Electronic Supplementary Information

Investigation of Facet Effects on the Catalytic Activity of Cu_2O Nanocrystals for Efficient Regioselective Synthesis of 3,5-Disubstituted Isoxazoles

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Experimental section

Chemicals

Anhydrous copper (II) chloride ($CuCl_2$; 97%) and hydroxylamine hydrochloride ($NH_2OH\cdot HCl$; 99%) were purchased from Aldrich. Sodium hydroxide (98.2%) and sodium dodecyl sulfate (SDS; 100%) were acquired from Mallinckrodt. All chemicals were used as received without further purification along with deionized water for all solution preparations. Commercially available reagents were used for the [3+2] cycloaddition reactions.

Synthesis of Cu_2O nanocubes and rhombic dodecahedra

The synthetic method described here is adopted from our previously reported procedure.[14] For the synthesis of Cu_2O nanocrystals with cubic and rhombic dodecahedral shapes, 8.92 and 6.95 ml of deionized water were added respectively to sample vials. The volume of water added to each vials was adjusted in such a manner that after the addition of $NH_2OH\cdot HCl$, total volume of the final solution is 10 mL. The sample vials were placed in a water bath set at 30–32 °C. Then 0.5 mL of 0.1 M $CuCl_2$ solution and 0.087 g of SDS powder were added to the vials with vigorous stirring. When the solution became clear, 0.18 mL of 1.0 M NaOH solution was added and shaken for ~10 s. The solution turned light blue immediately, due to the formation of threadlike $Cu(OH)_2$ precipitate. Finally, 0.40 and 2.37 mL of 0.1 M $NH_2OH\cdot HCl$ were quickly injected in 5 s for the synthesis of nanocubes and rhombic dodecahedra, respectively. After stirring for 20 s, the solutions were kept in the water bath for 1 h for nanocrystal growth. The concentrations of Cu^{2+} ions and SDS surfactant in the final solution are 1.0×10^{-3} M and 3.0×10^{-2} M, respectively. The reaction mixtures were centrifuged at 5000 rpm for 3 min. After decanting the top solution, the precipitate was washed with 6 mL of 1:1 volume ratio of water and ethanol for three times to remove unreacted chemicals and SDS surfactant. The final washing step used 5 mL of ethanol, and the precipitate was dispersed in 0.6 mL of ethanol for storage and analysis.

Synthesis of Cu_2O octahedra

The synthetic procedure used for making octahedral Cu_2O nanocrystals is based on our reported procedure with a slight modification in the volume of $NH_2OH{\cdot}HCl$ solution added.[15] First, 9.02 ml of deionized water was added to a sample vial. The sample vial was placed in a water bath set at 30–32 °C. Next, 0.1 mL of 0.1 M $CuCl_2$ and 0.2 mL of 1.0 M NaOH solution were added and the vial was shaken for ~10 s. Then 0.087 g of SDS powder was introduced with vigorous stirring. Finally, 0.68 mL of 0.2 M $NH_2OH{\cdot}HCl$ was quickly injected. After stirring for 20 s, the solution was kept in the water bath for 2 h for nanocrystal growth. The concentrations of Cu^{2+} ions and SDS surfactant in the final solution are 1.0×10^{-3} M and 3.0×10^{-2} M. The reaction mixture was centrifuged at 3500 rpm for 2 min. After decanting the top solution, the precipitate was washed with 6 mL of 1:1 volume ratio of water and ethanol for three times to remove unreacted chemicals and SDS surfactant. The final washing step used 5 mL of ethanol, and the precipitate was dispersed in 0.6 mL of ethanol for storage and analysis.

Turnover frequency calculations

Since surface copper atoms are considered to be the active catalytic sites, we define TOF as moles of products formed / (moles of total surface copper atoms × reaction time). The surface copper atom area density for a particular lattice plane can be calculated by determining the number of surface copper atoms within a chosen area. The chosen areas are shown in Figure S4. Here the unit cell parameter *a* is taken as 4.267 Å. For the (100) plane with the area shown in panel a of Figure S4, the surface copper atom density is $32 / (4 \times 4.267 \times 4 \times 4.267) = 0.1098$ Å^{-2}, or 10.98 nm^{-2}. For the (111) plane with the area shown in panel c of Figure S4, a total of 36 surface copper atoms are counted from line 1 to line 8. The surface copper atom density is $36 / (4\sqrt{2} \times 4.267 \times 2\sqrt{6} \times 4.267 / 2) = 0.1427$ Å^{-2}, or 14.27 nm^{-2}. For the (110) plane with the area shown in panel e of Figure S4, the surface copper atom density is $32 / (4 \times 4.267 \times 4\sqrt{2} \times 4.267) = 0.0776$ Å^{-2}, or 7.76 nm^{-2}.

All catalysts have approximately the same total surface area of 0.0028 m^2 or 2.8×10^{15} nm^2. For nanocubes, this surface area contains $(10.98 \times 2.8 \times 10^{15}) / 6.023 \times 10^{23}$, or 5.104×10^{-8}, mole of surface Cu atoms. For octahedra and rhombic dodecahedra, this area contains 6.634×10^{-8} and 3.608×10^{-8} mole of surface Cu atoms, respectively.

For the reaction shown in Table 1 (1a to product 3aa), 0.050 g of 1a was used for each case. The molecular weight of 1a is 200.57 g/mole and that of 3aa is 266.25

g/mole. Moles of product 3aa formed can be calculated from the percent product yield. For the nanocubes, weight of 3aa produced = (266.25/200.57 × 0.050) × 0.82 = 0.0544 g or 2.04×10^{-4} mol. For the octahedra, weight of 3aa produced = (266.25/200.57 × 0.050) × 0.89 = 0.0590 g or 2.22×10^{-4} mol. For the rhombic dodecahedra, it is 0.06305 g or 2.37×10^{-4} mol.

TOF of nanocubes = 2.04×10^{-4} mol / (5.104×10^{-8} mol × 7 h) = 571 h^{-1}.
TOF of octahedra = 2.22×10^{-4} mol / (6.634×10^{-8} mol × 5 h) = 669 h^{-1}.
TOF of rhombic dodecahedra = 2.37×10^{-4} mol / (3.608×10^{-8} mol × 2 h) = 3338 h^{-1}.

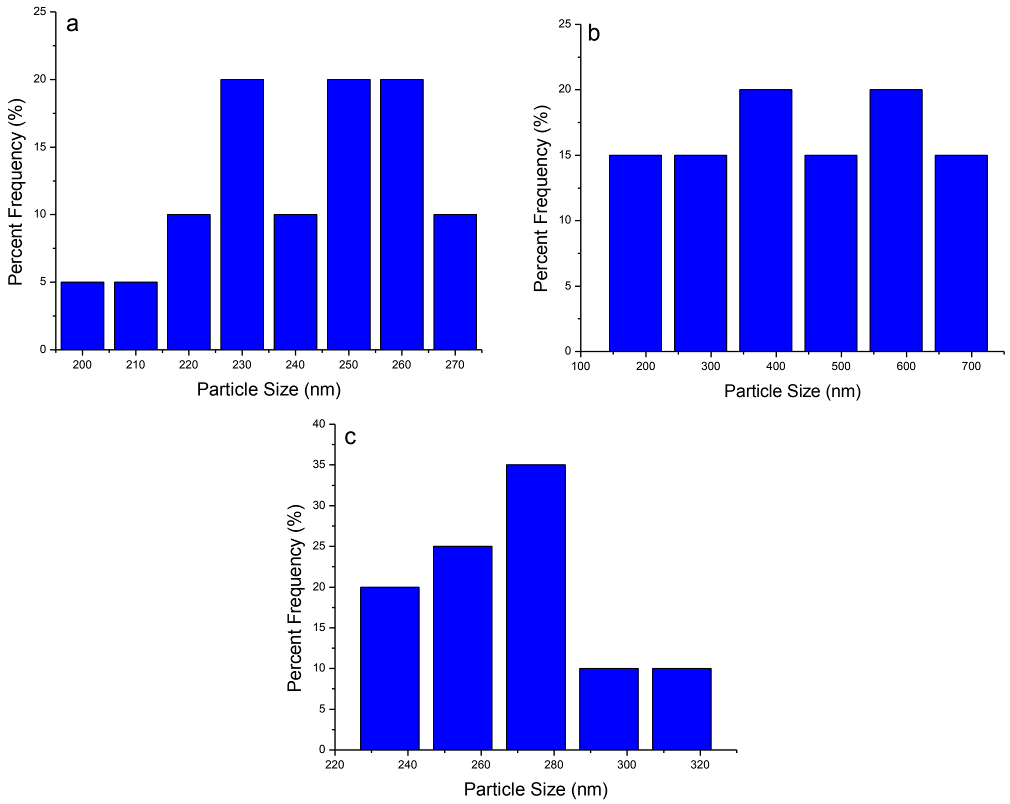


Fig. S1 Size distribution histograms of Cu_2O (a) nanocubes, (b) octahedra, and (c) rhombic dodecahedra.

Table S1. Average particle sizes and their relative standard deviations.

Shape	Average Particle Size	Relative Standard Deviation
Cubes	241 ± 20 nm	8%
Octahedra	427 ± 123 nm	29%
Rhombic dodecahedra	268 ± 17 nm	6%

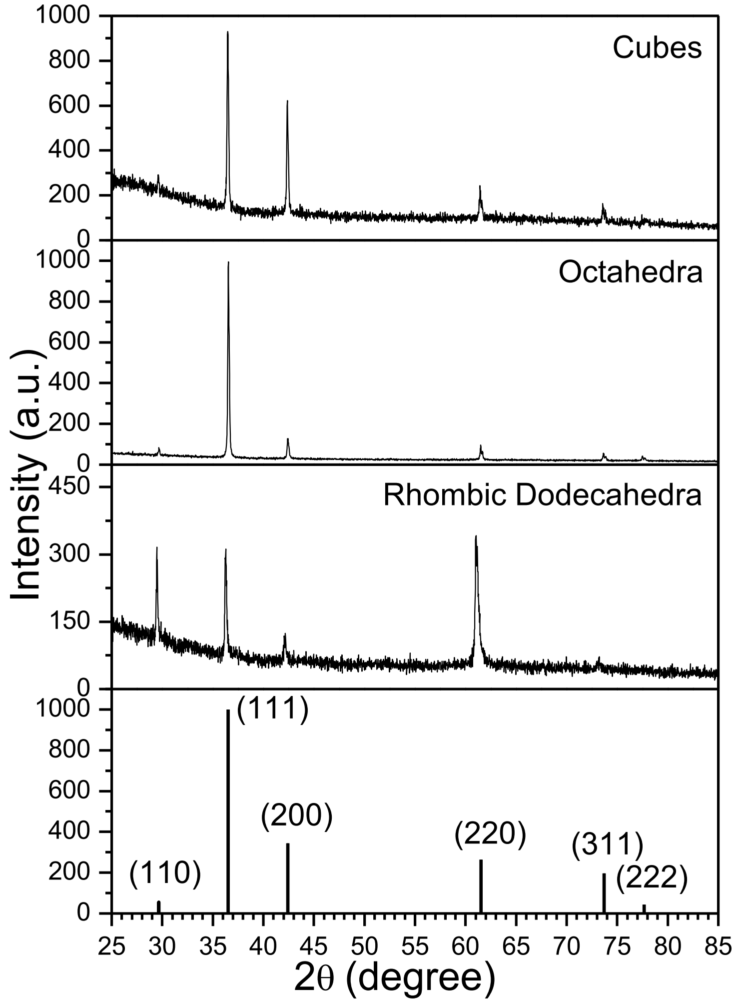


Fig. S2 XRD patterns of the synthesized Cu_2O nanocubes, octahedra, and rhombic dodecahedra. A standard diffraction pattern of Cu_2O is also given (JCPDS card no. 77-0199 for cuprite Cu_2O with a lattice constant a_o of 4.26 Å). Due to random orientation of the nanocubes, the (200) peak intensity is not enhanced. Octahedra display an exceptionally strong (111) reflection peak because of their {111} facets. Rhombic dodecahedra show enhanced (110) and (220) peaks as a result of their {110} faces.

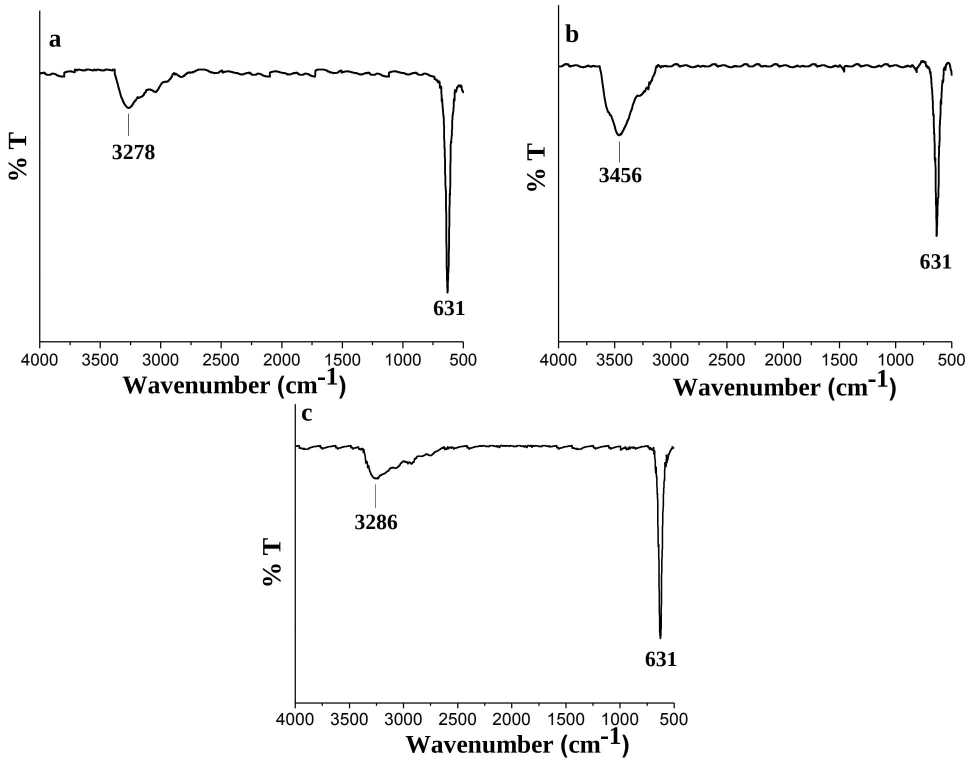


Fig. S3 FI-IR spectra of the synthesized Cu_2O (a) nanocubes, (b) octahedra, and (c) rhombic dodecahedra.

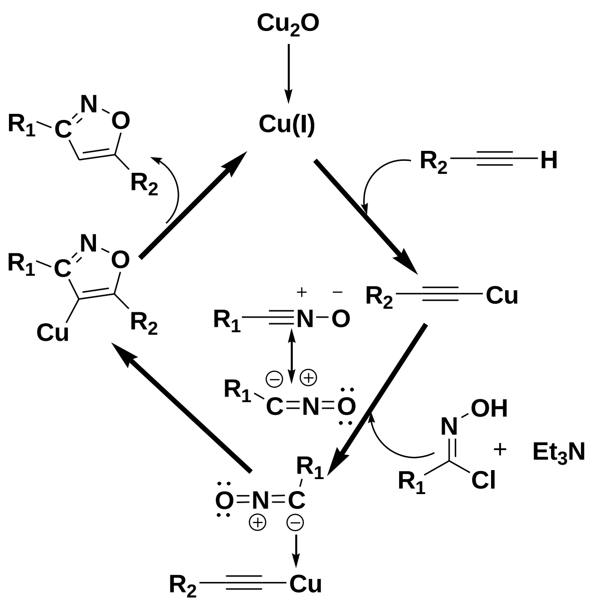
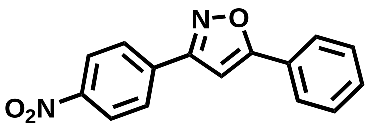


Fig. S4 Possible mechanism for the Cu_2O-catalyzed [3 + 2] cycloaddition addition.

