Rhodium-Catalyzed Hydroformylation of Alkynes Employing a Self-Assembling Ligand System

Vladislav Agabekov, Wolfgang Seiche and Bernhard Breit*

Institut für Organische Chemie
Albert-Ludwigs-Universität Freiburg, Germany

Supporting Information

I General

All reactions were carried out in oven-dried glassware under an atmosphere of argon (argon 5.0 from Sauerstoffwerke Friedrichshafen). [$Rh(CO)_2acac$] was a gift from BASF. All solvents were dried and distilled by standard procedures. Chromatographic purification of products was accomplished using flash chromatography[1] on Machery-Nagel silica gel 60® (230-400 mesh). Hydroformylation reactions at 50-55 °C were performed in an Endeavor parallel autoclave with 8 reaction vessels from Argonaut Technologies. Gases: Carbon monoxide 3.7, hydrogen 4.3 (1:1, Messer-Griesheim).

Melting points were measured on a Büchi melting point apparatus using open glass capillaries, and the values are uncorrected.

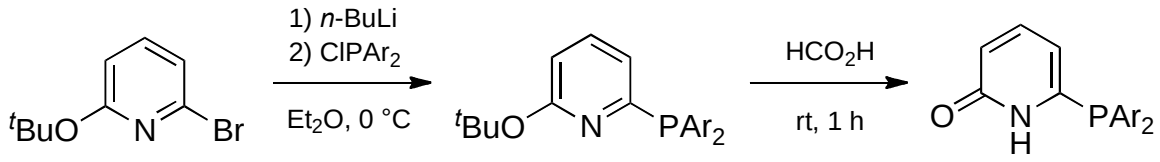
Nuclear magnetic resonance spectra were acquired on a Bruker DRX 500 spectrometer, a Bruker Avance 400 spectrometer, a Bruker Avance DRX 250 spectrometer and on a Varian Mercury 300 spectrometer. NMR-spectra are referenced internally according to TMS [0.00 ppm (^1H)] or residual protio solvent signals [$CDCl_3$: 77.10 ppm (^{13}C)].[2] Data for ^1H-NMR are reported as follows: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; m_c, symmetrical multiplet; br, broad signal; *p*, pseudo), coupling constant (Hz), integration. Data for ^{13}C-NMR are reported in terms of chemical shift, integration.

II Experimental procedures and characterizations

Synthesis of ligands

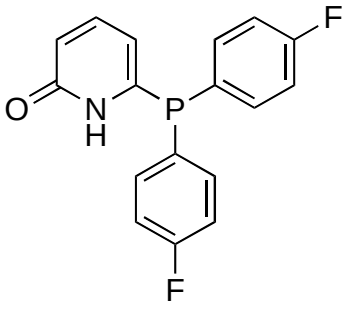
PPh_3 and Biphephos are commercially available. The 6-DPPon ligand (**L1**) was prepared applying a methodology developed in our group.[3]

General procedure A: Synthesis of L2-4



To a solution of 2-bromo-6-(*tert*-butoxy)pyridine (1.0 equiv.) in Et_2O was added slowly at 0 °C *n*BuLi (1.1 equiv.). The reaction mixture was stirred for 60 min, then bisarylchlorphosphine (1.15 equiv.) was added and the reaction mixture was stirred for further 60 min at room temperature. The reaction was quenched with H_2O (1.15 equiv.) and the solution concentrated in vacuo. The resulting oil was directly dissolved in degased formic acid and was stirred at room temperature for 60 min. Afterwards the mixture was diluted with H_2O and extracted with Et_2O three times. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (CH_2Cl_2/EtOAc) and subsequently trituration in pentane yielded the desired compounds **L2-4**.

Synthesis of 6-bis-(4-fluorophenyl)-phosphino-pyridin-2(1*H*)-one (L2)



Following the **general procedure A** the title compound was isolated by flash chromatography (SiO_2, CH_2Cl_2:EtOAc = 10:1, R_f = 0.5) as a colorless solid in 75% (0.64 g, 2.03 mmol) yield. Mp = 185 °C.

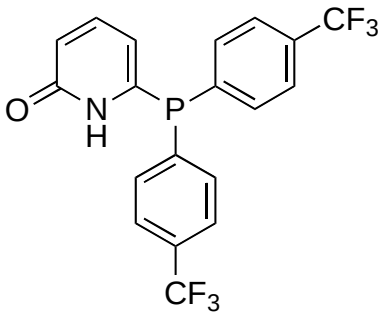
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 6.06 (dd, ^{3}J = 6.1 Hz, ^{3}J = 5.1 Hz, 1H, Ar*H*), 6.46 (d, ^{3}J = 9.2 Hz, 1H, Ar*H*), 7.10 (dd, ^{3}J = 8.4 Hz, ^{4}J = 8.4 Hz, 1H, Ar*H*), 7.30 (m_c, 4H Ar*H*), 7.35 (m_c, 4H, Ar*H*), 9.63 (bs, 1H, N*H*).

^{13}C{^{1}H}-NMR (125.692 MHz, $CDCl_3$): δ (ppm) = 113.3 (d, $^{2}J_{C-P}$ = 17.0 Hz), 116.7 (dd, $^{2}J_{C-F}$ = 21.2 Hz, $^{3}J_{C-P}$ = 8.3 Hz, 4C), 121.0 (b), 128.2 (dd, $^{1}J_{C-P}$ = 9.6 Hz, $^{4}J_{C-F}$ = 3.5 Hz, 2C), 136.1 (dd, $^{2}J_{C-P}$ = 22.1 Hz, $^{3}J_{C-F}$ = 8.3 Hz, 4C), 140.3 (d, $^{3}J_{C-P}$ = 5.7 Hz), 146.6 (d, $^{1}J_{C-P}$ = 23.2 Hz), 164.2 (d, $^{1}J_{C-F}$ = 251.8 Hz, 2C), 164.2 (b).

^{31}P{^{1}H}-NMR (121.468 MHz, C_6D_6): δ (ppm) = − 10.9 (t, $^{5}J_{P-F}$ = 4.2 Hz).

CHN: Calcd. C: 64.77, H: 3.84, N: 4.44; Found C: 64.58, H: 3.90, N: 4.53.

Synthesis of 6-bis-((4-trifluoromethyl)-phenyl)-phosphino-pyridin-2(1*H*)-one (L3)



Following the **general procedure A** the title compound was isolated by flash chromatography (SiO_2, CH_2Cl_2:EtOAc = 10:1, R_f = 0.6) as a colorless solid in 62% (1.19 g, 2.87 mmol) yield. Mp =166-169 °C.

^{1}H-NMR (400.130 MHz, $CDCl_3$, $(CD_3)_2SO$): δ (ppm) = 5.59 (dd, ^{3}J = 6.7 Hz, ^{4}J = 2.7 Hz, 1H, Ar*H*), 6.18 (d, ^{3}J = 9.3 Hz, 1H, Ar*H*), 7.01 (dd, ^{3}J = 8.1 Hz, ^{3}J = 8.1 Hz, 1H, Ar*H*), 7.18 (m_c, 4H Ar*H*), 7.35 (m_c, 4H, Ar*H*), 7.75 (bs, 1H, N*H*).

^{13}C{^{1}H}-NMR (100.613 MHz, $CDCl_3$, $(CD_3)_2SO$): δ (ppm) = 112.9 (d, $^{2}J_{C-P}$ = 10.7 Hz), 120.0 (bs), 123.1 (q, $^{1}J_{C-F}$ = 271.6 Hz, 2C), 125.0 (dq, $^{3}J_{C-P}$ = 7.4 Hz, $^{3}J_{C-F}$ = 3.6 Hz, 4C), 131.0 (q, $^{2}J_{C-F}$ = 32.6 Hz, 2C), 132.0 (d, $^{1}J_{C-P}$ = 10.0 Hz, 2C), 133.7 (d, $^{2}J_{C-P}$ = 20.5 Hz, 4C), 137.4 (d, $^{3}J_{C-P}$ = 12.6 Hz), 139.4 (d, $^{3}J_{C-P}$ = 3.9 Hz), 163.4 (d, $^{3}J_{C-P}$ = 4.9 Hz).

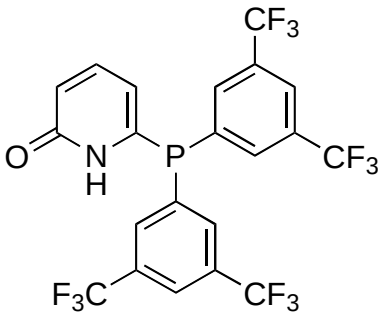
^{19}F-NMR (235.357 MHz, $CDCl_3$, $(CD_3)_2SO$): δ (ppm) = − 57.95 (s).

^{31}P{^{1}H}-NMR (161.976 MHz, $CDCl_3$, $(CD_3)_2SO$): δ (ppm) = − 5.5 (s).

MS (APCI, $C_{19}H_{12}F_6NOP$, M = 415.27 g/mol): m/z (%) = 432.0 (12), 416.1 (100), 395.1 (1), 353.1 (1).

HRMS (APCI): Calcd. for $C_{19}H_{13}NOF_6P[M+H]^+$: 416.06390; Found: 416.06360.

Synthesis of 6-bis-(3,5-bis-(trifluoromethyl)-phenyl)-phosphino-pyridin-2(1*H*)-one (L4)



Following the **general procedure A** the title compound was isolated by flash chromatography (SiO_2, CH_2Cl_2:EtOAc = 10:1, R_f = 0.3) as a colorless solid in 61% (584 mg, 1.06 mmol) yield. Mp = 213 °C.

^{1}H-NMR (300.066 MHz, $CDCl_3$): δ (ppm) = 6.27 (d, ^3J = 9.2 Hz, 1H, Ar*H*), 6.45 (dd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, 1H, Ar*H*), 7.37 (ddd, ^3J = 8.8 Hz, ^3J = 7.0 Hz, $^4J_{H\text{-}P}$ = 1.8 Hz, 1H, Ar*H*), 7.91 (bs, 4H, Ar*H*), 7.94 (bs, 2H, Ar*H*), 11.00 (bs, 1H, N*H*).

^{13}C{^{1}H}-NMR (100.613 MHz, $CDCl_3$): δ (ppm) = 116.8 (d, $^2J_{C\text{-}P}$ = 31.2 Hz), 122.9, 123.0 (q, $^1J_{C\text{-}F}$ = 273.3 Hz, 4C), 123.9-124.3 (m, 2C), 132.5 (qd, $^2J_{C\text{-}F}$ = 33.7 Hz, $^3J_{C\text{-}P}$ = 6.8 Hz, 4C), 133.7 (m, 4C), 136.1 (d, $^1J_{C\text{-}P}$ = 15.0 Hz, 2C), 140.4 (d, $^3J_{C\text{-}P}$ = 11.1 Hz), 142.7 (d, $^1J_{C\text{-}P}$ = 25.4 Hz), 165.3 (d, $^4J_{C\text{-}P}$ = 1.4 Hz).

^{31}P{^{1}H}-NMR (161.976 MHz, $CDCl_3$): δ (ppm) = − 5.7 (s).

HRMS (EI, [M^+]): Calcd.: 551.030802; Found: 551.030056.

Synthesis of substrates

Alkynes **1a-d**, **4a**, **7a-b** are commercially available. Alkynes **4b-n** were prepared in accordance with a literature procedure developed by P. A. Grieco.[4]

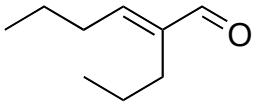
General procedure B: Synthesis of 2 and 8

An oven dried glass inlet was purged with argon and charged with [$Rh(CO)_2$acac] (3.0 mg, 11.6 μmol, 1.0 mol%), **L4** (19.2 mg, 34.8 μmol, 3.0 mol%) and **1** or **7** (1.16 mmol, 100 mol%). Toluene (2 ml) was added via syringe and the glass inlet was transferred into the autoclave. The autoclave was sealed and purged three times with 5 bar of the CO/H_2 gas-mixture (1:1). Then it was pressurized with 5 bar of CO/H_2 (1:1), heated to 55 °C and stirred for 20 h. Subsequently, the autoclave was cooled to room temperature, the CO/H_2 gas was released and the reaction mixture was analyzed and purified.

General procedure C: Synthesis of 5

An oven dried glass inlet was purged with argon and charged with [$Rh(CO)_2acac$] (1.5 mg, 5.8 µmol, 0.5 mol%), **L4** (9.6 mg, 17.4 µmol, 1.5 mol%) and **4** (1.16 mmol, 100 mol%). Toluene (2 ml) was added via syringe and the glass inlet was transferred into the autoclave. The autoclave was sealed and purged three times with 5 bar of the CO/H_2 gas-mixture (1:1). Then it was pressurized with 5 bar of CO/H_2 (1:1), heated to 55 °C and stirred for 20 h. Subsequently, the autoclave was cooled to room temperature, the CO/H_2 gas was released and the reaction mixture was analyzed and purified.

Synthesis of (*E*)-2-propylhex-2-enal (2a)

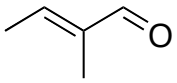


Following the **general procedure B** the title compound was isolated by flash chromatography (SiO_2, pentane:CH_2Cl_2 = 1.5:1, R_f = 0.3) as a colorless oil in 92% (150 mg, 1.068 mmol) yield. The analytical data are in agreement with those reported previously.[5]

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 0.89 (t, ^3J = 7.4 Hz, 3H), 0.98 (t, ^3J = 7.4 Hz, 3H), 1.38 (qt, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H), 1.54 (qt, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H), 2.22 (t, ^3J = 7.4 Hz, 2H), 2.34 (dt, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H), 6.45 (t, ^3J = 7.4 Hz, 1H), 9.37 (s, 1H, C*H*O).

^{13}C-NMR (100.613 MHz, $CDCl_3$): δ (ppm) = 14.0, 14.2, 22.0, 22.1, 26.0, 31.0, 143.9, 155.3, 195.5 (*C*HO).

Synthesis of tiglic aldehyde (2b)

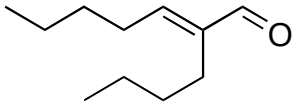


Following the **general procedure B** the title compound was isolated by flash chromatography (SiO_2, pentane:Et_2O = 5:1, R_f = 0.5) as a colorless oil in 78% (76 mg, 0.903 mmol) yield. The analytical data are in agreement with those reported previously.[6]

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 1.74 (d, ^4J = 1.0 Hz, 3H), 1.97 (d, ^3J = 7.0 Hz, 3H), 6.59 (qq, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H), 9.37 (s, 1H, C*H*O).

^{13}C-NMR (100.613 MHz, $CDCl_3$): δ (ppm) = 8.9, 14.8, 140.9, 149.4, 194.7 (*C*HO).

Synthesis of (*E*)-2-butylhept-2-enal (2c)

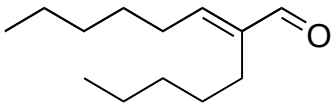


Following the **general procedure B** the title compound was isolated by flash chromatography (SiO_2, pentane:Et_2O = 5:1, R_f = 0.3) as a colorless oil in 86% (168 mg, 0.998 mmol) yield. The analytical data are in agreement with those reported previously.[7]

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 0.90 (t, ^3J = 7.0 Hz, 3H), 0.95 (t, ^3J = 7.2 Hz, 3H), 1.26-1.55 (m, 8H), 2.24 (t, ^3J = 7.4 Hz, 2H), 2.36 (dt, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H), 6.44 (t, ^3J = 7.4 Hz, 1H), 9.36 (s, 1H, C*H*O).

^{13}C-NMR (100.613 MHz, $CDCl_3$): δ (ppm) = 14.0, 14.2, 20.5, 22.1, 22.8, 28.5, 28.9, 31.3, 146.3, 156.9, 194.0 (*C*HO).

Synthesis of (*E*)-2-pentyloct-2-enal (2d)

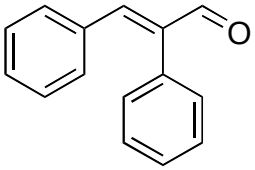


Following the **general procedure B** the title compound was isolated by flash chromatography (SiO_2, pentane:Et_2O = 5:1, R_f = 0.3) as a colorless oil in 97% (220 mg, 1.125 mg) yield. The analytical data are in agreement with those reported previously.[7]

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 0.88 (t, ^3J = 7.1 Hz, 3H), 0.92 (t, ^3J = 7.1 Hz, 3H), 1.24-1.39 (m, 10H), 1.45-157 (m, 2H), 2.23 (t, ^3J = 7.4 Hz, 2H), 2.35 (dt, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H), 6.44 (t, ^3J = 7.4 Hz, 1H), 9.36 (s, 1H, C*H*O).

^{13}C-NMR (100.613 MHz, $CDCl_3$): δ (ppm) = 14.0, 14.2, 20.9, 22.8 (2C), 26.7, 29.4 (2C), 31.1, 31.9, 144.8, 156.4, 195.1 (*C*HO).

Synthesis of (*E*)-2,3-diphenylacrylaldehyde (5a)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 5:1, R_f = 0.26) as a colorless solid in 92% (223 mg, 1.071 mmol) yield. The analytical data are in agreement with those reported previously.[8]

Mp = 92-94 °C.

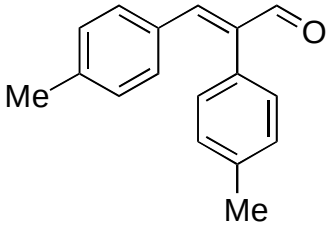
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 7.19-7.26 (m, 6H, Ar*H*), 7.28-7.32 (m, 1H, Ar*H*), 7.36-7.45 (m, 3H, Ar*H*), 7.40 (s, 1H, C*H*=C), 9.78 (s, 1H, C*H*O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 128.4 (2C), 128.6 (2C), 128.9 (2C), 129.4 (2C), 130.3, 130.8, 133.4, 134.1, 141.9, 150.1, 193.9 (*C*HO).

MS (EI, $C_{15}H_{12}O$, M = 208.09 g/mol): m/z (%) = 208.2 (49), 178.1 (100), 165.1 (33), 105.1 (8), 102.1 (22).

HRMS (EI): Calcd. for $C_{15}H_{12}O$: 208.08882; Found: 208.08860.

Synthesis of (*E*)-2,3-di-*p*-tolylacrylaldehyde (5b)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.26) as a pale yellow solid in 93% (255 mg, 1.078 mmol) yield.

Mp = 104-106 °C.

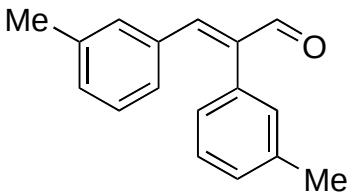
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 2.32 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 7.03-7.07 (m_c, 2H, Ar*H*), 7.08-7.11 (m_c, 2H, Ar*H*), 7.12-7.16 (m_c, 2H, Ar*H*), 7.21-7.24 (m_c, 2H, Ar*H*), 7.33 (s, 1H, C*H*=C), 9.74 (s, 1H, C*H*O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 21.4 (*C*H_3), 21.5 (*C*H_3), 129.2 (2C), 129.3 (2C), 129.7 (2C), 130.6, 130.9 (2C), 131.5, 138.1, 140.8, 141.1, 150.2 (*C*H=C), 194.2 (*C*HO).

MS (APCI, $C_{17}H_{16}O$, M = 236.31 g/mol): m/z (%) = 251.1 (4), 238.1 (22), 237.1 (100) 219.1 (5).

HRMS (APCI): Calcd. for $C_{17}H_{17}O[M+H]^+$: 237.12794; Found: 237.12800.

Synthesis of (*E*)-2,3-di-*m*-tolylacrylaldehyde (5c)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.35) as a colorless oil in 86% (236 mg, 1.000 mmol) yield.

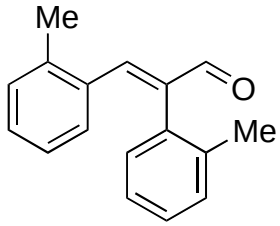
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 2.24 (s, 3H, C*H*$_3$), 2.36 (s, 3H, C*H*$_3$), 6.96-7.00 (m, 2H, Ar*H*), 7.02 (m$_c$, 1H, Ar*H*), 7.06 (m$_c$, 1H, Ar*H*), 7.08-7.13 (m, 2H, Ar*H*), 7.18-7.22 (m, 1H, Ar*H*), 7.30 (dd, 1H, ^{3}J = 7.6 Hz, ^{3}J = 7.6 Hz, Ar*H*), 7.34 (s, 1H, C*H*=C), 9.76 (s, 1H, C*H*=O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 21.3 (*C*H$_3$), 21.5 (*C*H$_3$), 126.4, 127.8, 128.4, 128.8, 129.1, 129.8, 131.1, 131.9, 133.5, 134.1, 138.1, 138.5, 142.0, 150.3 (*C*H=C), 194.2 (*C*H=O).

