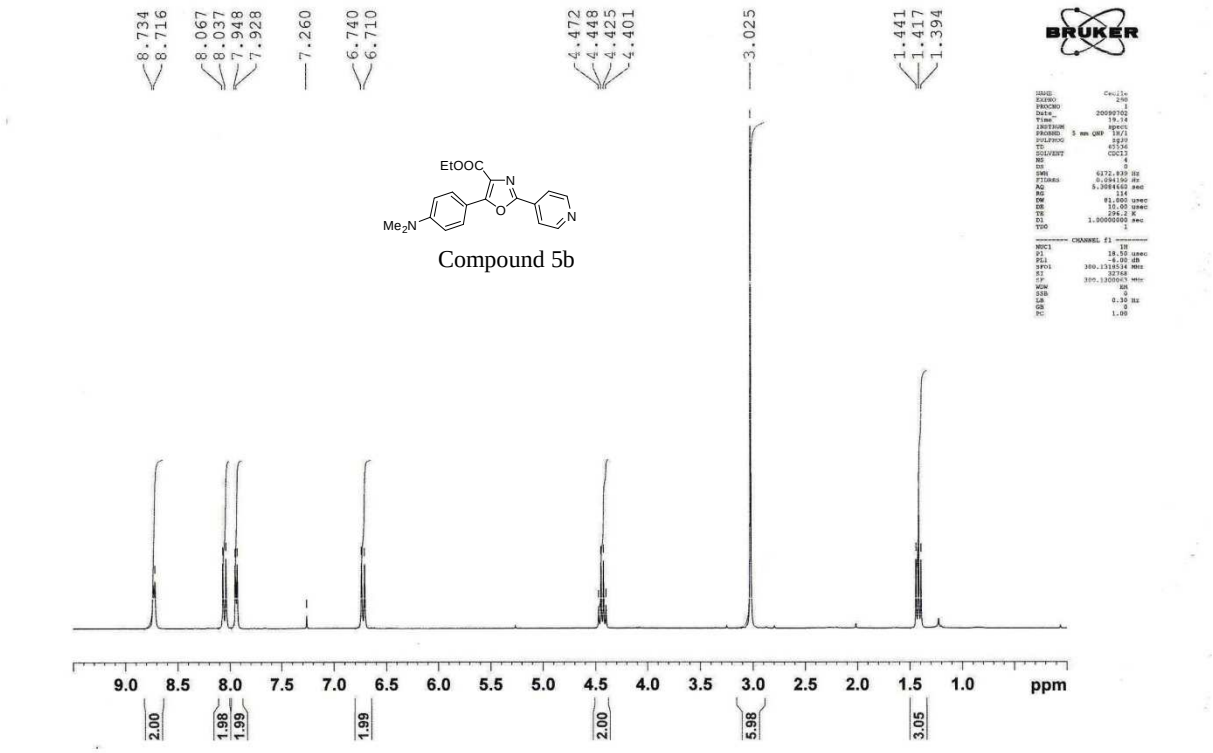
Compound 4b


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

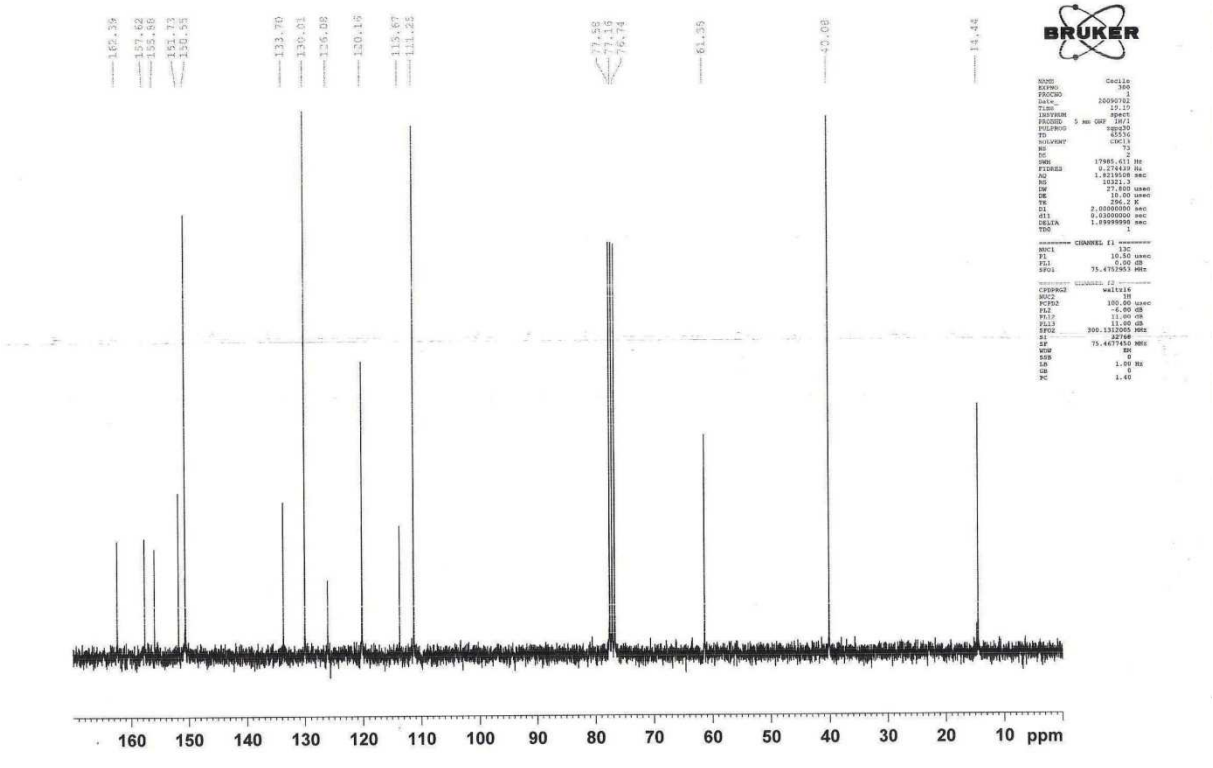

8.210
8.182
8.064
8.034
7.745
7.718
7.260
6.757
6.728
4.475
4.451
4.428
4.404
3.043
1.447
1.423
1.400
EtOOC
N
O
Me2N
CN
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.02
1.96
2.00
1.93
2.00
5.75
3.04

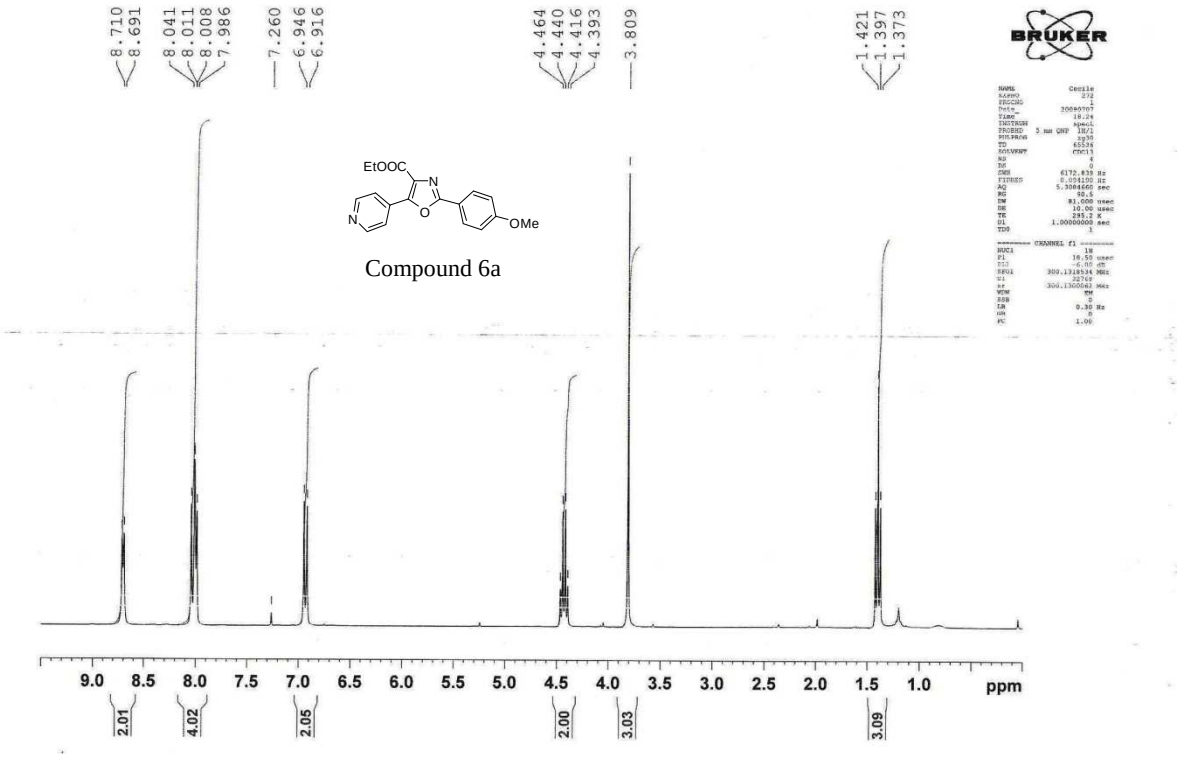
Compound 5a


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

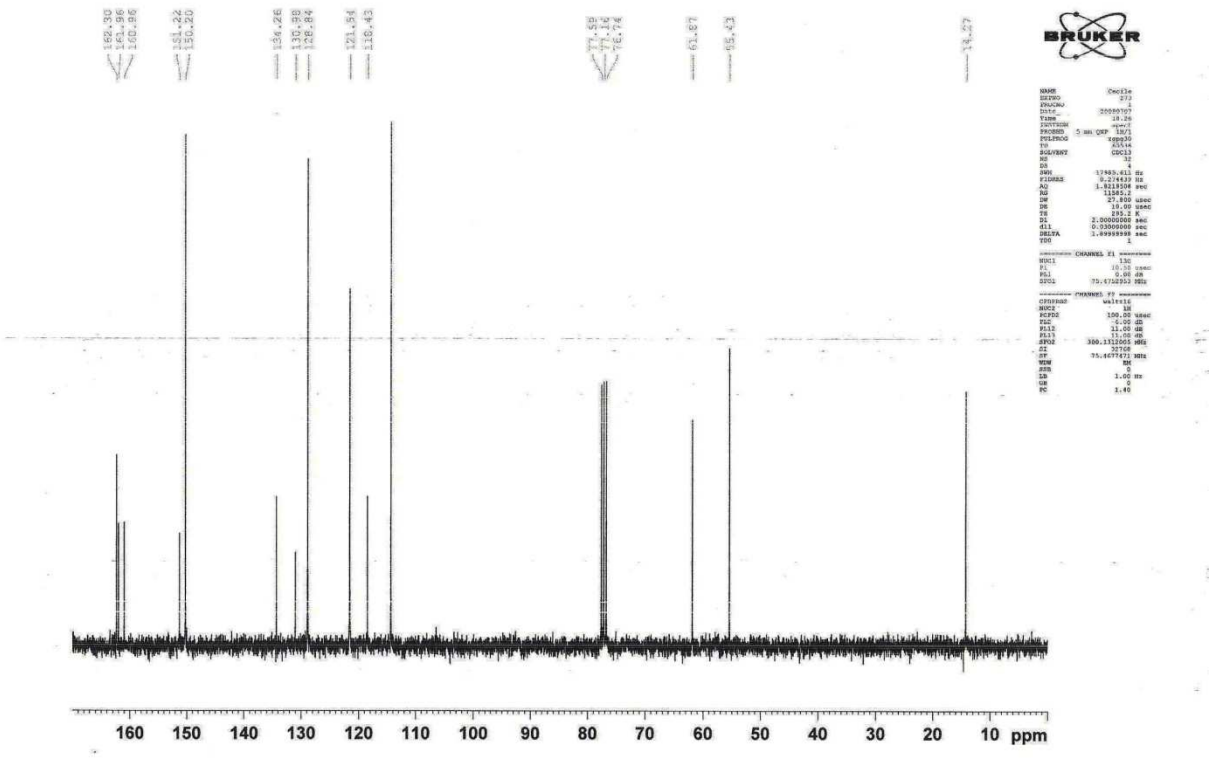

8.734
8.716
8.067
8.037
7.948
7.928
7.260
6.740
6.710
4.472
4.448
4.425
4.401
3.025
1.441
1.417
1.394
BRUKER
EtOOC
N
O
N
Me2N
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
1.98
1.99
1.99
2.00
5.98
3.05