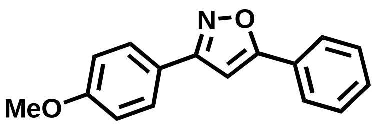
Spectral Data of Synthesized Compounds from Table 2

3-(4-Nitrophenyl)-5-phenylisoxazole (3aa)



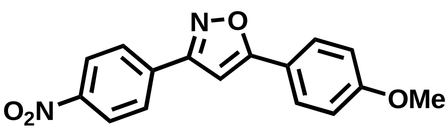
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 7.6 Hz, 2H), 7.51-7.48 (m, 3H), 6.88 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.5, 161.2, 148.7, 135.2, 130.7, 129.2, 127.7, 126.9, 125.9, 124.2, 97.5; MS (EI) *m/z*: 266 (M^+); HRMS (EI, m/z) calcd for $C_{15}H_{10}N_2O_3$: *m/z* 266.0691; Found 266.0693 (M^+).

3-(4-Methoxyphenyl)-5-phenylisoxazole (3ba)



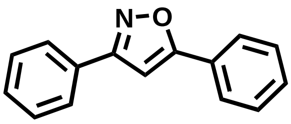
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, J = 8.0, 1.5 Hz, 2H), 7.78 (dd, J = 6.8, 2.0 Hz, 2H), 7.48-7.43 (m, 3H), 6.97 (dd, J = 6.8, 2.0 Hz, 2H), 6.76 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 162.6, 161.0, 130.1, 128.9, 128.2, 127.6, 125.8, 121.7, 114.3, 97.2, 55.4; MS (EI) *m/z*: 251 (M^+); HRMS (EI, m/z) calcd for $C_{16}H_{13}NO_2$: *m/z* 251.0946; Found 251.0938 (M^+).

5-(4-Methoxyphenyl)-3-(4-nitropheny)isoxazole (3ab)



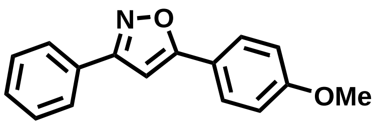
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, J = 8.9 Hz, 2H), 8.02 (d, J = 8.9 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 7.51-7.48 (m, 3H), 6.75 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.5, 161.5, 161.1, 148.6, 135.4, 127.5, 124.5, 124.2, 119.7, 114.5, 96.1, 55.4; MS (EI) *m/z*: 296 (M^+); HRMS (EI, m/z) calcd for $C_{16}H_{12}N_2O_4$: *m/z* 296.0797; Found 296.0801 (M^+).

3,5-Diphenylisoxazole (3ca)



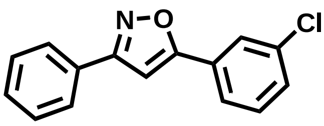
[1]H NMR (600 MHz, $CDCl_3$) δ 7.86-7.82 (m, 5H), 7.48-7.44 (m, 5H), 6.82 (s, 1H); [13]C NMR (150 MHz, $CDCl_3$) δ 170.4, 162.9, 130.2, 130.0, 129.1, 129.0, 128.9, 127.5, 126.8, 125.8, 97.5; MS (EI) *m/z*: 221 (M^+); HRMS (EI, m/z) calcd for $C_{15}H_{11}NO$: *m/z* 221.0841; Found 221.0842 (M^+).

5-(4-Methoxyphenyl)-3-phenyisoxazole (3cb)



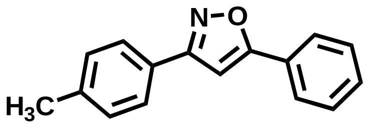
[1]H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.5, 1.5 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.48-7.44 (m, 3H), 6.98 (d, J = 8.6 Hz, 2H), 6.69 (s, 1H), 3.85 (s, 3H); [13]C NMR (150 MHz, $CDCl_3$) δ 170.4, 162.9, 161.1, 129.9, 129.3, 128.9, 127.5, 126.8, 120.3, 114.4, 96.1, 55.4; MS (EI) *m/z*: 251 (M^+); HRMS (EI, m/z) calcd for $C_{16}H_{13}NO_2$: *m/z* 251.0946; Found 251.0939 (M^+).

5-(3-Chlorophenyl)-3-phenylisoxazole (3cc)



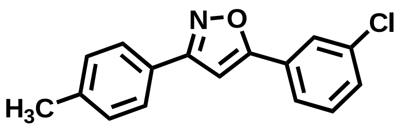
[1]H NMR (600 MHz, $CDCl_3$) δ 7.85-7.81 (m, 2H), 7.80 (t, J = 1.6 Hz, 1H), 7.71-7.70 (m, 1H), 7.47-7.45 (m, 3H), 7.41-7.40 (m, 2H), 6.84 (s, 1H); [13]C NMR (150 MHz, $CDCl_3$) δ 168.9, 163.1, 135.1, 130.2, 130.1, 129.0, 128.9, 128.8, 126.8, 125.9, 123.9, 98.3; MS (EI) *m/z*: 255 (M^+); HRMS (EI, m/z) calcd for $C_{15}H_{10}ClNO$: *m/z* 255.0451; Found 255.0456 (M^+).

3-(4-Methylphenyl)-5-phenylisoxazole (3ca)



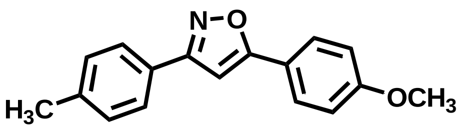
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.1, 1.5 Hz, 2H), 7.74 (d, J = 8,5 Hz, 2H), 7.48-7.43 (m, 3H), 7.26 (dd, J = 8.1, 1.5 Hz, 2H), 6.79 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 162.9, 140.2, 130.2, 129.6, 128.9, 127.6, 126.3, 125.8, 97.4, 21.4; MS (EI) *m/z*: 235 (M^+); HRMS (EI, m/z) calcd for $C_{16}H_{13}NO$: *m/z* 235.0997; Found 235.0990 (M^+).

5-(3-Chlorophenyl)-3-*p*-tolylsooxazole (3dc)



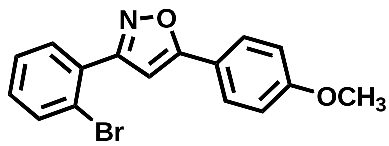
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (t, J = 1.4 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.68 (dt, J = 6.0, 1.4 Hz, 1H), 7.38 (dd, J = 5.0, 3.6 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.79 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 162.9, 140.3, 134.9, 130.3, 130.1, 129.6, 129.0, 126.6, 125.9, 125.8, 123.8, 98.2, 21.4; MS (EI) *m/z*: 269 (M^+); HRMS (EI, m/z) calcd for $C_{16}H_{12}ClNO$: *m/z* 269.0607; Found 269.0600 (M^+).

5-(4-Methoxyphenyl)-3-*p*-tolylisooxazole (3db)



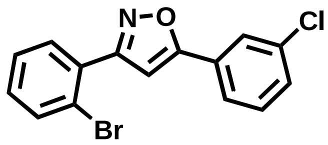
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, J = 6.8, 1.8 Hz, 2H), 7.73 (dd, J = 8.0, 0.5 Hz, 2H), 7.25 (dd, J = 8.0, 0.5 Hz, 2H), 6.96 (dd, J = 6.8, 1.8 Hz, 2H), 6.66 (s, 1H), 3.84 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 162.9, 161.0, 140.0, 129.6, 127.4, 126.7, 126.7, 126.4, 120.4, 114.4, 96.0, 55.4, 21.4; MS (EI) *m/z*: 265 (M^+); HRMS (EI, m/z) calcd for $C_{17}H_{15}NO_2$: *m/z* 265.1103; Found 265.1098 (M^+).

3-(2-Bromophenyl)-5-(4-methoxyphenyl)isoxazole (3eb)



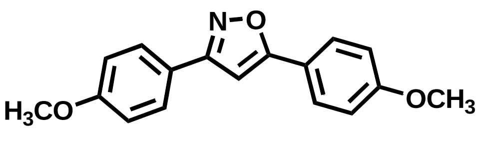
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.5 Hz, 2H), 7.67 (t, J = 8.6 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.5 Hz, 2H), 6.81 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 162.9, 161.1, 13.6, 130.9, 130.7, 127.6, 127.5, 122.3, 120.3, 114.4, 95.5, 55.4; MS (EI) *m/z*: 330 (M^+); HRMS (EI, m/z) calcd for $C_{16}H_{12}BrNO_2$: *m/z* 329.0051 ; Found 329.0054 (M^+).

3-(2-Bromophenyl)-5-(3-chlorophenyl)isoxazole (3ec)



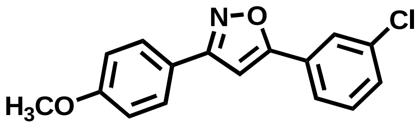
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J = 0.9 Hz, 1H), 7.75-7.72 (m, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.70 (dd, J = 8.0, 1.6 Hz, 1H), 7.44-7.42 (m, 3H), 7.35 (dt, J = 7.4, 0.9 Hz, 1H), 6.99 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 163.1, 135.1, 133.7, 131.5, 131.3, 131.2, 130.4, 130.2, 128.9, 127.7, 125.9, 123.9, 122.4, 101.7; MS (EI) *m/z*: 334 (M^+); HRMS (EI, m/z) calcd for $C_{15}H_9ClBrNO$: *m/z* 332.9556; Found 332.9554 (M^+).

3,5-Bis(4-methoxyphenyl)isoxazole (3bb)



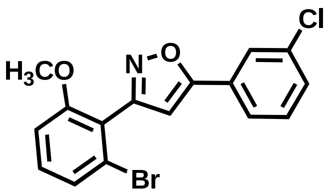
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.8, 2.0 Hz, 2H), 7.73 (dd, J = 8.8, 2.0 Hz, 2H), 6.96 (dd, J = 8.8, 2.0 Hz, 2H), 6.95 (dd, J = 8.8, 2.0 Hz, 2H), 6.63 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 162.5, 161.0, 160.9, 128.1, 127.4, 121.7, 120.4, 14.3, 114.2, 95.9, 55.4, 55.3; MS (EI) *m/z*: 281 (M^+); HRMS (EI, m/z) calcd for $C_{17}H_{15}NO_3$: *m/z* 281.1052; Found 281.1050 (M^+).

5-(3-Chlorophenyl)-3-(4-methoxyphenyl)isoxazole (3bc)



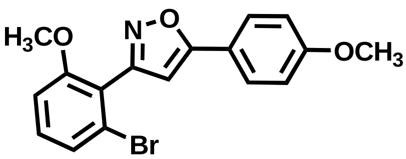
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.7 Hz, 3H), 7.61 (m, 1H), 7.37 (d, J = 4.6 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 6.75 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 162.6, 161.1, 134.9, 130.3, 130.1, 129.0, 128.2, 125.8, 123.8, 121.2, 114.3, 98.0, 55.3; MS (EI) *m/z*: 285 (M^+); HRMS (EI, m/z) calcd for $C_{16}H_{12}ClNO_2$: *m/z* 285.0557; Found 285.0565 (M^+).

3-(2-Bromo-6-methoxyphenyl)-5-(3-chlorophenyl)isoxazole (3fc)



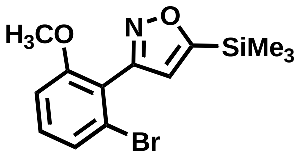
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.80 (m, 1H),7.71 (dt, J = 4.3, 1.6 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7 6.88 (dd, J = 8.8, 3.0 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 163.1, 158.9, 135.1, 130.8, 130.4, 130.2, 128.9, 125.9, 123.9, 117.8, 116.0, 112.5, 101.7, 55.7; MS (EI) *m/z*: 364 (M^+); HRMS (EI, m/z) calcd for $C_{16}H_{11}BrClNO_2$: *m/z* 362.9662; Found 362.9664 (M^+).

3-(2-Bromo-6-methoxyphenyl)-5-(4-methoxyphenyl)isoxazole (3fb)



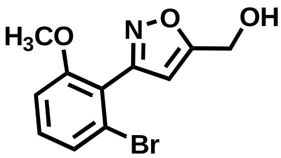
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, J = 6.8, 2.0 Hz, 2H), 7.53 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 3.1 Hz, 1H), 6.96 (dd, J = 6.8, 2.0 Hz, 2H), 6.84 (dd, J = 8.8, 3.1 Hz, 1H), 6.82 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 162.9, 161.1, 158.8, 134.3, 131.2, 127.4, 120.2, 117.5, 115.9, 114.4, 112.5, 99.4, 55.6, 55.4; MS (EI) *m/z*: 360 (M^+); HRMS (EI, m/z) calcd for $C_{17}H_{14}BrNO_3$: *m/z* 359.0157; Found 359.0154 (M^+).

3-(2-Bromo-6-methoxyphenyl)-5-(trimethylsilyl)isoxazole (3fe)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 8.8 Hz, 1H), 7.14 (d, J = 3.1 Hz, 1H), 6.83 (s, 1H), 6.80 (dd, J = 8.8, 3.1 Hz, 1H), 3.78 (s, 3H), 0.36 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 160.7, 158.7, 134.1, 131.2, 117.3, 116.1, 113.7, 112.5, 55.5, -1.94; MS (EI) *m/z*: 326 (M^+); HRMS (EI, m/z) calcd for $C_{13}H_{16}BrNO_2Si$: *m/z* 325.0134; Found 325.0132 (M^+).

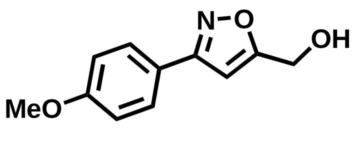
(3-(2-Bromo-6-methoxyphenyl)isoxazol-5-yl)methanol (3fd)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 3.1 Hz, 1H), 6.84 (dd, J = 8.8, 3.1 Hz, 1H), 6.69 (s, 1H), 4.82 (t, J = 3.0 Hz, 2H), 3.80 (s, 3H), 2.31 (brs, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 162.7, 159.1, 134.5, 131.1, 117.9, 116.3, 112.7, 103.6, 56.8, 55.9; MS (EI) *m/z*: 284 (M^+); HRMS (EI, m/z) calcd for $C_{11}H_{10}BrNO_3$: *m/z* 282.9844; Found 282.9848 (M^+).

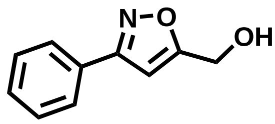
Spectral Data of Compounds from Table 3

3-(4-Methoxyphenyl)isoxazol-5-yl)methanol (3bd)



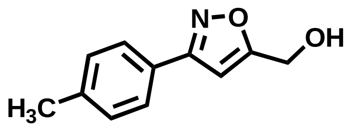
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.45 (s, 1H), 4.74 (s, 2H), 3.81 (s, 3H), 3.10 (brs, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.8, 162.0, 161.9, 128.2, 121.2, 114.3, 99.7, 56.4, 55.3; MS (EI) *m/z*: 205 (M^+); HRMS (EI, m/z) calcd for $C_{11}H_{11}NO_3$: *m/z* 205.0739; Found 205.0734 (M^+).

3-(Phenyl)isoxazol-5-yl)methanol (3cd)



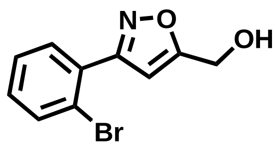
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.41-7.39 (m, 3H), 6.51 (s, 1H), 4.75 (s, 2H), 3.56 (brs, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.2, 162.4, 130.1, 128.9, 128.6, 126.7, 100.0, 56.3; MS (EI) *m/z*: 175 (M^+); HRMS (EI, m/z) calcd for $C_{10}H_9NO_2$: *m/z* 175.0633; Found 175.0639 (M^+).

3-(4-Methylphenyl)isoxazol-5-yl)methanol (3dd)



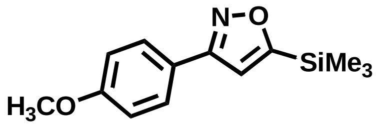
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.22 (dd, *J* = 8.1, 1.5 Hz, 2H), 6.48 (s, 1H), 4.76 (s, 2H), 3.70 (brs, OH), 2.39 (s, 3H),; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 162.4, 140.2 129.6, 126.6, 125.8, 99.9, 56.4, 21.3; MS (EI) *m/z*: 189 (M^+); HRMS (EI, m/z) calcd for $C_{11}H_{11}NO_2$: *m/z* 189.0790; Found 189.0799 (M^+).

(3-(2-Bromophenyl)isoxazol-5-yl)methanol (3ed)



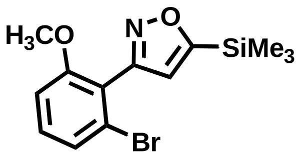
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.35 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.26 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.62 (s, 1H), 4.76 (s, 2H), 4.00 (brs, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 162.3, 133.5, 131.1, 131.0, 129.9, 127.5, 122.1, 103.2, 56.1; MS (EI) *m/z*: 254 (M^+); HRMS (EI, m/z) calcd for $C_{10}H_8BrNO_2$: *m/z* 252.9738; Found 252.9742 (M^+).