MS (APCI, $C_{17}H_{16}O$, M = 236.31 g/mol): m/z (%) = 237.1 (100).

HRMS (APCI): Calcd. for $C_{17}H_{17}O[M+H]^+$: 237.12794; Found: 237.12800.

Synthesis of (*E*)-2,3-di-*o*-tolylacrylaldehyde (5d)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.34) as a pale yellow oil in 93% (255 mg, 1.081 mmol) yield.

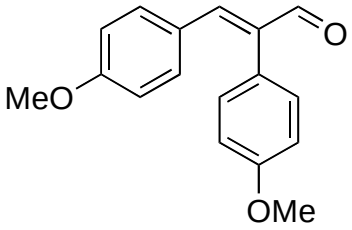
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 2.05 (s, 3H, C*H*$_3$), 2.51 (s, 3H, C*H*$_3$), 6.71 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.0 Hz, 1H, Ar*H*), 6.88 (dddd, ^{3}J = 7.5 Hz, ^{3}J = 7.5 Hz, ^{4}J = 0.6 Hz, ^{4}J = 0.6 Hz, 1H, Ar*H*), 7.00 (dd, ^{3}J = 7.5 Hz, ^{4}J = 1.4 Hz, 1H, Ar*H*) 7.15-7.29 (m, 5H, Ar*H*), 7.74 (s, 1H, C*H*=C), 9.84 (s, 1H, C*H*=O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 19.7 (*C*H$_3$), 20.1 (*C*H$_3$), 125.9, 126.2, 128.4, 129.1, 129.7, 130.0, 130.5, 130.6, 133.1, 133.2, 136.3, 138.1, 142.4, 148.1 (*C*H=C), 193.9 (*C*H=O).

MS (APCI, $C_{17}H_{16}O$, M = 236.31 g/mol): m/z (%) = 269.1 (11), 251.1 (4), 237.1 (100), 214.1 (3).

HRMS (APCI): Calcd. for $C_{17}H_{17}O[M+H]^+$: 237.12794; Found: 237.12800.

Synthesis of (*E*)-2,3-bis(4-methoxyphenyl)acrylaldehyde (5e)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.12) as a pale yellow solid in 92% (286 mg, 1.066 mmol) yield.

Mp = 96-98 °C.

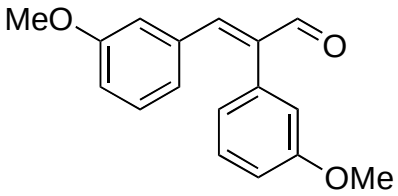
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 3.79 (s, 3H, OC*H*$_3$), 3.85 (s, 3H, OC*H*$_3$), 6.74-6.78 (m_c, 2H, Ar*H*), 6.94-6.98 (m_c, 2H, Ar*H*), 7.12-7.16 (m_c, 2H, Ar*H*), 7.19-7.23 (m_c, 2H, Ar*H*), 7.29 (s, 1H, C*H*=C), 9.70 (s, 1H, C*H*O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 55.3 (O*C*H$_3$), 55.4 (O*C*H$_3$), 114.1 (2C), 114.5 (2C), 125.8, 127.0, 130.7 (2C), 132.7 (2C), 139.6, 150.0 (*C*H=C), 159.6, 161.3, 194.3 (*C*HO).

MS (APCI, $C_{17}H_{16}O$, M = 268.31 g/mol): m/z (%) = 270.1 (26), 269.1 (100).

HRMS (APCI): Calcd. for $C_{17}H_{17}O_3[M+H]^+$: 269.11777; Found: 269.11770.

Synthesis of (*E*)-2,3-bis(3-methoxyphenyl)acrylaldehyde (5f)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.13) as a colorless solid in 90% (280 mg 1.044 mmol) yield.

Mp = 50-53 °C.

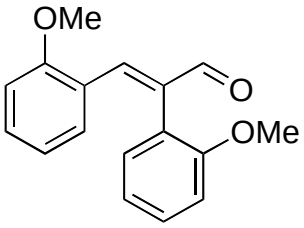
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 3.54 (s, 3H, OC*H*$_3$), 3.77 (s, 3H, OC*H*$_3$), 6.72 (dd, ^4J = 2.6 Hz, ^5J = 1.5 Hz, 1H, Ar*H*), 6.75 (dd, ^4J = 2.6 Hz, ^5J = 1.5 Hz, 1H, Ar*H*), 6.79 (ddd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, ^4J = 1.0 Hz, 1H, Ar*H*), 6.86 (ddd, ^3J = 8.2 Hz, ^4J = 2.6 Hz, ^4J = 1.0 Hz, 1H, Ar*H*), 6.88 (m, 1H, Ar*H*), 6.93 (ddd, ^3J = 8.2 Hz, ^4J = 2.6 Hz, ^4J = 1.0 Hz, 1H, Ar*H*), 7.18 (dd, ^3J = 8.0 Hz, ^3J = 8.0 Hz, 1H, Ar*H*), 7.34 (dd, ^3J = 8.0 Hz, ^3J = 2.0 Hz, 1H, Ar*H*), 7.36 (s, 1H, C*H*=C), 9.76 (s, 1H, C*H*=O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 55.0, 55.3, 114.2, 114.7, 114.7, 117.2, 121.7, 124.0, 129.6, 130.1, 135.0, 135.2, 141.9, 149.9 (*C*H=C), 159.4, 160.1, 193.8 (*C*H=O).

MS (APCI, $C_{17}H_{16}O_3$, M = 268.31 g/mol): m/z (%) = 269.1 (100).

HRMS (APCI): Calcd. for $C_{17}H_{17}O_3[M+H]^+$: 269.11777; Found: 269.11767.

Synthesis of (*E*)-2,3-bis(2-methoxyphenyl)acrylaldehyde (5g)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.17) as a pale yellow solid in 78% (243 mg, 0.905 mmol) yield.

Mp = 116-119 °C.

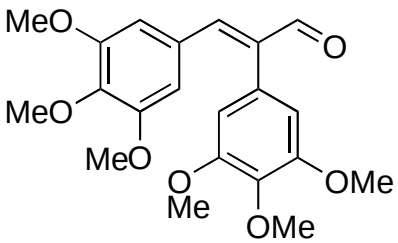
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 3.69 (s, 3H, OC*H*$_3$), 3.90 (s, 3H, OC*H*$_3$), 6.65 (dddd, ^3J = 7.6 Hz, ^3J = 7.6 Hz, ^4J = 0.5 Hz, ^4J = 0.5 Hz, 1H, Ar*H*), 6.89 (dd, ^3J = 8.5 Hz, ^4J = 0.8 Hz, 1H, Ar*H*), 6.93 (dd, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, Ar*H*), 6.95-6.98 (m, 2H, Ar*H*), 7.02 (dd, ^3J = 7.3 Hz, ^4J = 1.9 Hz, 1H, Ar*H*), 7.26 (ddd, ^3J = 7.6 Hz, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 1H, Ar*H*), 7.35 (ddd, ^3J = 7.6 Hz, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 1H, Ar*H*), 7.93 (s, 1H, C*H*=C), 9.77 (s, 1H, C*H*=O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 55.67 (O*C*H$_3$), 55.69 (O*C*H$_3$), 110.7, 111.5, 120.3, 121.1, 123.3, 123.6, 129.8, 129.9, 130.8, 131.5, 138.8, 144.4 (*C*H=C), 157.2, 158.1, 193.9 (*C*H=O).

MS (APCI, $C_{17}H_{16}O_3$, M = 268.31 g/mol): m/z (%) = 283.1 (7), 270.1 (19), 269.1 (100), 241.1 (4), 237.1 (3).

HRMS (APCI): Calcd. for $C_{17}H_{17}O_3[M+H]^+$: 269.11777; Found: 269.11770.

Synthesis of (*E*)-2,3-bis(3,4,5-trimethoxyphenyl)acrylaldehyde (5h)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 1:1, R_f = 0.36) as a yellow solid in 61% (276 mg, 0.710 mmol) yield.

Mp = 71-74 °C.

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 3.62 (s, 6H, 2×OC*H*$_3$), 3.80 (s, 6H, 2×OC*H*$_3$), 3.84 (s, 3H, OC*H*$_3$), 3.85 (s, 3H, OC*H*$_3$), 6.43 (s, 2H, Ar*H*), 6.52 (s, 2H, Ar*H*), 7.28 (s, 1H, C*H*=C), 9.73 (s, 1H, C*H*O).

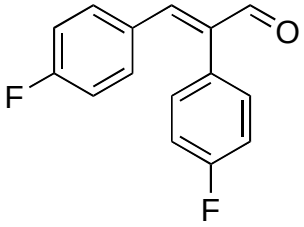
^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 55.9 (2C, 2×O*C*H$_3$), 56.3 (2C, 2×O*C*H$_3$), 60.8 (O*C*H$_3$), 61.0 (O*C*H$_3$), 106.4 (2C), 108.5 (2C), 129.0, 129.3, 138.0, 140.3, 141.2, 150.2 (*C*H=C), 152.9 (2C), 154.0 (2C), 193.7 (*C*HO).

HRMS: Calcd. for $C_{21}H_{24}O_7$: 388.15220; Found: 388.15200.

MS (EI, $C_{21}H_{24}O_7$, M = 388.41 g/mol): m/z (%) = 388.2 (100), 373.2 (19), 360.2 (16), 345.2 (60).

HRMS (EI): Calcd. for $C_{21}H_{24}O_7$: 388.15220; Found: 388.15200.

Synthesis of (*E*)-2,3-bis(4-fluorophenyl)acrylaldehyde (5i)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.18) as a colorless solid in 90% (255 mg, 1.046 mmol) yield. Mp = 109-111 °C.

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 6.92-6.98 (m_c, 2H, Ar*H*), 7.08-7.14 (m_c, 2H, Ar*H*), 7.15-7.23 (m, 4H, Ar*H*), 7.36 (s, 1H, C*H*=C), 9.74 (s, 1H, C*H*O).

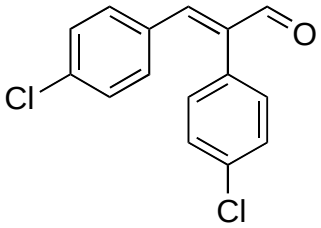
^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 116.0 (d, ^{2}J = 21.8 Hz, 2C), 116.2 (d, ^{2}J = 21.6 Hz, 2C), 128.9 (d, ^{4}J = 3.5 Hz), 130.2 (d, ^{4}J = 3.5 Hz), 131.3 (d, ^{3}J = 8.1 Hz, 2C), 132.8 (d, ^{3}J = 8.6 Hz, 2C), 140.6 (d, ^{5}J = 1.9 Hz), 149.2 (*C*H=C), 162.0 (d, ^{1}J = 80.5 Hz), 164.5 (d, ^{1}J = 85.5 Hz), 193.6 (*C*HO).

^{19}F-NMR (235.357 MHz, $CDCl_3$): δ (ppm) = −108.4 (m_c), −112.9 (m_c).

MS (APCI, $C_{15}H_{10}F_2O$, M = 244.24 g/mol): m/z (%) = 262.1 (6), 245.1 (100), 214.1 (3).

HRMS (APCI): Calcd. for $C_{15}H_{11}OF_2[M+H]^+$: 245.07780; Found: 245.07780.

Synthesis of (*E*)-2,3-bis(4-chlorophenyl)acrylaldehyde (5j)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.12) as a colorless solid in 78% (251 mg, 0.904 mmol) yield.

Mp = 108-110 °C.

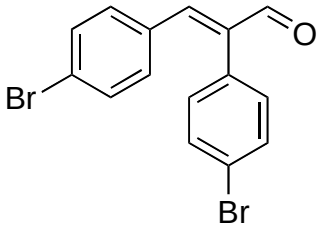
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 7.11-7.13 (m_c, 2H, Ar*H*), 7.14-7.16 (m_c, 2H, Ar*H*), 7.22-7.26 (m_c, 2H, Ar*H*), 7.35 (s, 1H, C*H*=C), 7.38-7.41 (m_c, 2H, Ar*H*), 9.74 (s, 1H, C*H*O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 129.1 (2C), 129.4 (2C), 130.9 (2C), 131.3, 131.8 (2C), 132.3, 134.7, 136.6, 141.0, 148.9 (*C*H=C), 193.2 (*C*HO).

MS (APCI, $C_{15}H_{10}Cl_2O$, M = 276.01 g/mol): m/z (%) = 277.0 (100), 214.1 (21).

HRMS (APCI): Calcd. for $C_{15}H_{11}O^{35}Cl_2[M+H]^+$: 277.01870; Found: 277.01880.

Synthesis of (*E*)-2,3-bis(4-bromophenyl)acrylaldehyde (5k)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.19) as a colorless solid in 78% (332 mg, 0.908 mmol) yield.

Mp = 108-110 °C.

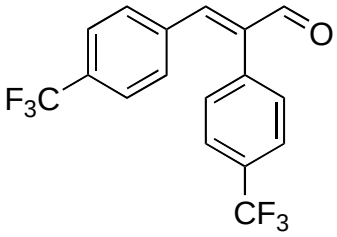
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 7.04-7.06 (m_c, 2H, Ar*H*), 7.07-7.09 (m_c, 2H, Ar*H*), 7.33 (s, 1H, C*H*=C), 7.38-7.42 (m_c, 2H, Ar*H*), 7.53-7.56 (m_c, 2H, Ar*H*), 9.74 (s, 1H, C*H*O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 123.0, 125.0, 131.1 (2H), 131.8, 132.0 (2C), 132.1 (2C), 132.3 (2C), 132.7, 141.1, 149.0 (*C*H=C), 193.1 (*C*HO).

MS (APCI, $C_{15}H_{10}Br_2O$, M = 366.05 g/mol): m/z (%) = 419.3 (8), 383.9 (10), 366.9 (100), 214.1 (12), 101.1 (32), 87.1 (28).

HRMS (APCI): Calcd. for $C_{15}H_{11}O^{79}Br_2[M+H]^+$: 364.91766; Found: 364.91780.

Synthesis of (*E*)-2,3-bis(4-(trifluoromethyl)phenyl)acrylaldehyde (5l)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.36) as a pale yellow solid in 33% (133 mg, 0.385 mmol) yield.

Mp = 56-60 °C.

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 7.27-7.34 (m_c, 4H, Ar*H*), 7.50 (s, 1H, C*H*=C), 7.51-7.55 (m_c, 2H, Ar*H*), 7.67-7.70 (m_c, 4H, Ar*H*), 9.81 (s, 1H, C*H*O).

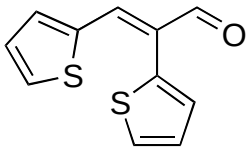
^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 123.7 (q, ^{1}J = 272.1 Hz), 124.0 (q, ^{1}J = 272.1 Hz), 125.7 (q, ^{3}J = 3.8 Hz, 2C), 126.0 (q, ^{3}J = 3.8 Hz, 2C), 130.0 (2C), 130.7 (2C), 131.0 (q, ^{2}J = 32.6 Hz), 132.0 (q, ^{2}J = 32.9 Hz), 136.4, 136.9, 142.3, 148.6 (*C*H=C), 192.7 (*C*HO).

^{19}F-NMR (235.357 MHz, $CDCl_3$): δ (ppm) = −62.7 (m_c, 3F), −63.1 (m_c, 3F).

MS (APCI, $C_{17}H_{10}F_6O$, M = 344.25 g/mol): m/z (%) = 345.1 (100), 327.1 (23), 288.0 (14), 207.0 (8), 173.0 (11), 77.0 (8).

HRMS (APCI): Calcd. for $C_{17}H_{11}OF_6[M+H]^+$: 345.07141; Found: 345.07140.

Synthesis of (*Z*)-2,3-di(thiophen-2-yl)acrylaldehyde (5m)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.15) as a pale brown solid in 82% (210 mg, 0.955 mmol) yield.

Mp = 72-74 °C.

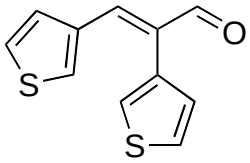
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 7.04-7.07 (m, 2H, Ar*H*), 7.18 (dd, ^{3}J = 5.1 Hz, ^{3}J = 5.1 Hz, 1H, Ar*H*), 7.38 (d, ^{3}J = 3.5 Hz, 1H, Ar*H*), 7.44 (d, ^{3}J = 5.1 Hz, 1H, Ar*H*), 7.56 (dd, ^{3}J = 5.1 Hz, ^{4}J = 1.1 Hz, 1H, Ar*H*), 7.72 (s, 1H, C*H*=C), 9.70 (s, 1H, C*H*O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 127.3, 127.8, 128.5, 129.1, 132.0, 132.3, 133.0, 135.2, 137.8, 144.1 (*C*H=C), 191.9 (*C*HO).

MS (APCI, $C_{11}H_8OS_2$, M = 220.31 g/mol): m/z (%) = 235.0 (2), 221.0 (100), 193.1 (2).

HRMS (APCI): Calcd. for $C_{11}H_9OS_2[M+H]^+$: 221.00948; Found: 221.00940.

Synthesis of (*E*)-2,3-di(thiophen-3-yl)acrylaldehyde (5n)



Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.21) as a pale brown solid in 91% (233 mg, 1.056 mmol) yield.

Mp = 72-74 °C.

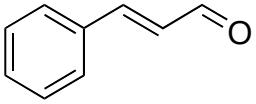
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 6.82 (ddd, ^3J = 5.1 Hz, ^4J = 1.3 Hz, ^5J = 0.4 Hz, 1H, Ar*H*), 6.98 (dd, ^3J = 4.9 Hz, ^4J = 1.3 Hz, 1H, Ar*H*), 7.21 (ddd, ^3J = 5.1 Hz, ^4J = 3.0 Hz, ^4J = 0.6 Hz, 1H, Ar*H*), 7.31 (dd, ^4J = 2.9 Hz, ^4J = 1.2 Hz, 1H, Ar*H*), 7.41 (dd, ^3J = 4.9 Hz, ^4J = 3.0 Hz, 1H, Ar*H*), 7.41 (d, ^4J = 0.6 Hz, 1H, C*H*=C), 7.43 (ddd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, ^5J = 0.4 Hz, 1H, Ar*H*), 9.70 (s, 1H, C*H*O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 125.3, 126.0, 126.2, 128.1, 128.4, 130.7, 133.0, 135.5, 136.5, 143.7 (*C*H=C), 193.4 (*C*HO).

MS (APCI, $C_{11}H_8OS_2$, M = 220.31 g/mol): m/z (%) = 238.0 (5), 229.0 (4), 221.0 (100).

HRMS (APCI): Calcd. for $C_{11}H_9OS_2[M+H]^+$: 221.00948; Found: 221.00950.

Synthesis of cinnamaldehyde (8a)

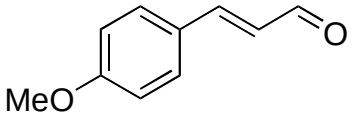


Following the **general procedure B** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 11:1, R_f = 0.31) as a colorless oil in 39% (59.8 mg, 0.453mmol) yield. The analytical data are in agreement with those reported previously.[9]

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 6.73 (dd, ^3J = 15.9 Hz, ^3J = 7.6 Hz, 1H), 7.39-7.46 (m, 3H, Ar-*H*), 7.48 (d, ^3J = 15.9 Hz, 1H), 7.54-7.60 (m, 2H, Ar-*H*), 9.71 (d, ^3J = 7.6 Hz, 1H, C*H*O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 128.6, 128.7 (2C), 129.2 (2C), 131.4, 134.1, 152.8, 193.8 (*C*HO).