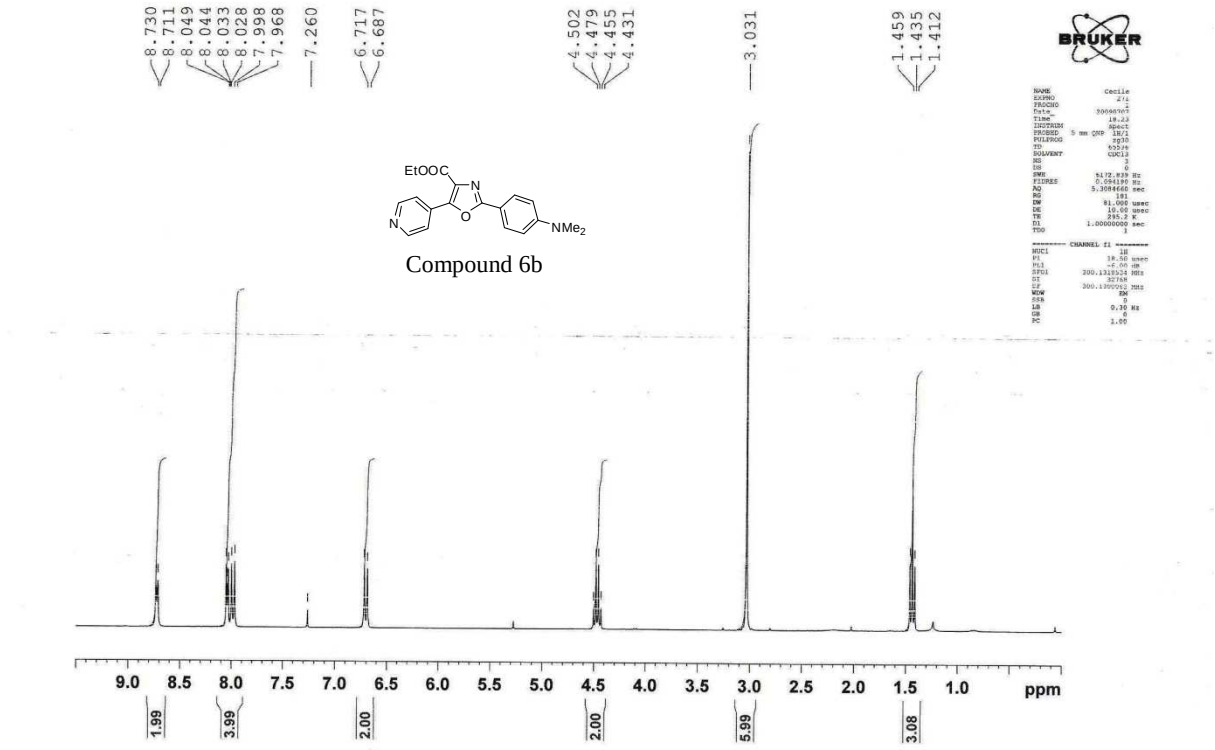
Compound 5b


162.39
157.62
155.58
151.73
150.55
133.70
130.01
126.09
120.16
115.67
111.25
77.58
77.16
76.74
61.35
40.08
14.44
BRUKER
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

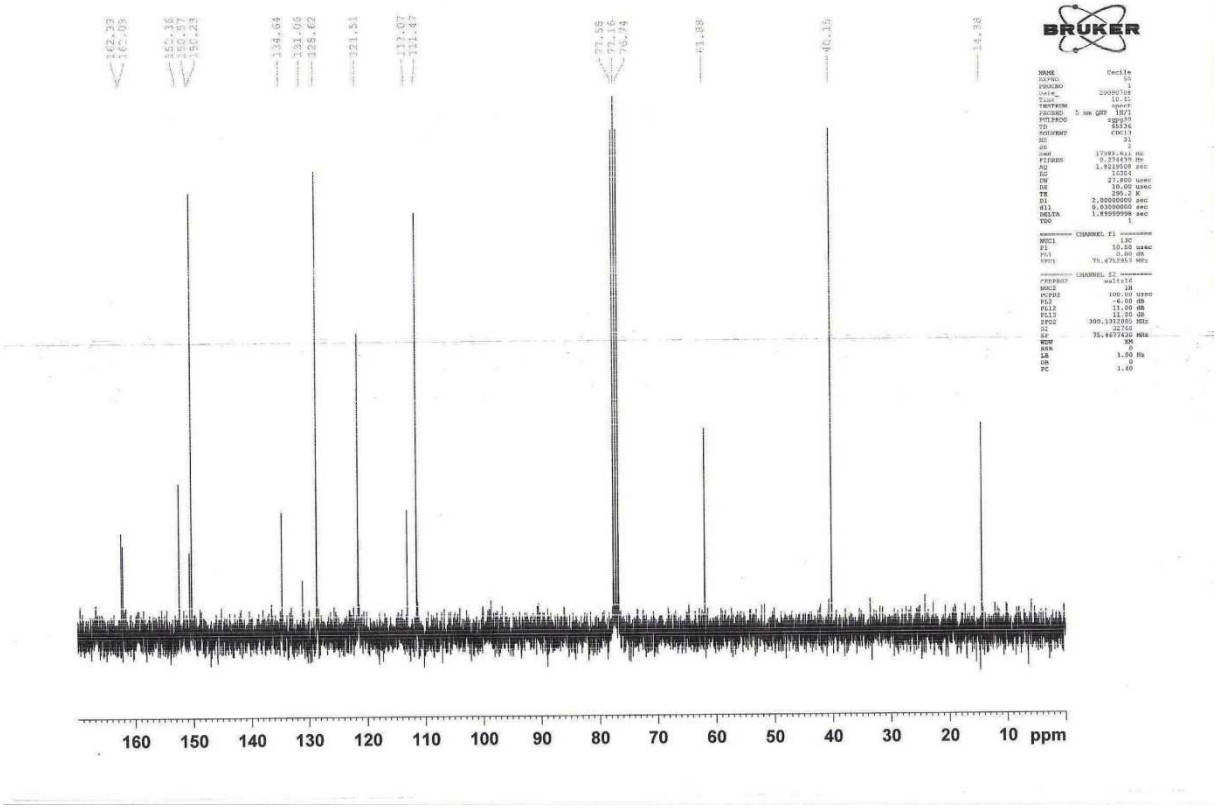

8.710
8.691
8.041
8.011
8.008
7.986
7.260
6.946
6.916
4.464
4.440
4.416
4.393
3.809
1.421
1.397
1.373
EtOOC
N
O
N
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.01
4.02
2.05
2.00
3.03
3.09

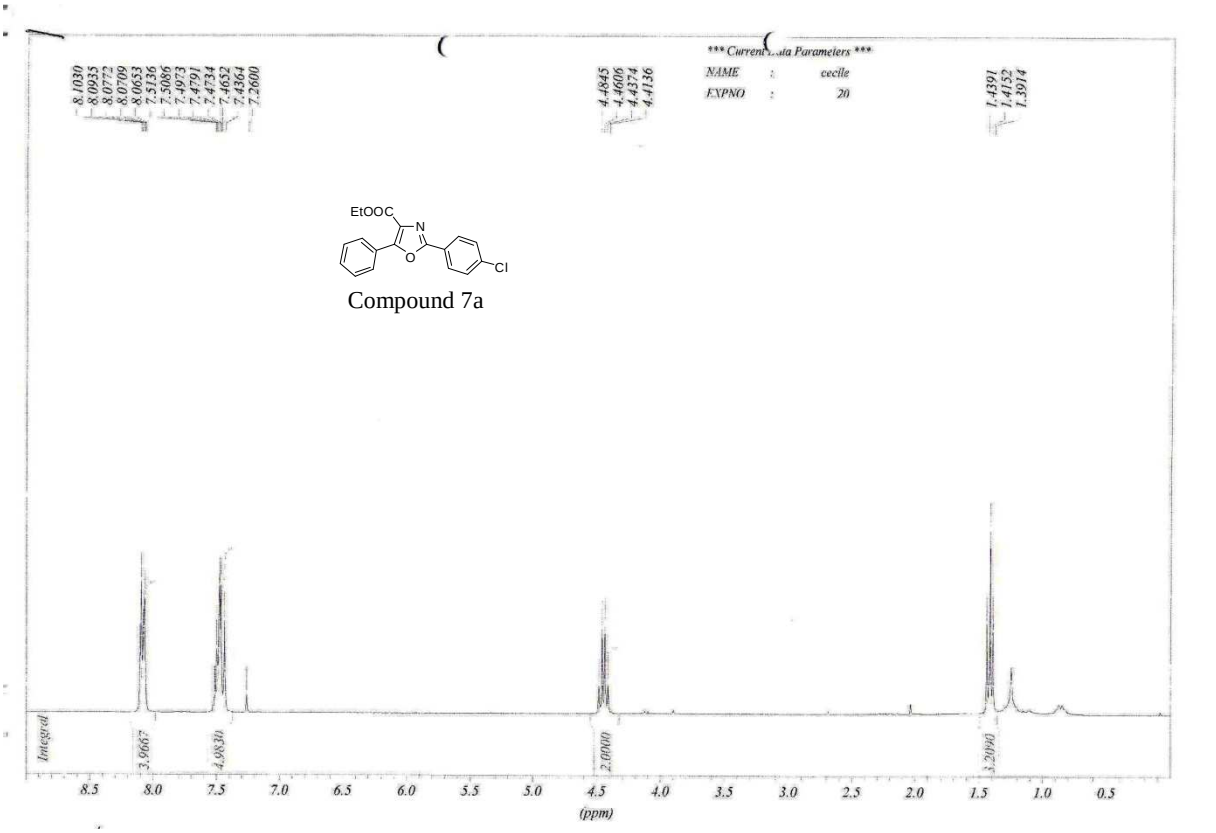
Compound 6a


162.30
161.96
160.96
151.22
150.20
134.26
130.98
128.84
121.54
116.43
77.59
77.16
76.74
61.67
55.43
14.27
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