3-(4-Methoxyphenyl)-5-(trimethylsilyl)isoxazole (3be)



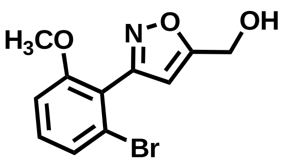
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, J = 6.8, 2.0 Hz, 2H), 6.93 (dd, J = 6.8, 2.0 Hz, 2H), 6.67 (s, 1H), 3.81 (s, 3H), 0.35 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.4, 160.7, 160.3, 128.3, 121.6, 114.2, 110.2, 55.2, -1.96; MS (EI) *m/z*: 247 (M^+); HRMS (EI, m/z) calcd for $C_{13}H_{17}NO_2Si$: *m/z* 247.1029; Found 247.1026 (M^+).

3-(2-Bromo-6-methoxyphenyl)-5-(trimethylsilyl)isoxazole (3fe)



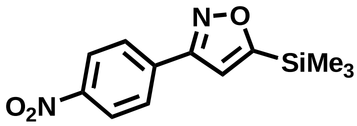
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 8.8 Hz, 1H), 7.14 (d, J = 3.1 Hz, 1H), 6.83 (s, 1H), 6.80 (dd, J = 8.8, 3.1 Hz, 1H), 3.78 (s, 3H), 0.36 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 160.7, 158.7, 134.1, 131.2, 117.3, 116.1, 113.7, 112.5, 55.5, -1.94; MS (EI) *m/z*: 326 (M^+); HRMS (EI, m/z) calcd for $C_{13}H_{16}BrNO_2Si$: *m/z* 325.0134; Found 325.0132 (M^+).

(3-(2-Bromo-6-methoxyphenyl)isoxazol-5-yl)methanol (3fd)



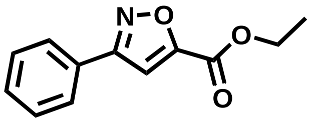
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 3.1 Hz, 1H), 6.84 (dd, J = 8.8, 3.1 Hz, 1H), 6.69 (s, 1H), 4.82 (t, J = 3.0 Hz, 2H), 3.80 (s, 3H), 2.31 (brs, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 162.7, 159.1, 134.5, 131.1, 117.9, 116.3, 112.7, 103.6, 56.8, 55.9; MS (EI) *m/z*: 284 (M^+); HRMS (EI, m/z) calcd for $C_{11}H_{10}BrNO_3$: *m/z* 282.9844; Found 282.9848 (M^+).

3-(4-Nitrophenyl)-5-(trimethylsilyl)isoxazole (3ae)



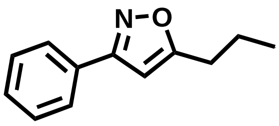
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, J = 8.9 Hz, 2H), 7.99 (d, J = 8.9 Hz, 2H), 6.79 (s, 1H), 0.38 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.3, 159.1, 148.5, 127.8, 124.5, 123.5, 110.6, -1.94; MS (EI) *m/z*: 262 (M^+); HRMS (EI, m/z) calcd for $C_{12}H_{14}N_2O_3Si$: *m/z* 262.0774; Found 262.0776 (M^+).

Ethyl-3-phenylisoxazole-5-carboxylate (3cf)

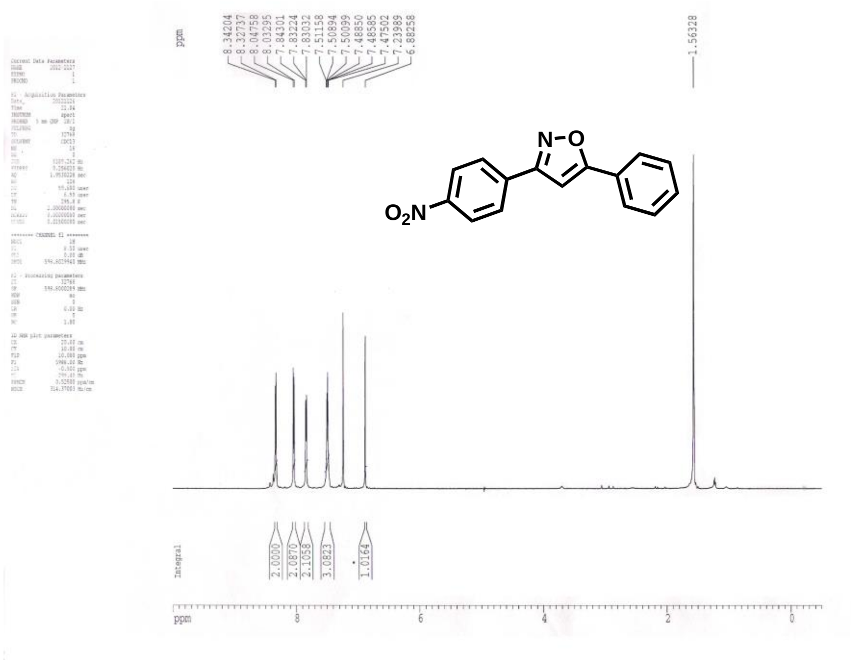


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H), 7.44-7.42 (m, 3H), 7.22 (s, 1H), 4.42 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.1, 162.8, 156.7, 130.4, 129.3, 128.9, 126.7, 107.2, 62.2, 14.0; MS (EI) *m/z*: 217 (M^+); HRMS (EI, m/z) calcd for $C_{12}H_{11}NO_3$: *m/z* 217.0739; Found 217.0740 (M^+).

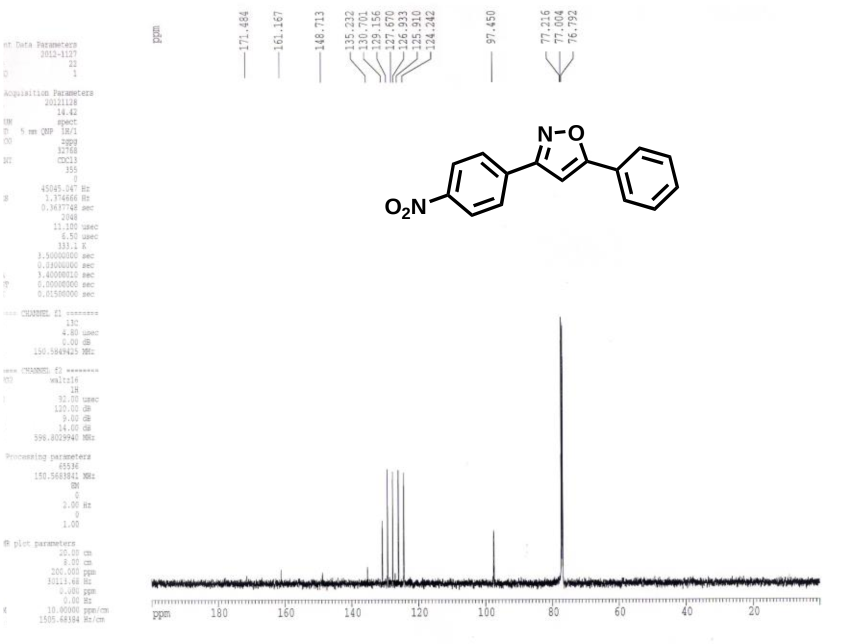
3-Phenyl-5-propylisoxazole (3cg)



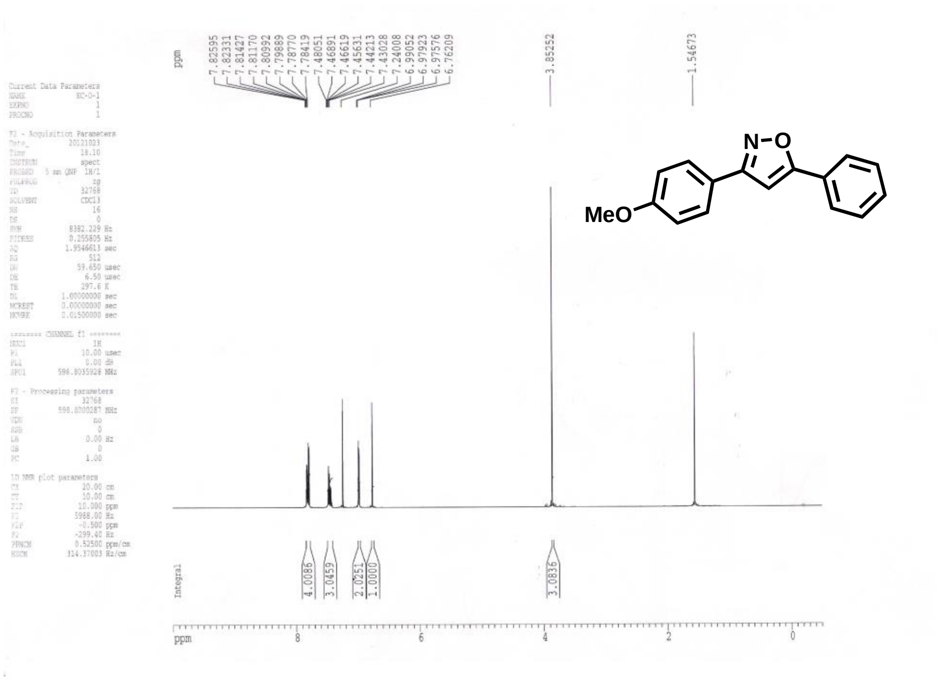
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83-7.76 (m, 2H), 7.42-7.41 (m, 3H), 6.27 (s, 1H), 2.75 (t, J = 7.5 Hz, 2H), 1.78-1.74 (m, 2H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ174.0, 162.3, 129.7, 128.8, 128.6, 126.7, 98.8, 28.7, 20.9, 13.6;MS (EI) *m/z*: 187 (M^+); HRMS (EI, m/z) calcd for $C_{12}H_{13}NO$: *m/z* 187.0997; Found 187.0990 (M^+).



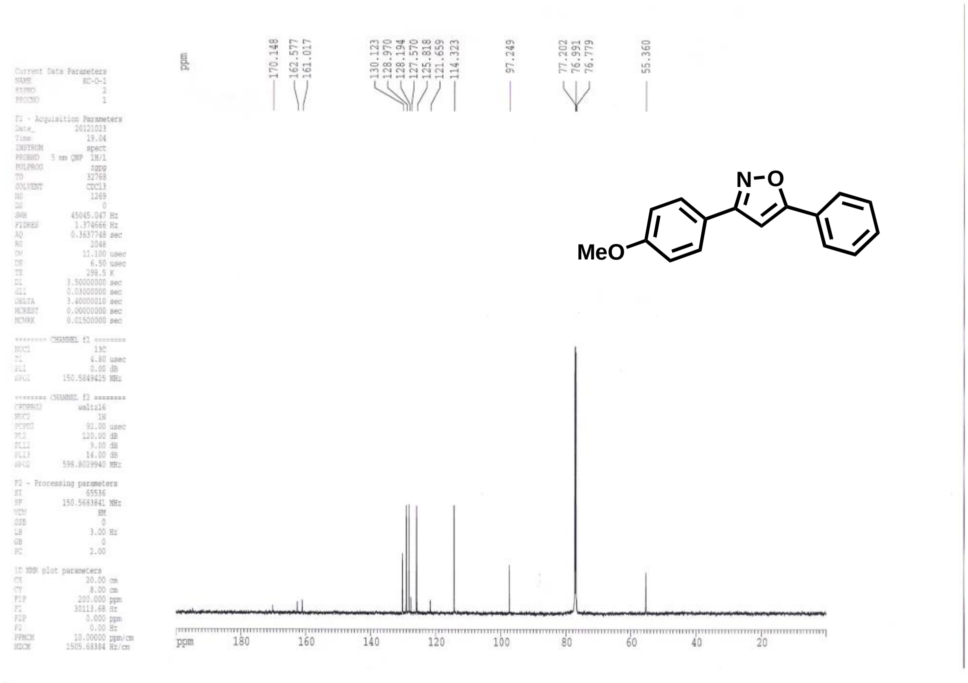
^{1}H NMR spectrum of compound 3aa in $CDCl_3$ in 600 MHz



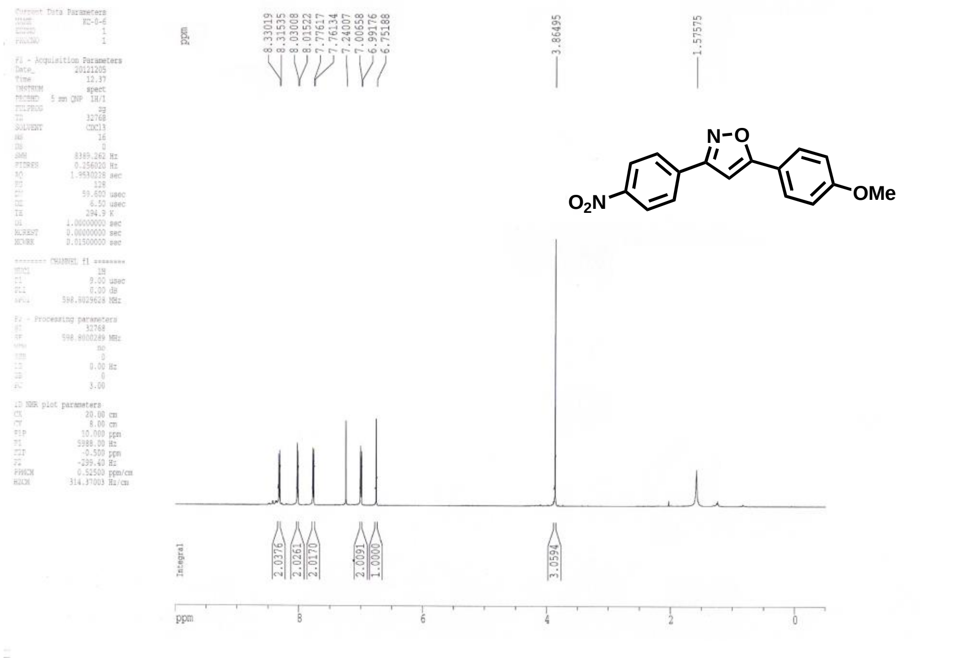
^{13}C NMR spectrum of compound 3aa in $CDCl_3$ in 150 MHz



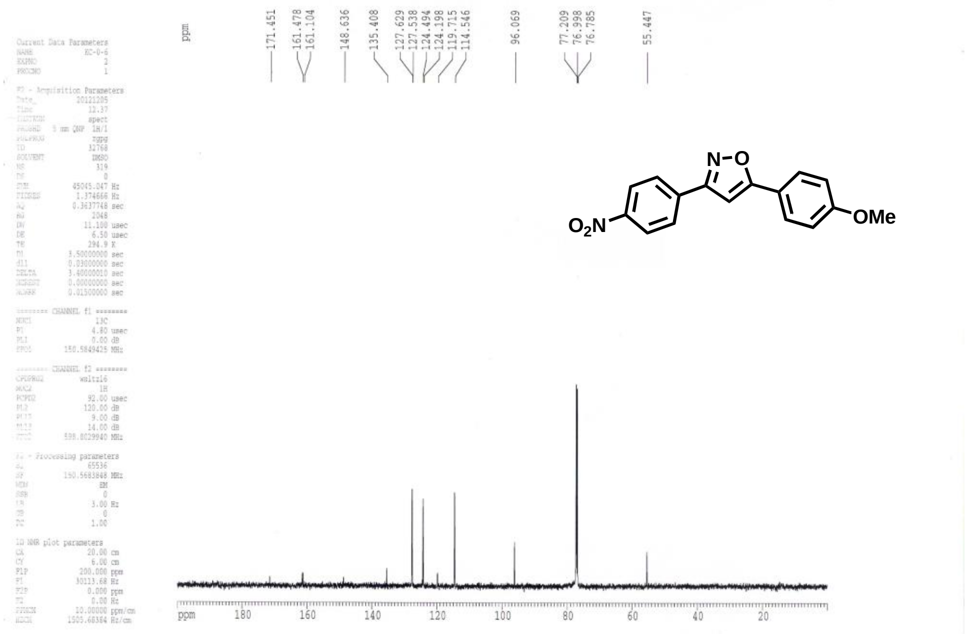
[1]H NMR spectrum of compound 3ba in $CDCl_3$ in 600 MHz