Synthesis of (*E*)-3-(4-methoxyphenyl)acrylaldehyde (8b)

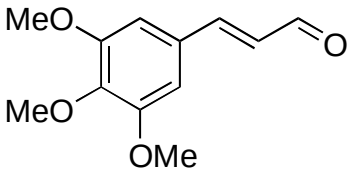


Following the **general procedure B** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.29) as a colorless oil in 45% (84.5 mg, 0.522 mmol) yield. The analytical data are in agreement with those reported previously.[10]

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 3.86 (s, 3H, OC*H*$_3$), 6.60 (dd, ^3J = 16.0 Hz, ^3J = 7.6 Hz, 1H), 6.94 (m$_c$, 2H, Ar*H*), 7.42 (d, ^3J = 16.0 Hz, 1H), 7.52 (m$_c$, 2H, Ar*H*), 9.64 (d, ^3J = 7.6 Hz, 1H, C*H*O).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ (ppm) = 55.5 (O*C*H$_3$), 114.5 (2C), 126.5, 128.7, 130.3 (2C), 152.7, 162.2, 193.7 (*C*HO).

Synthesis of (*E*)-3-(3,4,5-trimethoxyphenyl)acrylaldehyde (8c)



Following the **general procedure B** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 1:1, R_f = 0.42) as a pale yellow solid in 62% (161.1 mg, 0.725 mmol) yield. The analytical data are in agreement with those reported previously.[11]

Mp = 108-110 °C.

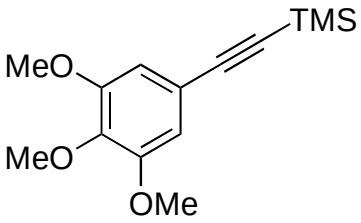
^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 3.89 (s, 9H, 3×OC*H*$_3$), 6.63 (dd, ^3J = 15.9 Hz, ^3J = 7.7 Hz, 1H), 6.79 (s, 2H, Ar*H*), 7.39 (d, ^3J = 15.9 Hz, 1H), 9.67 (d, ^3J = 7.7 Hz, 1H, C*H*O).

^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 56.3 (2C, O*C*H$_3$), 61.1 (O*C*H$_3$), 105.8 (2C), 128.0, 129.5, 141.1, 152.7, 153.6 (2C), 193.4 (*C*HO).

MS (EI, $C_{12}H_{14}O_4$, M = 222.24 g/mol): m/z (%) = 222.2 (100), 207.1 (8), 191.1 (29), 180.1 (8), 179.1 (77), 151.1 (26), 136.1 (13), 121.1 (9), 91.1 (8).

HRMS (EI): Calcd. for $C_{12}H_{14}O_4$: 222.08921; Found: 222.08920.

Synthesis of Trimethyl((3,4,5-trimethoxyphenyl)ethynyl)silane (10)



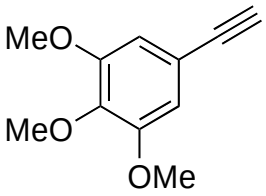
To a solution of 5-iodo-1,2,3-trimethoxybenzene (**9**) (5.00 g, 17.00 mmol, 1.0 equiv.) in THF (75 ml) $PdCl_2(PPh_3)_2$ (119.3 mg, 0.170 mmol, 0.01 equiv.), CuI (32.4 mg, 0.170 mmol, 0.01 equiv.) and dry HN^iPr_2 (7.2 ml, 5.16 g, 51.00 mmol, 3.0 equiv.) were added. The reaction flask was then packed in aluminum foil and ice-chilled trimethylsilylacetylene (2.6 ml, 1.84 g, 18.70 mmol, 1.05 equiv.) was added by syringe. After stirring for 1 h at room temperature the reaction mixture was quenched by addition of 5%-aqueous disodium EDTA solution (40 ml) and ^{t}BuOMe (40 ml). The aqueous phase was extracted with ^{t}BuOMe (2 × 40 ml) and the combined organic layers were washed with brine (40 ml), dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (PE/EtOAc, 10:1, R_f = 0.25) yielded the desired compound **10** (4.14 g, 15.65 mmol, 92%) as a pale brown solid.

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 0.25 (s, 9H, (SiCH_3)), 3.83 (s, 3H, OCH_3), 3.84 (s, 6H, 2×OCH_3), 6.70 (s, 2H, ArH).

^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 0.1 (3C, Si(CH$_3$)), 56.2 (2C, OCH$_3$), 61.0 (OCH$_3$), 93.2, 105.2, 109.3 (2C), 118.1, 139.2, 153.0 (2C).

The analytical data are in agreement with those reported previously.[12]

Synthesis of 5-ethynyl-1,2,3-trimethoxybenzene (7c)



To a solution of trimethyl((3,4,5-trimethoxyphenyl)ethynyl)silane (**10**) (3.96 g, 14.98 mmol, 1.0 equiv.) in MeOH (50 ml), K_2CO_3 (7.46 g, 53.96 mmol, 3.6 equiv.) was added and the reaction mixture was stirred for 3 h (TLC-control) at room temperature. Subsequently, water (40 ml) was added and the mixture was stirred for further 10 min. After dilution of the reaction mixture with ^{t}BuOMe (40 ml) the aqueous phase was separated and extracted with ^{t}BuOMe (3 × 30 ml). The combined organic layers were washed with brine (30 ml), dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (PE/EtOAc, 10:1, R_f = 0.23) yielded the desired compound **7c** (2.57 g, 14.50 mmol, 97%) as a pale yellow solid.

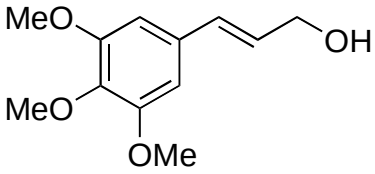
Mp = 70-71 °C.

^{1}H-NMR (400.130 MHz, $CDCl_3$): δ (ppm) = 3.01 (s, 1H, CC*H*), 3.83 (s, 3H, OCH_3), 3.84 (s, 6H, 2×OCH_3), 6.71 (s, 2H, Ar*H*).

^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 56.2 (2C, O*C*H_3), 61.0 (O*C*H_3), 76.0, 83.6, 109.3 (2C), 117.1, 139.2, 153.7 (2C).

The analytical data are in agreement with those reported previously.[13]

Synthesis of (*E*)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-ol (11)

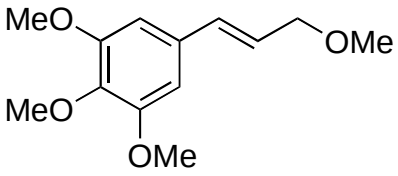


A solution of (*E*)-3-(3,4,5-trimethoxyphenyl)acrylaldehyde (**8c**) (100 mg, 0.450 mmol, 1.0 equiv.) in MeOH (3.5 ml) and CH_2Cl_2 (1.5 ml) was cooled to 0 °C followed by successive addition of $CeCl_3$•$7H_2O$ (83.8 mg, 0.225 mmol, 0.5 equiv.) and $NaBH_4$ (30.6 mg, 0.810 mmol, 1.8 equiv.). The reaction mixture was stirred at 0 °C for 1.5 h, subsequently quenched by addition of saturated aqueous NH_4Cl solution (3 ml) and diluted with CH_2Cl_2 (3 ml). The aqueous phase was separated and extracted with CH_2Cl_2 (3 × 3 ml). The combined organic layers were washed with brine (5 ml), dried over Na_2SO_4 and concentrated in vacuo. Filtration through a plug of silica gel yielded desired compound **11** (87.7 mg, 0.391 mmol, 87%) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.85 (s, 3H, OCH_3), 3.87 (s, 6H, 3×OCH_3), 4.32 (dd, ^{3}J = 5.6 Hz, ^{4}J = 1.5 Hz, 2H, H1) 5.29 (s, 1H, O*H*), 6.28 (dt, ^{3}J = 16.0 Hz, ^{3}J = 5.6 Hz, 1H, H2), 6.55 (d, ^{3}J = 16.0 Hz, 1H), 6.62 (s, 2H, Ar*H*).

The analytical data are in agreement with those reported previously.[14]

Synthesis of (*E*)-1,2,3-trimethoxy-5-(3-methoxyprop-1-en-1-yl)benzene (Boropinol B)



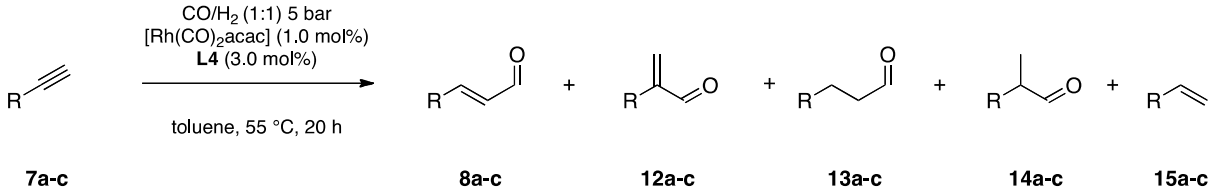
The solution of (*E*)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-ol (**11**) (80 mg, 0.357 mmol 1.0 equiv.) in THF (2.5 ml) was cooled to 0 °C and NaH (10.3 mg, 0.428 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at 0 °C for 1 h before adding MeI (29 µl, 65.8 mg, 0.463 mmol, 1.3 eq). The reaction mixture was allowed to warm to room temperature and stirred at this temperature for further 4 h. H_2O (3 ml) was added, and the solution was extracted with ^{t}BuOMe (3 × 3 ml). Combined organic layers were washed with brine (4 ml), dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (PE/EtOAc, 5:1, R_f = 0.3) yielded the desired compound **Boropinol B** (78.2 mg, 0.328 mmol, 92%) as a pale yellow oil.

The analytical data are identical to those reported for Boropinol B isolated from natural sources.[15]

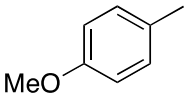
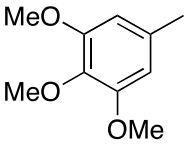
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.38 (s, 3H, OC*H*$_3$), 3.83 (s, 3H, ArOC*H*$_3$) 3.86 (s, 6H, 2×ArOC*H*$_3$), 4.07 (dd, ^3J = 6.0 Hz, ^4J = 1.4 Hz, 2H) 6.19 (dt, ^3J = 15.9 Hz, ^3J = 6.0 Hz, 1H), 6.53 (dt, ^3J = 15.9 Hz, ^4J = 1.4 Hz, 1H), 6.61 (s, 2H, Ar*H*).

^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 56.1 (2C, ArOCH_3), 58.1 (OCH_3), 60.9 (ArOCH_3), 73.0, 103.6 (2C), 125.6, 132.4, 138.0, 153.4 (2C).

Product ratios in the hydroformylation of terminal alkynes[a]



7a-c **8a-c** **12a-c** **13a-c** **14a-c** **15a-c**

Entry	R	Conv. (%)	8 : 12 : 13 : 14 : 15[b]
1	Ph	85	49 : 10 : 10 : 19 : 12
2		92	53 : 26 : 2 : 14 : 5
3		100	64 : 7 : 8 : 12 : 9

[a] Reaction conditions: CO/H_2 (1:1) 5 bar, $[Rh(CO)_2acac]$/**L4**/7a-c = 1/3/100 in 2 ml toluene, c_0(**7a-c**) = 0.6 M, 20 h at 55 °C.

[b] The conversion and product ratio were determined by GC and ^{1}H-NMR spectroscopy.

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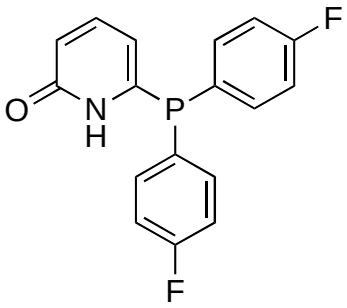
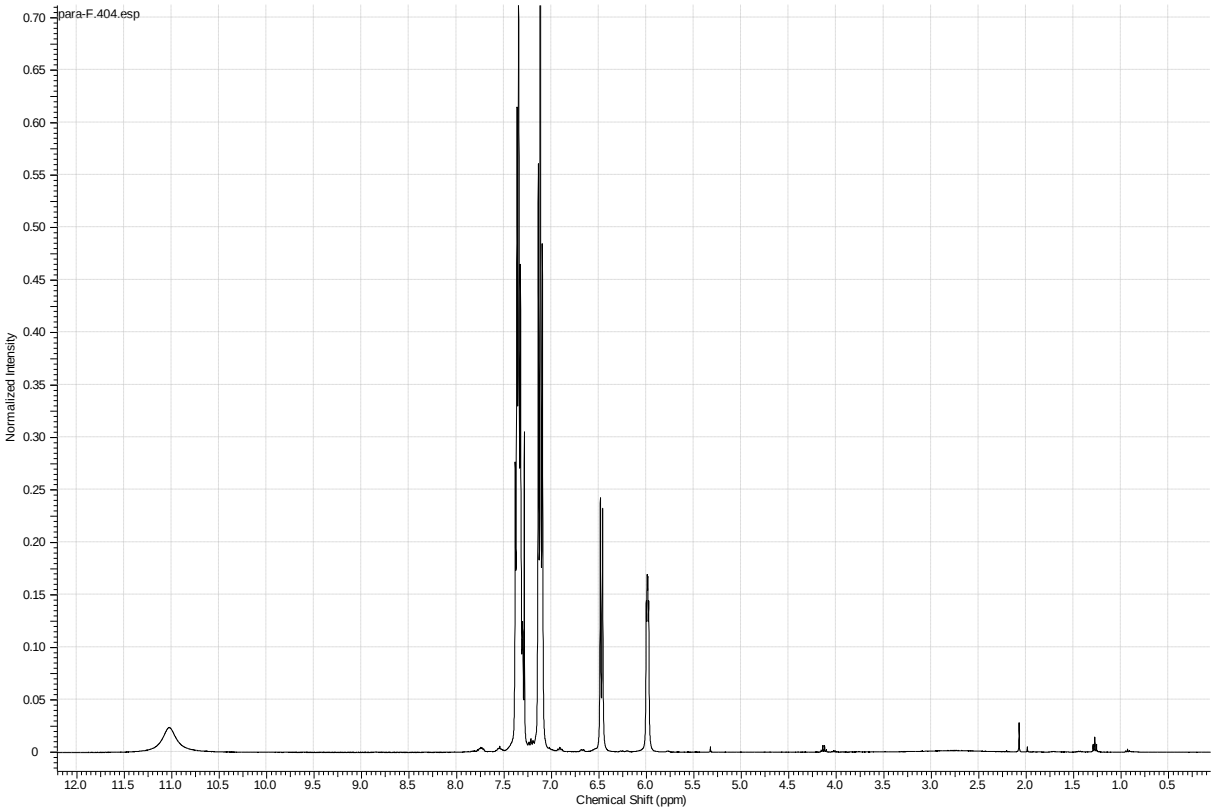
Appendix I

L2



^{1}H-NMR



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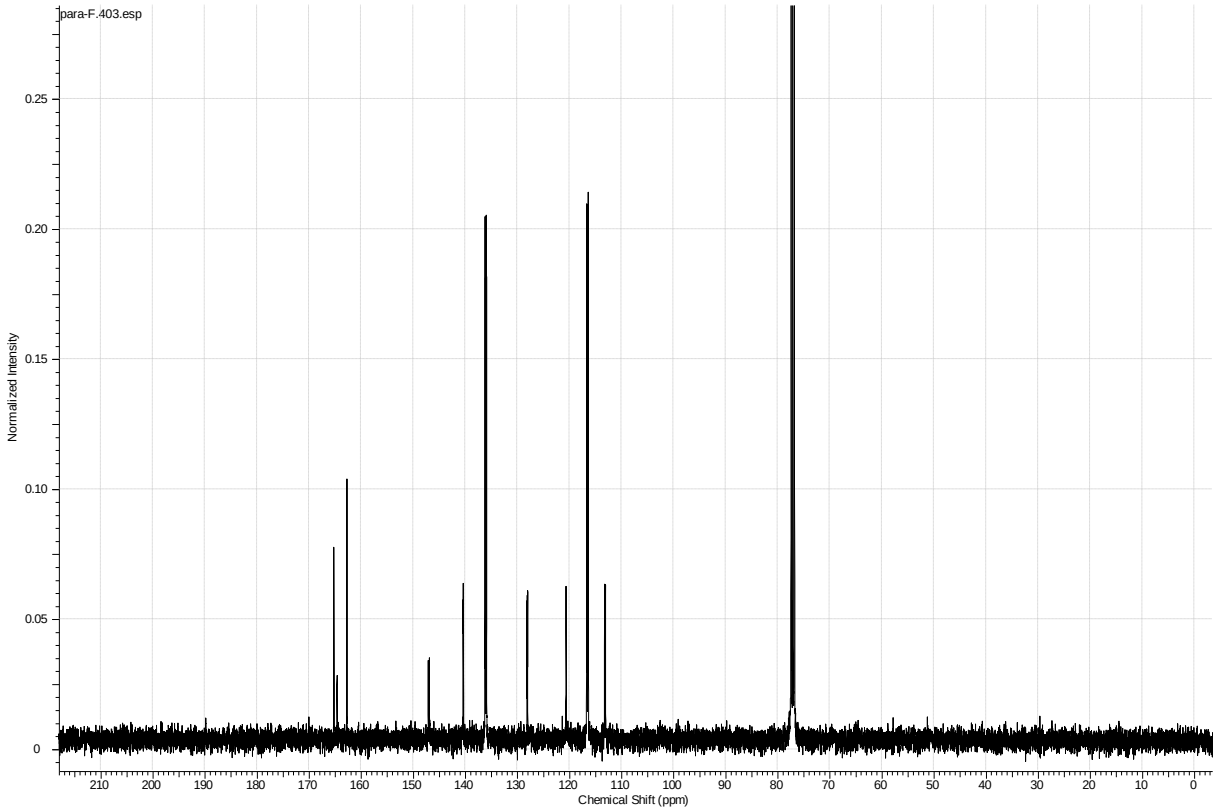