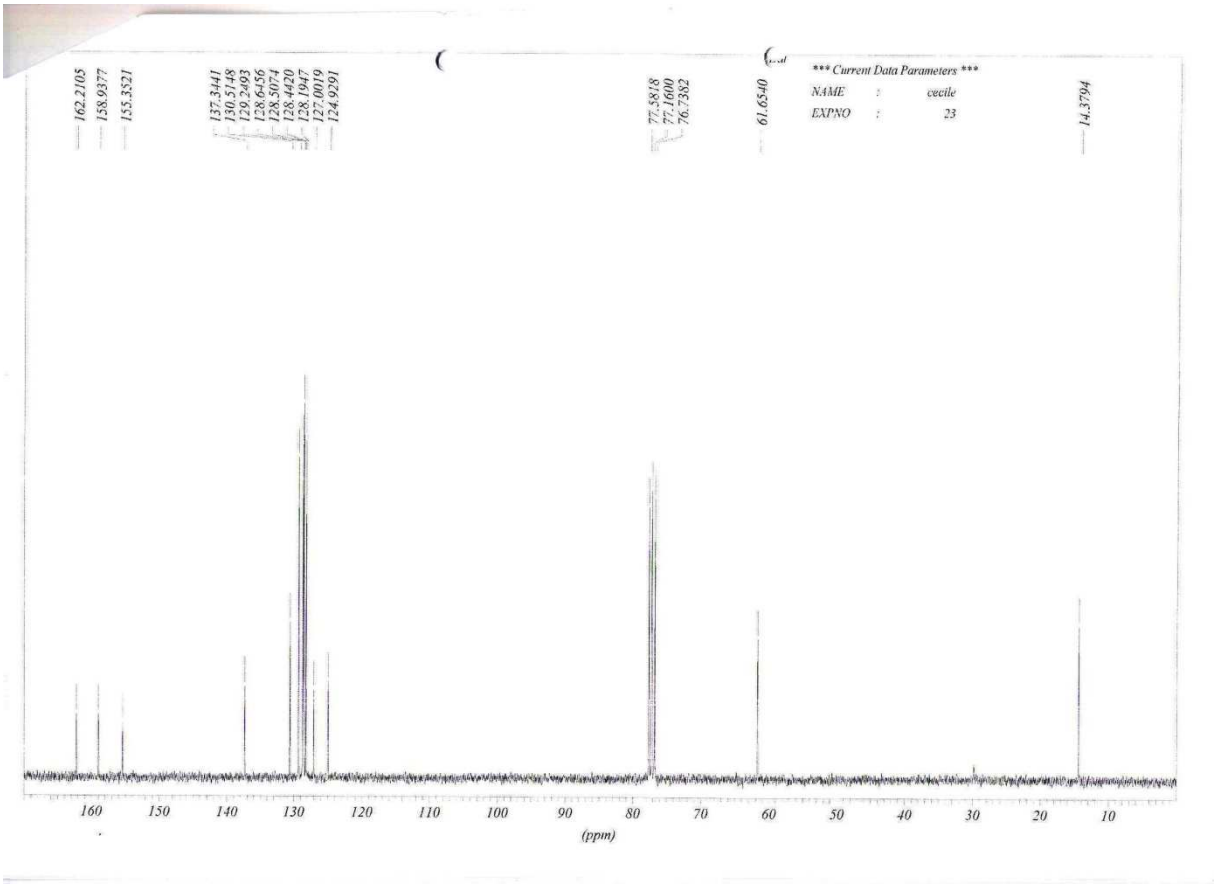

8.730
8.711
8.049
8.044
8.033
8.028
7.998
7.968
7.260
6.717
6.687
4.502
4.479
4.455
4.431
3.031
1.459
1.435
1.412
BRUKER
EtOOC
N
O
N
NMe2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.99
3.99
2.00
2.00
5.99
3.08

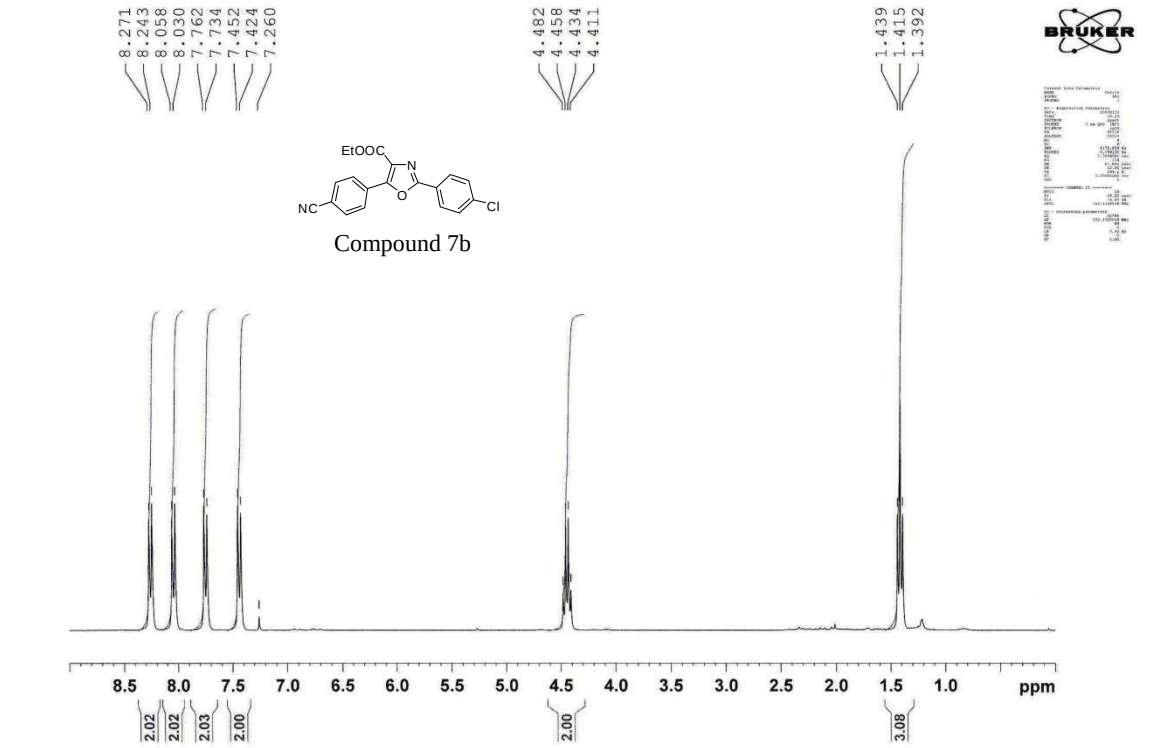
Compound 6b


BRUKER
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

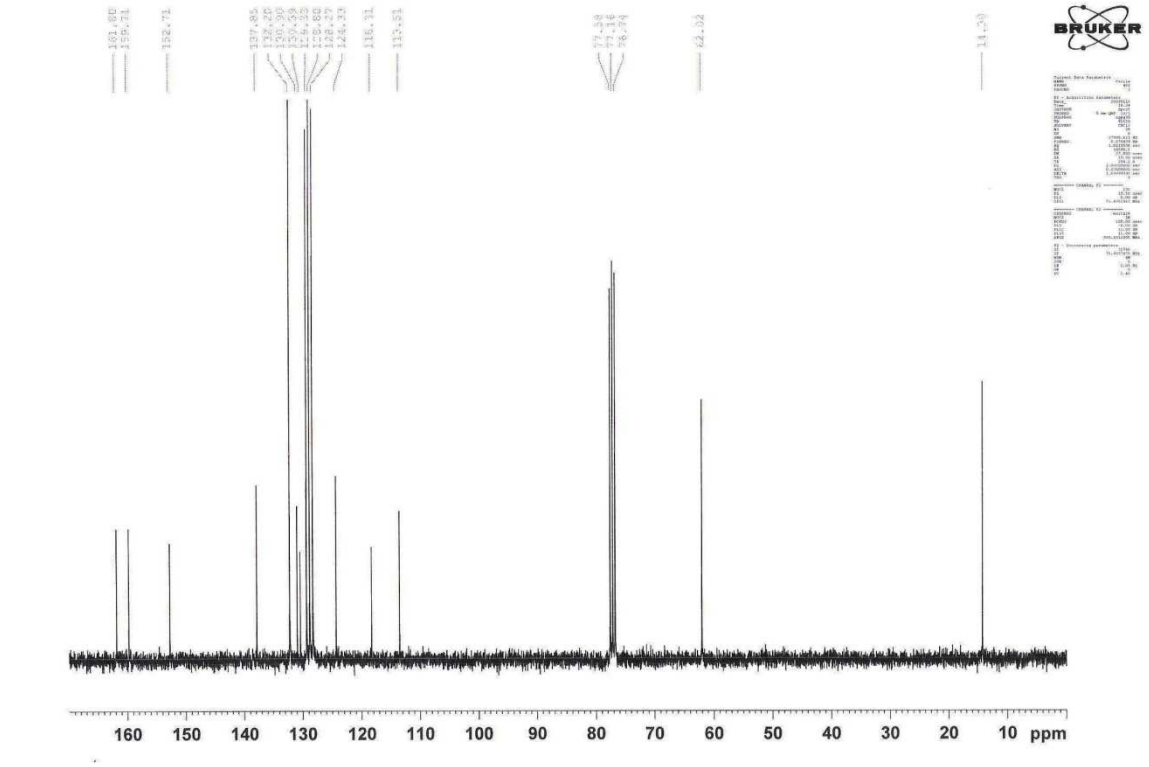

8.1030
8.0935
8.0772
8.0706
8.0653
7.5136
7.5086
7.4973
7.4791
7.4734
7.4652
7.4364
7.2600
4.4845
4.4606
4.4374
4.4136
*** Current Data Parameters ***
NAME : cecile
EXPNO : 20
1.4391
1.4152
1.3914
EtOOC
N
O
Cl
Integral
3.9667
4.9830
2.0000
3.2090
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

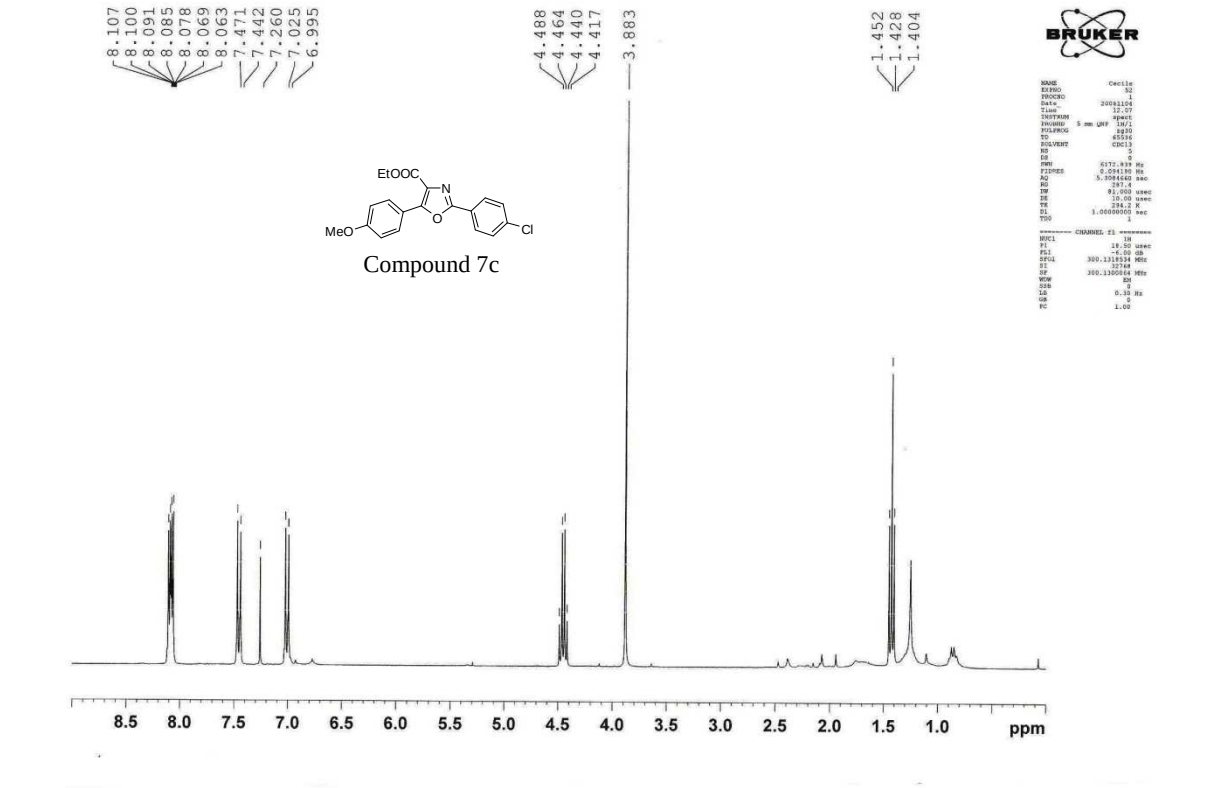
Compound 7a


162.2105
158.9377
155.3521
137.3441
130.5148
129.2493
128.6456
128.5074
128.4420
128.1947
127.0019
124.9291
77.5818
77.1600
76.7382
61.6540
*** Current Data Parameters ***
NAME : cecile
EXPNO : 23
14.3794
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