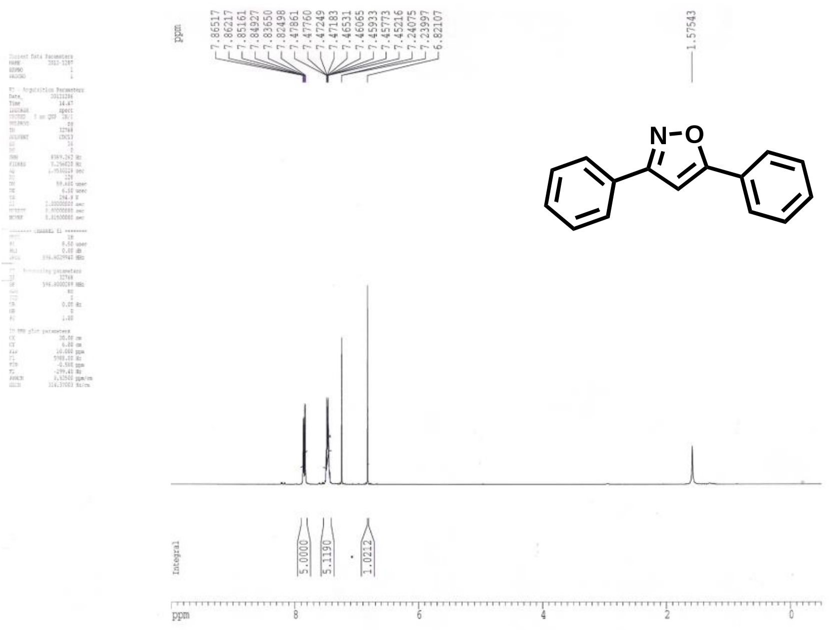
[13]C NMR spectrum of compound 3ba in $CDCl_3$ in 150 MHz



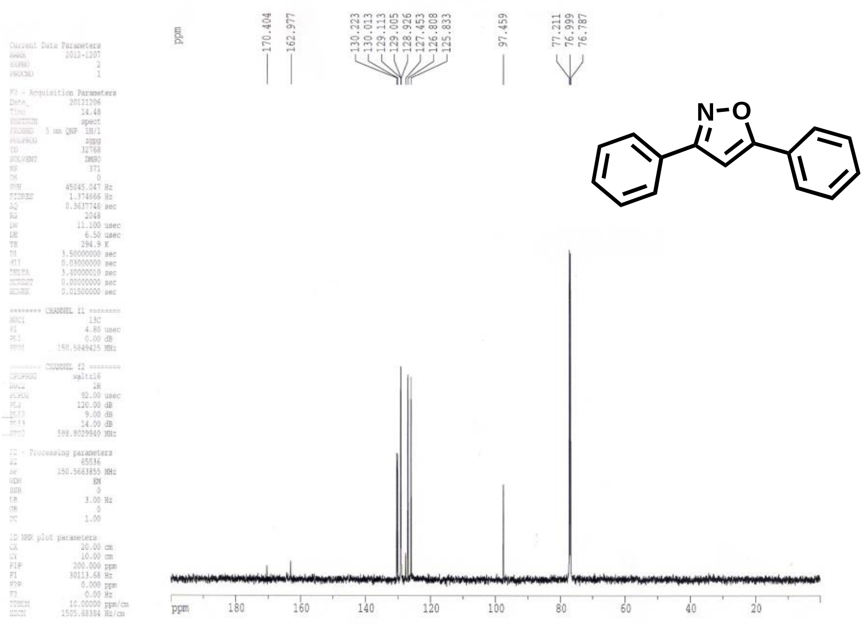
^{1}H NMR spectrum of compound 3ab in $CDCl_3$ in 600 MHz



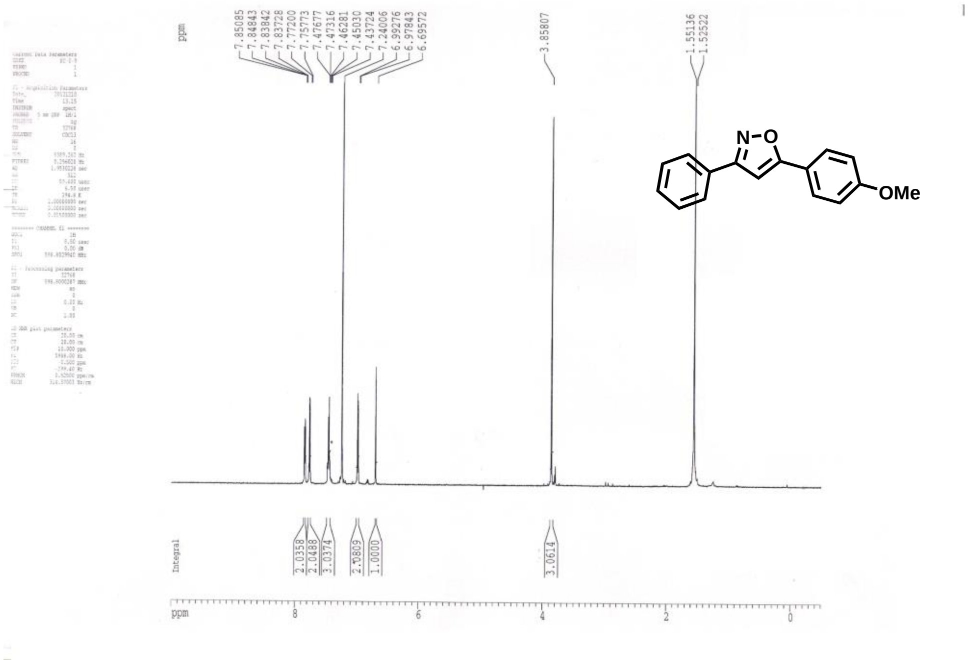
^{13}C NMR spectrum of compound 3ab in $CDCl_3$ in 150 MHz



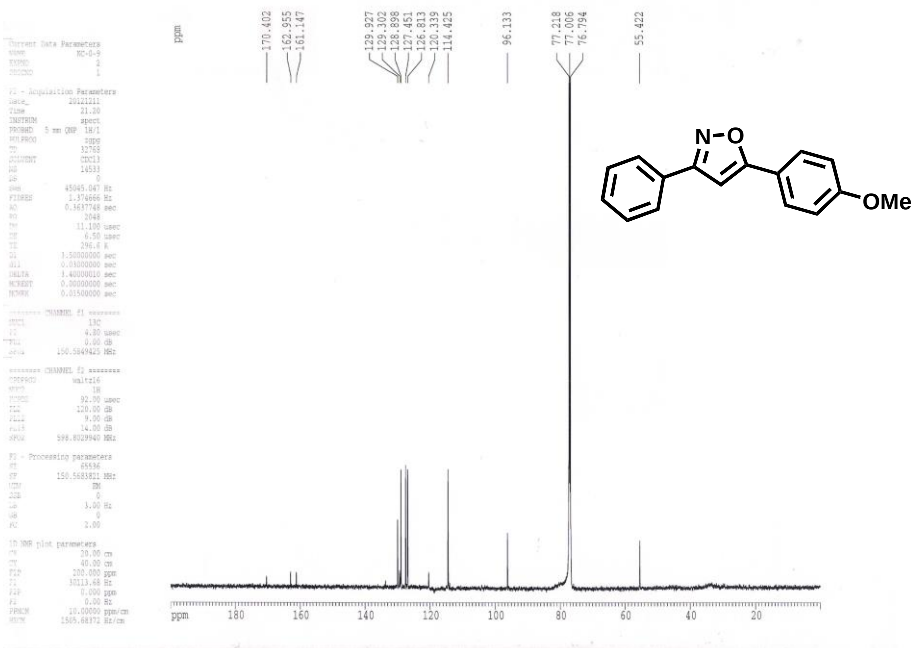
^{1}H NMR spectrum of compound 3ca in $CDCl_3$ in 600 MHz



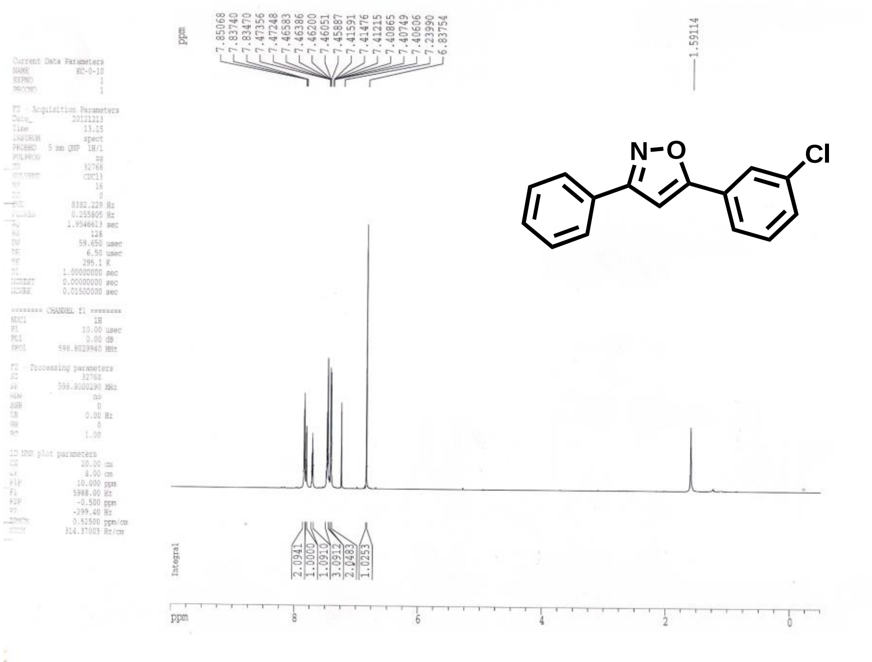
^{13}C NMR spectrum of compound 3ca in $CDCl_3$ in 150 MHz



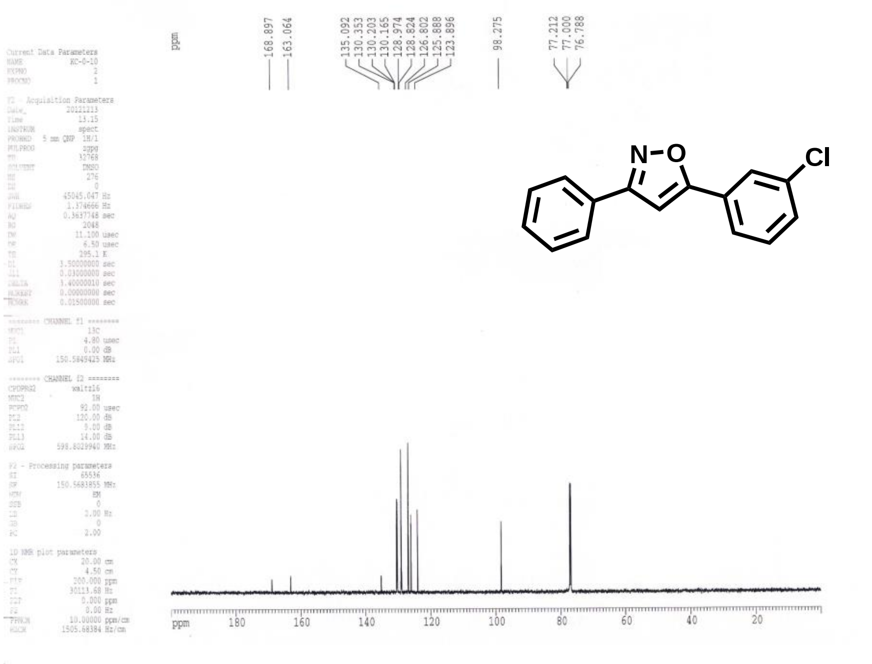
^{1}H NMR spectrum of compound 3cb in $CDCl_3$ in 600 MHz



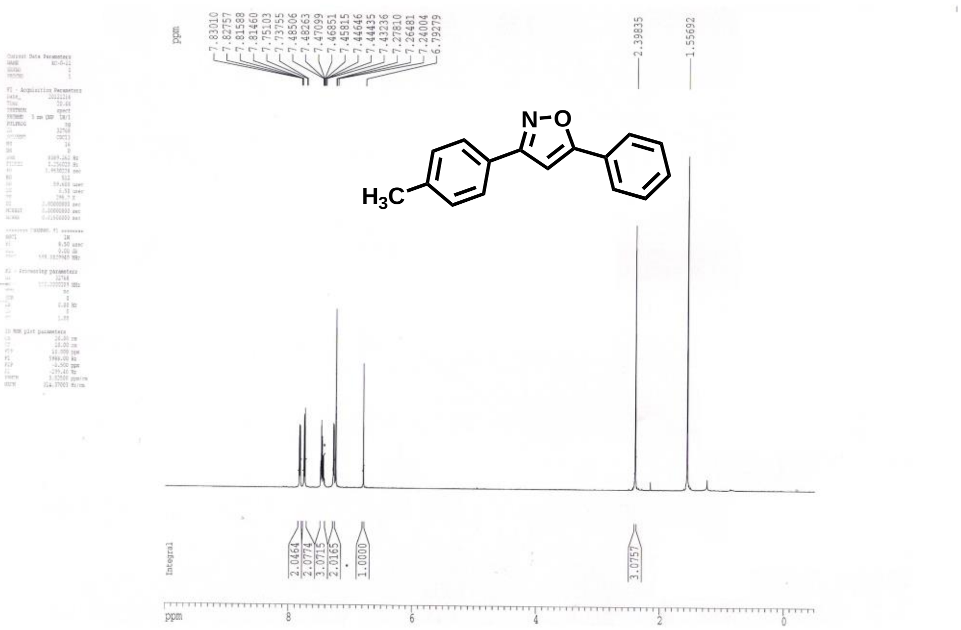
^{13}C NMR spectrum of compound 3cb in $CDCl_3$ in 150 MHz



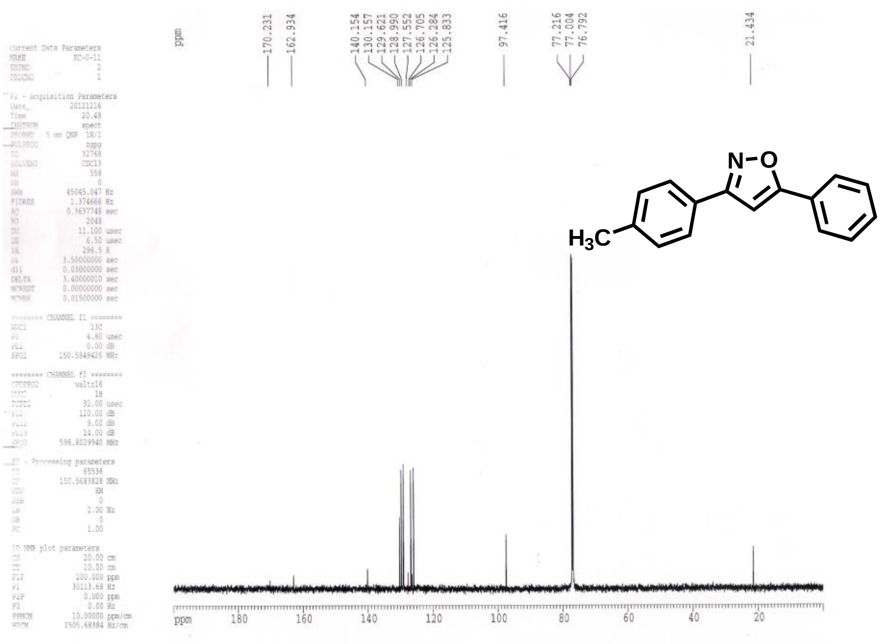
^{1}H NMR spectrum of compound 3cc in $CDCl_3$ in 600 MHz