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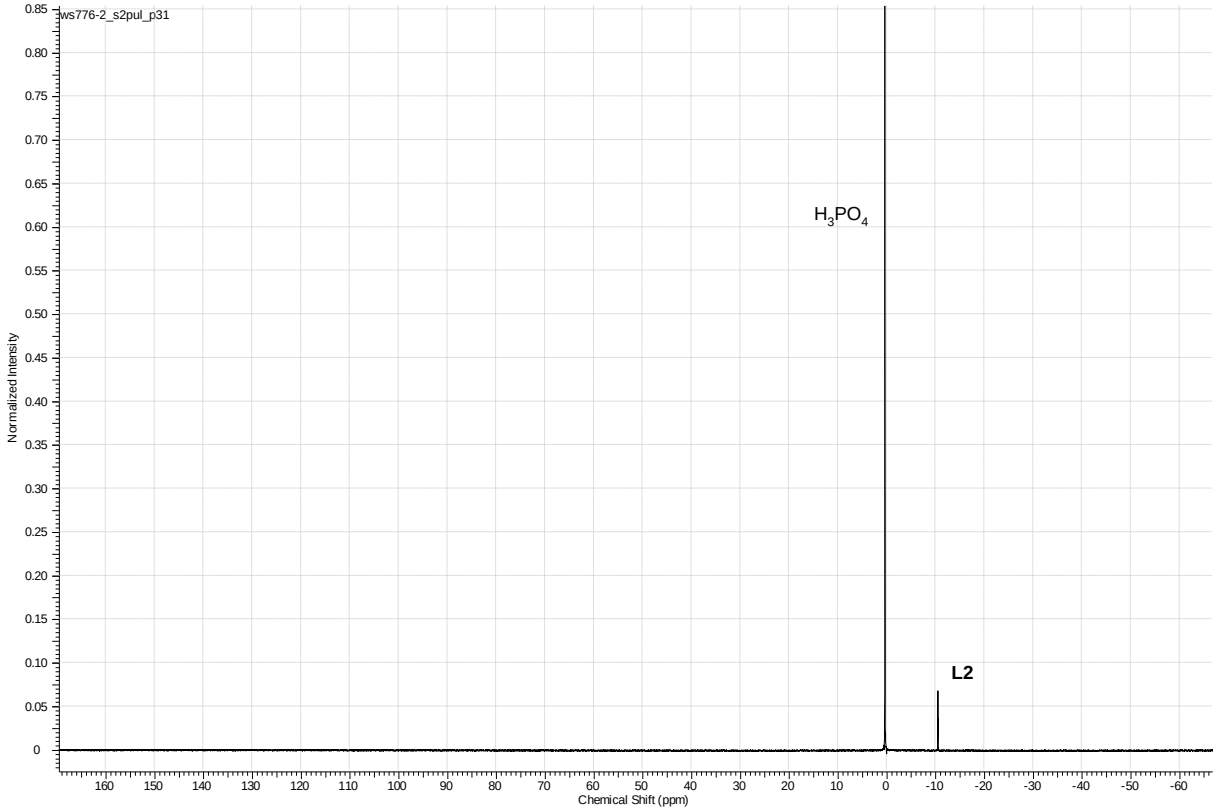
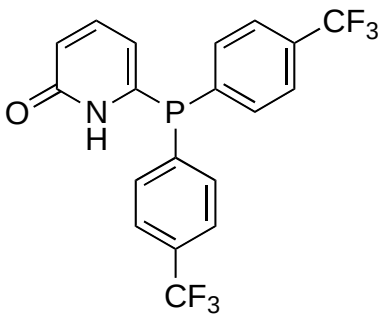
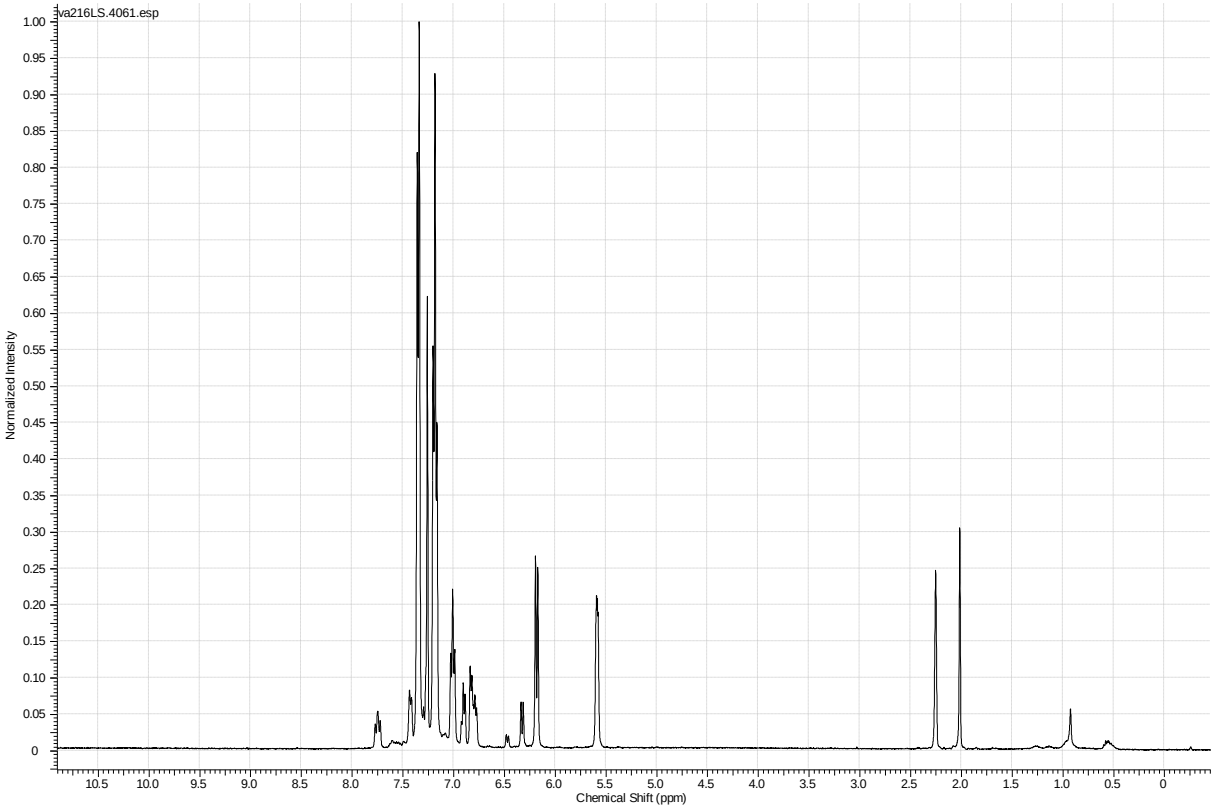


L3


CF3
O
N
H
P
CF3

^{1}H-NMR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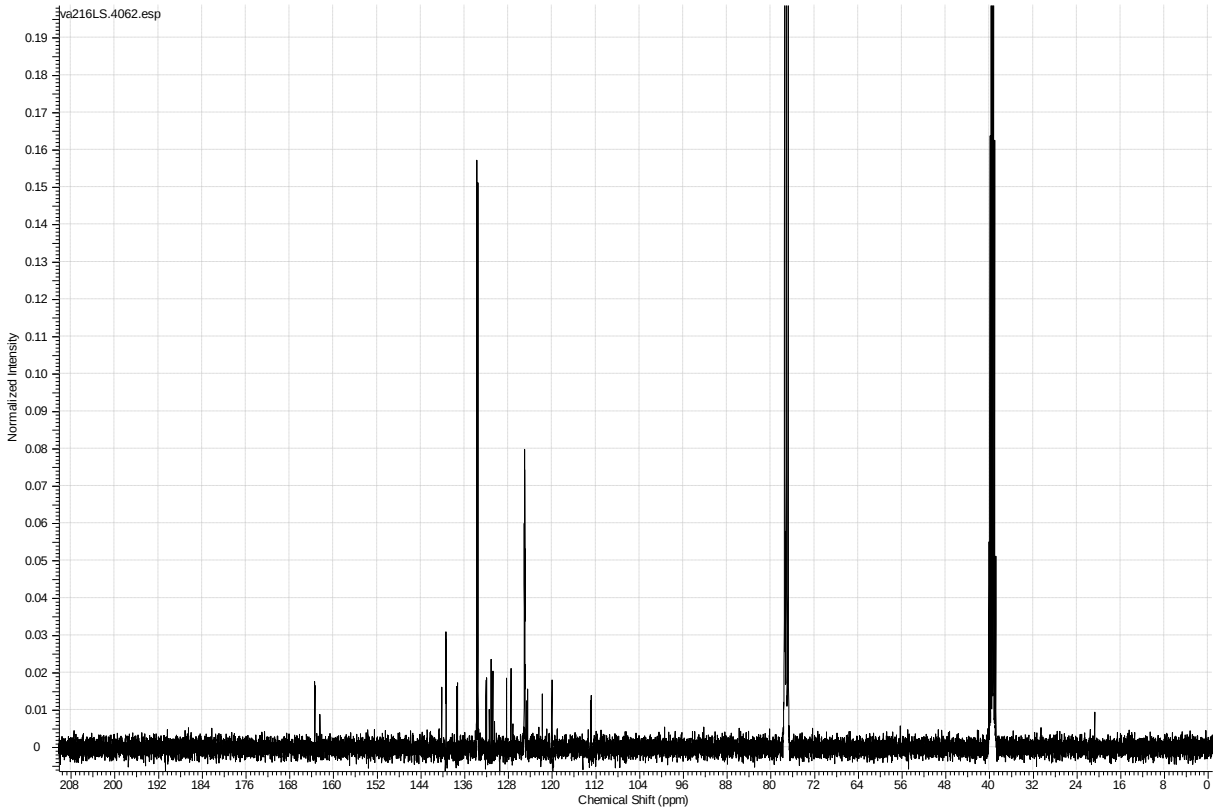
Normalized Intensity
Chemical Shift (ppm)

^{13}C-NMR



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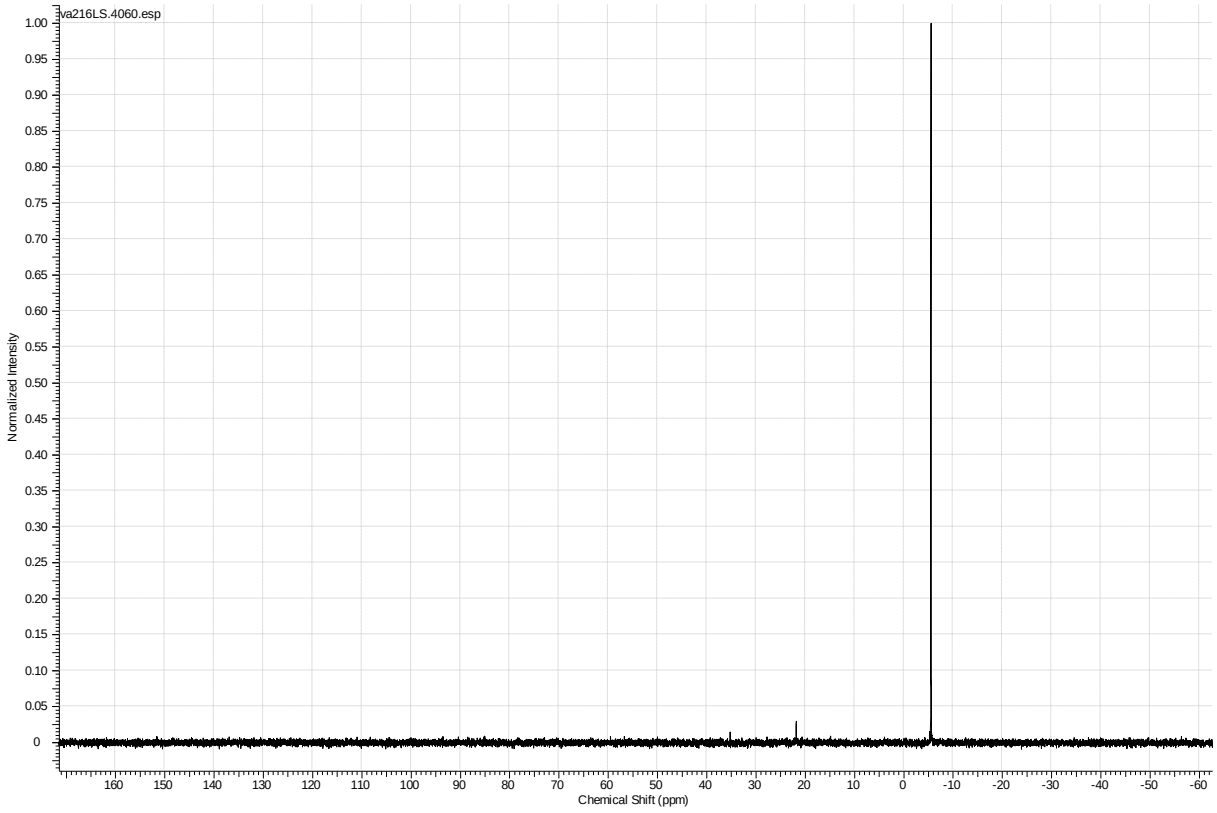
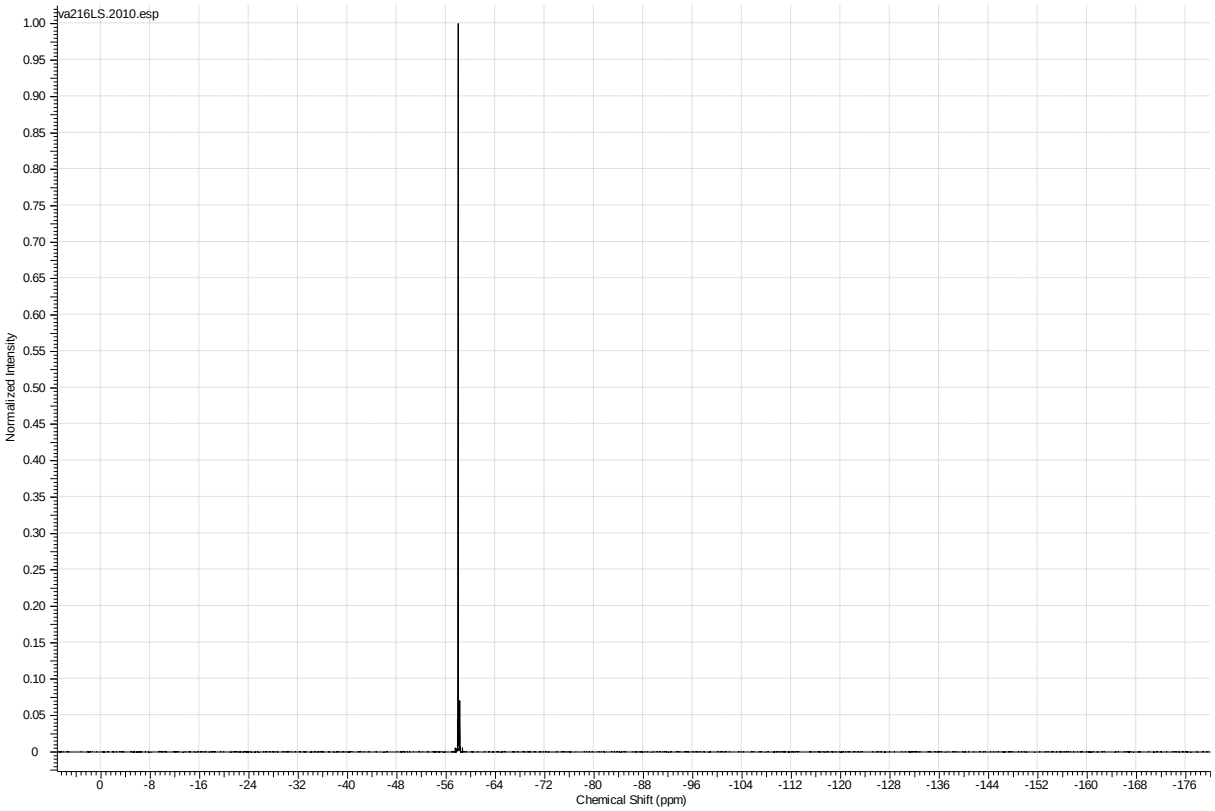


^{19}F-NMR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Normalized Intensity
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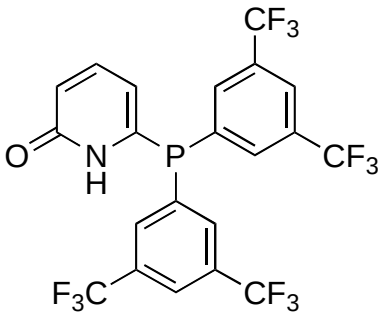
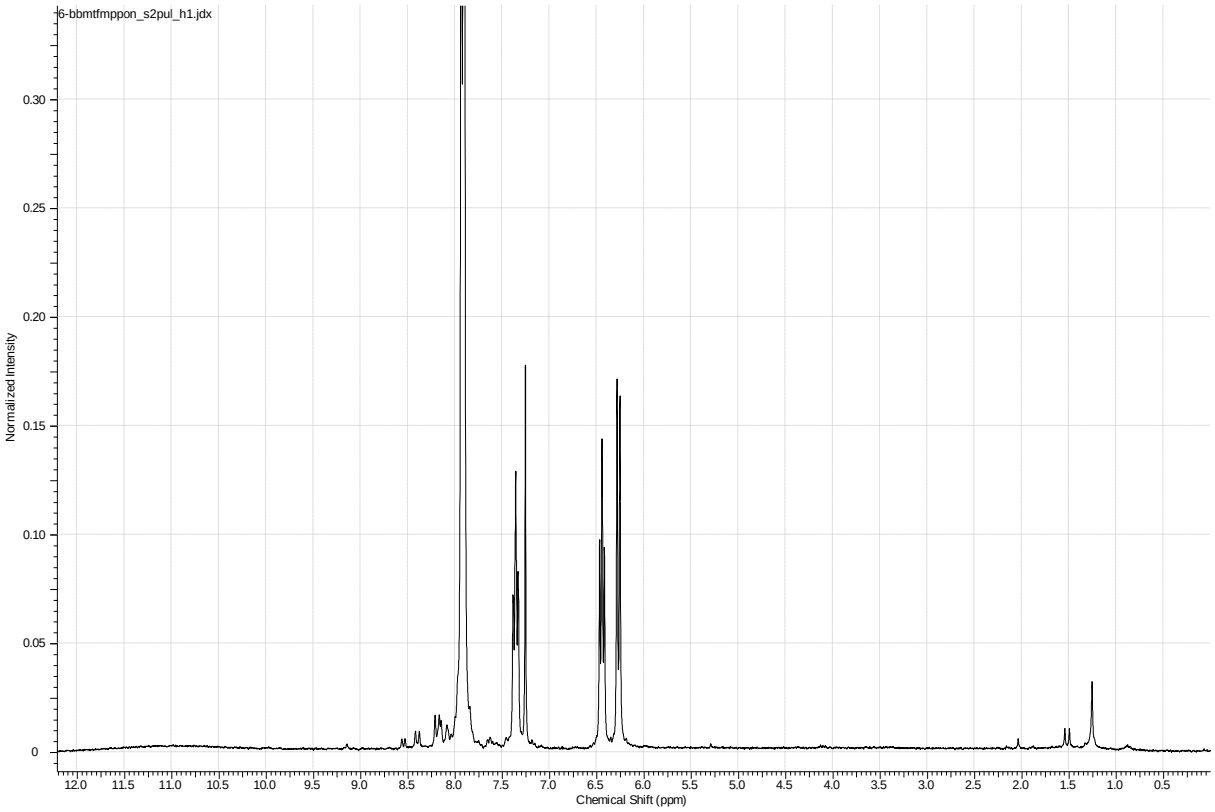
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
0 -8 -16 -24 -32 -40 -48 -56 -64 -72 -80 -88 -96 -104 -112 -120 -128 -136 -144 -152 -160 -168 -176
Chemical Shift (ppm)