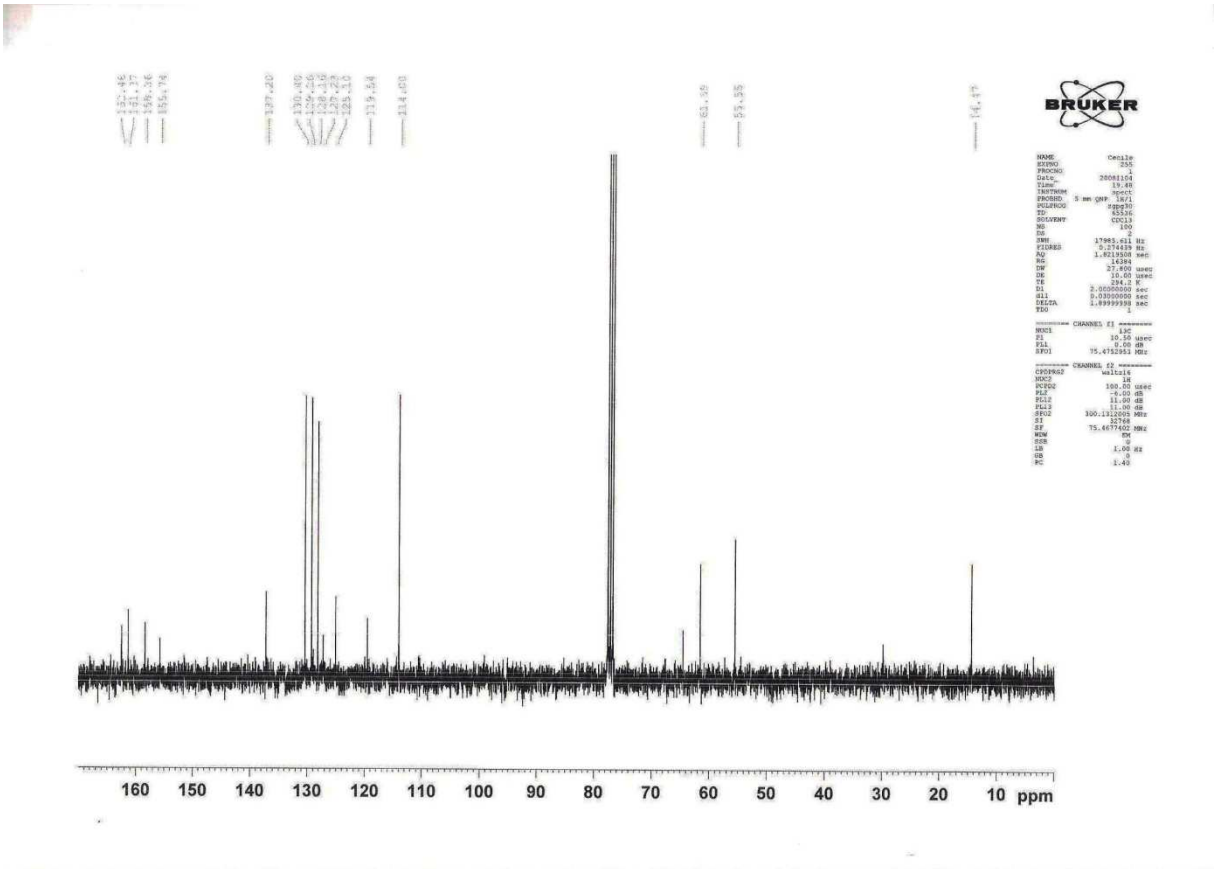

8.271
8.243
8.058
8.030
7.762
7.734
7.452
7.424
7.260
4.482
4.458
4.434
4.411
1.439
1.415
1.392
BRUKER
EtOOC
N
O
NC
Cl
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.02
2.02
2.03
2.00
2.00
3.08

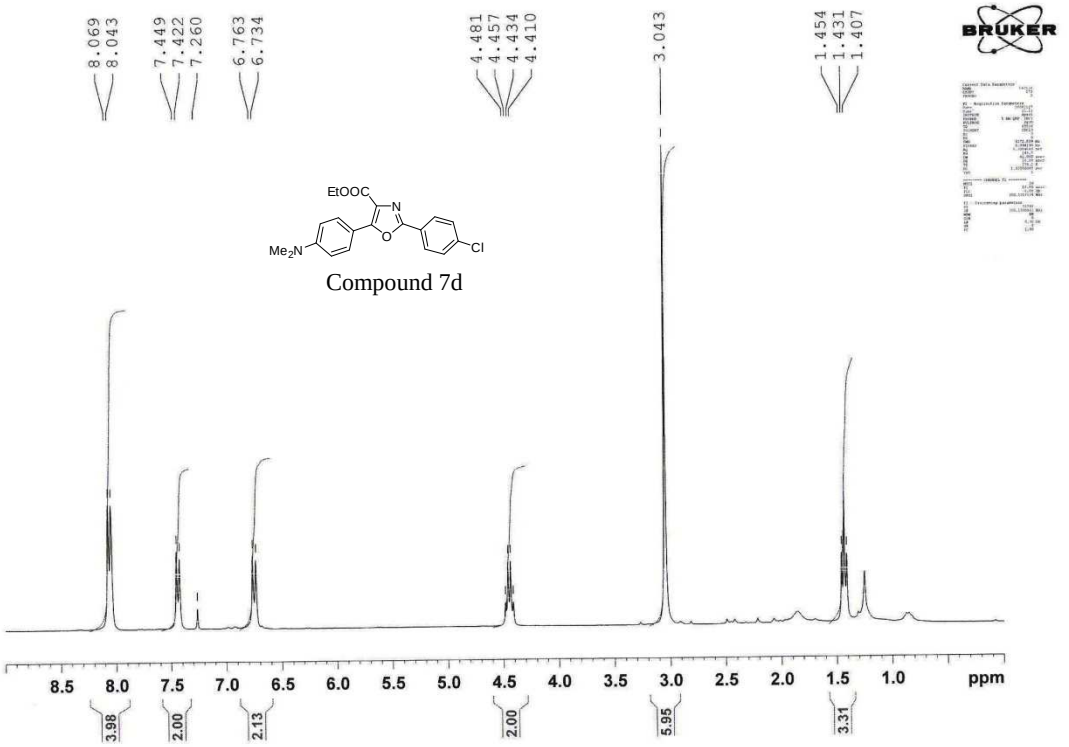
Compound 7b


BRUKER
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

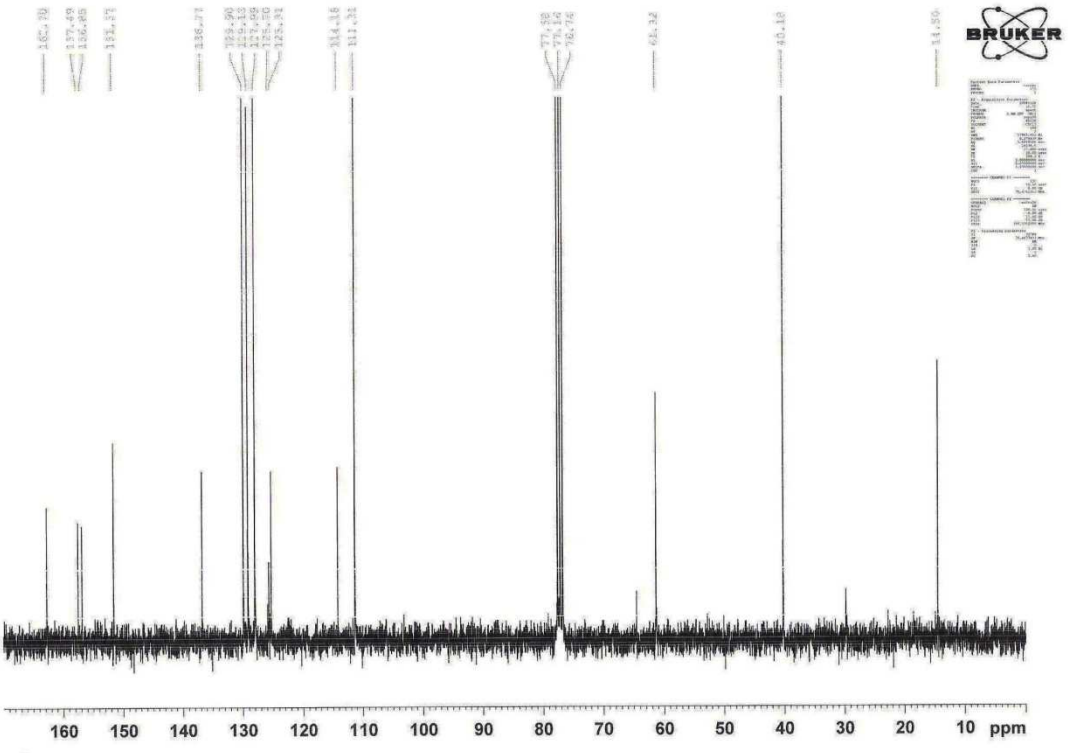

8.107
8.100
8.091
8.085
8.078
8.069
8.063
7.471
7.442
7.260
7.025
6.995
4.488
4.464
4.440
4.417
3.883
1.452
1.428
1.404
EtOOC
N
O
MeO
Cl
BRUKER
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