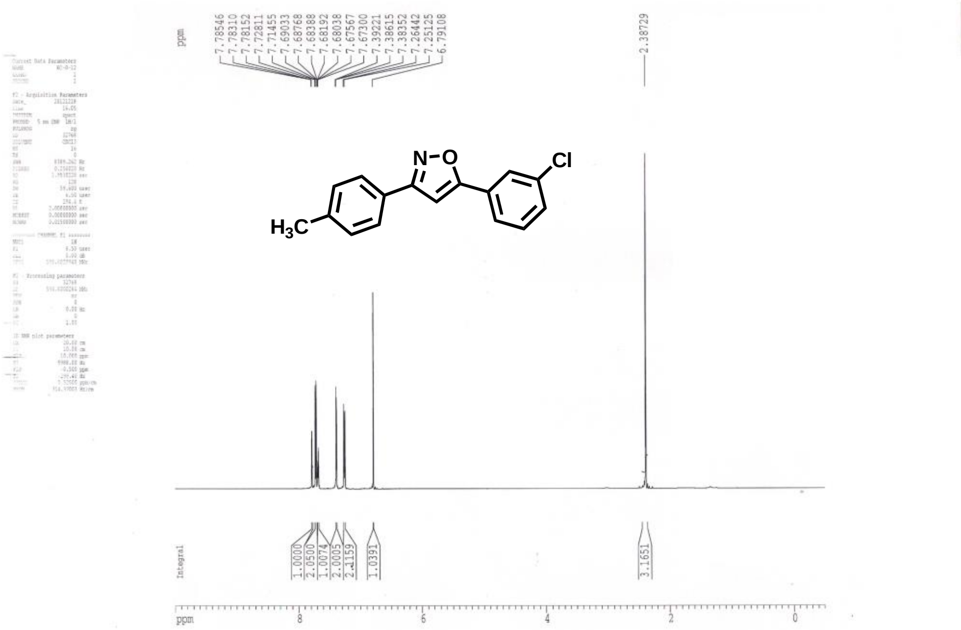
^{13}C NMR spectrum of compound 3cc in $CDCl_3$ in 150 MHz



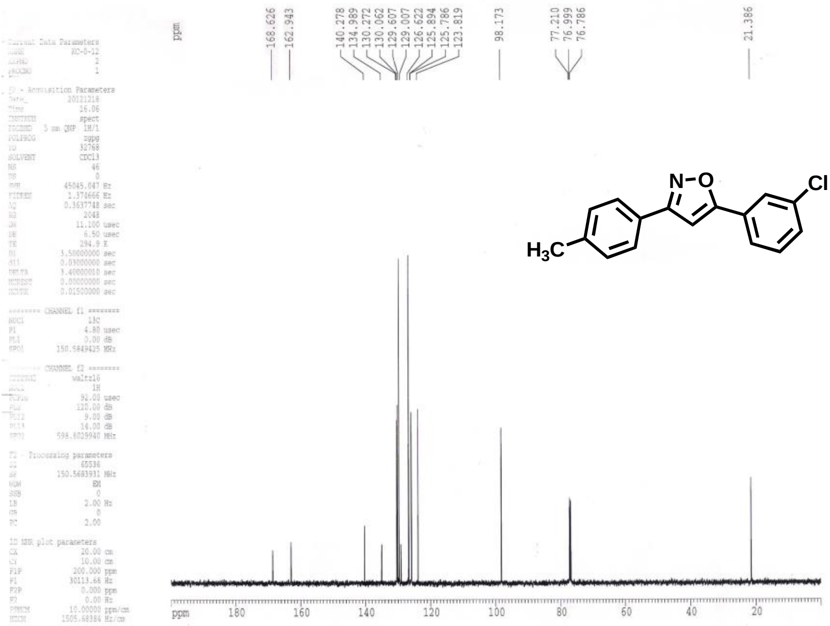
^{1}H NMR spectrum of compound 3da in $CDCl_3$ in 600 MHz



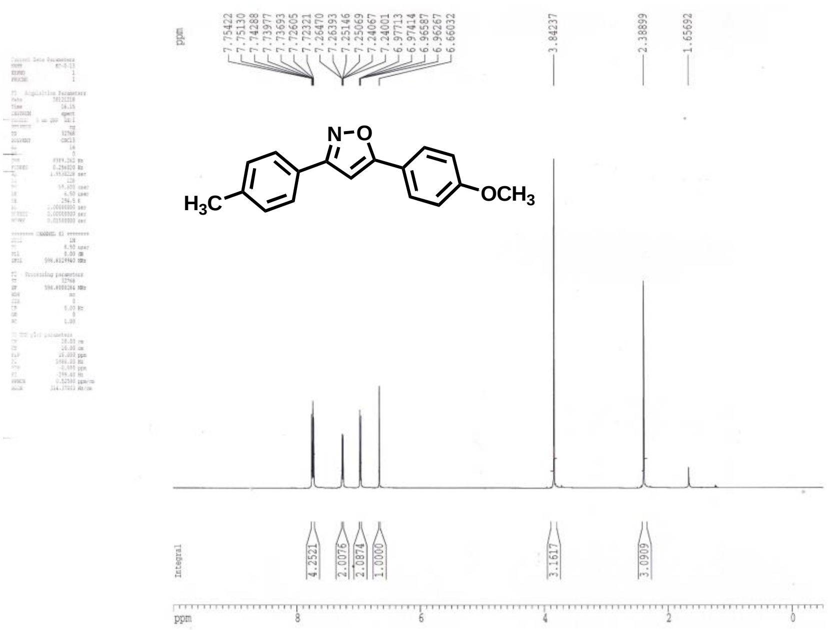
^{13}C NMR spectrum of compound 3da in $CDCl_3$ in 150 MHz



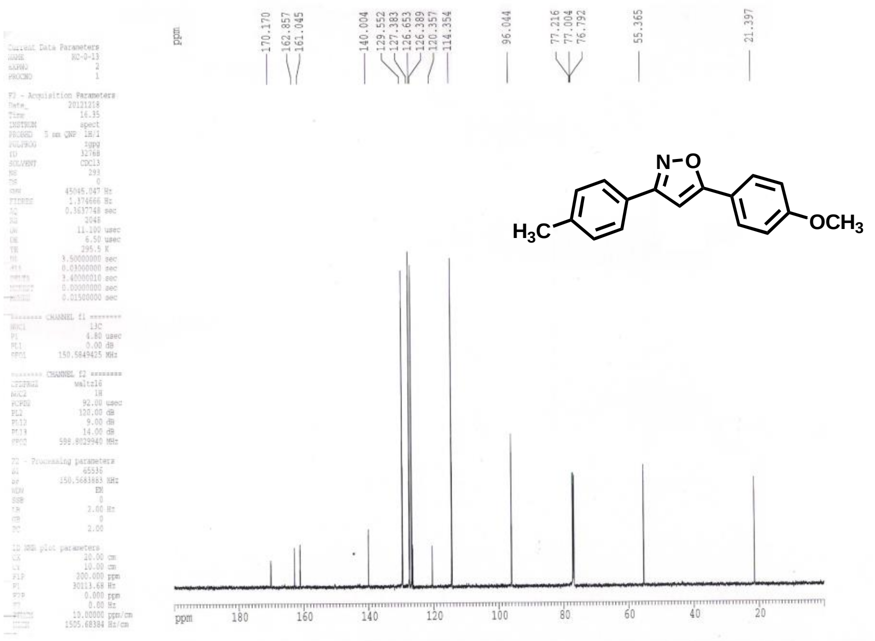
[1]H NMR spectrum of compound 3dc in $CDCl_3$ in 600 MHz



[13]C NMR spectrum of compound 3dc in $CDCl_3$ in 150 MHz

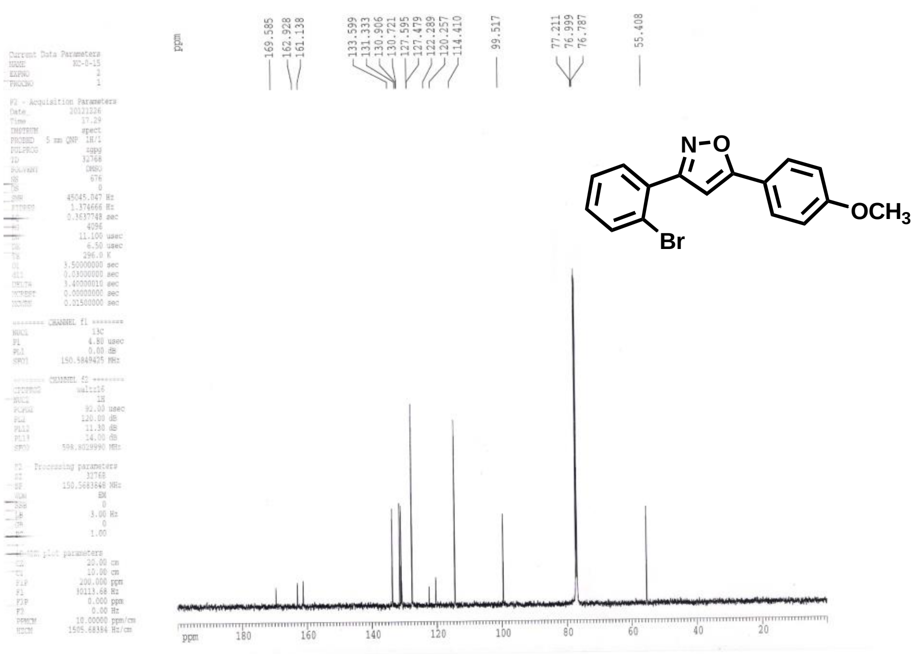


^{1}H NMR spectrum of compound 3db in $CDCl_3$ in 600 MHz

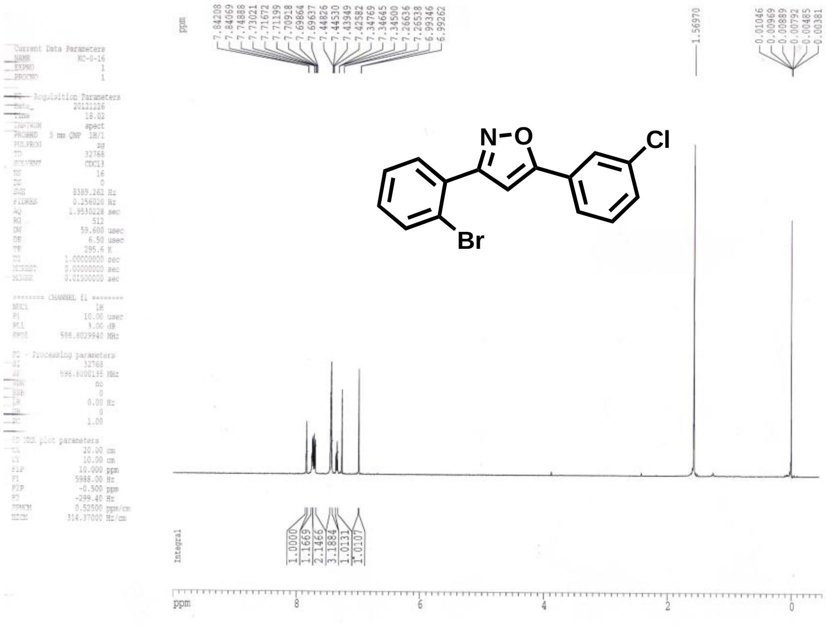


^{13}C NMR spectrum of compound 3db in $CDCl_3$ in 150 MHz

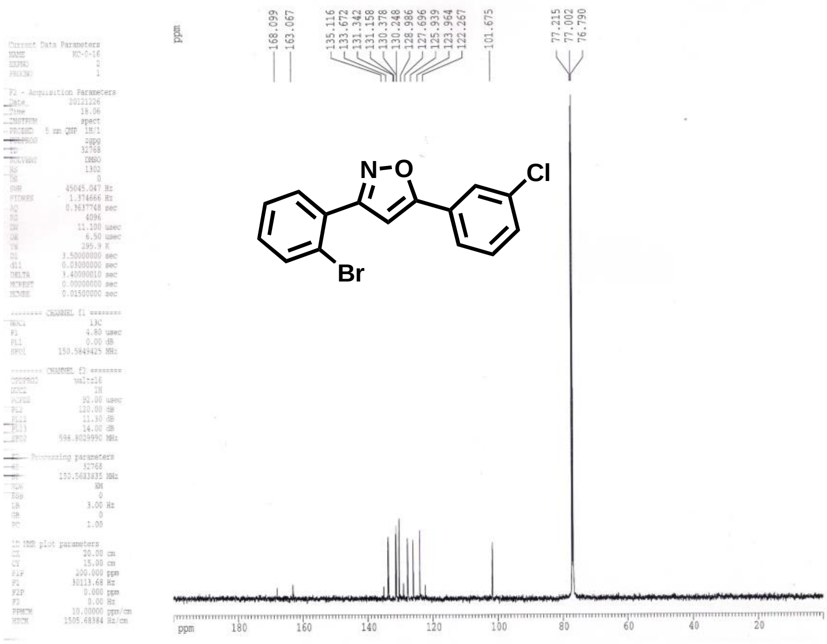
[1]H NMR spectrum of compound 3eb in $CDCl_3$ in 600 MHz



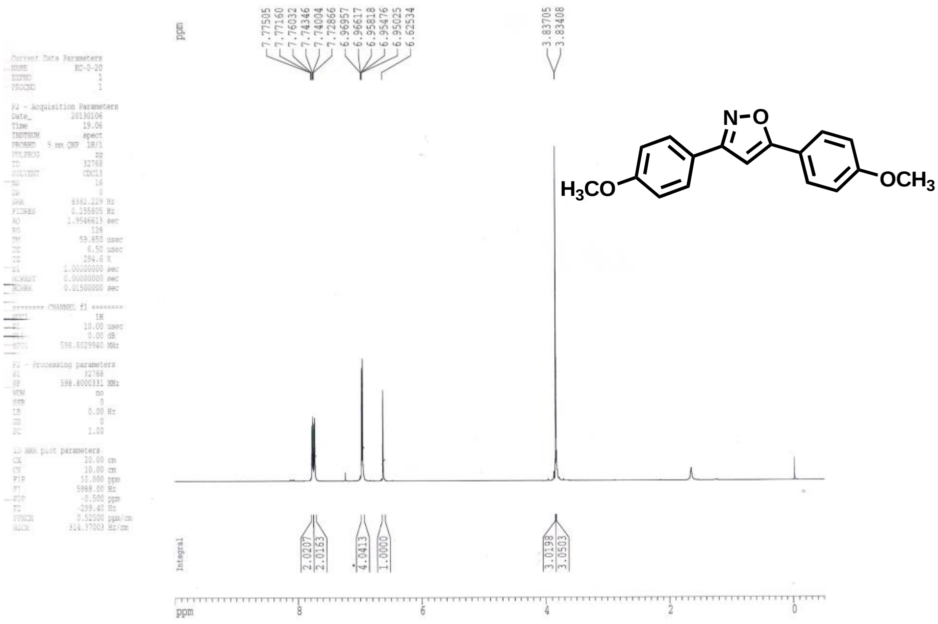
[13]C NMR spectrum of compound 3eb in $CDCl_3$ in 150 MHz



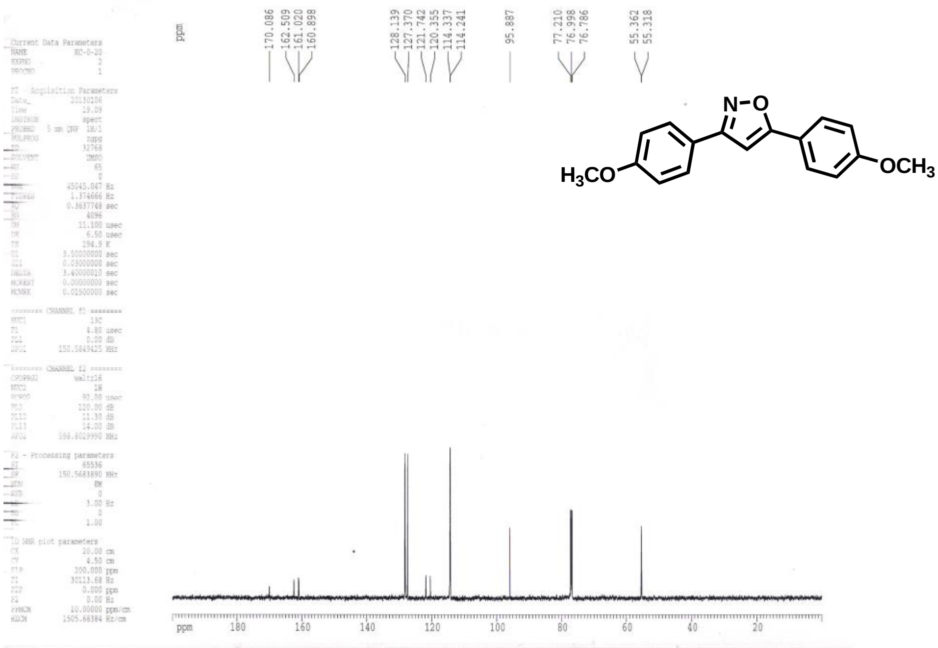
[1]H NMR spectrum of compound 3ec in $CDCl_3$ in 600 MHz