L4


CF3
O
N
H
P
CF3
F3C
CF3

^{1}H-NMR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Normalized Intensity
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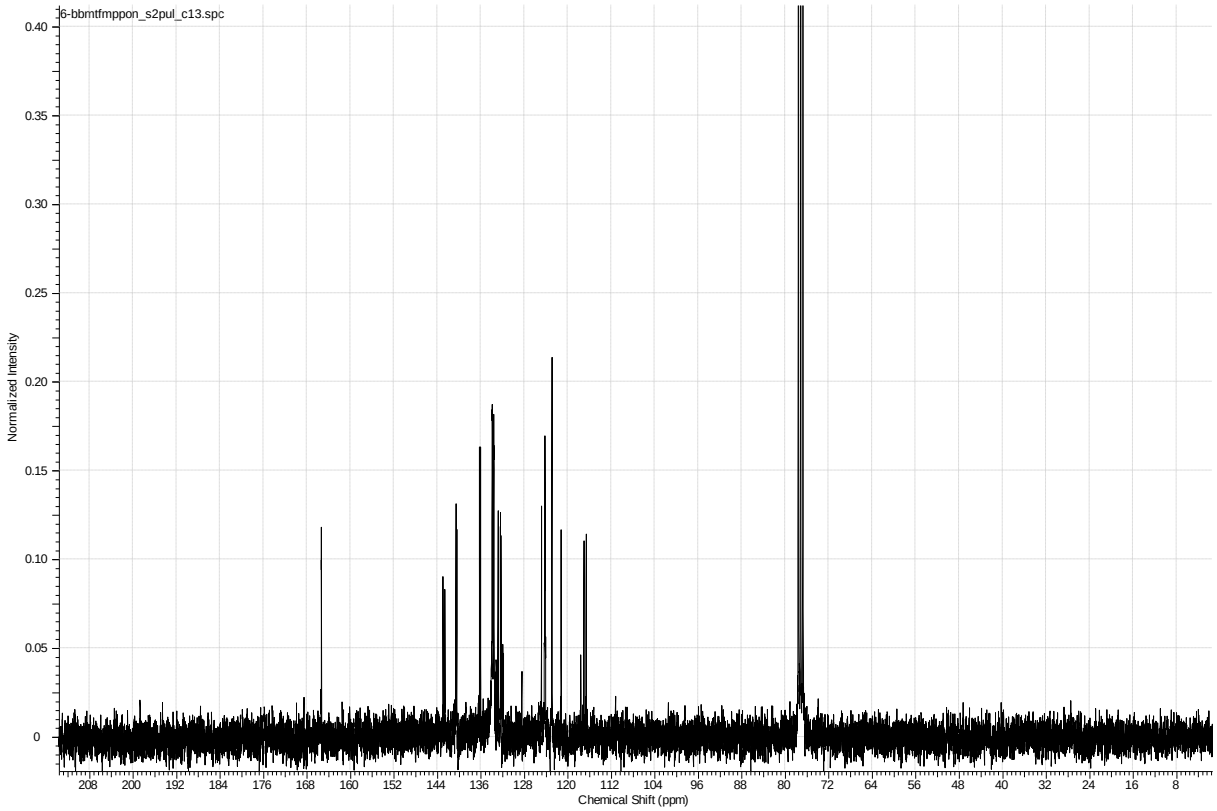
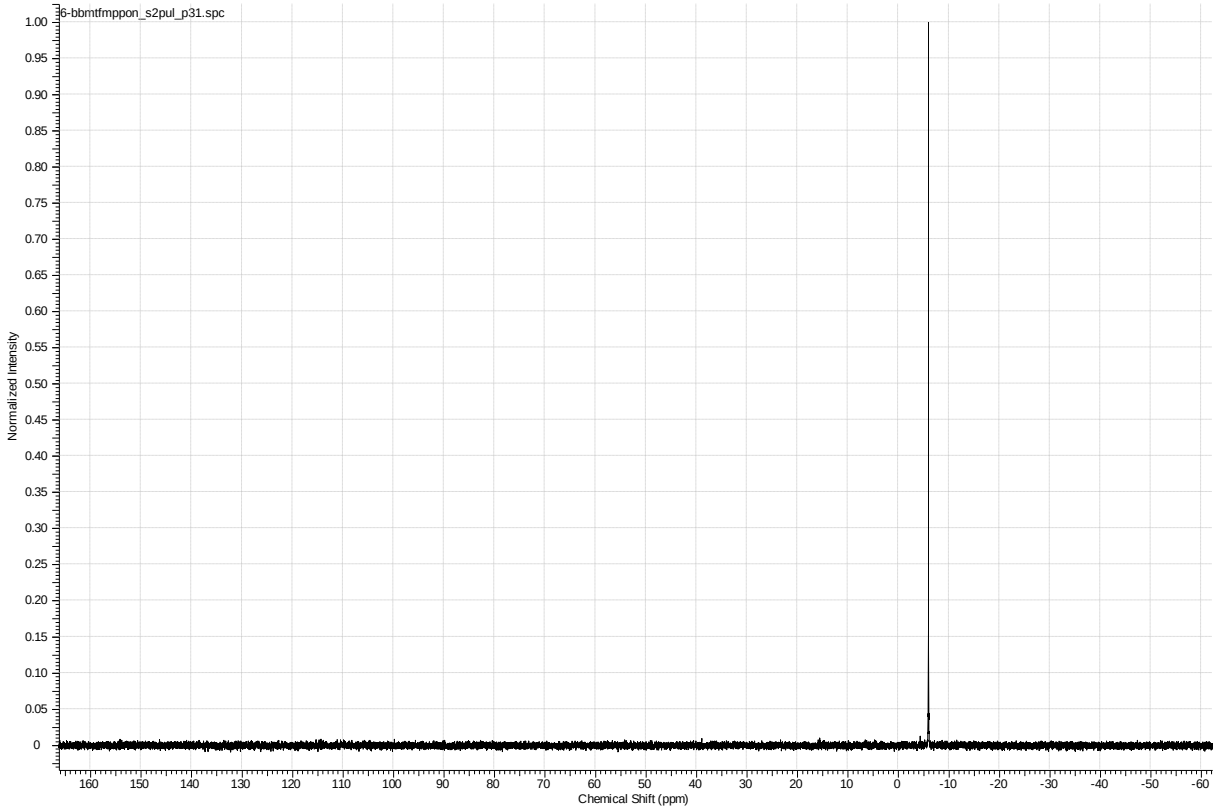
0.20
0.15
0.10
0.05
0
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

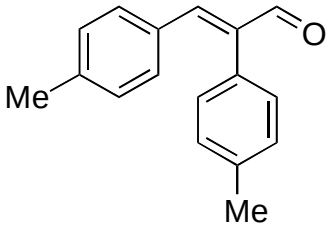
^{13}C-NMR



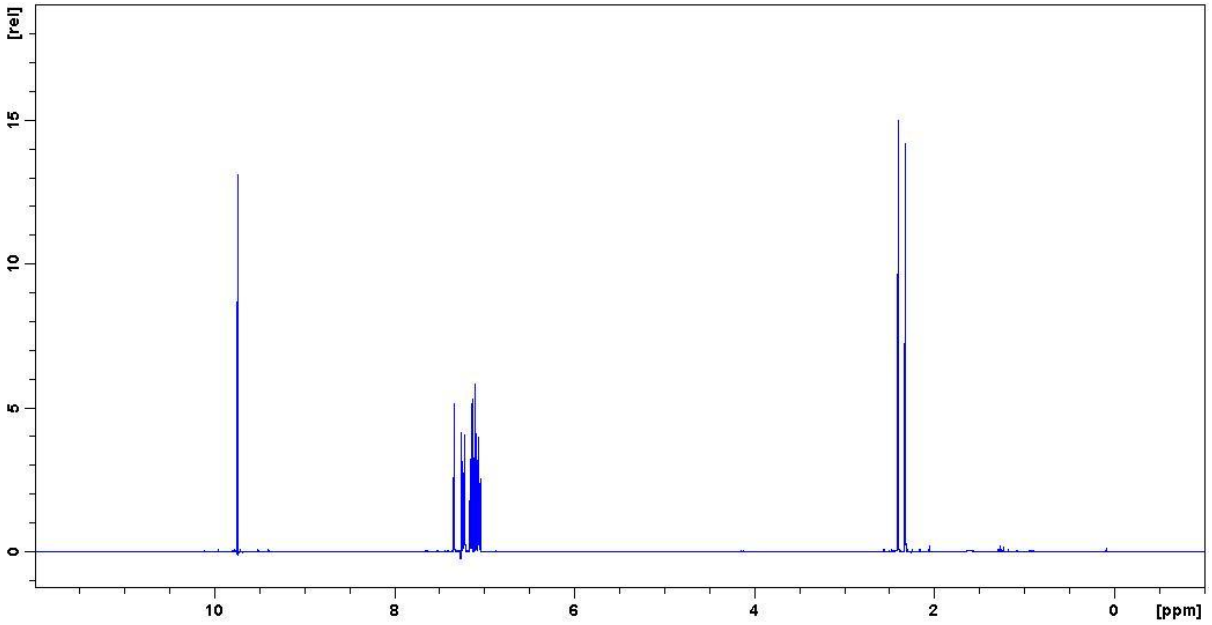
^{31}P-NMR



5b



^{1}H-NMR



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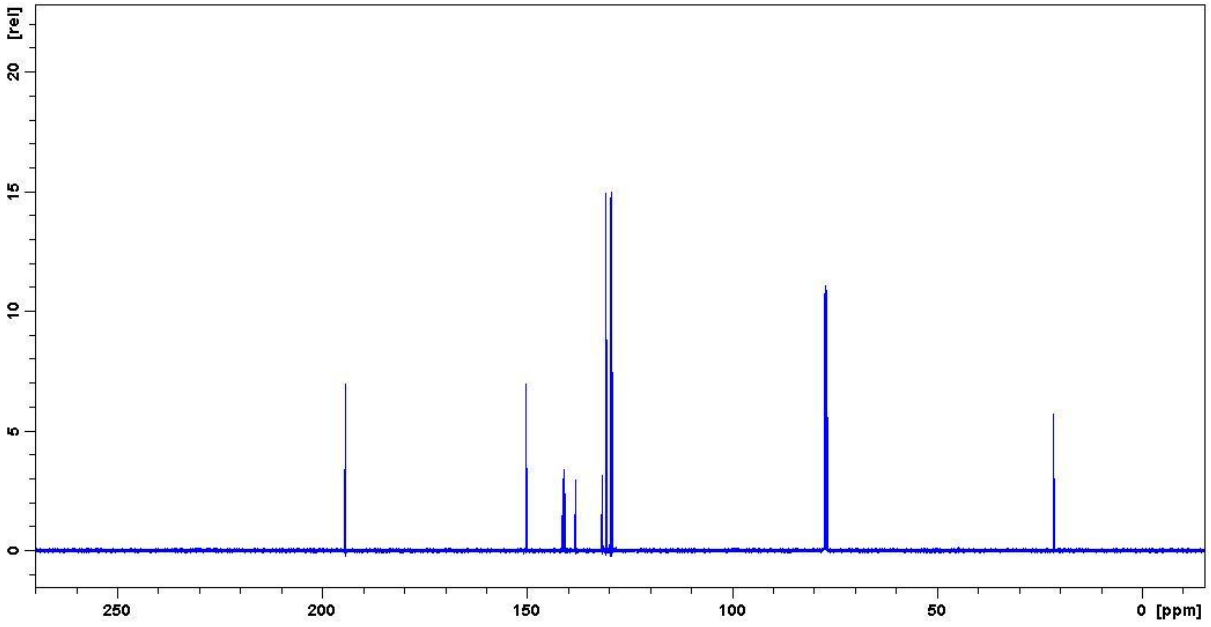

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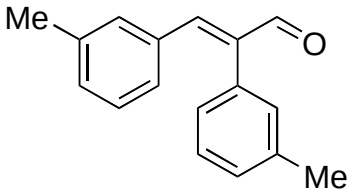

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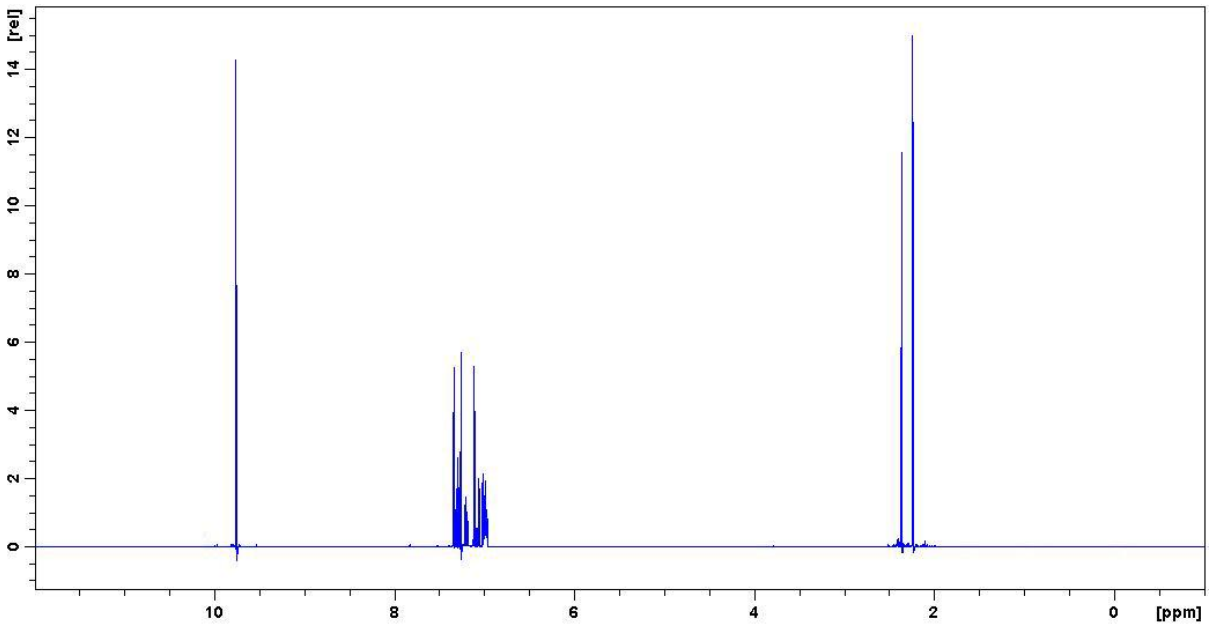

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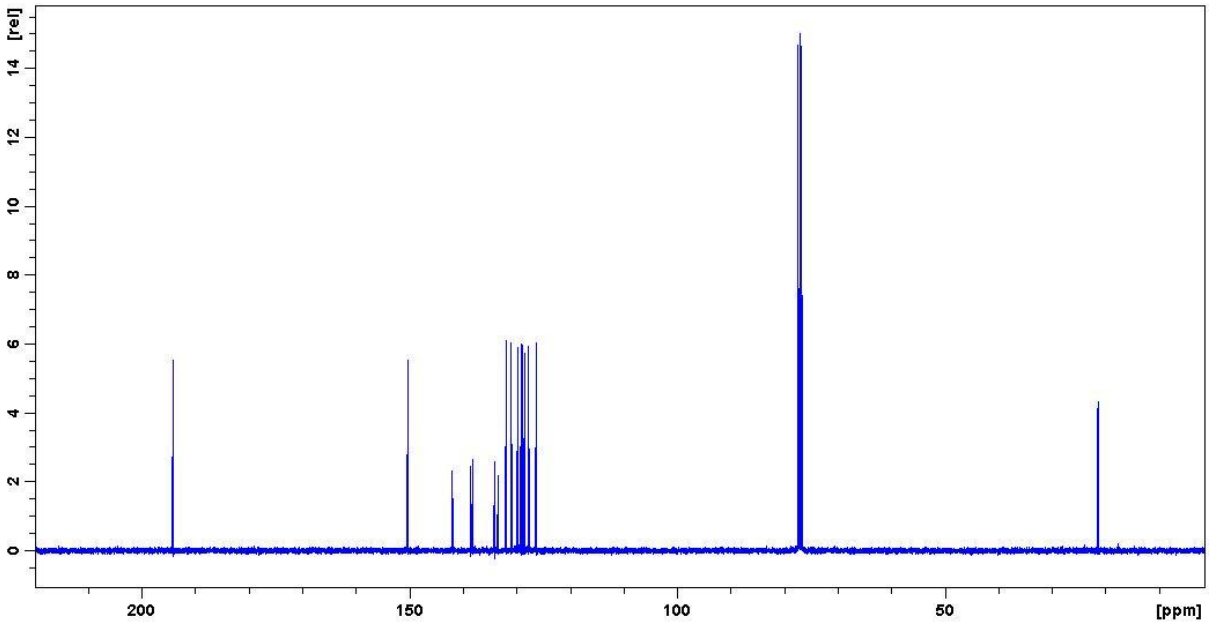

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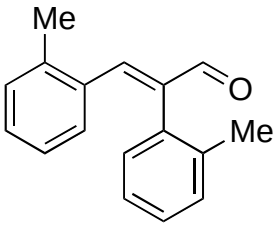

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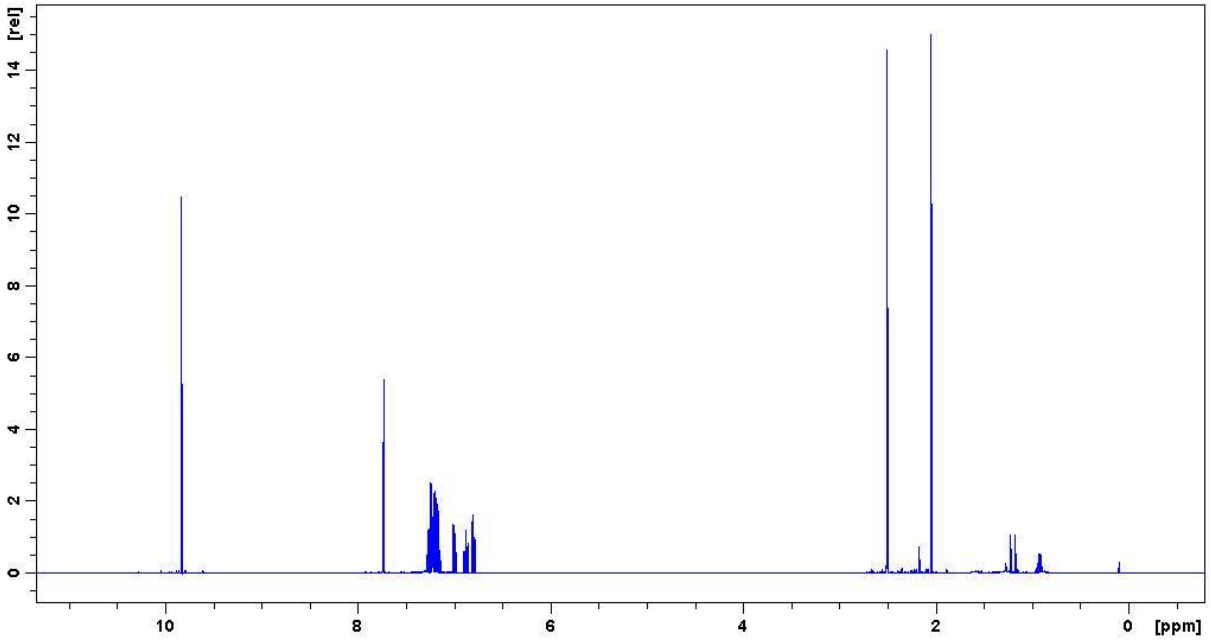

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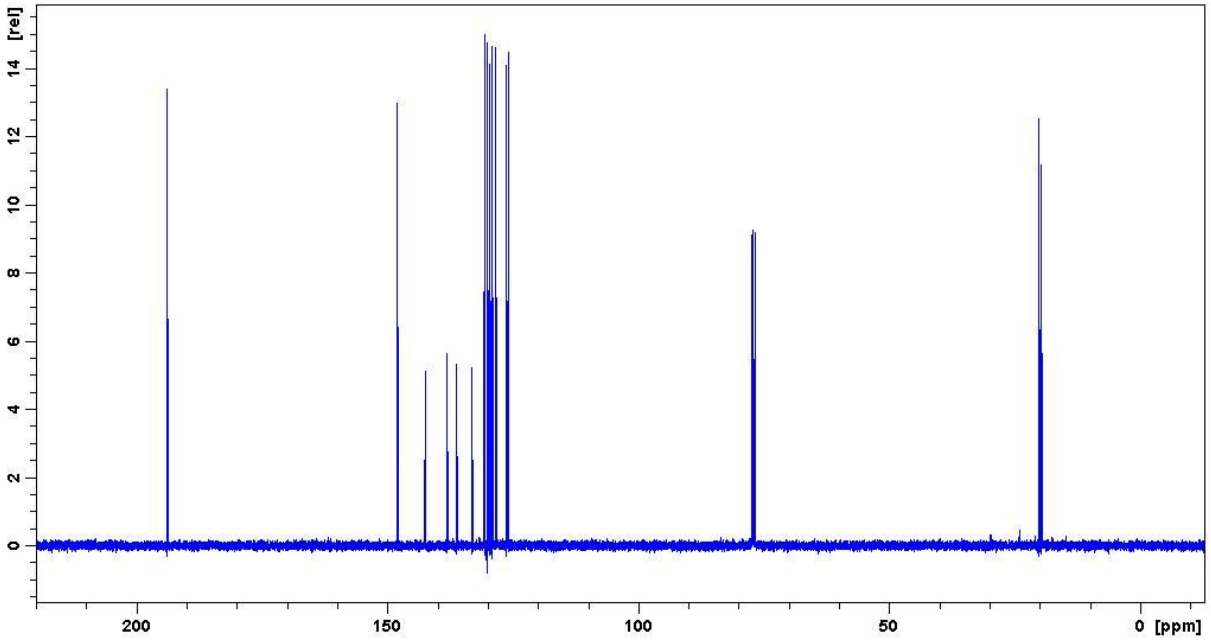

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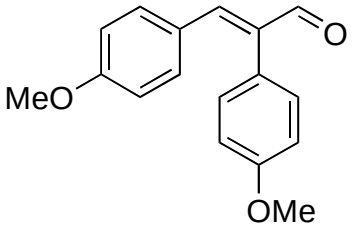

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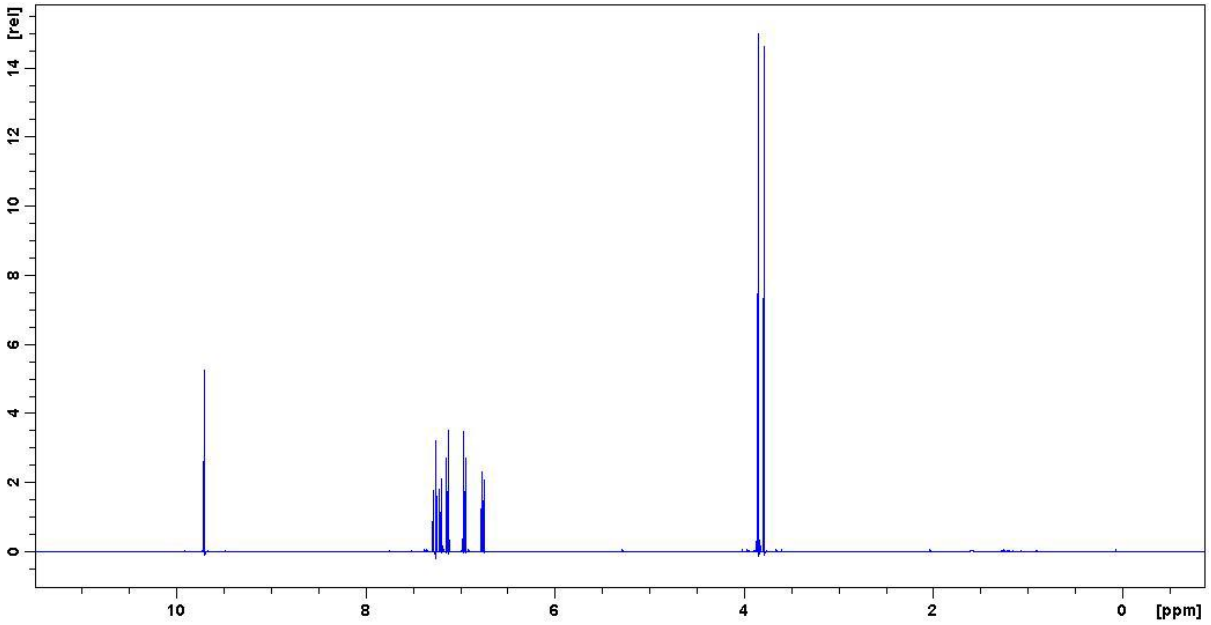

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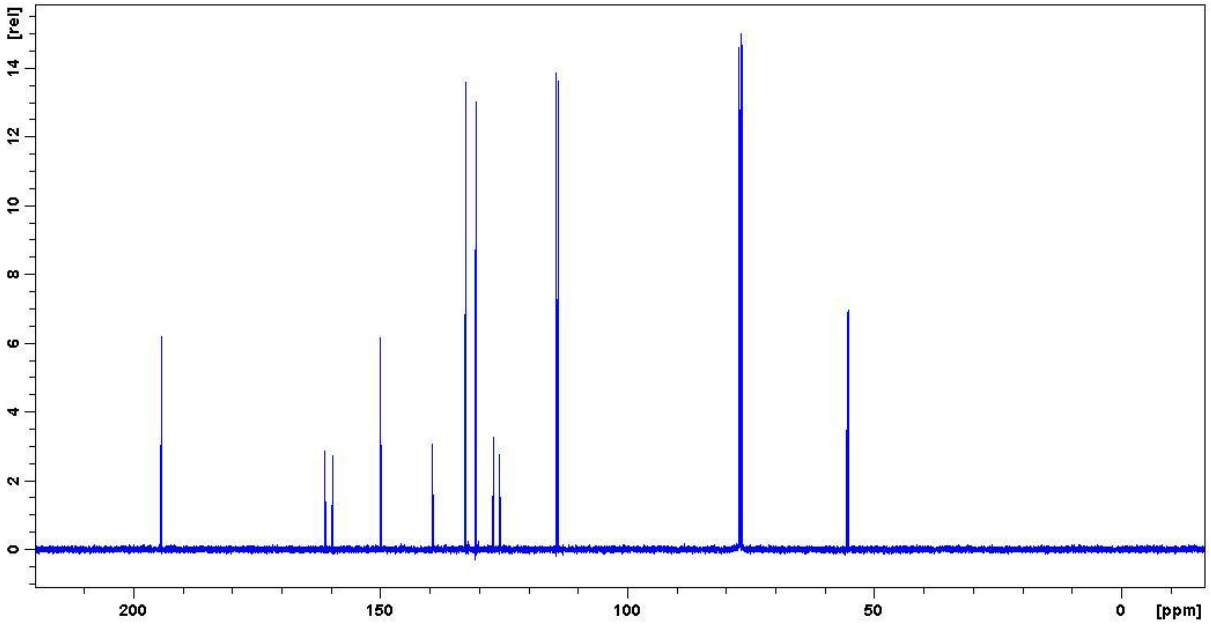

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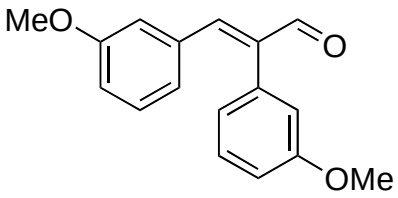

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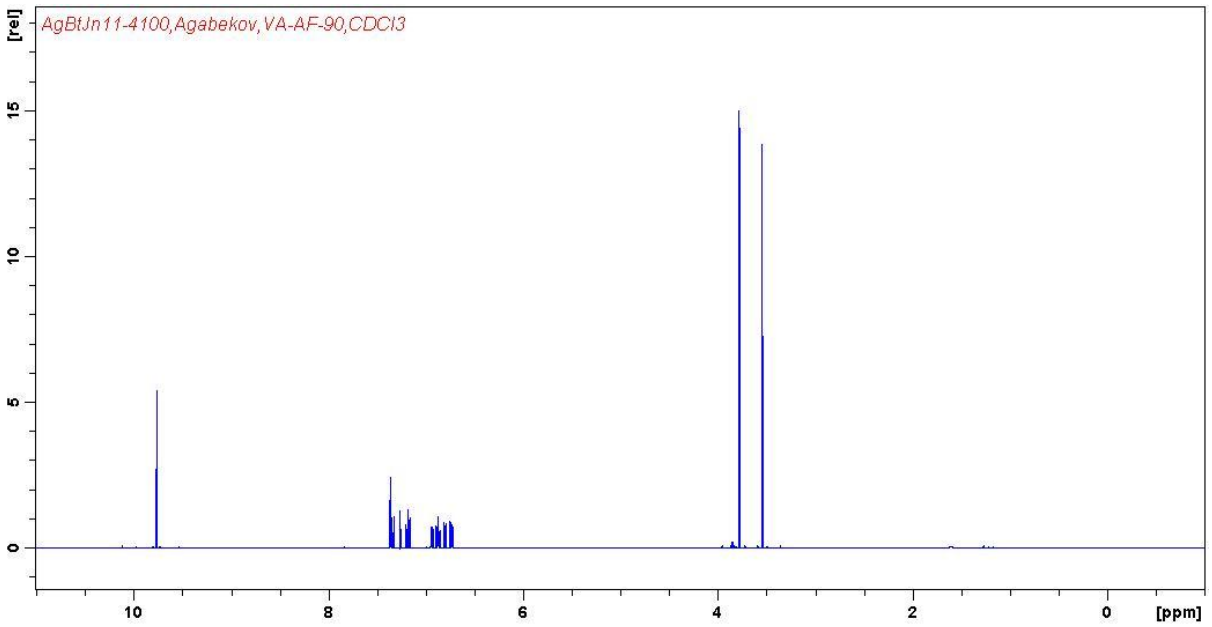

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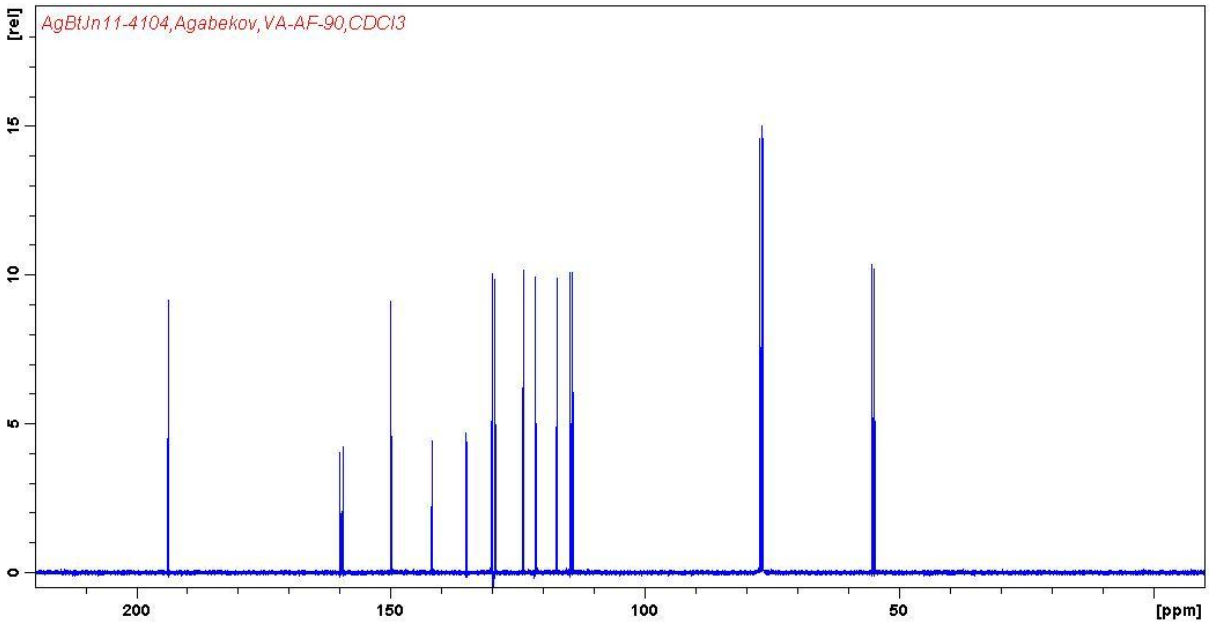

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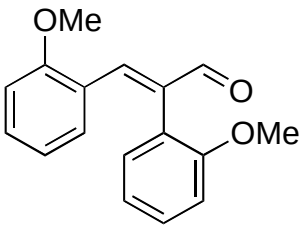
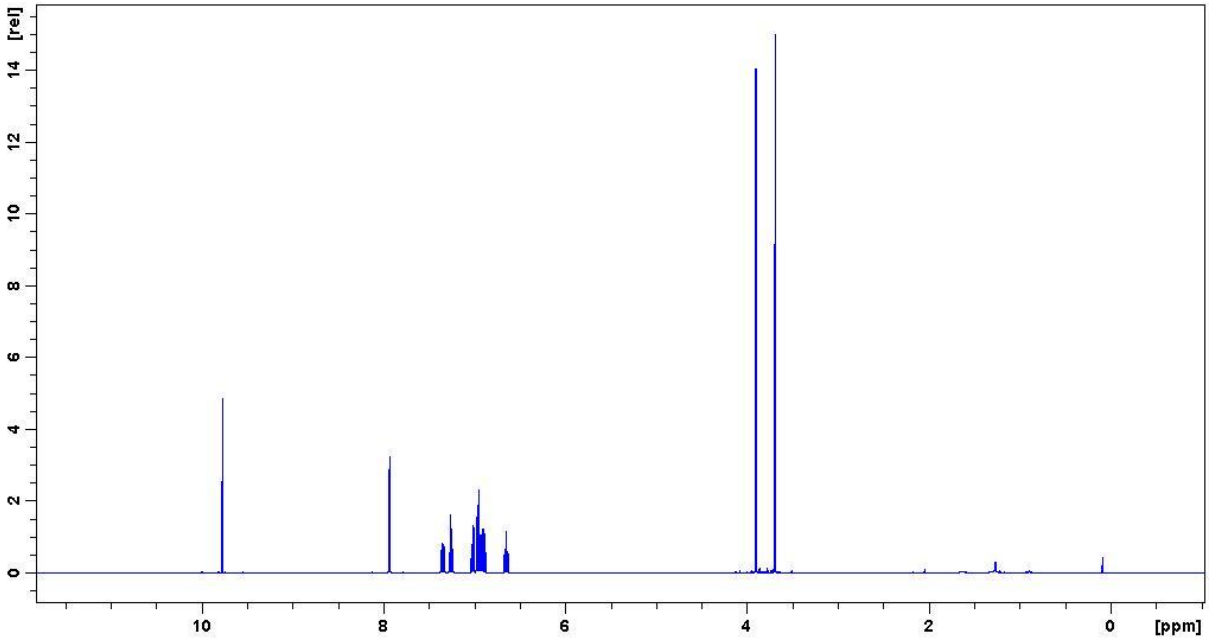
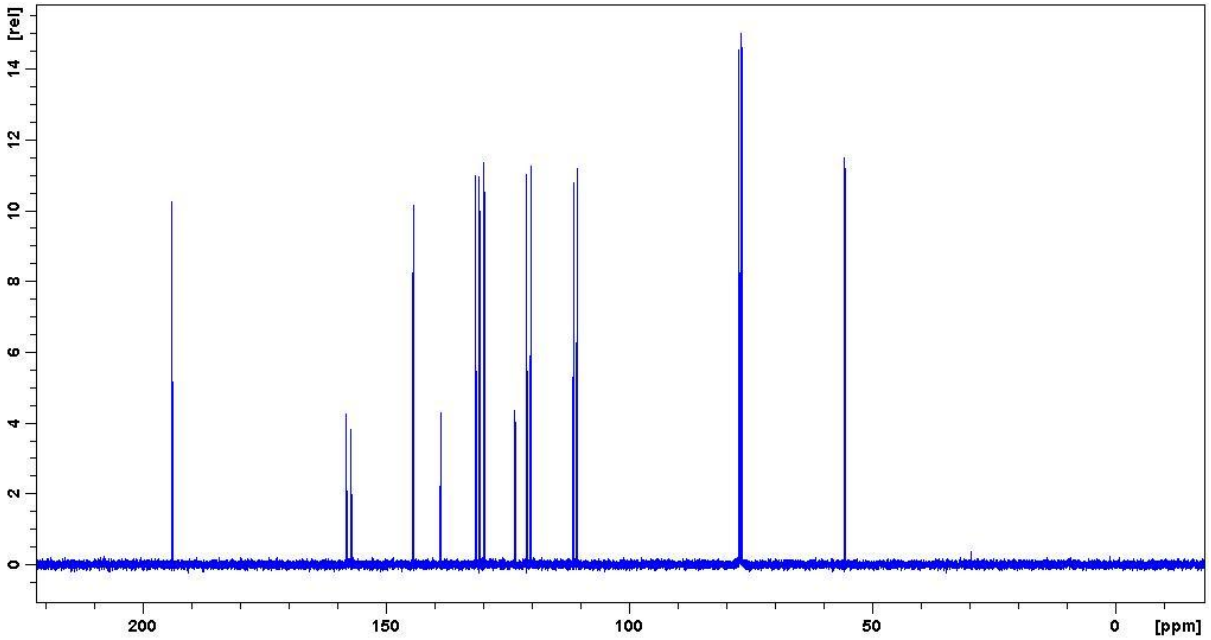