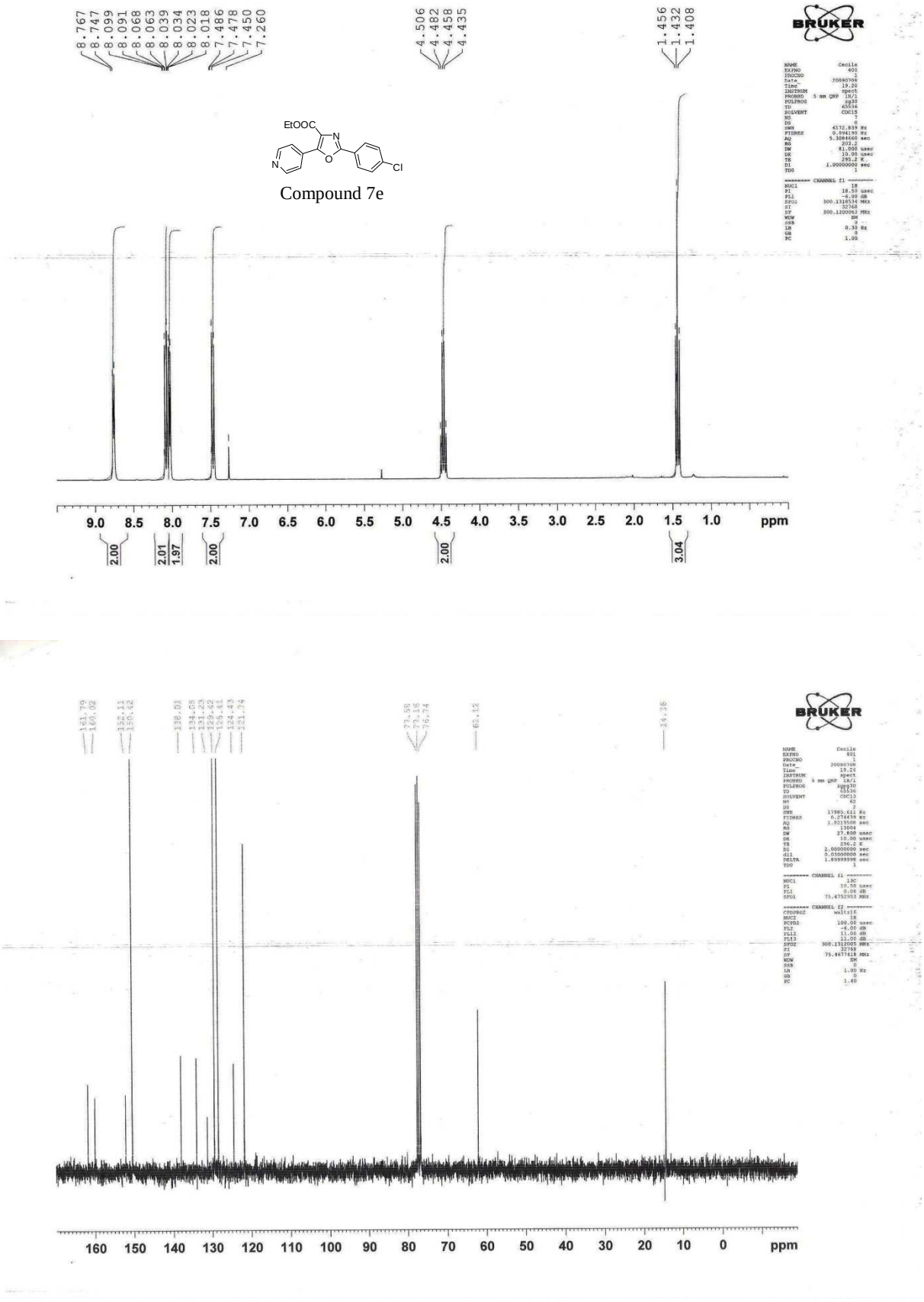
Compound 7c


BRUKER
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

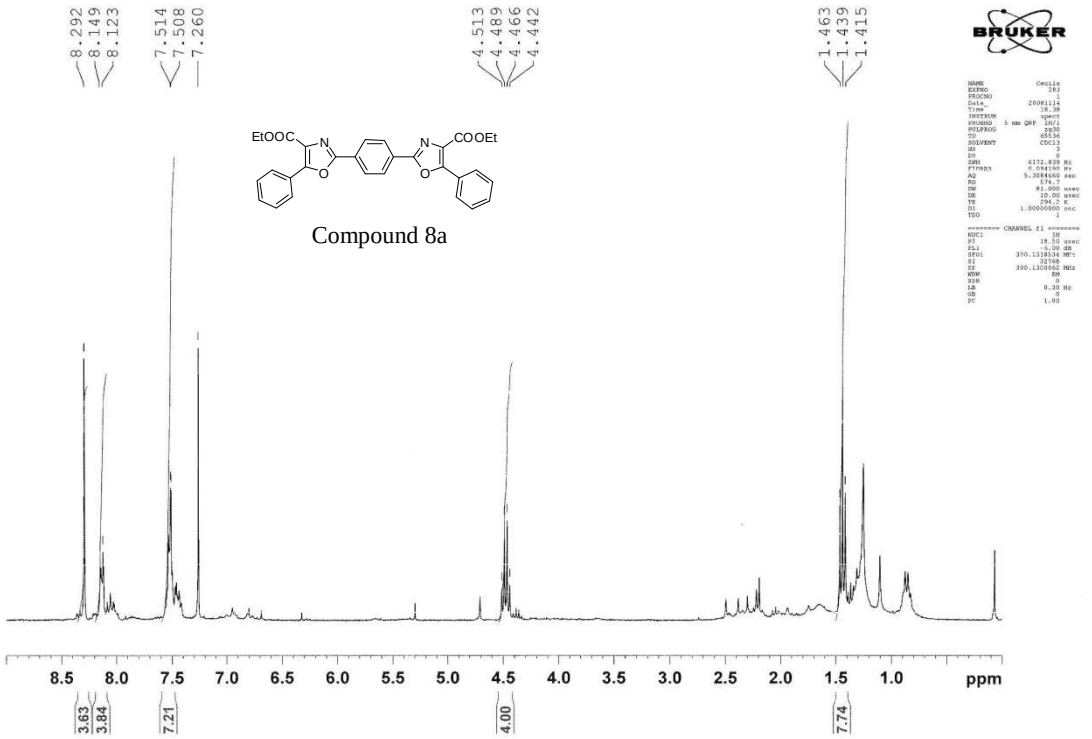

8.069
8.043
7.449
7.422
7.260
6.763
6.734
4.481
4.457
4.434
4.410
3.043
1.454
1.431
1.407
EtOOC
N
O
Me2N
Cl
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.98
2.00
2.13
2.00
5.95
3.31

Compound 7d

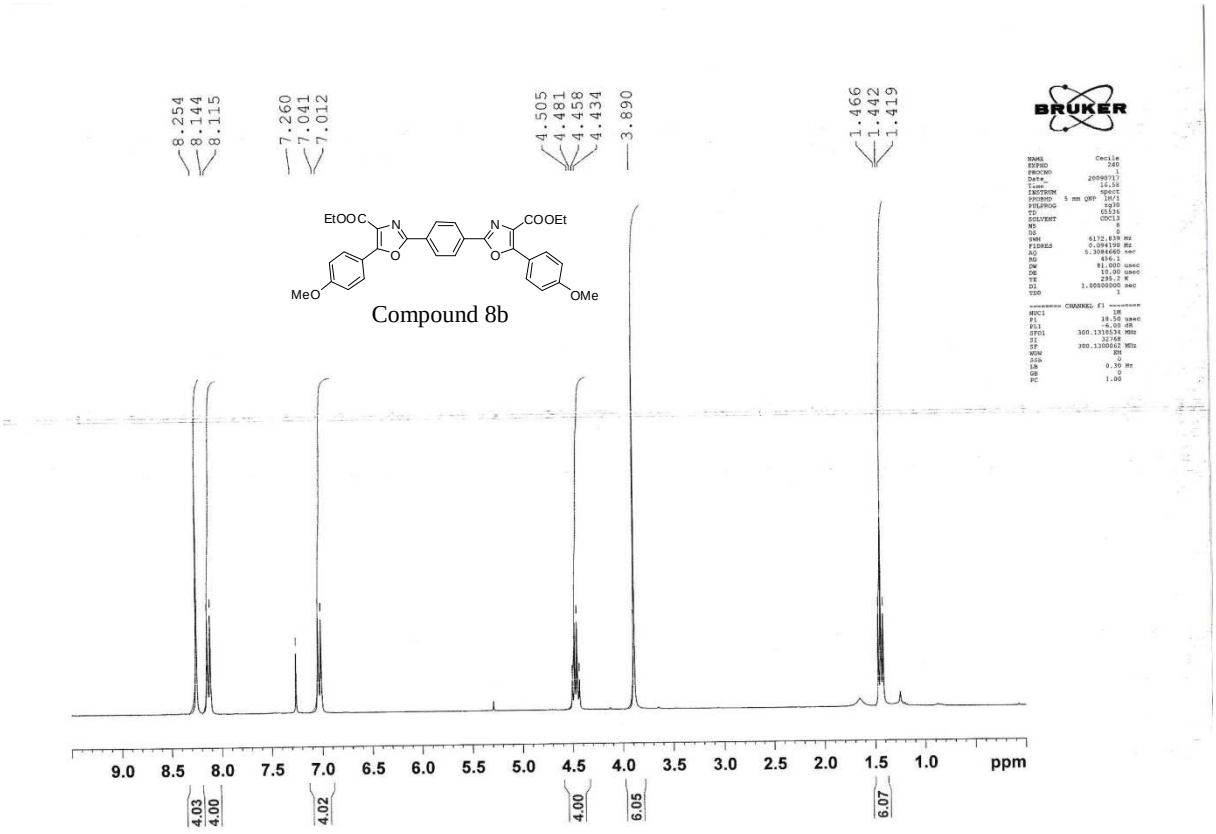

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.767
8.747
8.099
8.091
8.068
8.063
8.039
8.034
8.023
8.018
7.486
7.478
7.450
7.260
4.506
4.482
4.458
4.435
1.456
1.432
1.408
EtOOC
N
O
N
Cl
BRUKER
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00
2.01
1.97
2.00
2.00
3.04
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