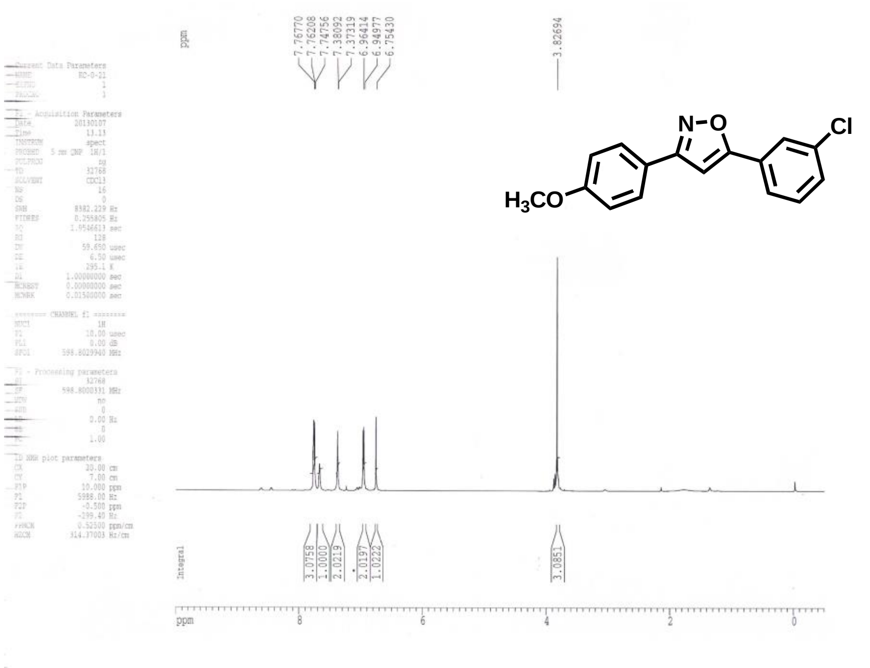
[13]C NMR spectrum of compound 3ec in $CDCl_3$ in 150 MHz



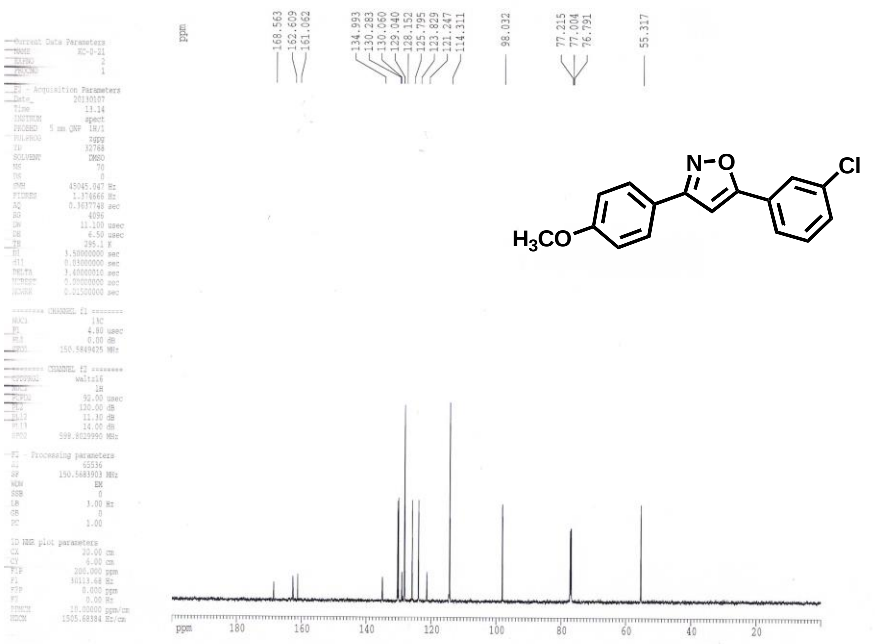
[1]H NMR spectrum of compound 3bb in $CDCl_3$ in 600 MHz



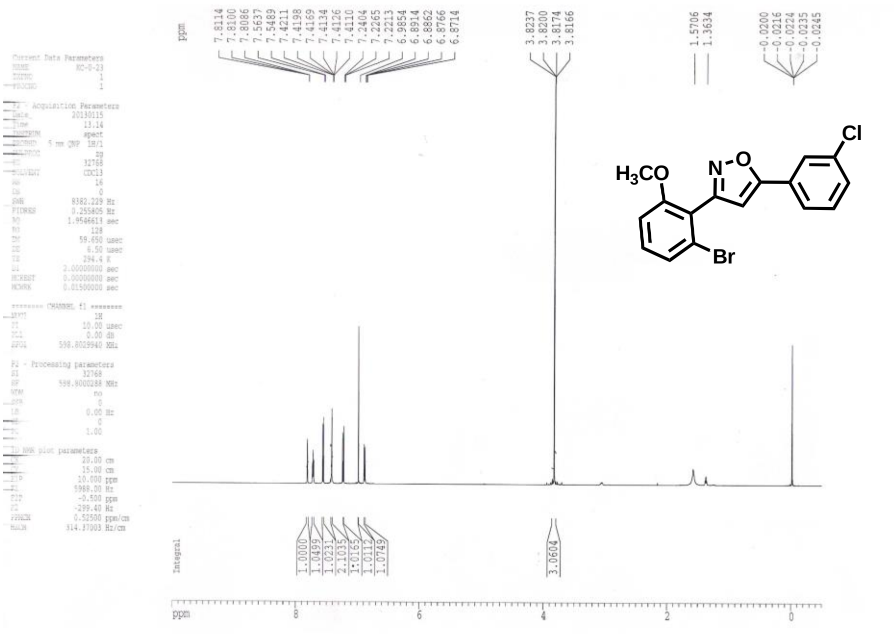
[13]C NMR spectrum of compound 3bb in $CDCl_3$ in 150 MHz



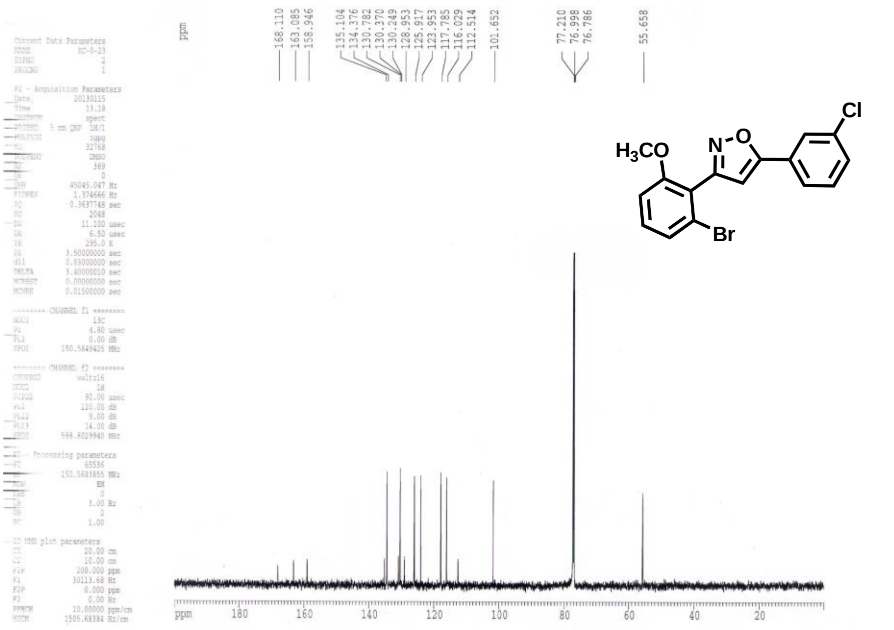
[1]H NMR spectrum of compound 3bc in $CDCl_3$ in 600 MHz



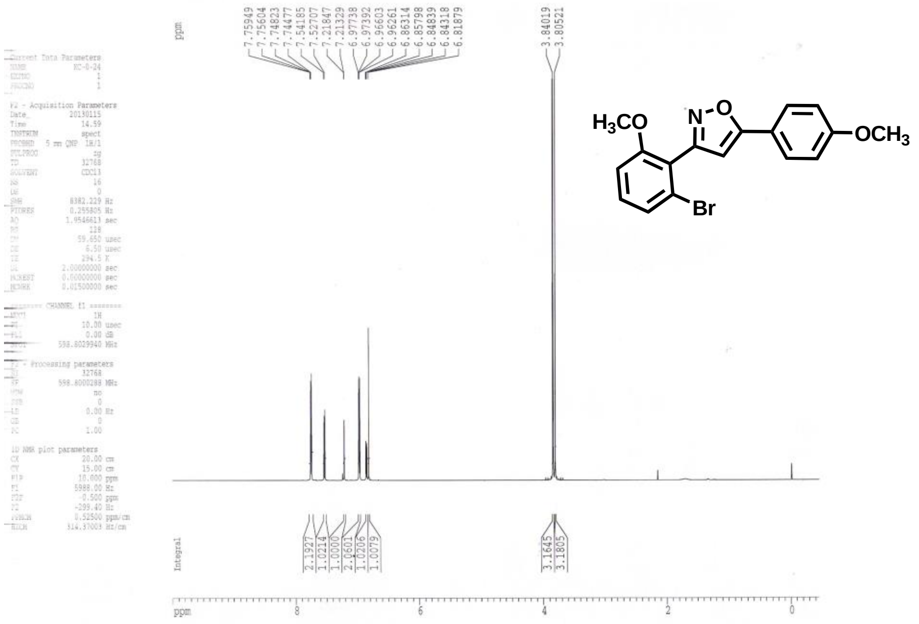
[13]C NMR spectrum of compound 3bc in $CDCl_3$ in 150 MHz



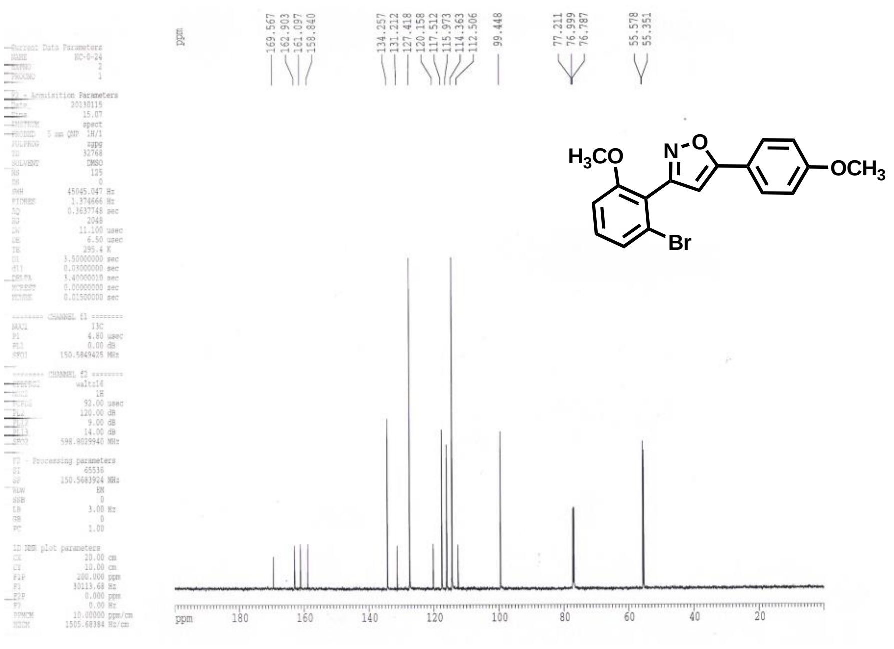
^{1}H NMR spectrum of compound 3fc in $CDCl_3$ in 600 MHz



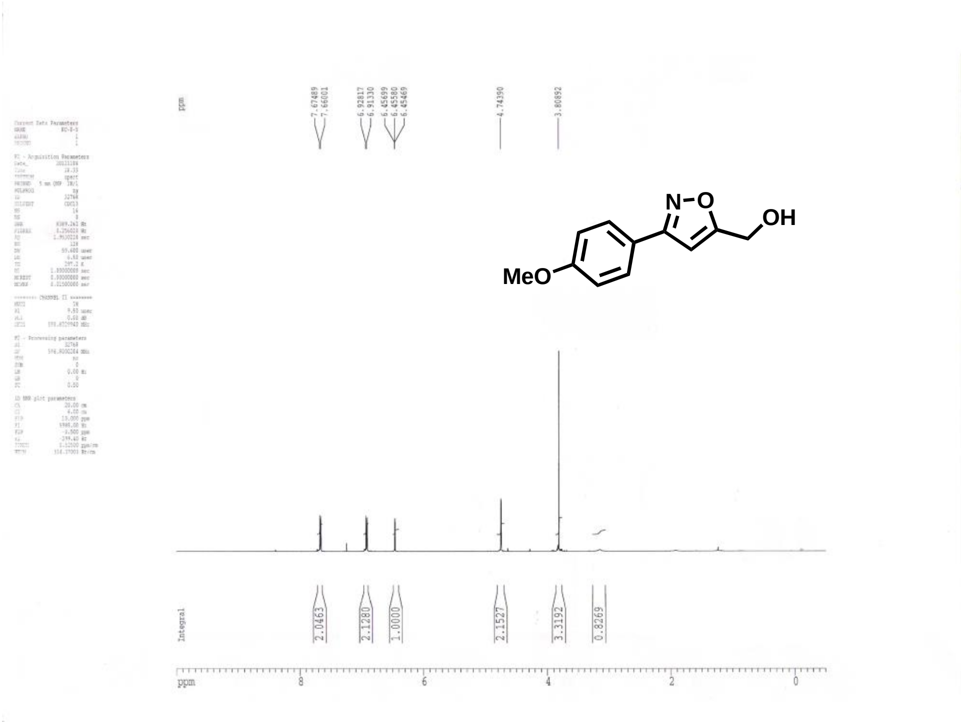
^{13}C NMR spectrum of compound 3fc in $CDCl_3$ in 150 MHz



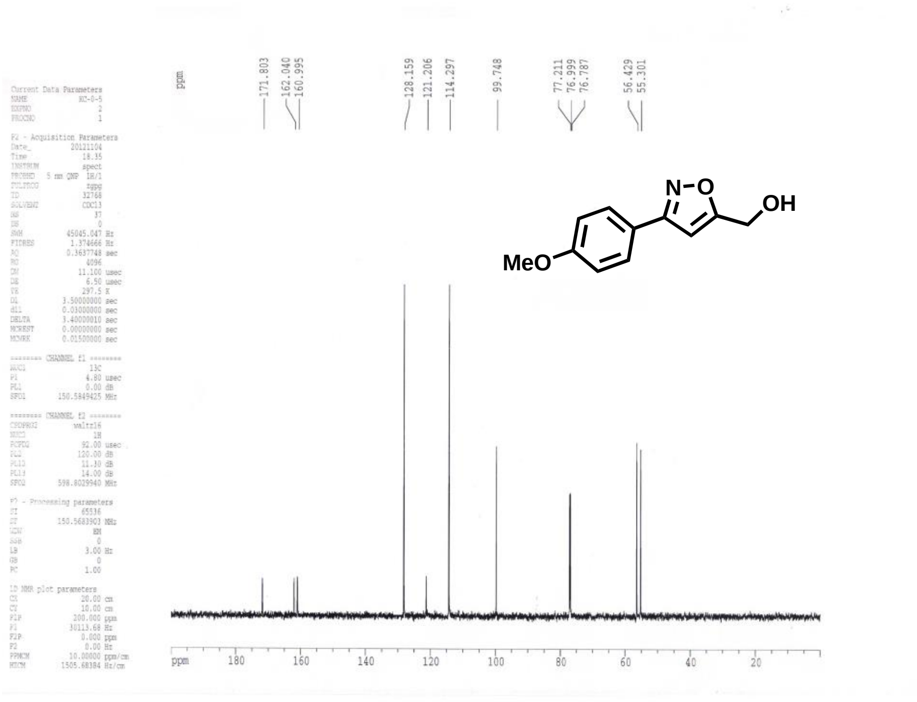
^{1}H NMR spectrum of compound 3fb in $CDCl_3$ in 600 MHz