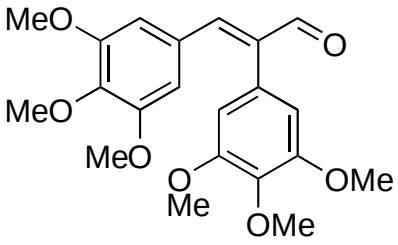
^{1}H-NMR



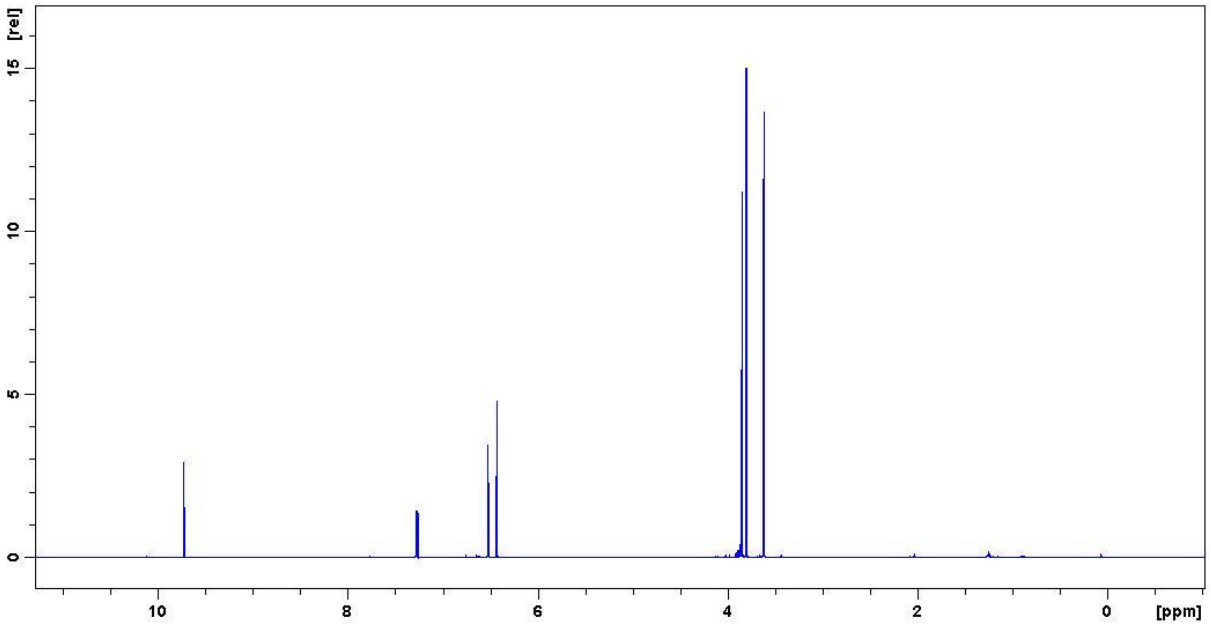
^{13}C-NMR



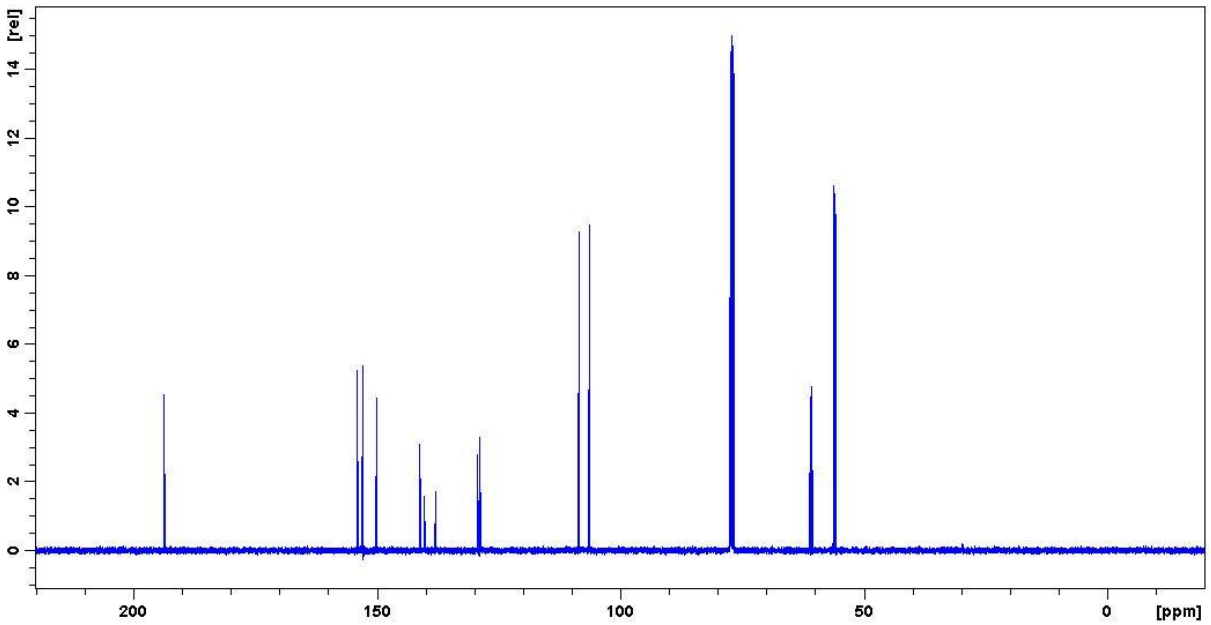
5h



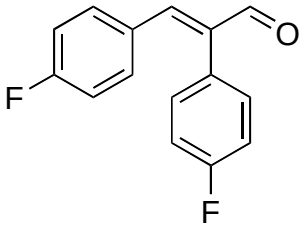
^{1}H-NMR



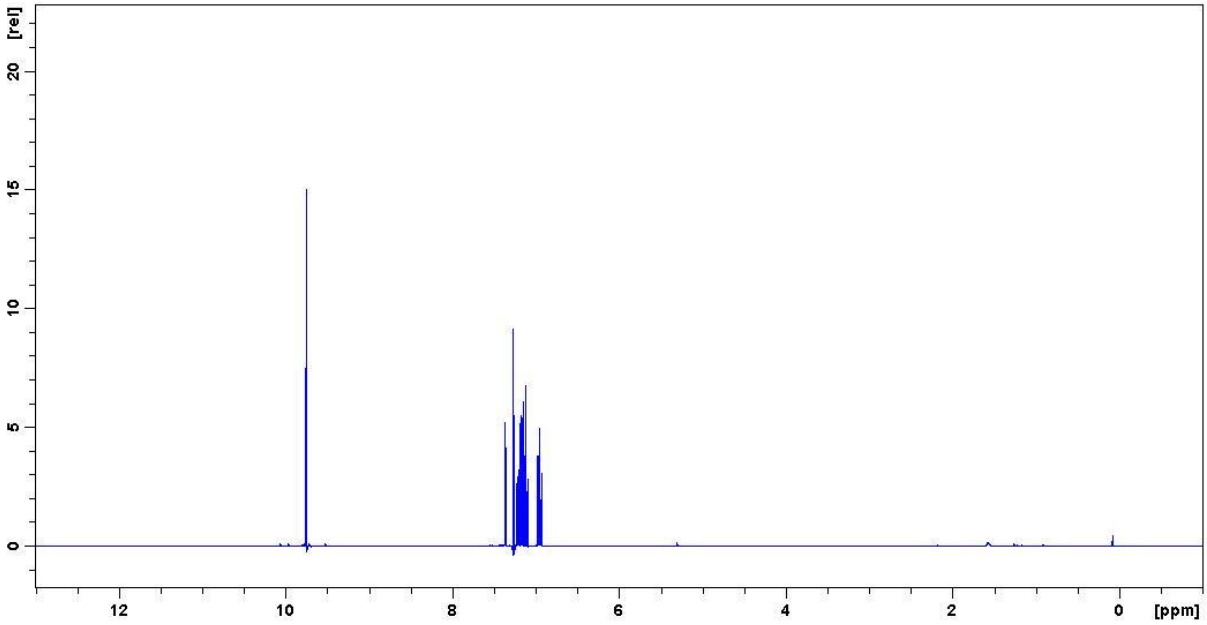
^{13}C-NMR



5i



^{1}H-NMR



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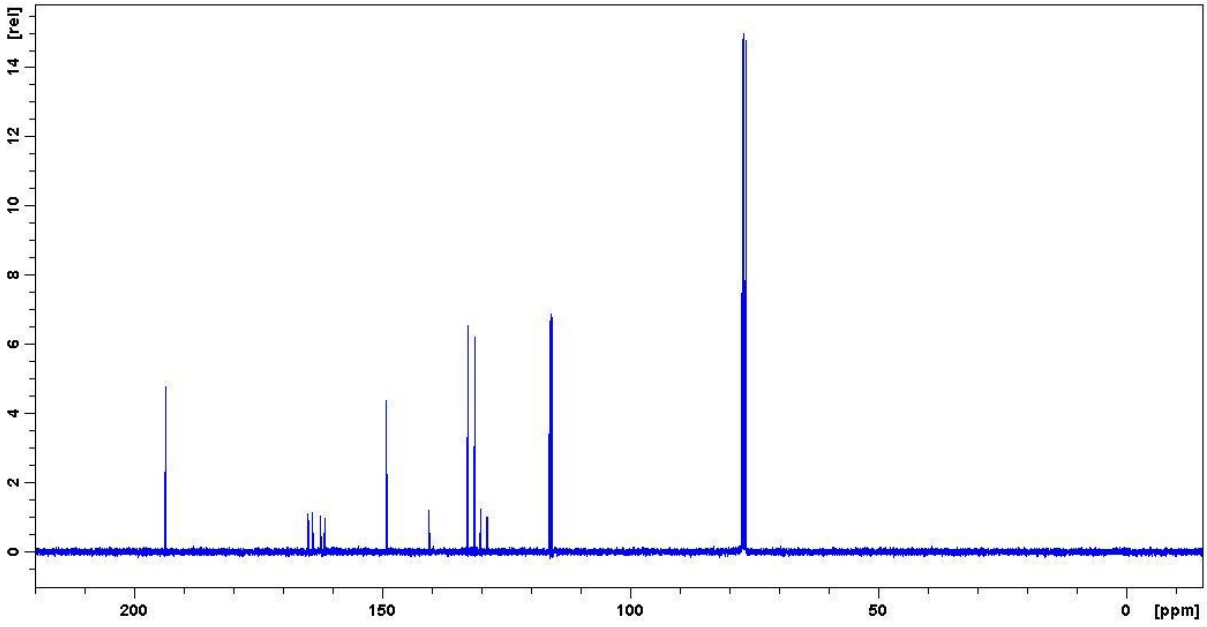

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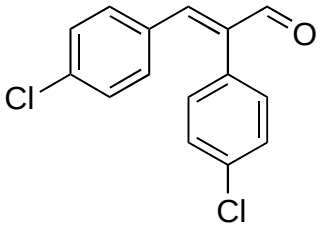

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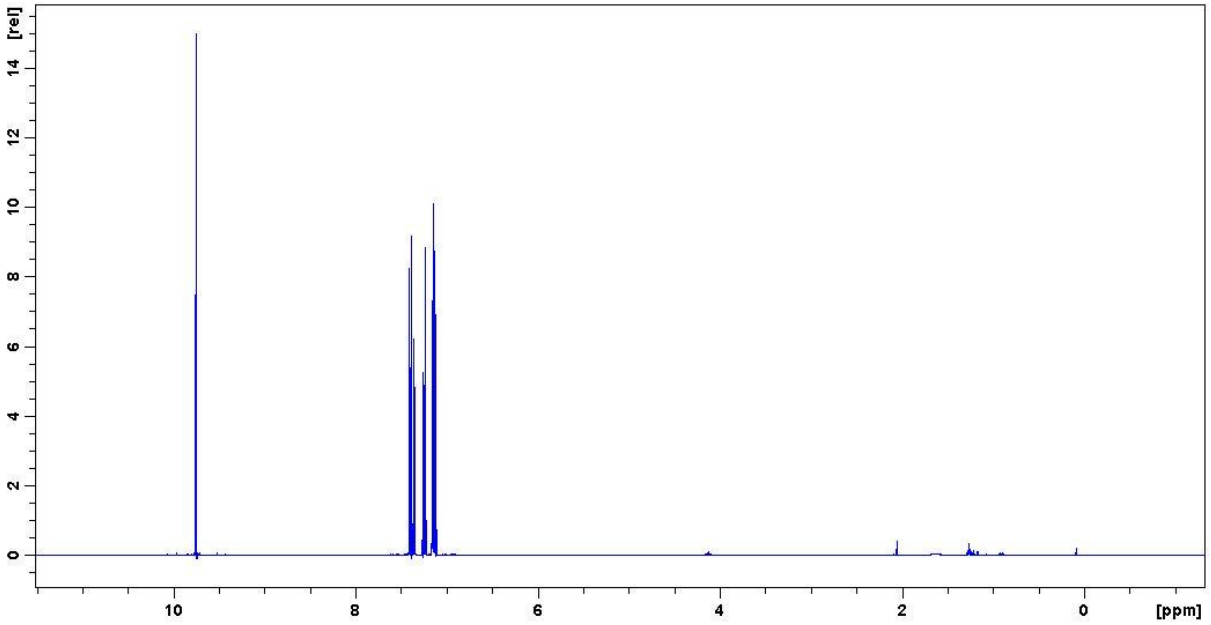

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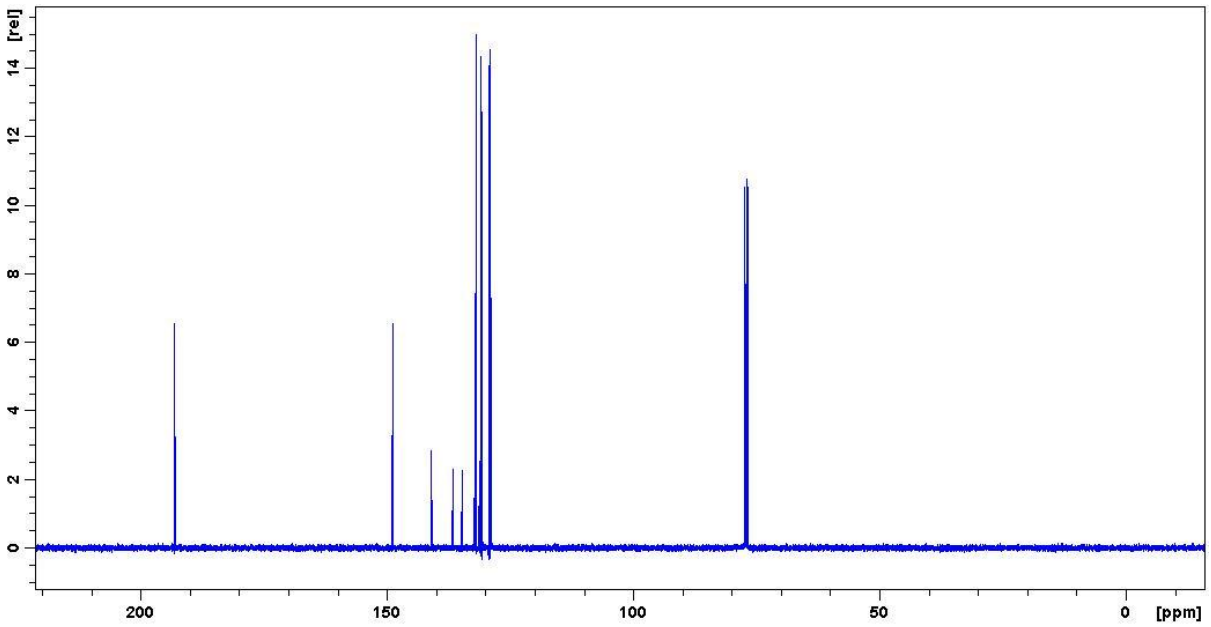
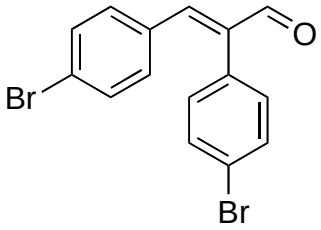
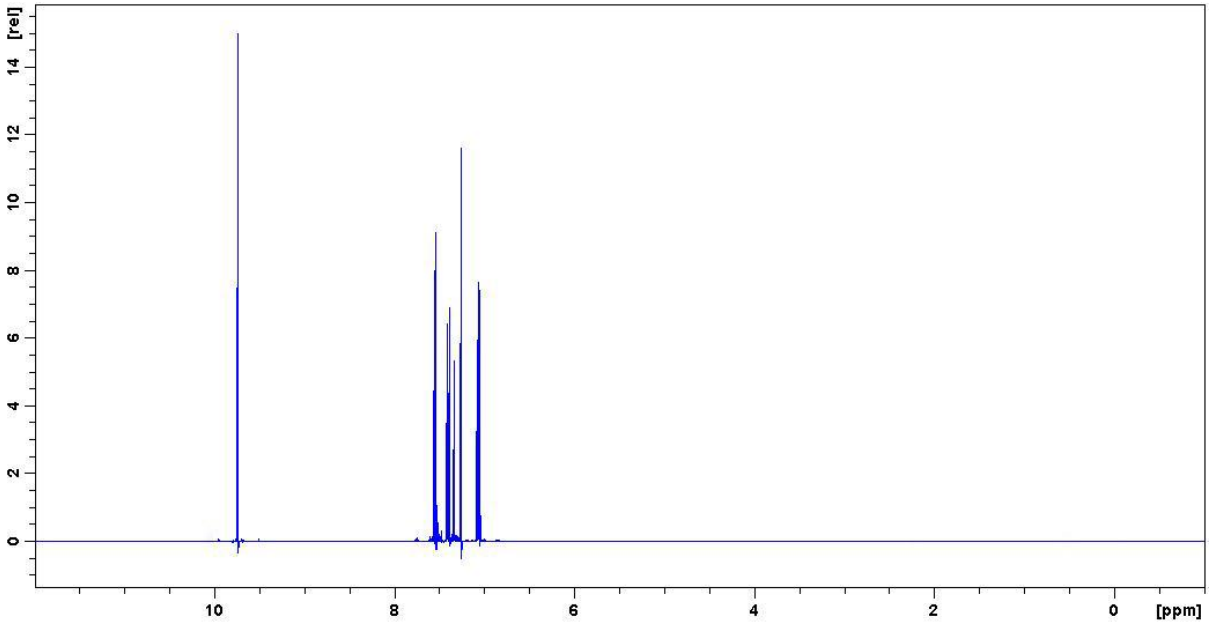


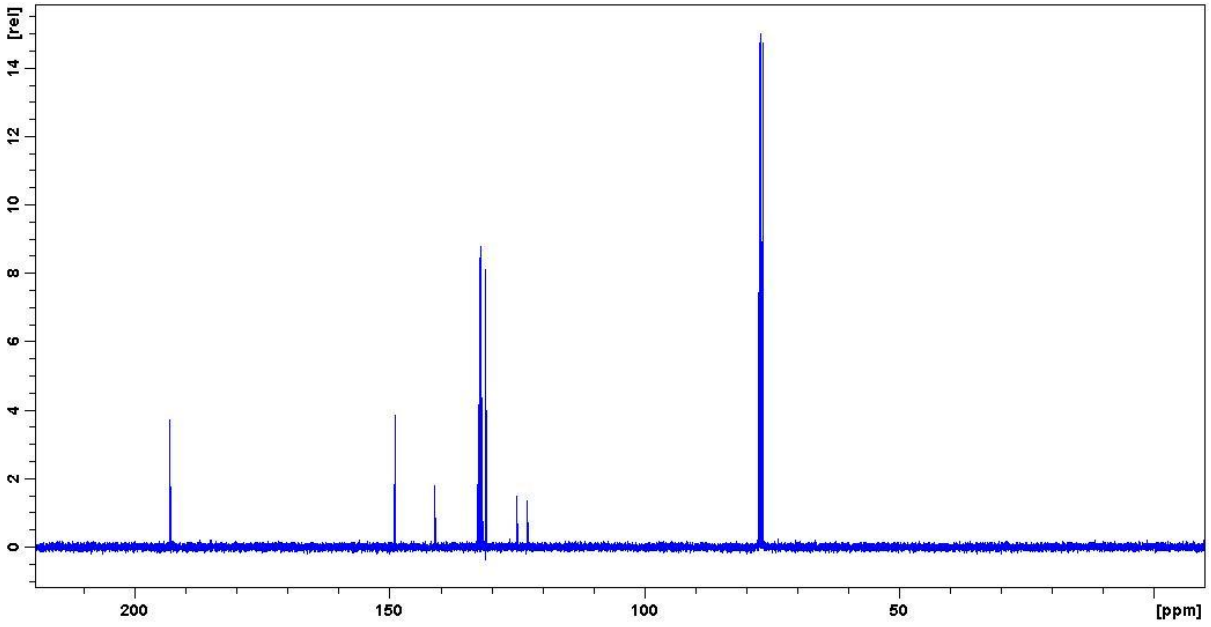
5k



^{1}H-NMR



^{13}C-NMR



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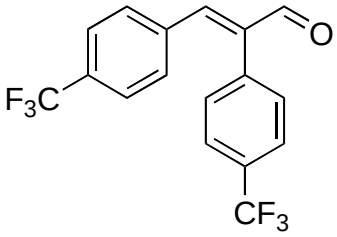
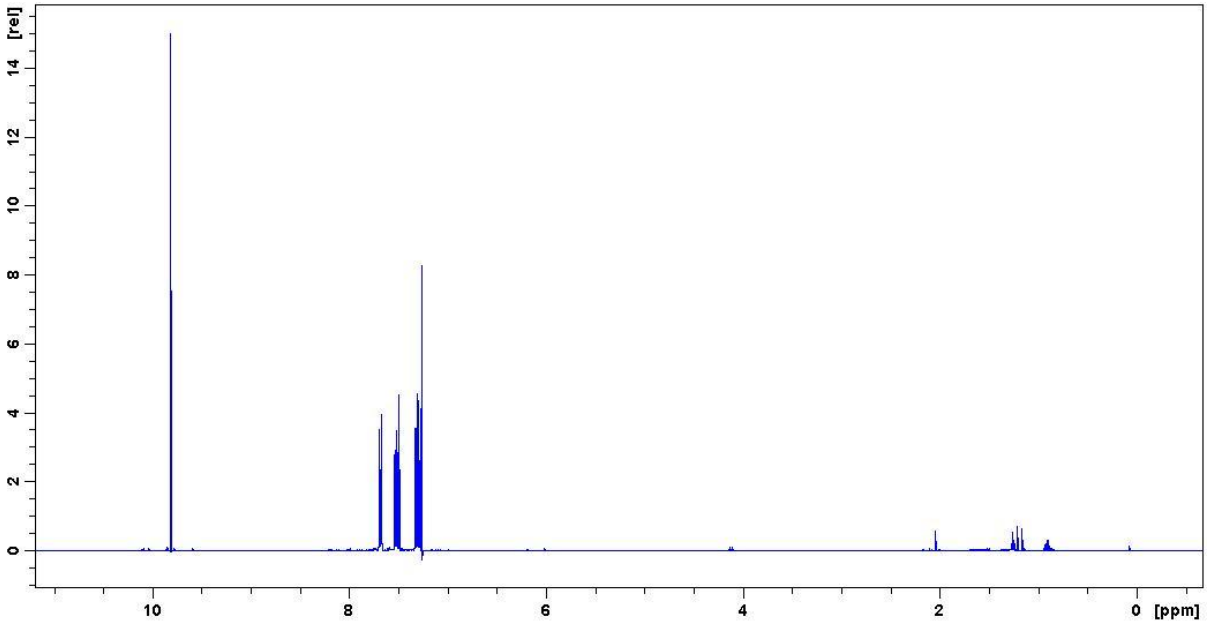
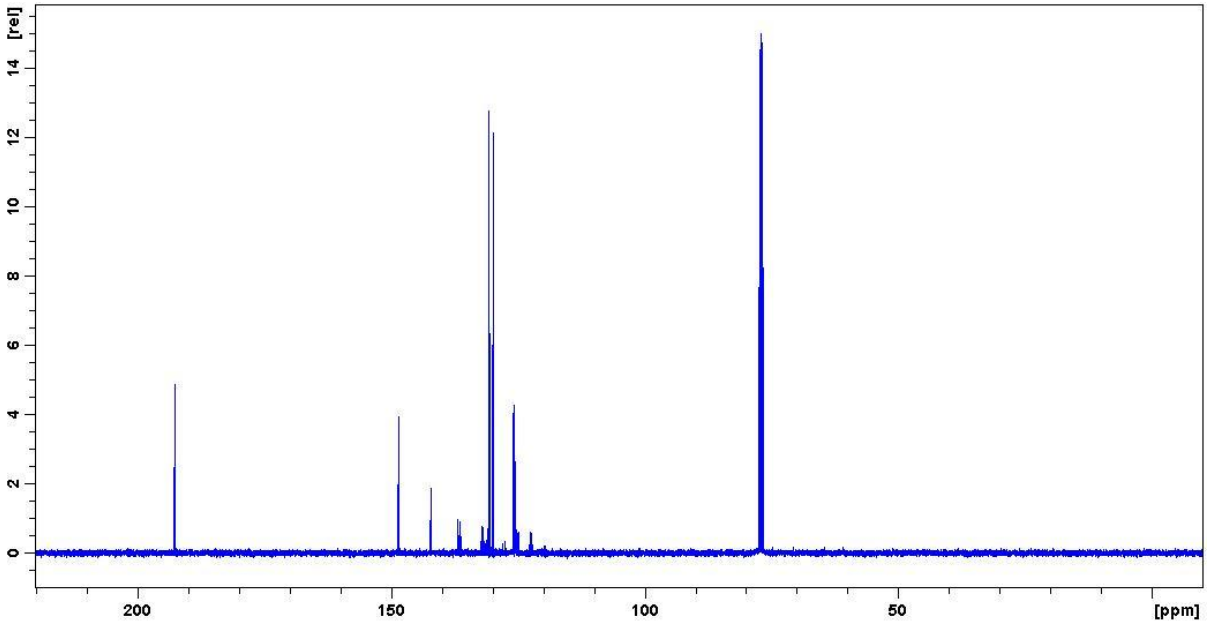