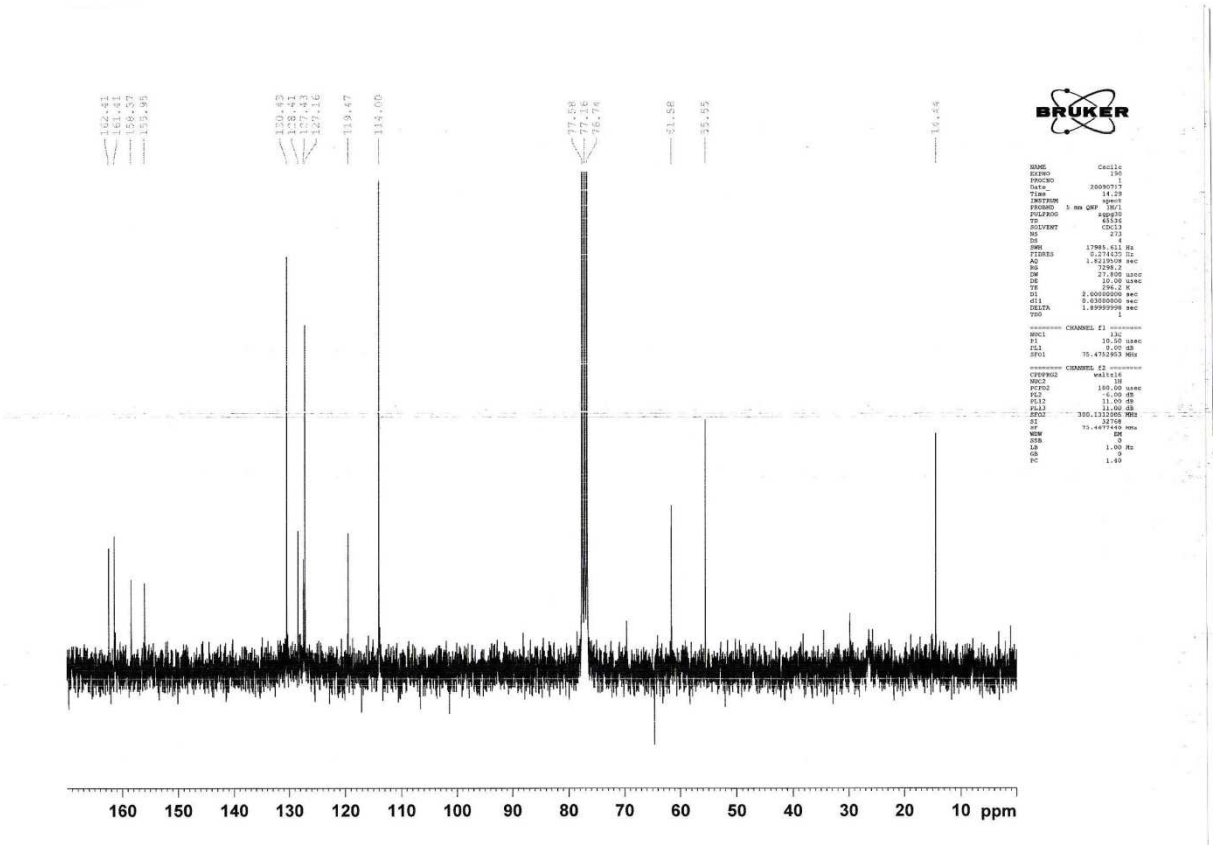
Compound 7e

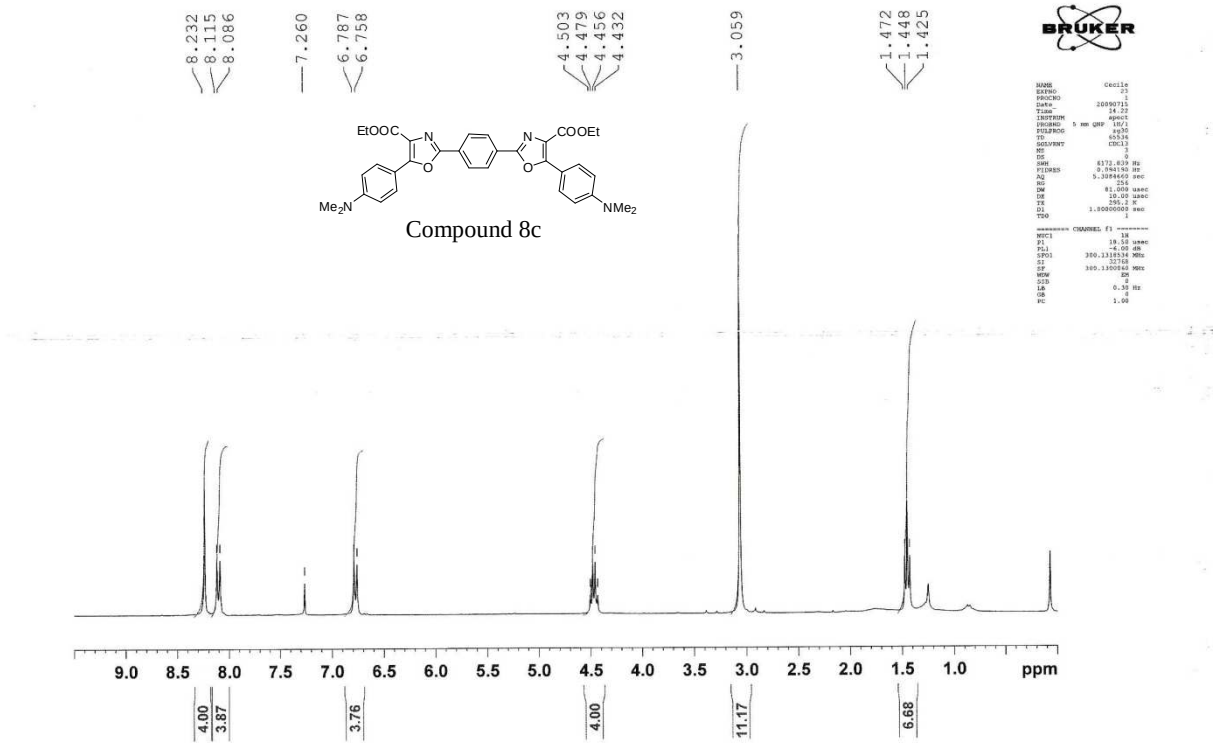


Compound 8a

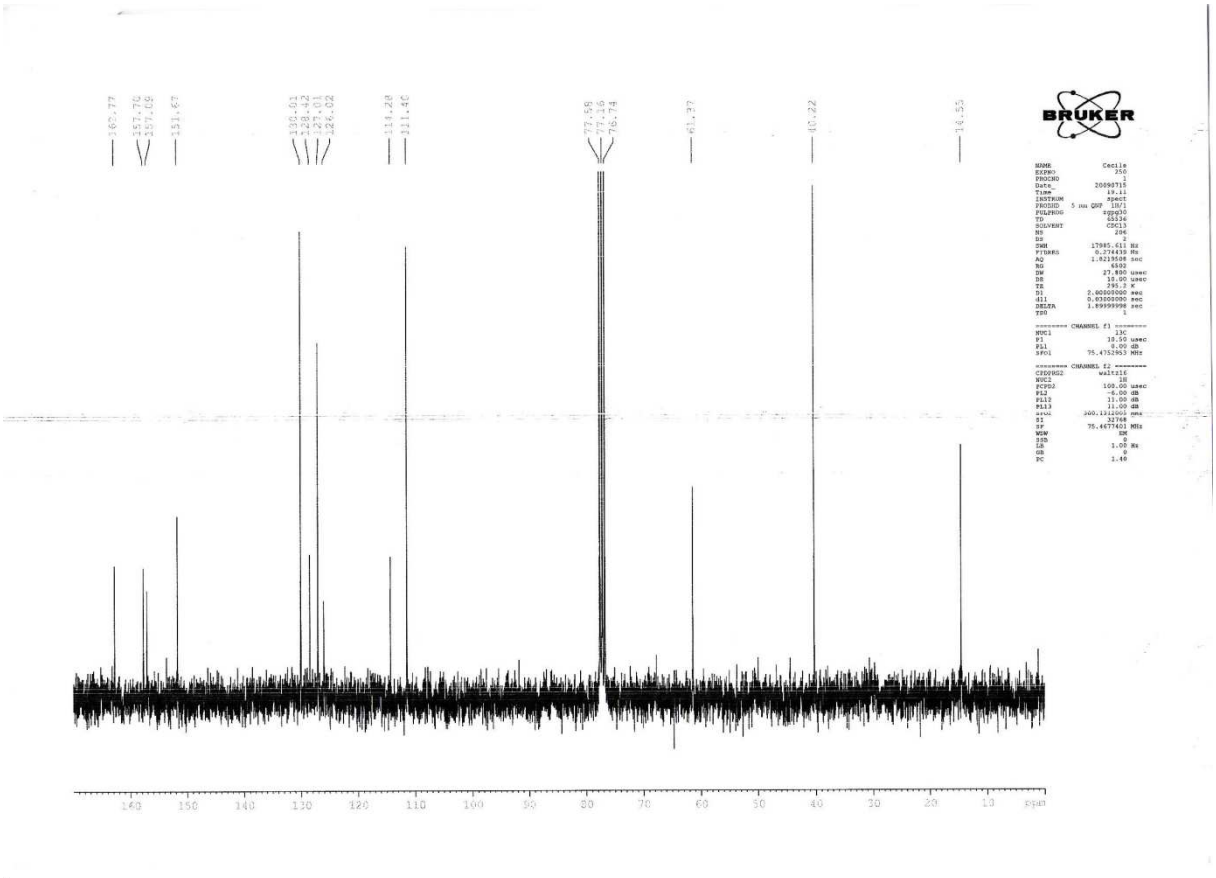

8.254
8.144
8.115
7.260
7.041
7.012
4.505
4.481
4.458
4.434
3.890
1.466
1.442
1.419
EtOOC
COOEt
MeO
OMe
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.03
4.00
4.02
4.00
6.05
6.07

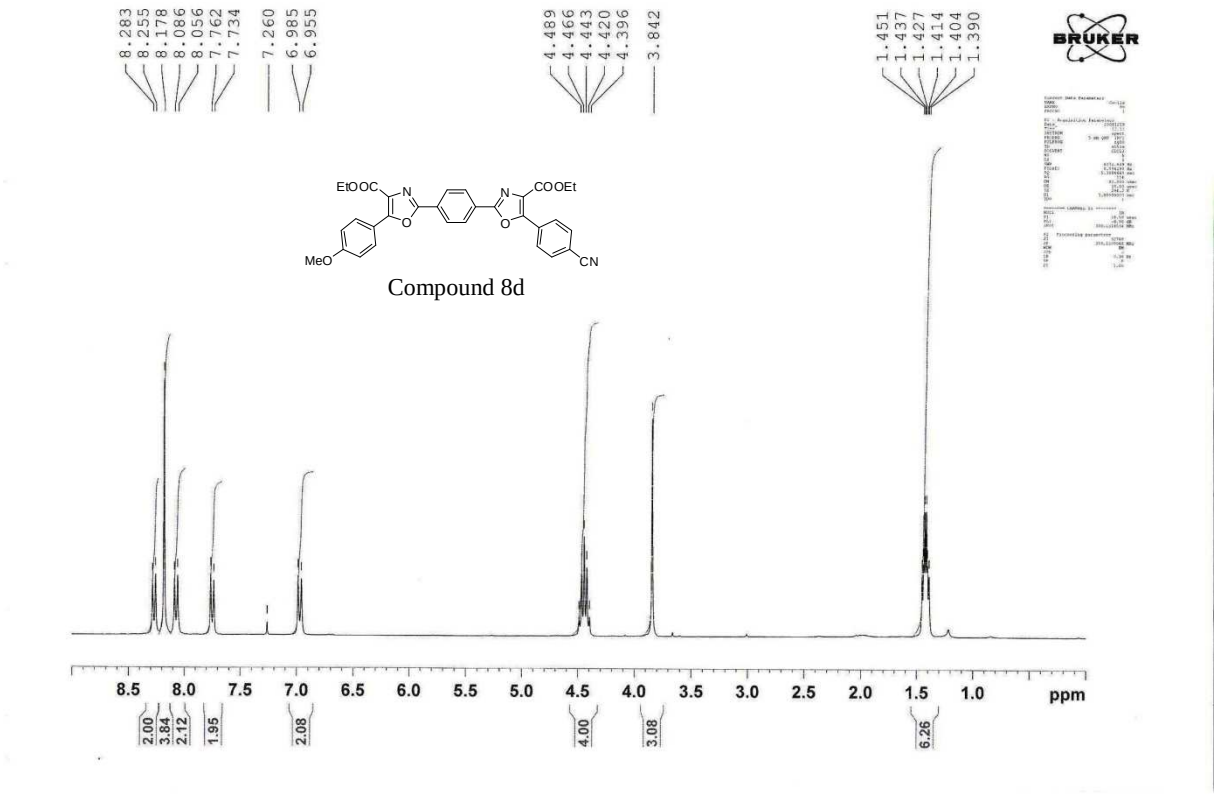
Compound 8b


160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

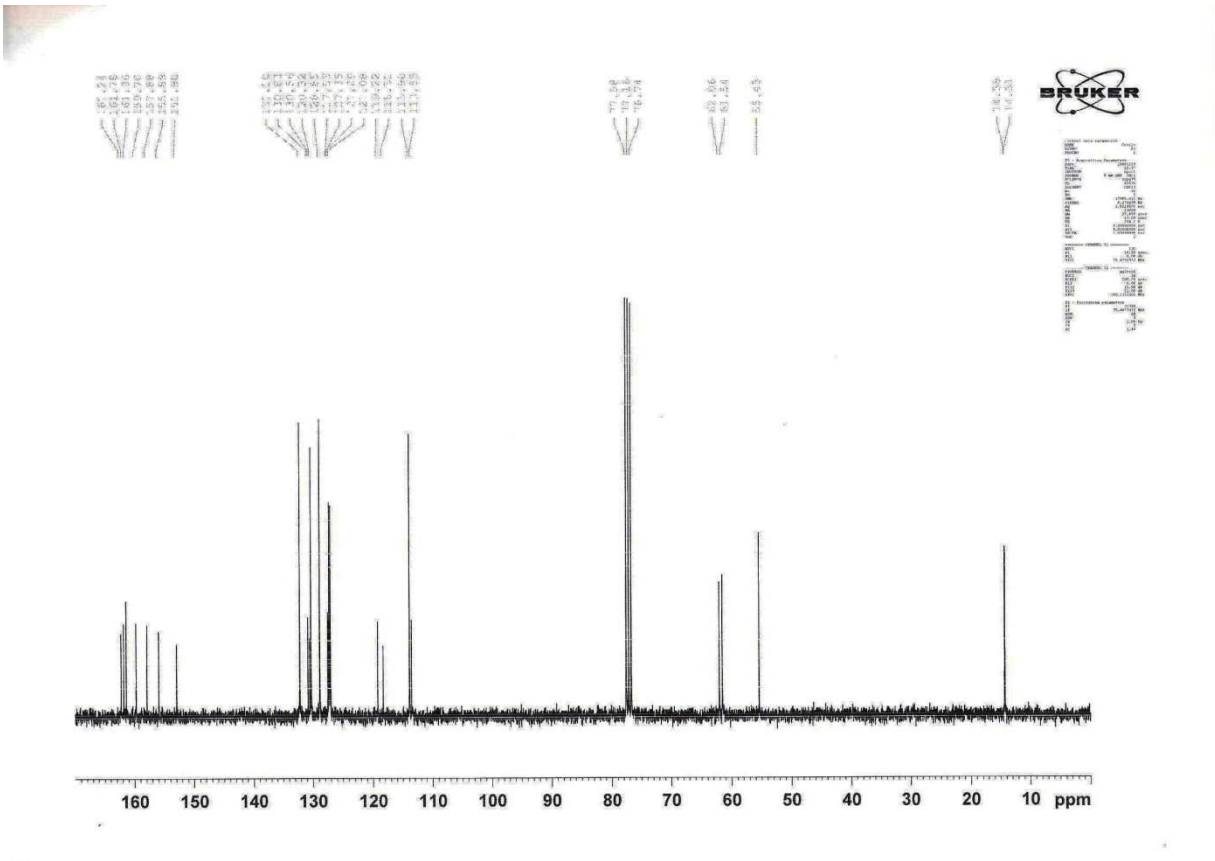

8.232
8.115
8.086
7.260
6.787
6.758
4.503
4.479
4.456
4.432
3.059
1.472
1.448
1.425
EtOOC
N
O
COOEt
Me2N
NMe2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.00
3.87
3.76
4.00
11.17
6.68