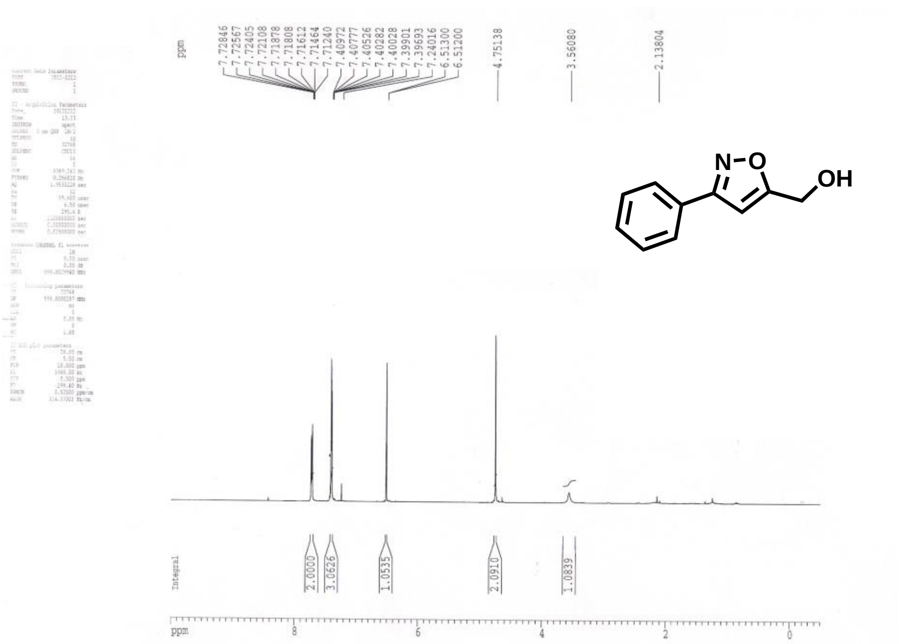
^{13}C NMR spectrum of compound 3fb in $CDCl_3$ in 150 MHz



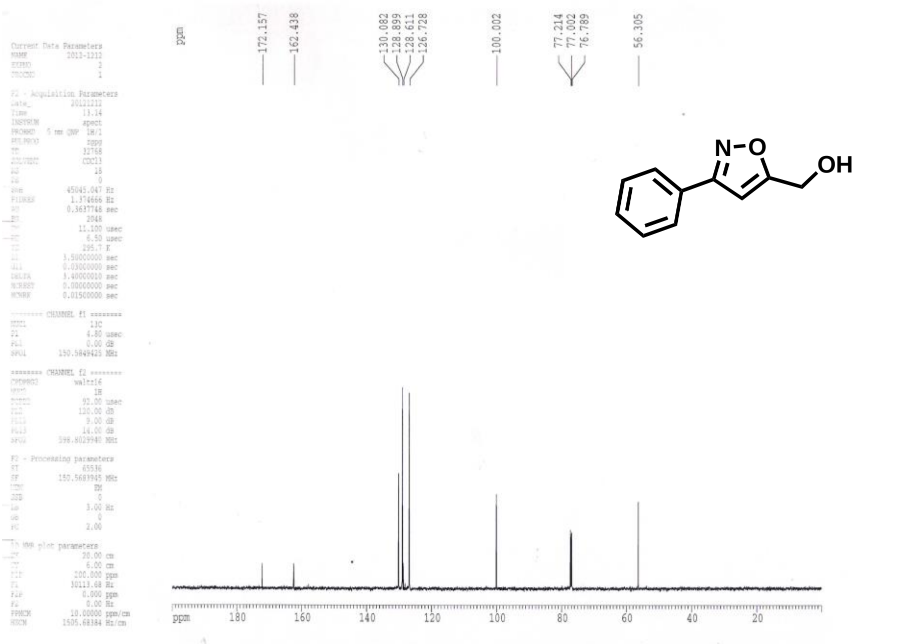
^{1}H NMR spectrum of compound 3bd in $CDCl_3$ in 600 MHz



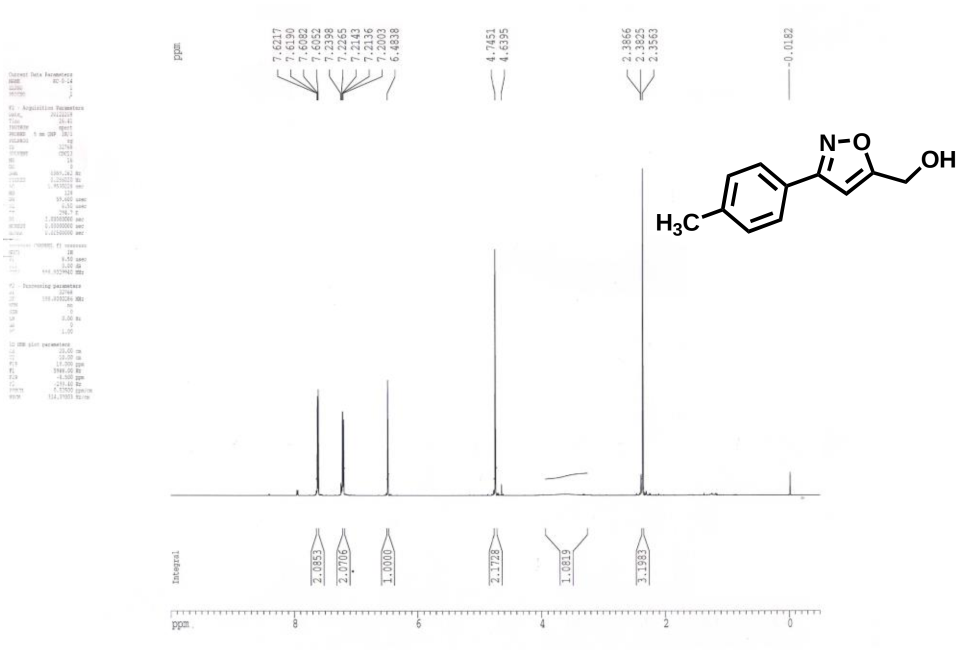
^{13}C NMR spectrum of compound 3bd in $CDCl_3$ in 150 MHz



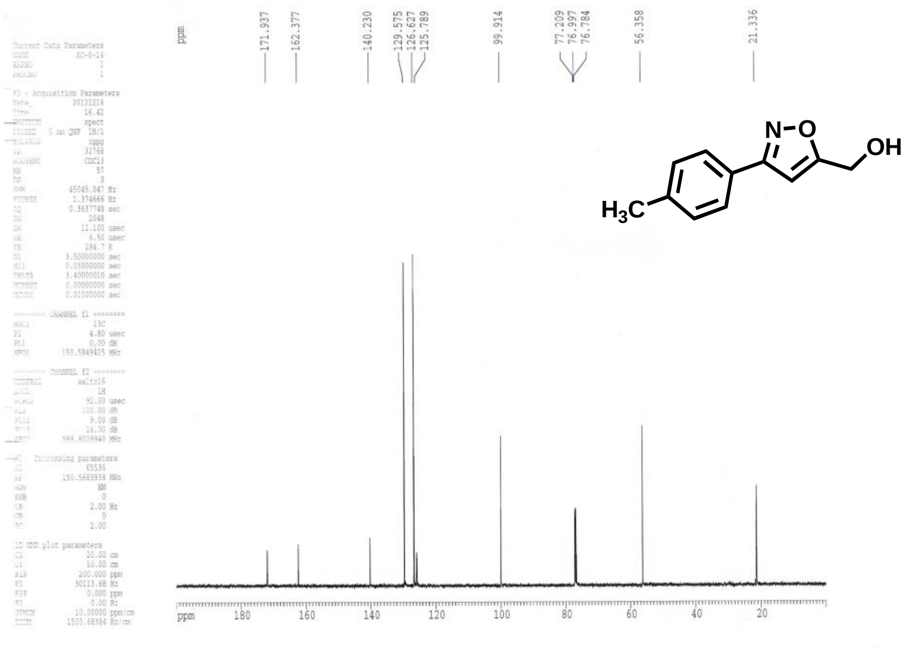
^{1}H NMR spectrum of compound 3cd in $CDCl_3$ in 600 MHz



^{13}C NMR spectrum of compound 3cd in $CDCl_3$ in 150 MHz

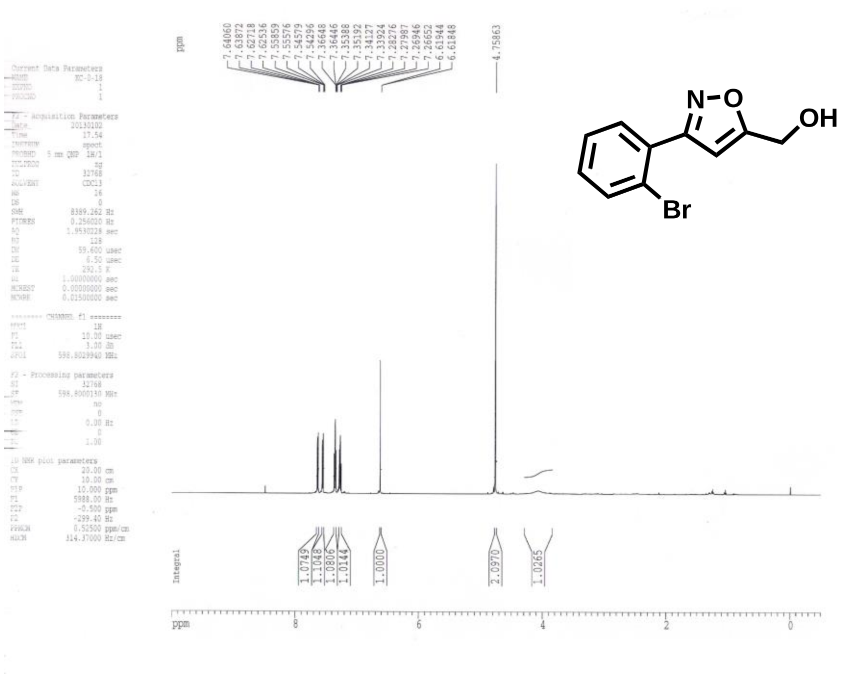


[1]H NMR spectrum of compound 3dd in $CDCl_3$ in 600 MHz

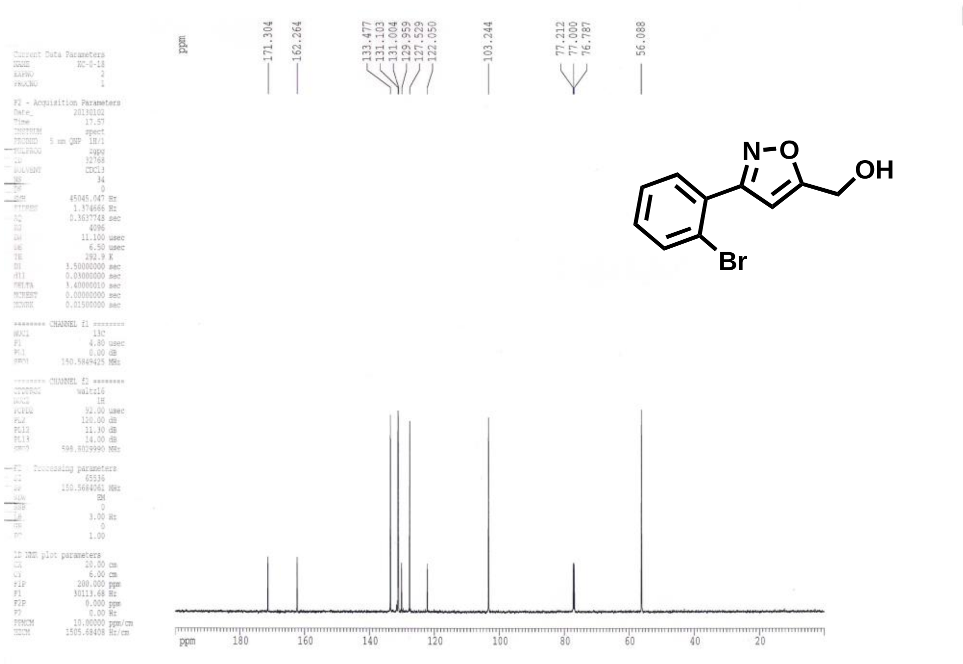


[13]C NMR spectrum of compound 3dd in $CDCl_3$ in 150 MHz

Electronic Supplementary Material (ESI) for Nanoscale



[1]H NMR spectrum of compound 3ed in $CDCl_3$ in 600 MHz



[13]C NMR spectrum of compound 3ed in $CDCl_3$ in 150 MHz

Electronic Supplementary Material (ESI) for Nanoscale
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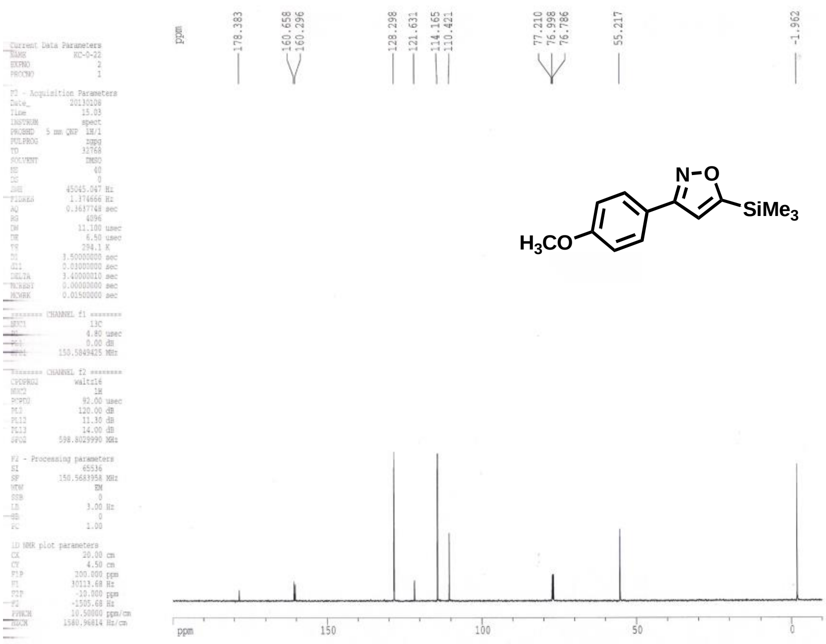
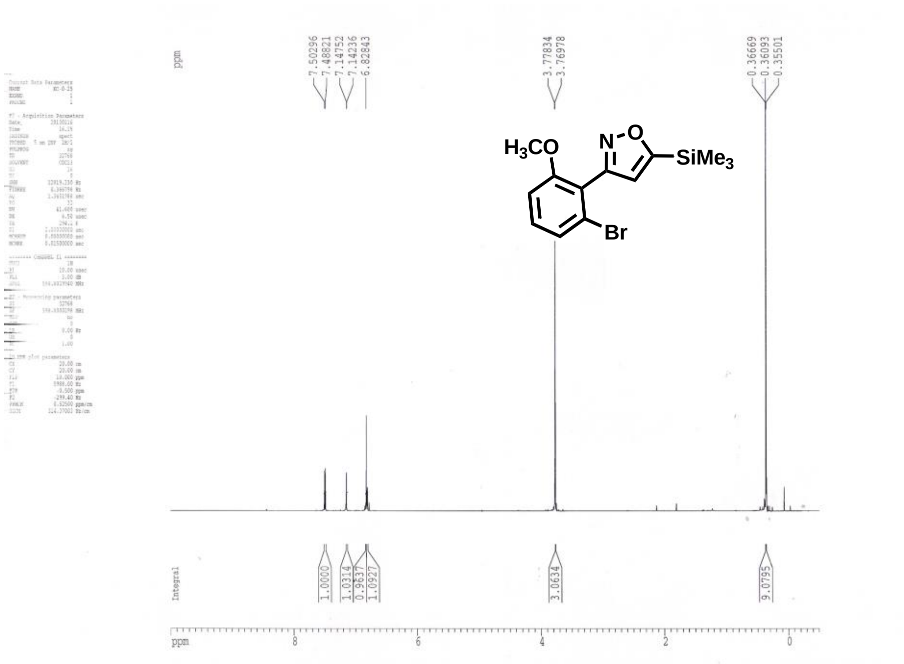
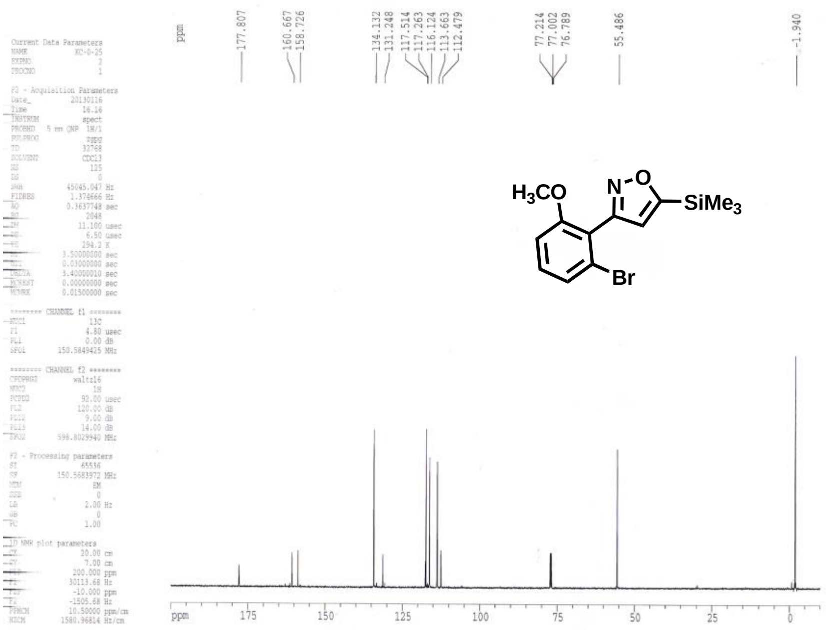
[1]H NMR spectrum of compound 3be in $CDCl_3$ in 600 MHz