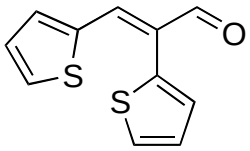
^{1}H-NMR



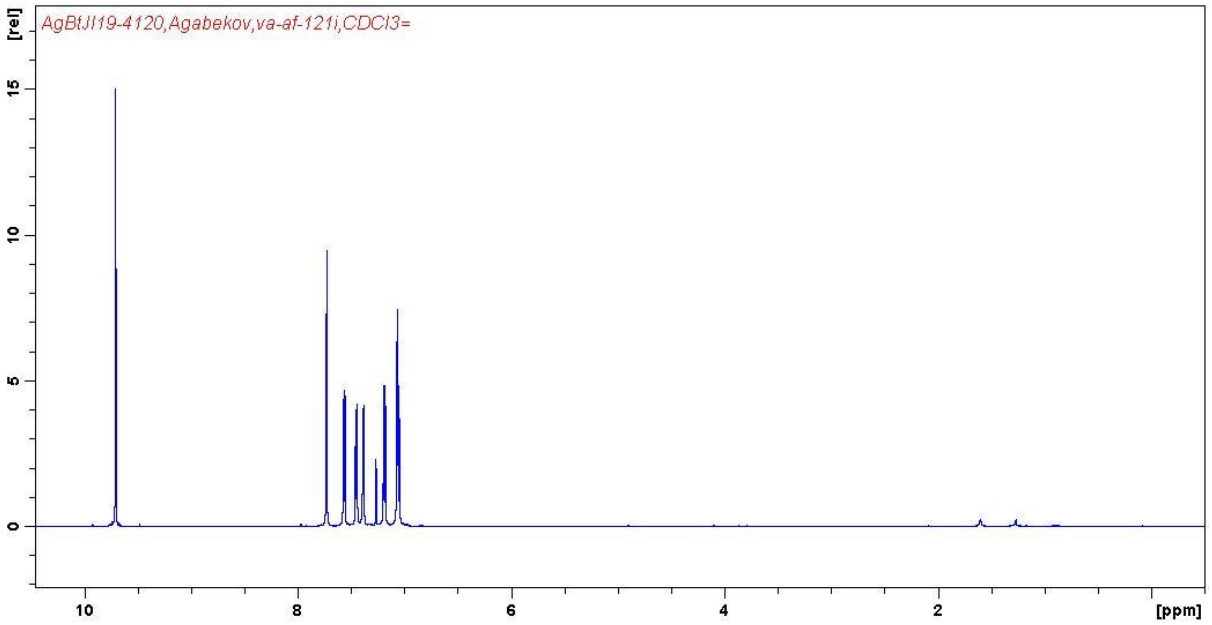
^{13}C-NMR



5m



^{1}H-NMR



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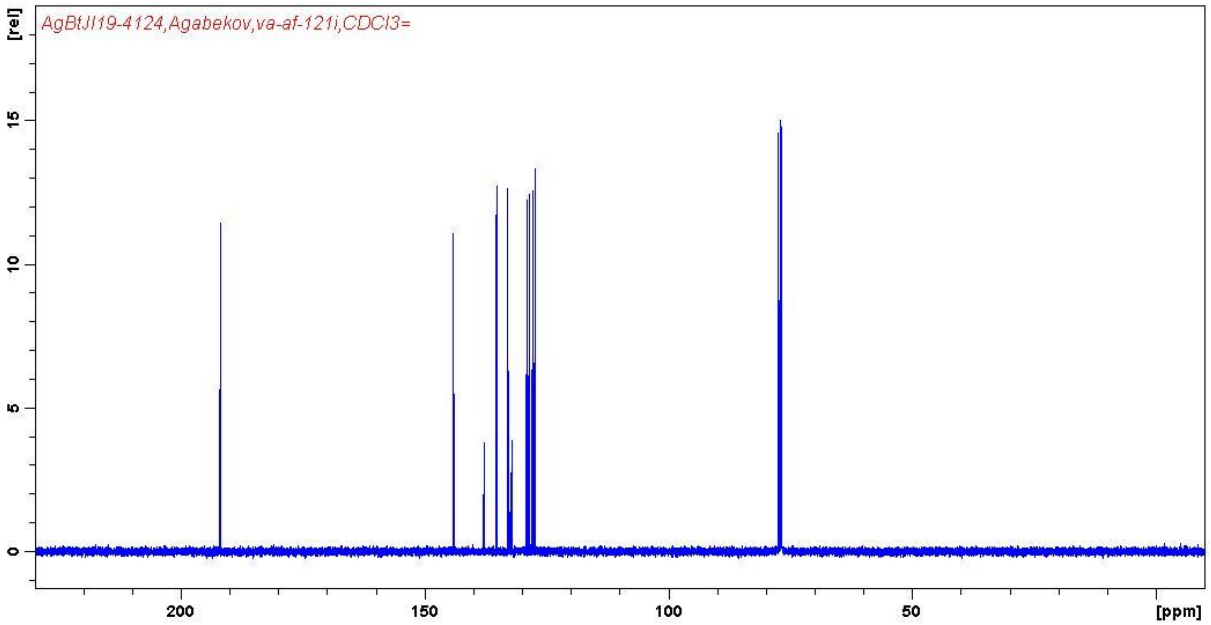
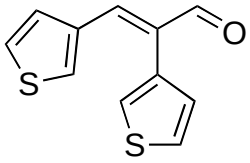
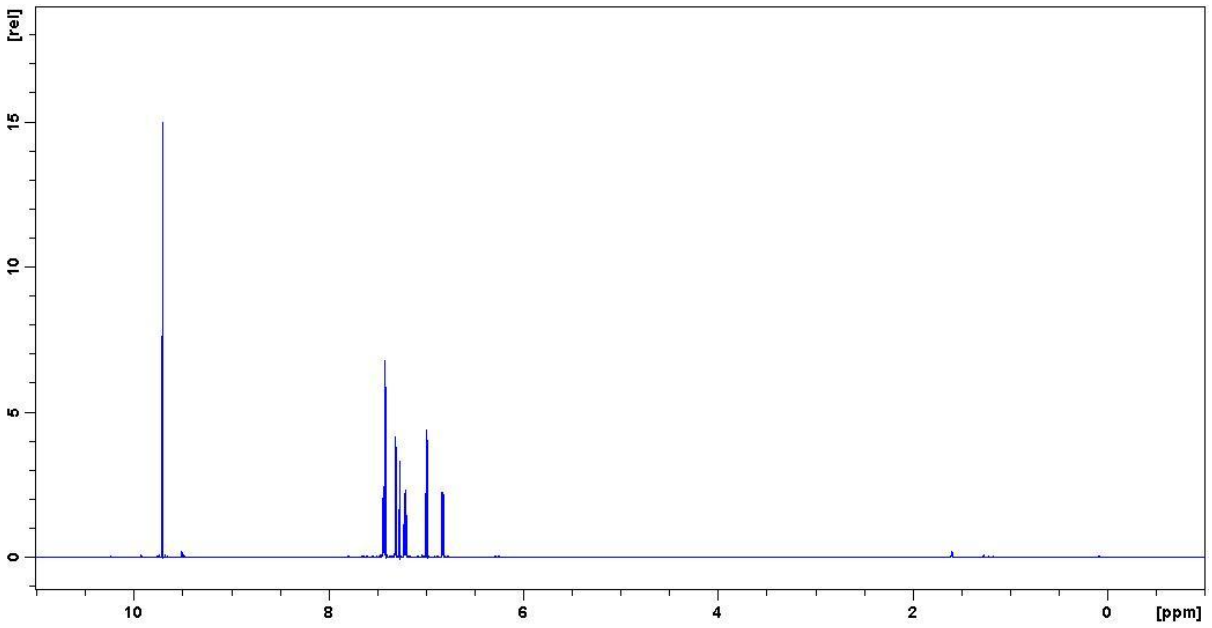


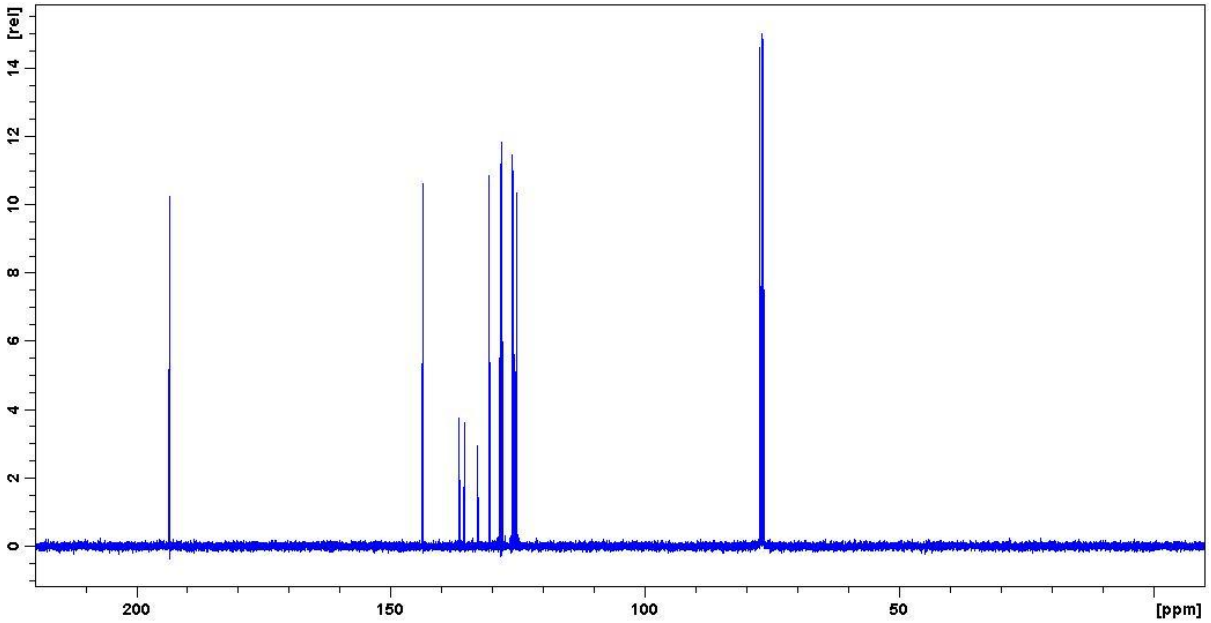
5n



^{1}H-NMR

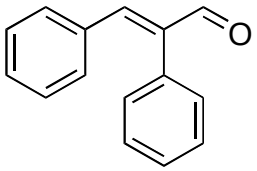


^{13}C-NMR



Appendix II (Crystallographic Data to 5a and 5i)

The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number **CCDC 923424**.



5a

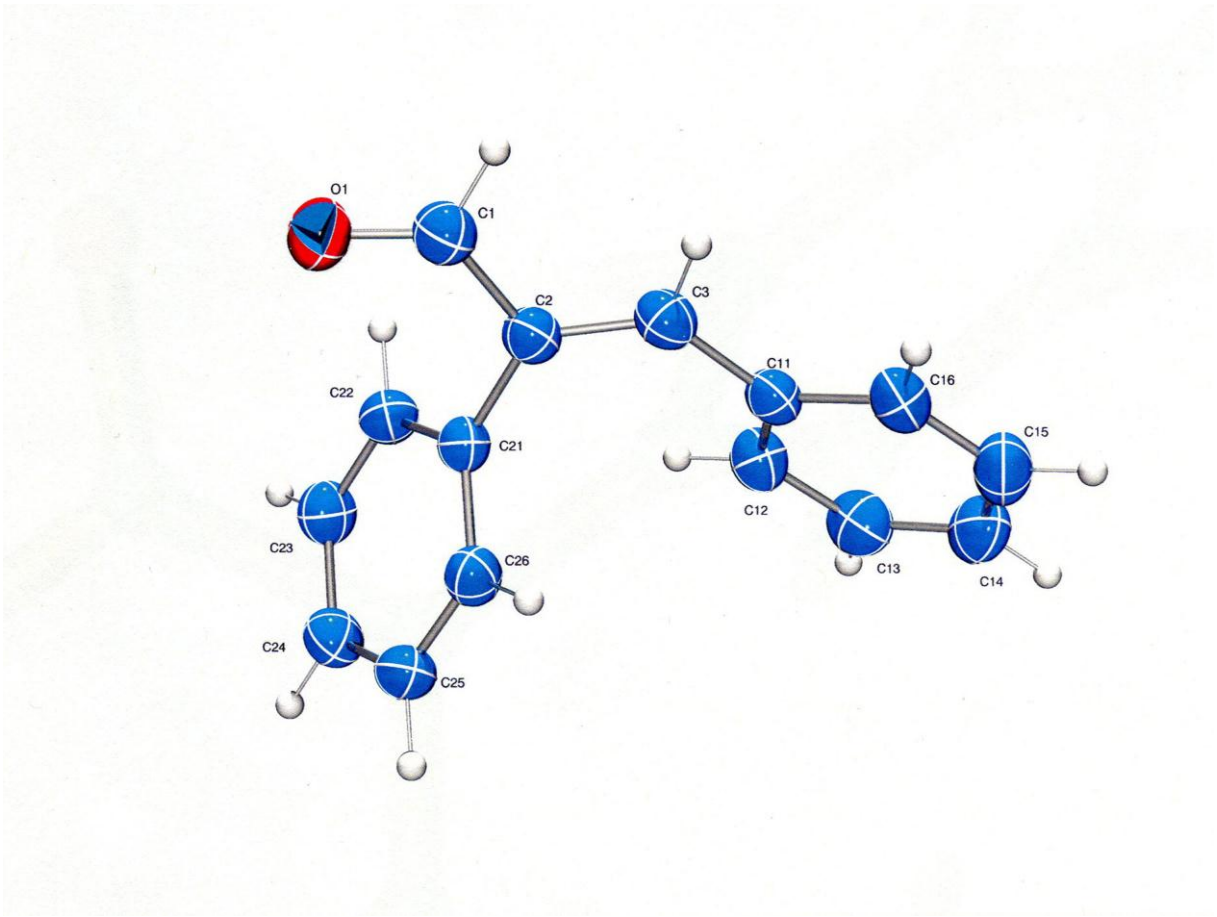
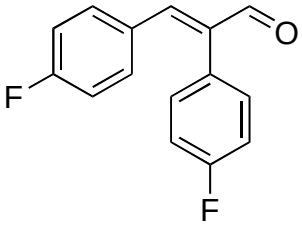


Table 1. Crystal data and structure refinement **5a**

Identification code	mk484bl
Empirical formula	C15 H12 O
Formula weight	208.25
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 5.8262(2) A alpha = 90 deg. b = 21.4617(13) A beta = 95.017(3) deg. c = 9.2279(4) A gamma = 90 deg.
Volume	1149.44(9) A^3
Z, Calculated density	4, 1.203 Mg/m^3
Absorption coefficient	0.074 mm^-1
F(000)	440
Crystal size	0.30 x 0.25 x 0.04 mm
Theta range for data collection	1.90 to 27.46 deg.
Limiting indices	-7<=h<=7, -27<=k<=26, -10<=l<=11
Reflections collected / unique	9998 / 2625 [R(int) = 0.0400]
Completeness to theta = 27.46	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.998 and 0.942
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2625 / 0 / 193
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.0969
R indices (all data)	R1 = 0.0703, wR2 = 0.1105
Largest diff. peak and hole	0.139 and -0.168 e.A^-3

The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number **CCDC 923423**.



5i

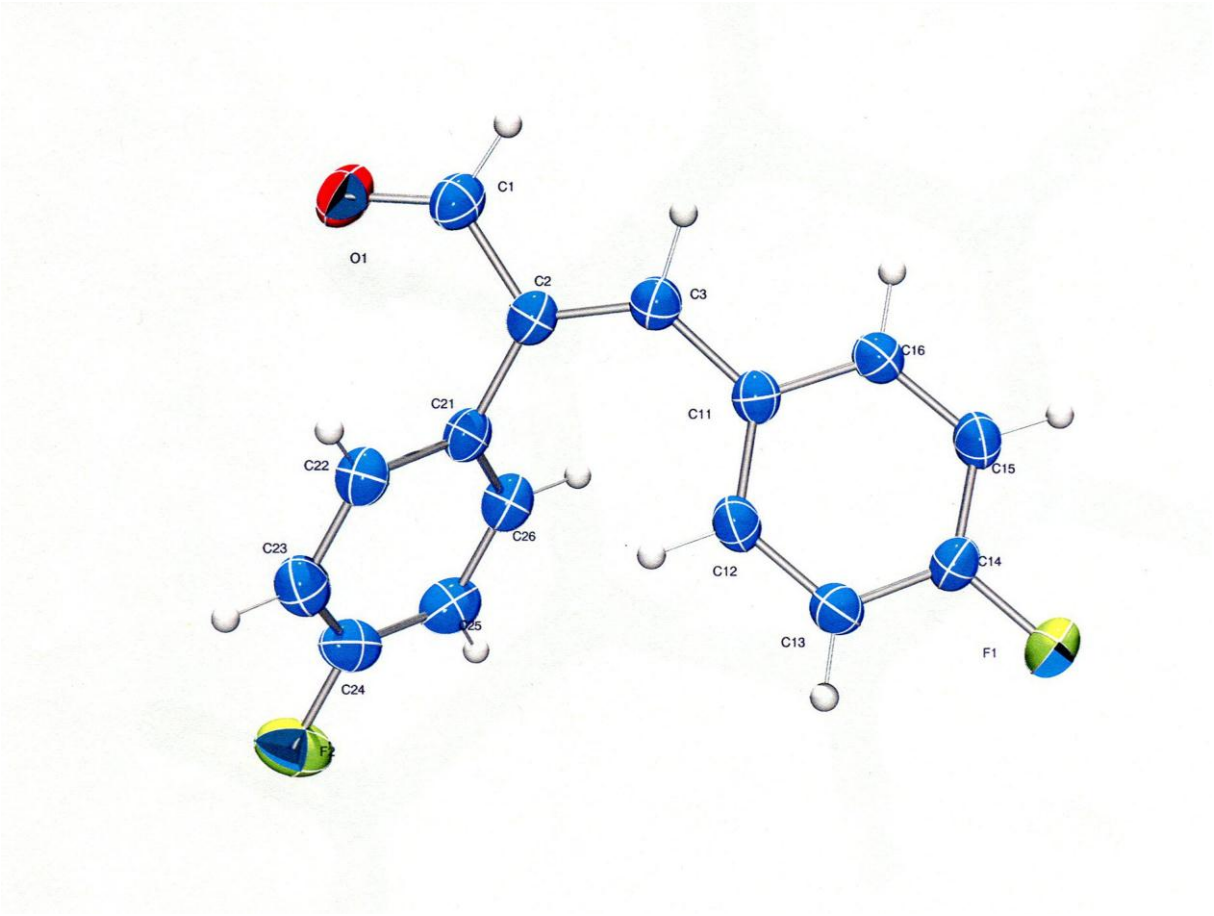


Table 1. Crystal data and structure refinement for **5i**

Identification code	mk473blp21c
Empirical formula	C15 H10 F2 O
Formula weight	244.23
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 6.6609(2) A alpha = 90 deg. b = 9.7886(5) A beta = 106.893(3) deg. c = 18.8033(8) A gamma = 90 deg.
Volume	1173.09(9) A^3
Z, Calculated density	4, 1.383 Mg/m^3
Absorption coefficient	0.107 mm^-1
F(000)	504
Crystal size	0.30 x 0.20 x 0.10 mm
Theta range for data collection	2.26 to 27.89 deg.
Limiting indices	-8<=h<=8, -11<=k<=12, -19<=l<=23
Reflections collected / unique	8538 / 2798 [R(int) = 0.0280]
Completeness to theta = 27.89	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.990 and 0.913
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2798 / 0 / 203
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0976
R indices (all data)	R1 = 0.0536, wR2 = 0.1070
Largest diff. peak and hole	0.127 and -0.194 e.A^-3