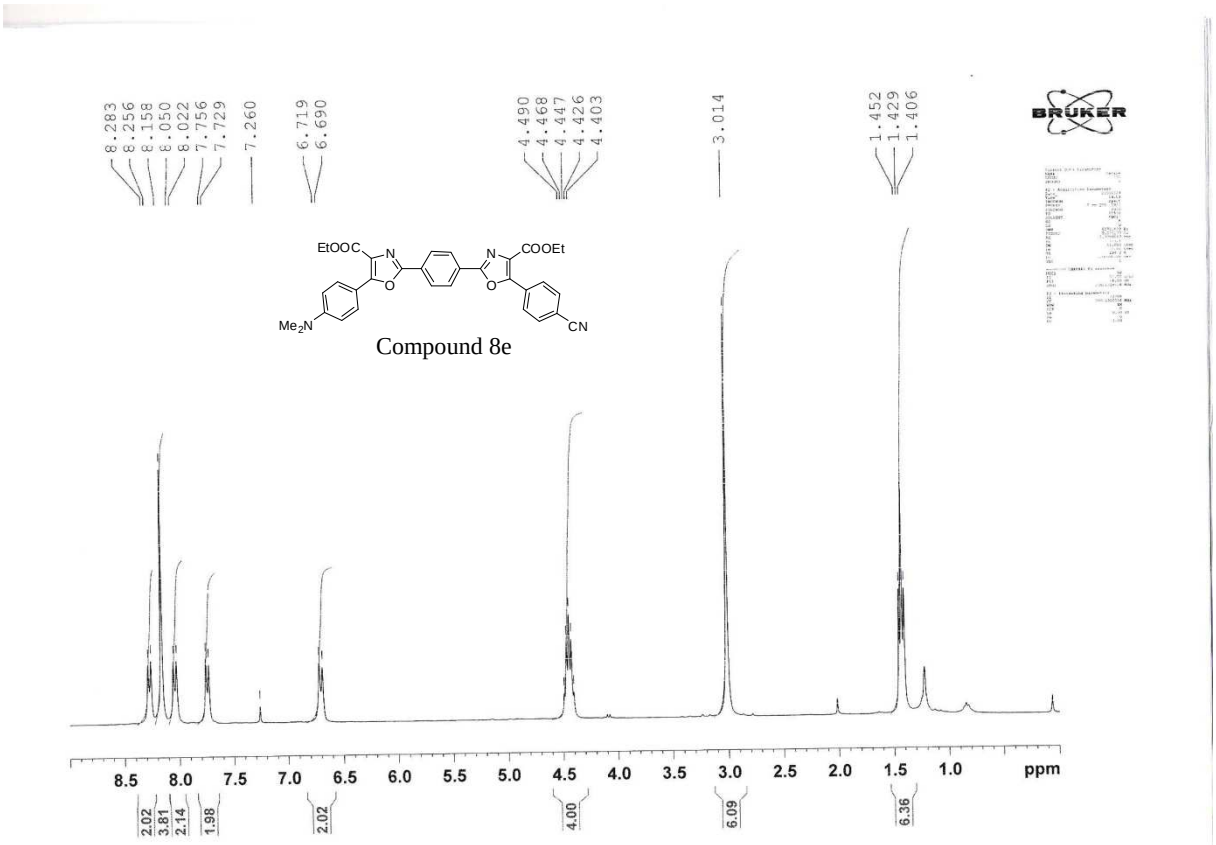
Compound 8c


160.77
157.76
157.09
151.67
130.01
129.12
128.10
126.02
114.28
111.46
77.56
77.16
76.74
61.97
60.22
14.55

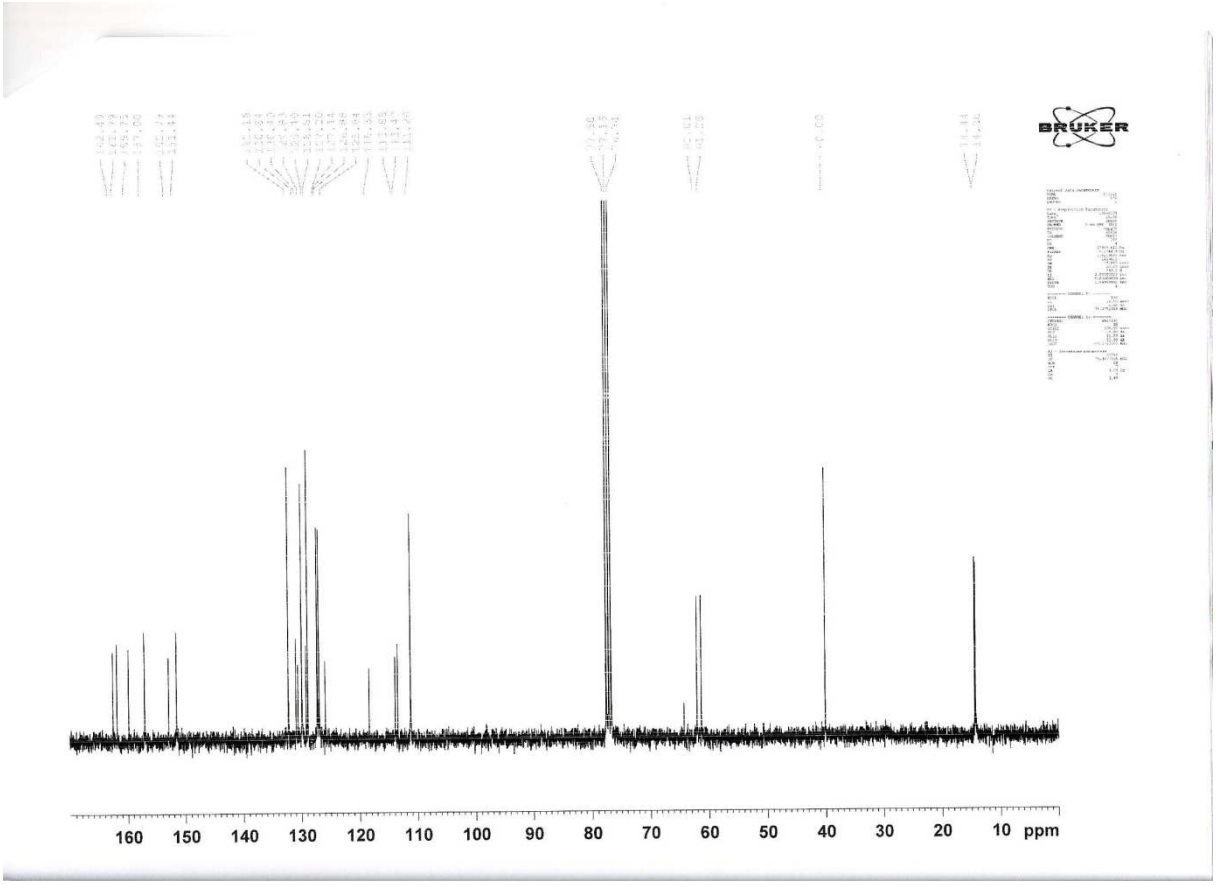

8.283
8.255
8.178
8.086
8.056
7.762
7.734
7.260
6.985
6.955
4.489
4.466
4.443
4.420
4.396
3.842
1.451
1.437
1.427
1.414
1.404
1.390
BRUKER
EtOOC
N
O
N
O
COOEt
MeO
CN
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
3.84
2.12
1.95
2.08
4.00
3.08
6.26