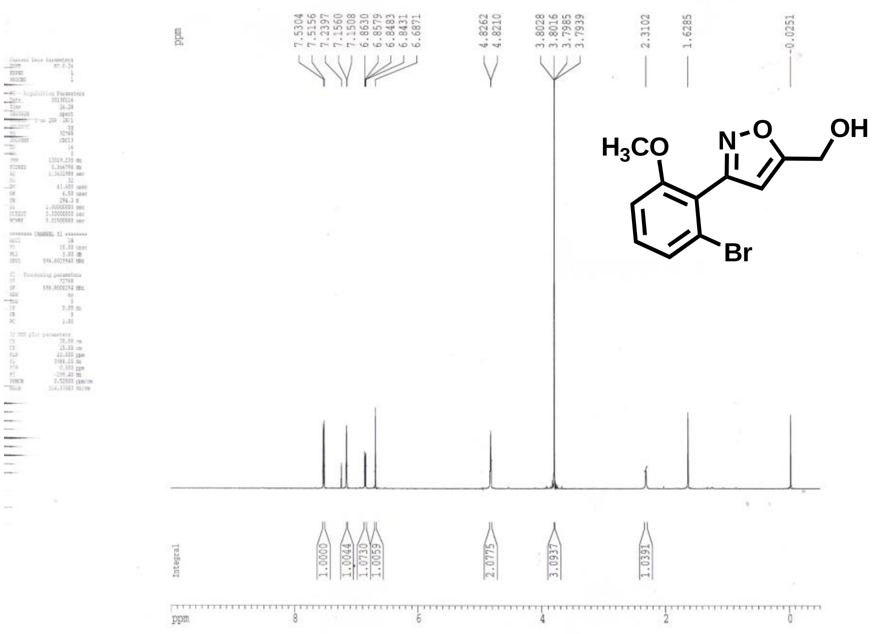
[13]C NMR spectrum of compound 3be in $CDCl_3$ in 150 MHz



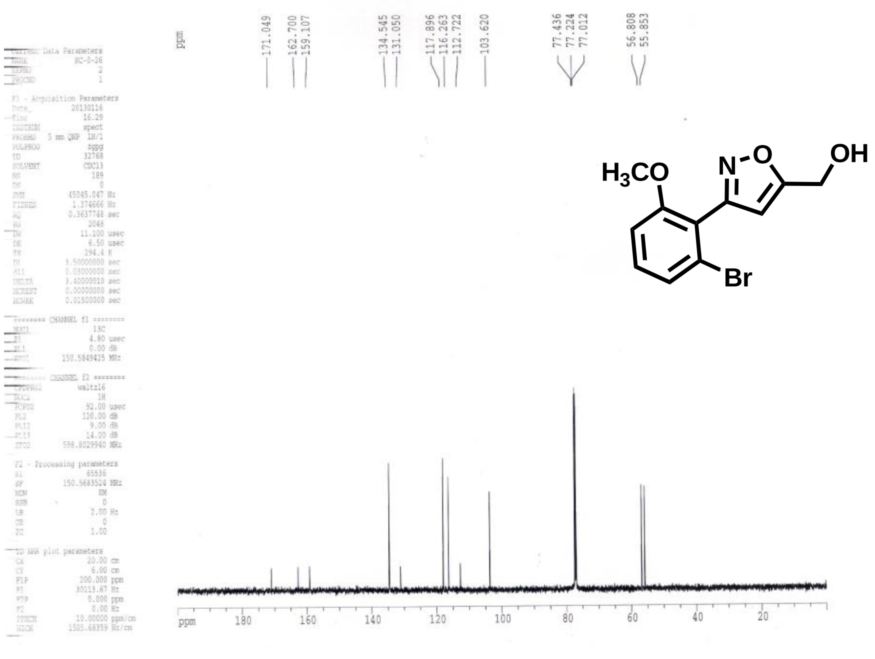
^{1}H NMR spectrum of compound 3fe in $CDCl_3$ in 600 MHz



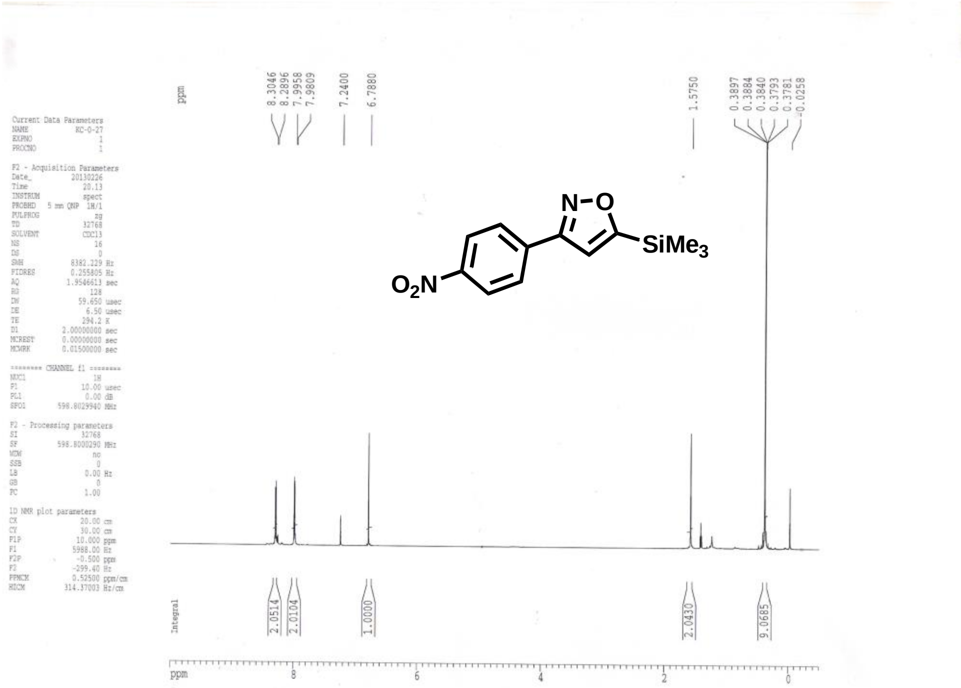
^{13}C NMR spectrum of compound 3fe in $CDCl_3$ in 150 MHz



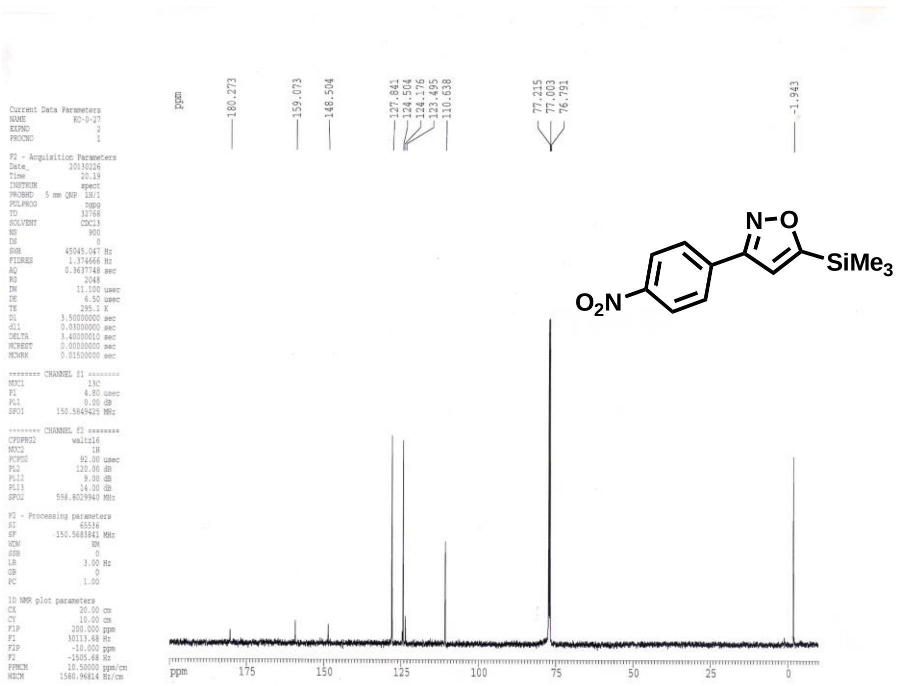
^{1}H NMR spectrum of compound 3fd in $CDCl_3$ in 600 MHz



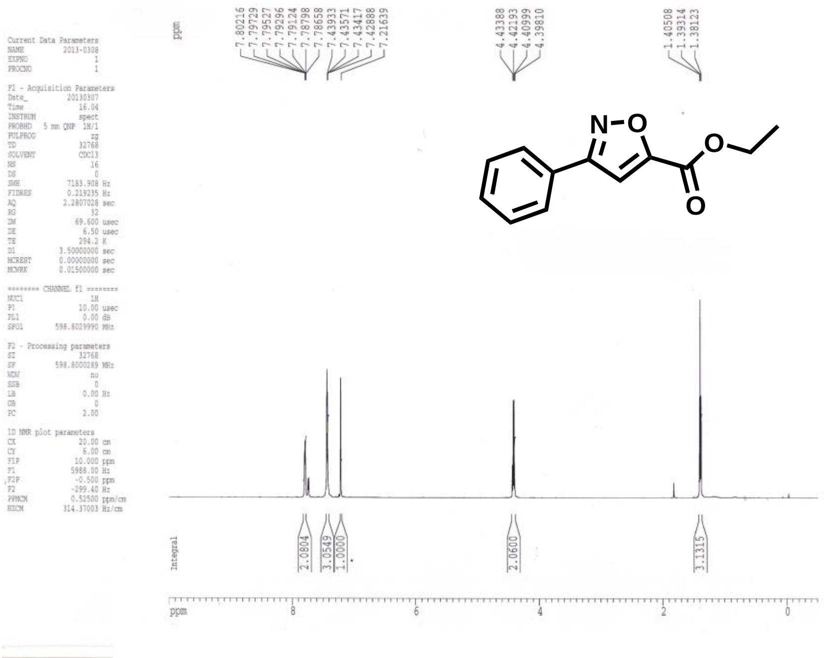
^{13}C NMR spectrum of compound 3fd in $CDCl_3$ in 150 MHz



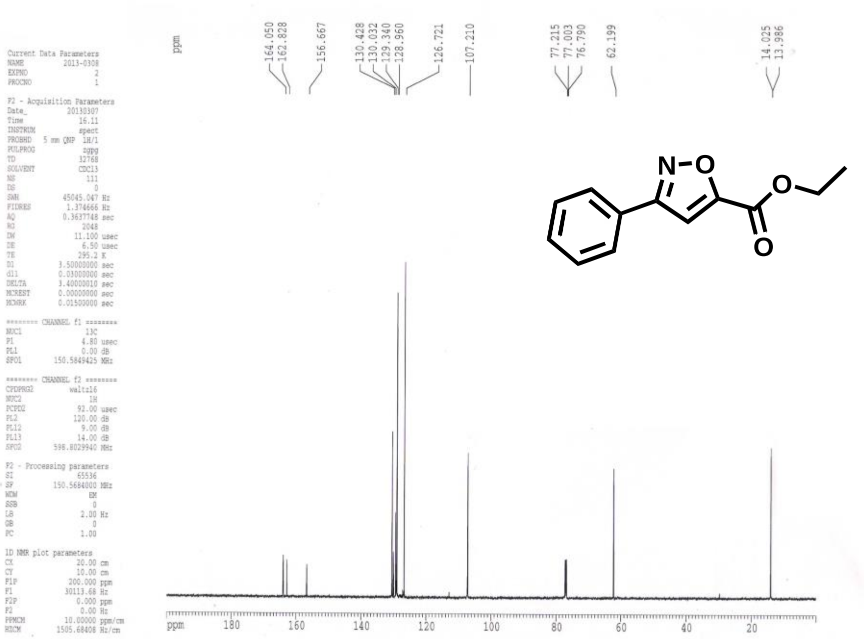
[1]H NMR spectrum of compound 3ae in $CDCl_3$ in 600 MHz



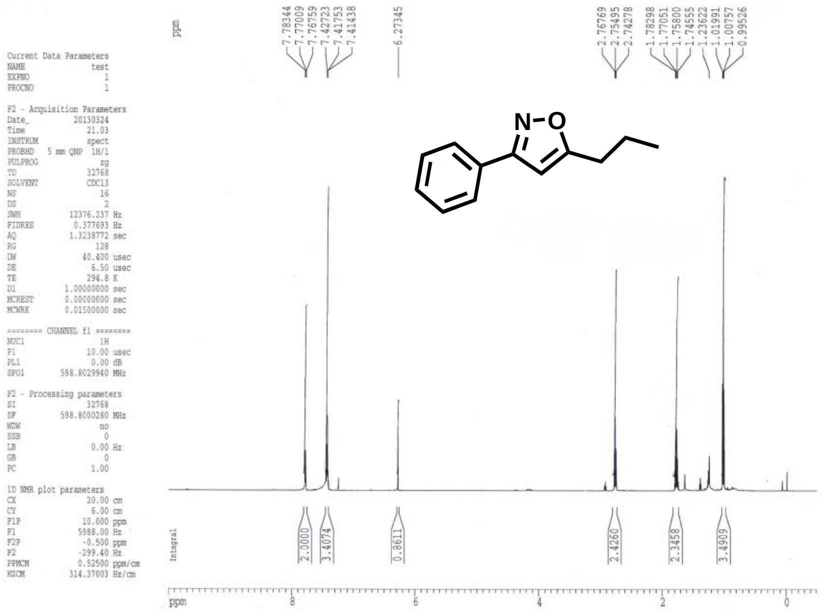
[13]C NMR spectrum of compound 3ae in $CDCl_3$ in 150 MHz



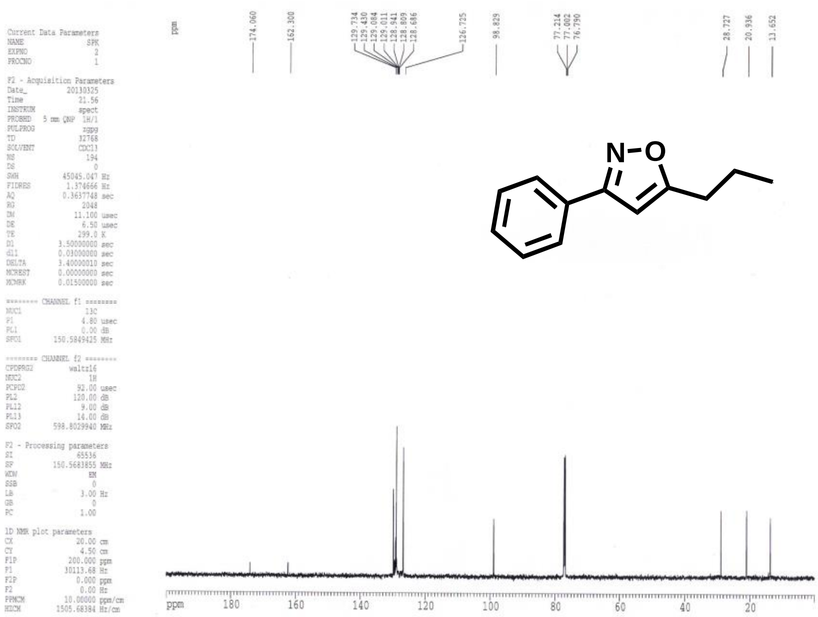
^{1}H NMR spectrum of compound 3cf in $CDCl_3$ in 600 MHz



^{13}C NMR spectrum of compound 3cf in $CDCl_3$ in 150 MHz



^{1}H NMR spectrum of compound 3cg in $CDCl_3$ in 600 MHz



^{13}C NMR spectrum of compound 3cg in $CDCl_3$ in 150 MHz