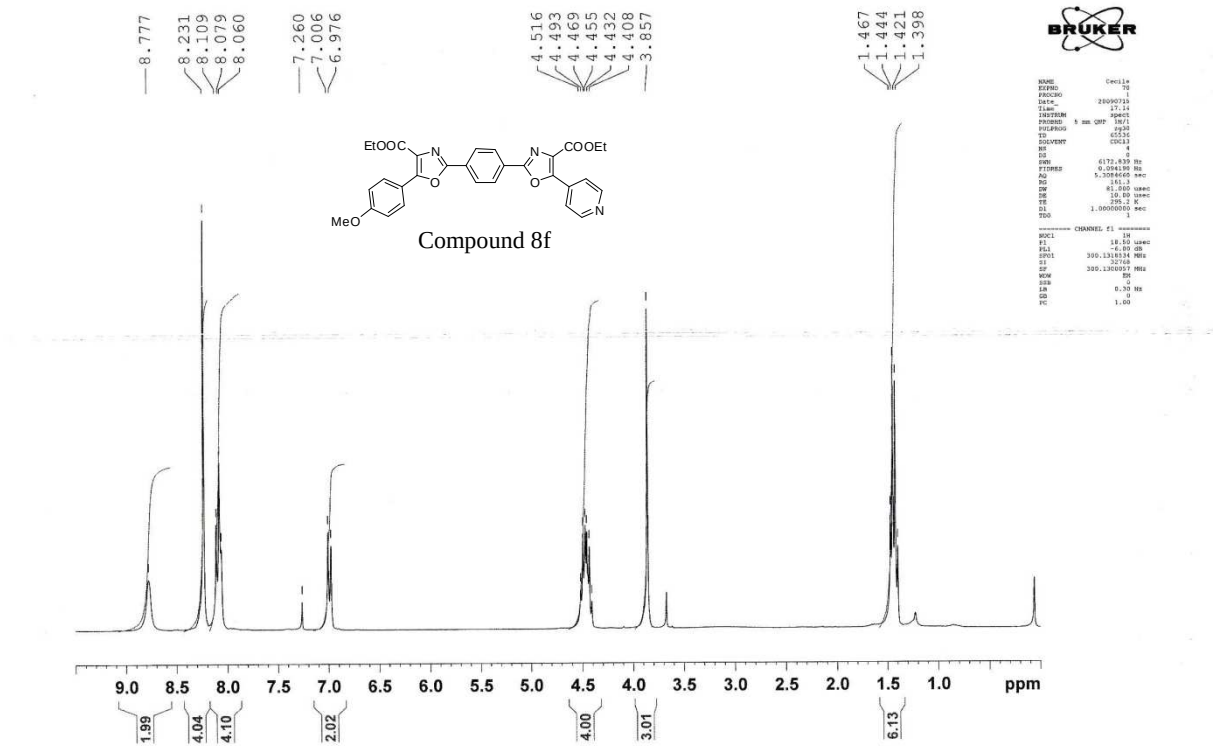
Compound 8d


BRUKER
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

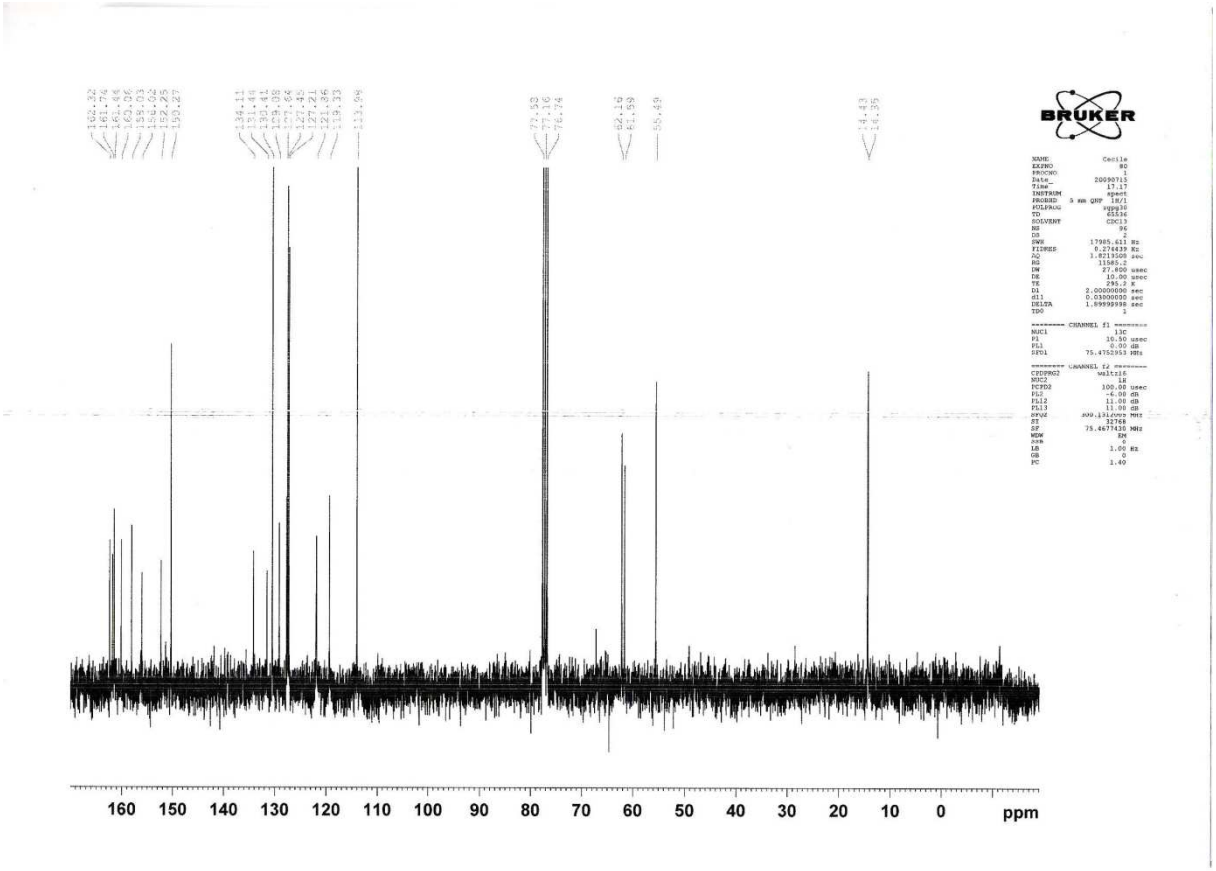

8.283
8.256
8.158
8.050
8.022
7.756
7.729
7.260
6.719
6.690
4.490
4.468
4.447
4.426
4.403
3.014
1.452
1.429
1.406
BRUKER
EtOOC
N
O
N
O
COOEt
Me2N
CN
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.02
3.81
2.14
1.98
2.02
4.00
6.09
6.36

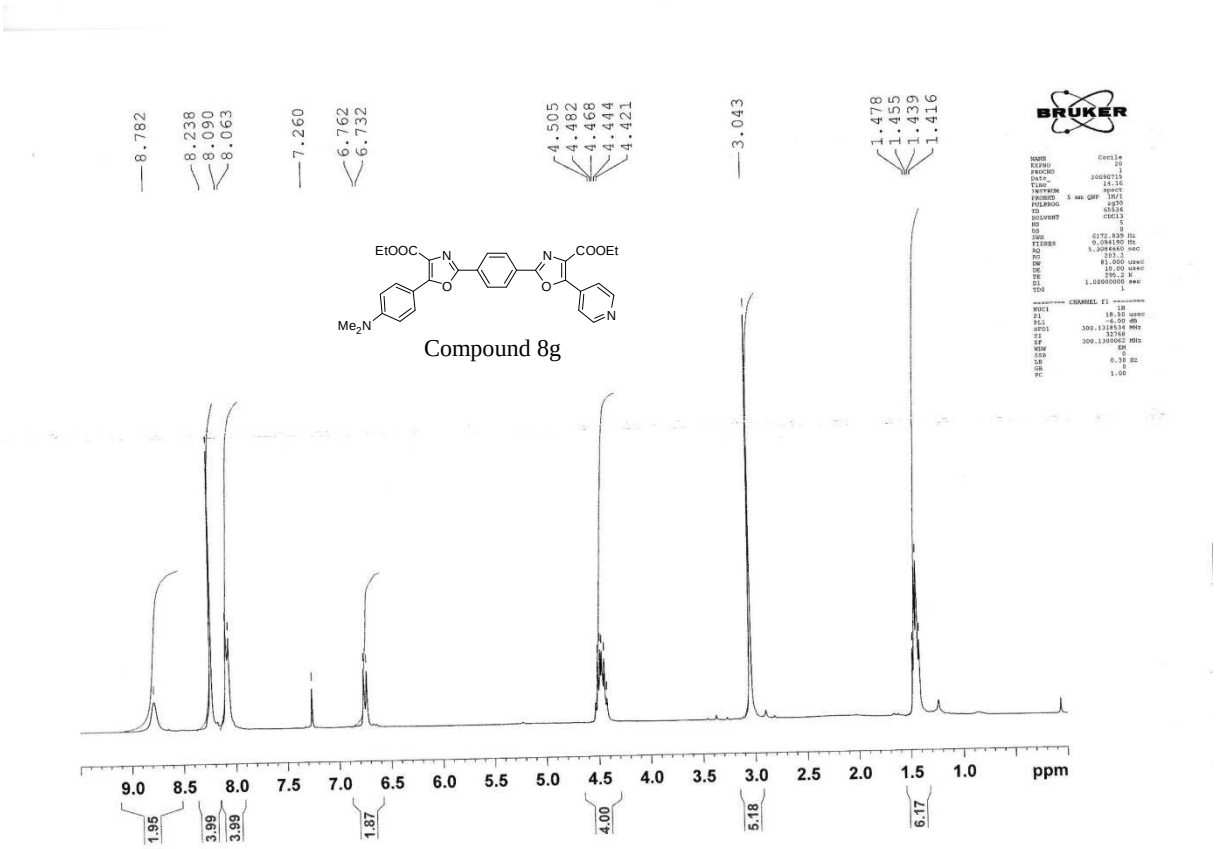
Compound 8e


BRUKER
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

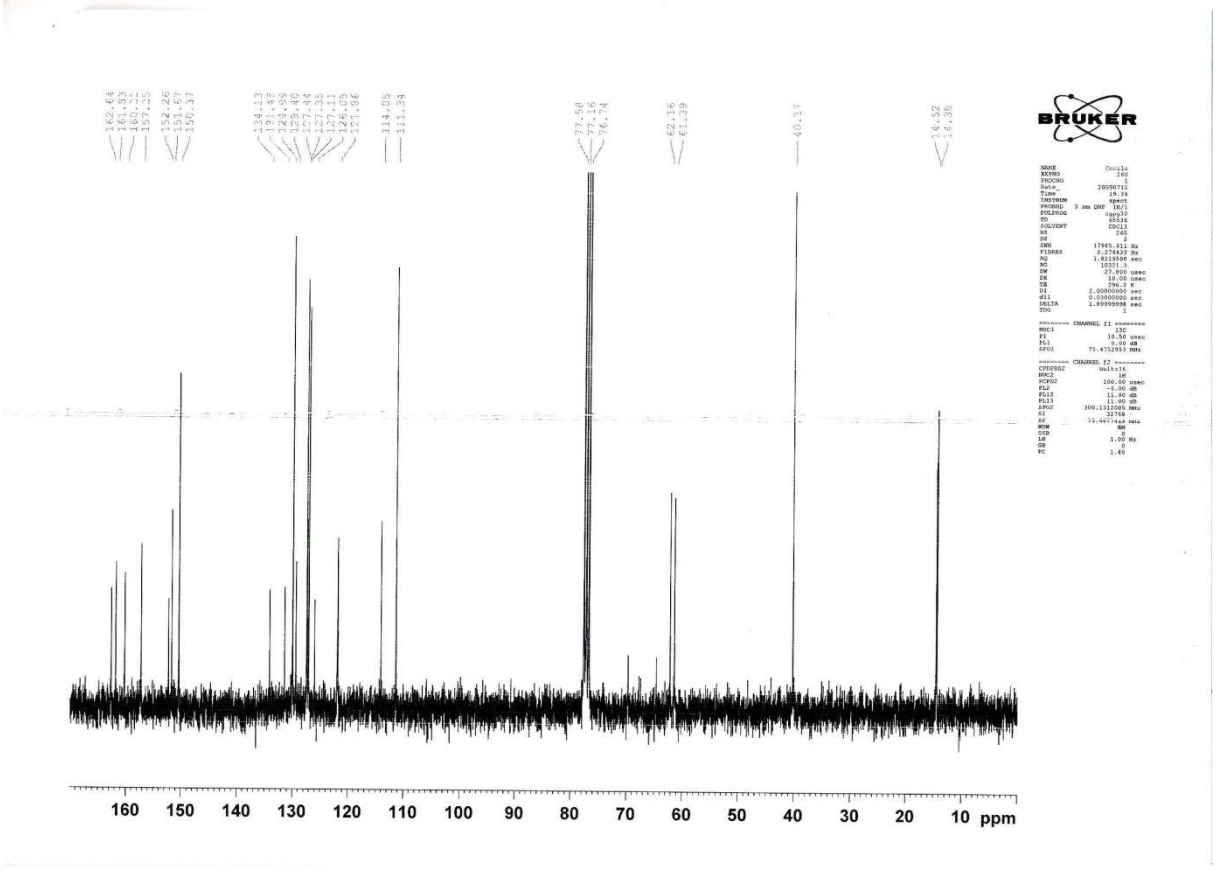

8.777
8.231
8.109
8.079
8.060
7.260
7.006
6.976
4.516
4.493
4.469
4.455
4.432
4.408
3.857
1.467
1.444
1.421
1.398
EtOOC
COOEt
MeO
N
O
BRUKER
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.99
4.04
4.10
2.02
4.00
3.01
6.13

Compound 8f


BRUKER
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.782
8.238
8.090
8.063
7.260
6.762
6.732
4.505
4.482
4.468
4.444
4.421
3.043
1.478
1.455
1.439
1.416
EtOOC
COOEt
Me2N
N
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.95
3.99
3.99
1.87
4.00
5.18
6.17

Compound 8g


162.64
160.53
160.32
157.05
152.26
150.37
134.13
131.43
129.09
128.80
127.94
127.35
127.21
126.05
121.06
114.05
111.34
77.50
77.16
76.74
62.16
61.99
40.17
14.52
14.36
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm