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Supporting Information

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Preparation of Aryl and Heteroaryl Indium(III) Reagents by the Direct Insertion of Indium in the Presence of LiCl

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General information: All reactions were carried out under an argon atmosphere in dried glassware. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95 % purity as determined by ^{1}H-NMR and capillary-GC. NMR spectra were recorded on solutions in deuterated chloroform ($CDCl_3$) with residual chloroform (d 7.24 ppm for ^{1}H NMR and d 77.0 ppm for ^{13}C NMR). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.
Starting Materials: Indium powder was purchased from ChemPur, Germany. Commercial available starting materials were purchased from commercial sources and used without further purification

General procedure for indium insertion (Table 1): LiCl was placed in an argon-flushed flask and dried additionally 5-10 min at 380 °C (heat gun) on high vacuum (1 mbar). Indium powder was added under argon and the flask was evacuated and refilled with argon three times. After the addition of THF, indium was activated by treatment first with 1,2-dibromoethane (5 mol%) and then with chlorotrimethylsilane (2 mol%).[1,2] The substrate (along with internal standard) was added as solution in THF at 25 °C and the resulting solution was stirred at the appropriate temperature. The completion of the insertion

reaction was checked by GC analysis of reaction aliquots quenched with a solution of saturated NH_4Cl in water (the conversion was more than 90 %). Yield was determined by GC analysis of the reaction aliquots quenched with iodine solution in anhydrous THF.

Reagent (1a). The general procedure was followed using indium powder (918 mg, 8 mmol), LiCl (340 mg, 8 mmol) in THF (1 mL). 4-iodoacetophenone **2a** (492 mg, 2 mmol) and tridecane (5 drops) in THF (1 mL). The reaction was carried out at 50 °C for 24 h and provided the indium reagent **1a** in 96% yield.

Reagent (1b). The general procedure was followed using indium powder (918 mg, 8 mmol), LiCl (340 mg, 8 mmol) in THF (1 mL). 1-(4-iodophenyl)-2-methyl-1-propanone **2b**[3] (550 mg, 2 mmol) and heptadecane (5 drops) in THF (1 mL). The reaction was carried out at 50 °C for 24 h and provided the indium reagent **1b** in 93% yield.

Reagent (1c). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). 2-iodoacetophenone **2c** (492 mg, 2 mmol) and tridecane (5 drops) in THF (2 mL). The reaction was carried out at 35 °C for 2 h and provided the indium reagent **1c** in 90% yield.

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Reagent (1d). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL).

Ethyl 2-iodobenzoate **2d** (563 mg, 2 mmol) and tetradecane (5 drops) in THF (2 mL). The reaction was carried out at 35 °C for 8 h and provided the indium reagent **1d** in 86% yield.

Reagent (1e). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). 4-(acetyloxy)-3-iodo-5-methoxybenzaldehyde **2e** (641 mg, 2 mmol) and heptadecane (5 drops) in THF (2 mL). The reaction was carried out at 35 °C for 4 h and provided the indium reagent **1e** in 70% yield.

Reagent (1f). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). Methyl 4-[(2,2-dimethylpropanoyl)oxy]-3-iodobenzoate **2f** (724 mg, 2 mmol) and heptadecane (5 drops) in THF (2 mL). The reaction was carried out at 40 °C for 13 h and provided the indium reagent **1f** in 70% yield.

Reagent (1g). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). Ethyl 3-cyano-5-iodobenzoate **2g**[3] (602 mg, 2 mmol) and tetradecane (5 drops) in THF (2 mL). The reaction was carried out at 40 °C for 6 h and provided the indium reagent **1g** in 78% yield.

Reagent (1h). The general procedure was followed using indium powder (460 mg, 4 mmol), LiCl (170 mg, 4 mmol) in THF (2 mL). 2-Acetyl-5-iodothiophene **2h** (520 mg, 2 mmol) and heptadecane (5 drops) in THF (2 mL). The reaction was carried out at 30 °C for 20 min and provided the indium reagent **1h** in 91% yield.

Reagent (1i). The general procedure was followed using indium powder (460 mg, 4 mmol), LiCl (170 mg, 4 mmol) in THF (2 mL). 2, 5-Diiodothiophene **2i** (672 mg, 2 mmol) and heptadecane (5

drops) in THF (2 mL). The reaction was carried out at 30 °C for 20 min and provided the indium reagent **1i** in 97% yield.

Reagent (1j). The general procedure was followed using indium powder (460 mg, 4 mmol), LiCl (170 mg, 4 mmol) in THF (2 mL). 2-Iodo-1-benzothiophene-3-carbaldehyde **2j**[4] (576 mg, 2 mmol) and tetradecane (5 drops) in THF (2 mL). The reaction was carried out at 30 °C for 20 min and provided the indium reagent **1j** in 78% yield.

Reagent (1k). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (3 mL). 3-Iodopyridine **2k** (410 mg, 2 mmol) and tetradecane (5 drops) in THF (3 mL). The reaction was carried out at 50 °C for 5 h and provided the indium reagent **1k** in 88% yield.

Reagent (1l). The general procedure was followed using indium powder (460 mg, 4 mmol), LiCl (170 mg, 4 mmol) in THF (2 mL). 5-Iodo-2-furancarboxaldehyde **2l** (448 mg, 2 mmol) and octadecane (5 drops) in THF (2 mL). The reaction was carried out at 30 °C for 20 min and provided the indium reagent **1l** in 83% yield.

Reagent (1m). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). Ethyl 5-bromo-2-furoate **2m** (440 mg, 2 mmol) and heptadecane (5 drops) in THF (2 mL). The reaction was carried out at 50 °C for 16 h and provided the indium reagent **1m** in 92% yield.

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General procedure A for cross-coupling (Table 2): The electrophile (1 equiv) and $Pd(dppf)Cl_2$ (4 mol%) were placed in

an argon-flushed flask. After the addition of NMP, the organoindium solution in THF was carefully transferred to the resulting solution from the rest of indium powder using syringe. Then, the reaction mixture was stirred at the indicated temperature. After the completion of the reaction (checked by GC analysis of reaction aliquots quenched with sat. aqueous NH_4Cl solution and TLC) the reaction mixture was quenched with acetic acid (0.5 mL) and water (2 mL). The aqueous layer was extracted with ethyl acetate or diethyl ether. The combined organic extracts were dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash column chromatography.

General procedure B for cross-coupling (Table 1): The electrophile (1 equiv), $Pd(OAc)_2$ (4 mol%) and S-Phos (8 mol%) were placed in an argon-flushed flask. After the addition of NMP and THF (0.5 mL), the organoindium solution in THF was carefully transferred to the resulting solution from the rest of indium powder using syringe. Then, the reaction mixture was stirred at the indicated temperature. After the completion of the reaction (checked by GC analysis of reaction aliquots quenched with sat. aqueous NH_4Cl solution and TLC) the reaction mixture was quenched with acetic acid (0.5 mL) and water (2 mL). The aqueous layer was extracted with ethyl acetate or diethyl ether. The combined organic extracts were dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash column chromatography.

Ethyl 4’-acetyl-1,1’-biphenyl-4-carboxylate (4a). The general procedure **A** was followed using $Pd(dppf)Cl_2$ (44 mg, 0.06 mmol), ethyl 4-iodobenzoate **3a** (414 mg, 1.50 mmol) and NMP (2 mL). The arylindium solution of **1a** was diluted with THF (2 mL) and transferred to the reaction mixture. The reaction mixture was stirred at 40 °C for 4 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:4) to yield

compound **4a** (380 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) d 8.20-8.03 (m, 4H), 7.77-7.67 (m, 4H), 4.44 (q, 2H, *J* = 7.1 Hz), 2.67 (s, 3H), 1.44 (t, 3H, *J* = 7.1) Hz); ^{13}C (75 MHz, $CDCl_3$) d 197.6, 166.3, 144.5, 144.1, 136.5, 130.2, 130.1, 129.0, 127.5, 127.2, 61.1, 26.7, 14.4; HRMS: *m/z* calcd. for $C_{17}H_{16}O_3$ (M^+) 268.1099, found 268.1083; FT-IR (Diamond-ATR, neat) 2993, 1703, 1678, 1607 cm^{-1}, mp (°C) = 106.7-107.7.

5-(4-(Isobutyryl)phenyl)furan-2-carboxaldehyde(4b). The general procedure **A** was followed using $Pd(dppf)Cl_2$ (44mg, 0.06 mmol), 5-iodo-2-furancarboxaldehyde **2l** (344 mg, 1.50 mmol) and NMP (2 mL). The arylindium solution of **1b** was diluted with THF (2 mL) and transferred to the reaction mixture. The reaction mixture was stirred at 60 °C for 12 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:3) to yield compound **4b** (255 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) d 9.62 (s, 1H), 7.95 (d, 2H, *J* = 12.0 Hz), 7.83 (d, 2H, *J* = 12.0 Hz), 7.28 (d, 1H, *J* = 3.7 Hz), 6.91 (d, 1H, *J* = 3.7 Hz), 3.49 (m, 1H), 1.16 (d, 6H, *J* = 6.9 Hz); ^{13}C (100 MHz, $CDCl_3$) d 203.5, 177.4, 157.8, 152.5, 136.4, 132.5, 128.9, 125.2, 123.2, 109.4, 35.4, 19.0; HRMS: *m/z* calcd. for $C_{15}H_{14}O_3$ (M^+) 242.0943, found 242.0929; FT-IR (Diamond-ATR, neat) 2813, 1740, 1664, 1605 cm^{-1}, mp (°C) = 74.0-76.7.

5-Formyl-3-methoxy-3’-methylbiphenyl-2-yl acetate (4c). The general procedure **B** was followed using $Pd(OAc)_2$ (10 mg, 0.04 mmol), S-Phos (33 mg, 0.08 mmol), 3-iodotoluene **3b** (197 mg, 0.89 mmol) and NMP (2 mL). The arylindium solution of **1e** was transferred to the reaction mixture. It was refluxed for 23 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:5) to yield compound **4c** (213 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) d 9.96 (s, 1H), 7.48 (dd, 2H, *J* = 10.6, 2.0 Hz), 7.34-7.26 (m, 1H), 7.23-7.17 (m, 3H), 3.92 (s, 3H), 2.39 (s, 3H), 2.15 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) d 191.1, 168.3, 152.4, 142.2, 138.2, 136.9, 136.1, 134.7, 129.4, 128.9,

128.3, 126.4, 125.7, 109.3, 56.3, 21.4, 20.4; HRMS: *m/z* calcd. for $C_{17}H_{16}O_4$ (M^+) 284.1049, found 284.1041; FT-IR (Diamond-ATR, neat) 1764, 1694, 1583 cm^{-1}.

Methyl 4'-cyano-6-[(2,2-dimethylpropanoyl)oxy]biphenyl-3-carboxylate (4d). The general procedure **B** was followed using $Pd(OAc)_2$ (10 mg, 0.04 mmol), S-Phos (33 mg, 0.08 mmol), 4-iodobenzonitrile **3c** (214 mg, 0.93 mmol) and NMP (2 mL). The arylindium solution of **1f** was transferred to the reaction mixture. The reaction mixture was refluxed for 22 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:6) to yield compound **4d** (210 mg, 68%, mixture of rotamers). ^1H NMR (400 MHz, $CDCl_3$) d 8.08 (dd, 1H, *J* = 8.4, 2.2 Hz), 8.03 (d, 1H, *J* = 2.2 Hz), 7.69 (d, 2H, *J* = 8.5 Hz), 7.49 (d, 2H, *J* = 8.5 Hz), 7.18 (d, 1H, *J* = 8.4 Hz), 3.91 (s, 3H), 1.12 (s, 9H); ^{13}C (100 MHz, $CDCl_3$) d 176.1, 165.9, 151.6, 141.3, 133.5, 132.0, 131.9, 130.0, 128.3, 123.3, 118.5, 111.8, 52.3, 39.0, 26.8; HRMS: *m/z* calcd. for $C_{20}H_{19}NO_4$ (M^+) 337.1314, found 337.1304; FT-IR (Diamond-ATR, neat) 2975, 2229, 1754, 1721 cm^{-1}.

Ethyl 4',5-dicyanobiphenyl-3-carboxylate (4e). The general procedure **B** was followed using $Pd(OAc)_2$ (11 mg, 0.05 mmol), S-Phos (40 mg, 0.10 mmol), 4-iodoacetophenone **2a** (296 mg, 1.20 mmol) and NMP (2 mL). The arylindium solution of **1g** was transferred to the reaction mixture. The reaction mixture was refluxed for 16 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:3) to yield compound **4e** (298 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$) d 8.47 (s, 1H), 8.30 (s, 1H), 8.10-8.00 (m, 3H), 7.69-7.67 (m, 2H), 4.43 (q, 2H, *J* = 8.0 Hz), 2.63 (s, 3H), 1.42 (t, 3H, *J* = 8.0 Hz); ^{13}C (100 MHz, $CDCl_3$) d 197.3, 164.4, 142.2, 141.6, 137.1, 134.3, 132.5, 132.3, 132.2, 129.2, 127.3, 117.7, 113.7, 62.0, 26.7, 14.2; HRMS: *m/z* calcd. for $C_{18}H_{15}NO_3$ (M^+) 293.1052, found

293.1047; FT-IR (Diamond-ATR, neat) 2235, 1712, 1684, 1593 cm^{-1}, mp (°C) = 133.6-135.1.

1-(5-(3-(Trifluoromethyl)phenyl)thiophene-2-yl)ethanone (4f). The general procedure **A** was followed using $Pd(dppf)Cl_2$ (44 mg, 0.06 mmol), 3-iodobenzotrifluoride **3d** (416 mg, 1.5 mmol) and NMP (2 mL). The arylindium solution of **1h** was transferred to the reaction mixture. The reaction mixture was stirred at 40 °C for 4 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:4) to yield compound **4f** (386 mg, 95%). ^1H NMR (300 MHz, $CDCl_3$) d 7.90 (s, 1H), 7.83 (d, 1H, *J* = 9.0 Hz), 7.70 (d, 1H, *J* = 3.9 Hz), 7.67-7.52 (m, 2H), 7.40 (d, 1H, *J* = 3.9 Hz), 2.60 (s, 3H); ^{13}C (75 MHz, $CDCl_3$) d 190.5, 150.5, 144.1, 134.2, 133.3, 131.7 (q, *J* = 32.4 Hz), 129.7, 129.5 (q, *J* = 1.4 Hz), 125.5 (q, *J* = 3.8 Hz), 124.9, 123.8 (q, *J* = 270.9 Hz), 122.9 (q, *J* = 3.8 Hz), 26.6; HRMS: *m/z* calcd. for $C_{13}H_9F_3OS$ (M^+) 270.0326, found 270.0314; FT-IR (Diamond-ATR, neat) 1652, 1614, 1534 cm^{-1}, mp (°C) = 100.7-102.4.

2-Iodo-5-(4-nitrophenyl)thiophene (4g). The general procedure **A** was followed using $Pd(dppf)Cl_2$ (57 mg, 0.08 mmol), 1-iodo-4-nitrobenzene **3e** (634 mg, 2.52 mmol) and NMP (2 mL). The arylindium solution of **1i** was transferred to the reaction mixture. The reaction mixture was stirred at 25 °C for 24 h. The residue was purified by flash chromatography on silica gel (ethyl acetate/pentane = 1:15) to yield compound **4g** (466 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$) d 8.24-8.19 (m, 2H), 7.65-7.61 (m, 2H), 7.28 (d, 1H, *J* = 3.8 Hz), 7.11 (d, 1H, *J* = 3.8 Hz); ^{13}C (100 MHz, $CDCl_3$) d 147.4, 146.9, 139.4, 138.5, 126.9, 125.9, 124.5, 76.1; HRMS: *m/z* calcd. for $C_{10}H_6INO_2S$ (M^+) 330.9164, found 330.9161; FT-IR (Diamond-ATR, neat) 1589, 1530, 1496, 1418, 1325 cm^{-1}, mp (°C) = 166.3-169.3.

4-(3-Formylbenzo[*b*]thiophen-2-yl)benzonitrile (4h). The general procedure **B** was followed using $Pd(OAc)_2$ (10 mg, 0.04

mmol), S-Phos (34 mg, 0.08 mmol), 4-iodobenzonitrile **3c** (240 mg, 1.04 mmol) and NMP (2 mL). The solution of the arylindium reagent **1j** was transferred to the reaction mixture. It was refluxed for 15 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:6) to yield compound **4h** (246 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) d 10.01 (s, 1H), 8.75 (d, 1H, *J* = 7.8 Hz), 7.85 (d, 1H, *J* = 8.0 Hz), 7.82-7.76 (m, 2H), 7.71-7.65 (m, 2H), 7.55-7.44 (m, 2H); ^{13}C (100 MHz, $CDCl_3$) d 185.6, 156.9, 138.2, 136.8, 136.2, 132.5, 131.1, 131.0, 126.7, 126.5, 125.4, 121.7, 117.9, 113.7; HRMS: *m/z* calcd. for $C_{16}H_9NOS$ (M^+) 263.0405, found 263.0383; FT-IR (Diamond-ATR, neat) 2230, 1669, 1603 cm^{-1}, mp (°C) = 164.8-167.7.

Ethyl 4-(pyridine-3-yl)benzoate (4i). The general procedure **A** was followed using $Pd(dppf)Cl_2$ (48 mg, 0.06 mmol), ethyl 4-iodobenzoate **3a** (414 mg, 1.50 mmol) and NMP (3 mL). The solution of the arylindium reagent **1k** was transferred to the reaction mixture. It was refluxed for 17 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:1) to yield compound **4i** (312 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) d 8.96 (bs, 1H), 8.71 (bs, 1H), 8.15-8.09 (m, 2H), 7.89 (d, 1H, *J* = 7.8 Hz), 7.65-7.59 (m, 2H), 7.41 (dd, 1H, *J* = 7.9, 4.6 Hz), 4.38 (q, 2H, *J* = 7.2 Hz), 1.39 (t, 3H, *J* = 7.2 Hz); ^{13}C (100 MHz, $CDCl_3$) d 166.2, 148.9, 148.0, 142.1, 136.0, 134.5, 130.3, 130.1, 127.0, 124.1, 61.1, 14.3; HRMS: *m/z* calcd. for $C_{14}H_{13}NO_2$ (M^+) 227.0946, found 227.0934; FT-IR (Diamond-ATR, neat) 2984, 1700, 1608 cm^{-1}, mp (°C) = 49.1-50.3.

Ethyl 4-(5-formylfuran-2-yl)benzoate (4j). The general procedure **A** was followed using $Pd(dppf)Cl_2$ (40 mg, 0.05 mmol), ethyl 4-iodobenzoate **3a** (382 mg, 1.38 mmol) and NMP (2 mL). The solution of the arylindium reagent **1l** was transferred to the reaction mixture. The reaction mixture was stirred at 25 °C for 1.5 h. The residue was purified by flash chromatography

on silica gel (ether/pentane = 1:4) to yield compound **4j** (260 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) d 9.68 (s, 1H), 8.11-8.07 (m, 2H), 7.88-7.84 (m, 2H), 7.32 (d, 1H, *J* = 3.9 Hz), 6.93 (d, 1H, *J* = 3.9 Hz), 4.38 (q, 2H, *J* = 7.1 Hz), 1.39 (t, 3H, *J* = 7.1 Hz); ^{13}C (100 MHz, $CDCl_3$) d 177.4, 165.9, 158.0, 152.5, 132.7, 131.1, 130.2, 125.0, 123.0, 109.3, 61.2, 14.3; HRMS: *m/z* calcd. for $C_{14}H_{12}O_4$ (M^+) 244.0736, found 244.0724; FT-IR (Diamond-ATR, neat) 1708, 1658, 1609 cm^{-1}, mp (°C) = 127.1-128.6.

5-((*E*)-oct-1-enyl)furan-2-carboxaldehyde (4k). The general procedure **A** was followed using $Pd(dppf)Cl_2$ (40 mg, 0.05 mmol), (*E*)-1-iodooct-1-ene **3f** (321 mg, 1.35 mmol) and NMP (2 mL). The solution of the arylindium reagent **1l** was transferred to the reaction mixture. It was stirred at 60 °C for 1.5 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:8) to yield compound **4k** (204 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) d 9.55 (s, 1H), 7.21 (d, 1H, *J* = 3.7 Hz), 6.60 (dt, 1H, *J* = 15.0, 7.1 Hz), 6.35 (d, 1H, *J* = 3.7 Hz), 6.28 (dt, 1H, *J* = 15.0, 1.5 Hz), 2.29-2.19 (m, 2H), 1.56-1.21 (m, 8H), 0.91 (t, 3H, *J* = 9.0 Hz); ^{13}C (75 MHz, $CDCl_3$) d 176.9, 159.0, 151.4, 137.7, 123.7, 117.6, 108.6, 33.0, 31.7, 28.8, 28.7, 22.6, 14.1; HRMS: *m/z* calcd. for $C_{13}H_{18}O_2$ (M^+) 206.1307, found 206.1301; FT-IR (Diamond-ATR, neat) 2925, 1675, 1517 cm^{-1}.

1-(2-(1*H*-indol-5-yl)phenyl)ethanone (4l). The general procedure **B** was followed using $Pd(OAc)_2$ (11 mg, 0.05 mmol), S-Phos (41 mg, 0.10 mmol), 5-iodoindole **3g** (280 mg, 1.13 mmol) and NMP (2 mL). The arylindium solution of **1c** was transferred to the reaction mixture. The reaction mixture was refluxed for 27 h. The residue was purified by flash chromatography on silica gel (ethyl acetate/pentane = 1:2) to yield compound **4l** (188 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) d 8.67 (bs), 7.63 (s, 1H), 7.60-7.57 (m, 1H), 7.55-7.46 (m, 2H), 7.43-7.35 (m, 2H),

7.21 (t, 1H, *J* = 2.8 Hz), 7.15 (dd, 1H, *J* = 8.4, 1.8 Hz), 6.59-6.56 (m, 1H), 1.97 (d, 3H, *J* = 0.8 Hz); ^{13}C (100 MHz, $CDCl_3$) d 206.5, 141.9, 141.2, 135.6, 132.3, 130.7, 130.6, 128.2, 127.7, 126.7, 125.4, 123.2, 121.0, 111.4, 102.8, 30.5; HRMS: *m/z* calcd. for $C_{16}H_{13}NO$ (M^+) 235.0997, found 235.0988; FT-IR (Diamond-ATR, neat) 3340, 1670, 1593 cm^{-1}.

Ethyl 2'-(1-hydroxyethyl)biphenyl-2-carboxylate (4m). The general procedure **A** was followed using Pd(dppf)Cl_2 (32mg, 0.04 mmol), 1-(3-iodophenyl)ethanol **3h** (248 mg, 1.0 mmol) and NMP (2 mL). The arylindium solution of **1d** was transferred to the reaction mixture. It was refluxed for 23 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:1) to yield compound **4m** (188 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) d 7.84 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.58-7.49 (m, 1H), 7.44 (dd, 1H, *J* = 7.6, 1.4 Hz), 7.42-7.31 (m, 4H), 7.23-7.19 (m, 1H), 4.94 (q, 1H, *J* = 6.4 Hz), 4.10 (q, 2H, *J* = 7.1 Hz), 2.14 (1H, bs), 1.53 (d, 3H, *J* = 6.43 Hz), 1.02 (t, 3H, *J* = 7.1 Hz); ^{13}C (75 MHz, $CDCl_3$) d 168.8, 145.7, 142.4, 141.7, 131.3, 131.1, 130.6, 129.7, 128.2, 127.5, 127.2, 125.5, 124.2, 70.3, 60.9, 25.3, 13.7; HRMS: *m/z* calcd. for $C_{17}H_{18}O_3$ (M^+) 270.1256, found 270.1261; FT-IR (Diamond-ATR, neat) 3418, 2975, 1709, 1598 cm^{-1}.

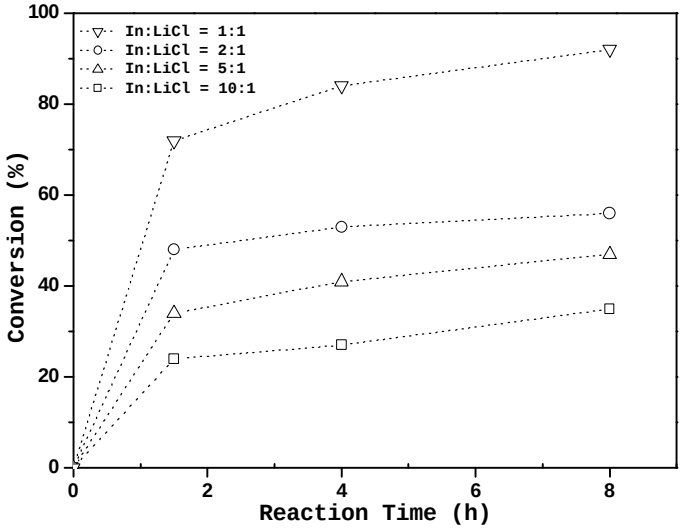
Ethyl 5-(3-hydroxyphenyl)furan-2-carboxylate (4n). The general procedure **A** was followed using Pd(dppf)Cl_2 (38 mg, 0.05 mmol), 3-iodophenol **3i** (292 mg, 1.31 mmol) and NMP (2 mL). The solution of the arylindium reagent **1m** was transferred to the reaction mixture. The reaction mixture was sitrred at 40 °C for 4 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:2) to yield compound **4n** (256 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) d 7.31 (dt, 1H, *J* = 8.0, 1.3 Hz), 7.29-7.23 (m, 2H), 7.21 (d, 1H, *J* = 3.5 Hz), 6.82 (ddd, 1H, *J* = 8.0, 2.5, 1.3 Hz), 6.69 (d, 1H, *J* = 3.5 Hz), 4.37 (q, 2H, *J* = 7.2 Hz), 1.38 (t, 3H, *J* = 7.2 Hz); ^{13}C (100 MHz, $CDCl_3$) d

159.0, 157.1, 156.1, 143.7, 130.9, 130.1, 119.8, 117.3, 116.0, 111.6, 107.1, 61.0, 14.3; HRMS: *m/z* calcd. for $C_{13}H_{12}O_4$ (M^+) 232.0736, found 232.0722; FT-IR (Diamond-ATR, neat) 3271, 1678, 1591 cm^{-1}, mp (°C) = 144.1-147.1.

Studying of indium insertion in the presence of LiCl with 2-iodothiophene

LiCl (0.4 mmol-4 mmol) was placed in an argon-flushed flask and dried additionally 5-10 min at 380 °C (using heat gun) on high vacuum (1 mbar). Indium powder (459 mg, 4 mmol) was added under argon and the flask was evacuated and refilled with argon three times. After the addition of THF (2 mL), indium was activated by treatment first with 1,2-dibromoethane (5 mol%) and then with chlorotrimethylsilane (2 mol%) (gentle heating with heat gun) . A solution of 2-iodothiophene (420 mg, 2 mmol) (along with internal standard) in THF (2 mL) was added at 25 °C and the resulting solution was stirred at 25 °C for 8 h. These reactions were followed by GC analysis of reaction aliquots quenched with a solution of saturated NH_4Cl in water (Figure 1). The indium powder gave the best results when it was activated by 1,2-dibromoethane and TMSCl. Without the addition of LiCl, a fast aggregation of the indium powder occurs in THF solution. The addition of an equal amount of LiCl prevented the metal to aggregate which decreased the reactivity dramatically.

Figure 1.



Preparation of Aryl and Heteroaryl Indium(III)-Reagents by the Direct Insertion of Indium in the Presence of LiCl

^{1}H and ^{13}C spectra

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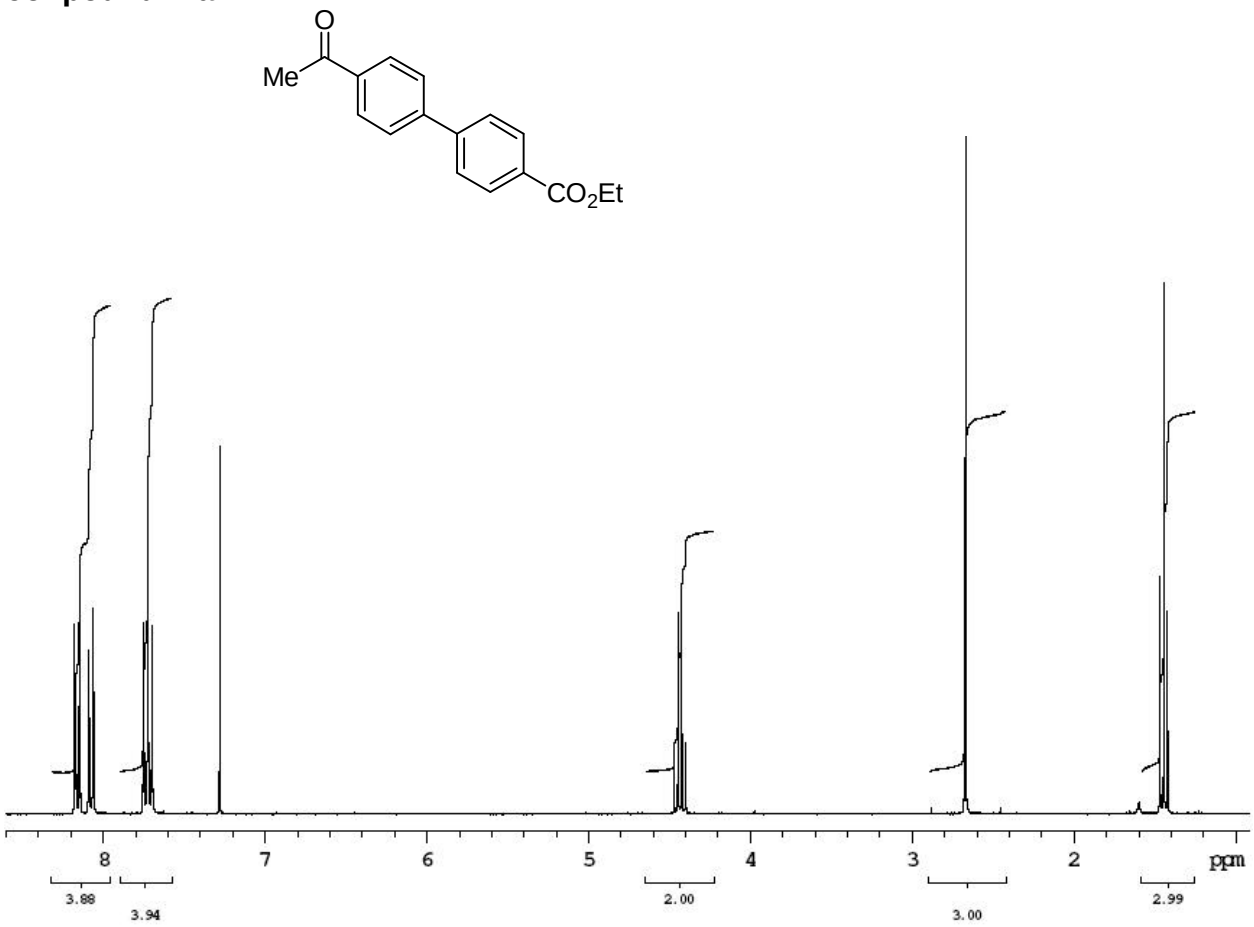
e-mail: paul.knochel@cup.uni-muenchen.de

Compound 4a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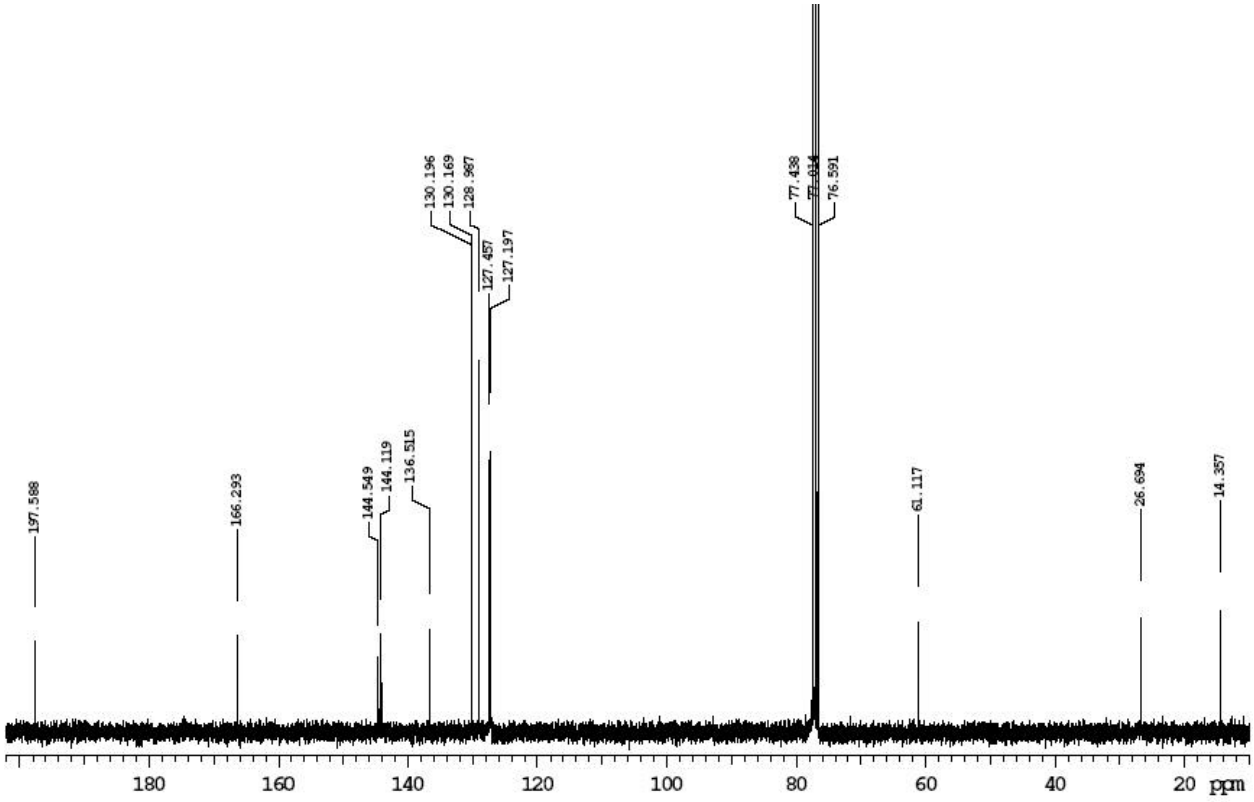
3.00
2.99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40
20
ppm

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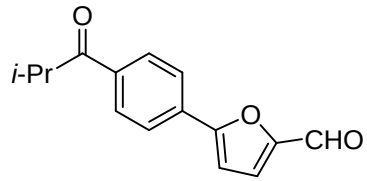
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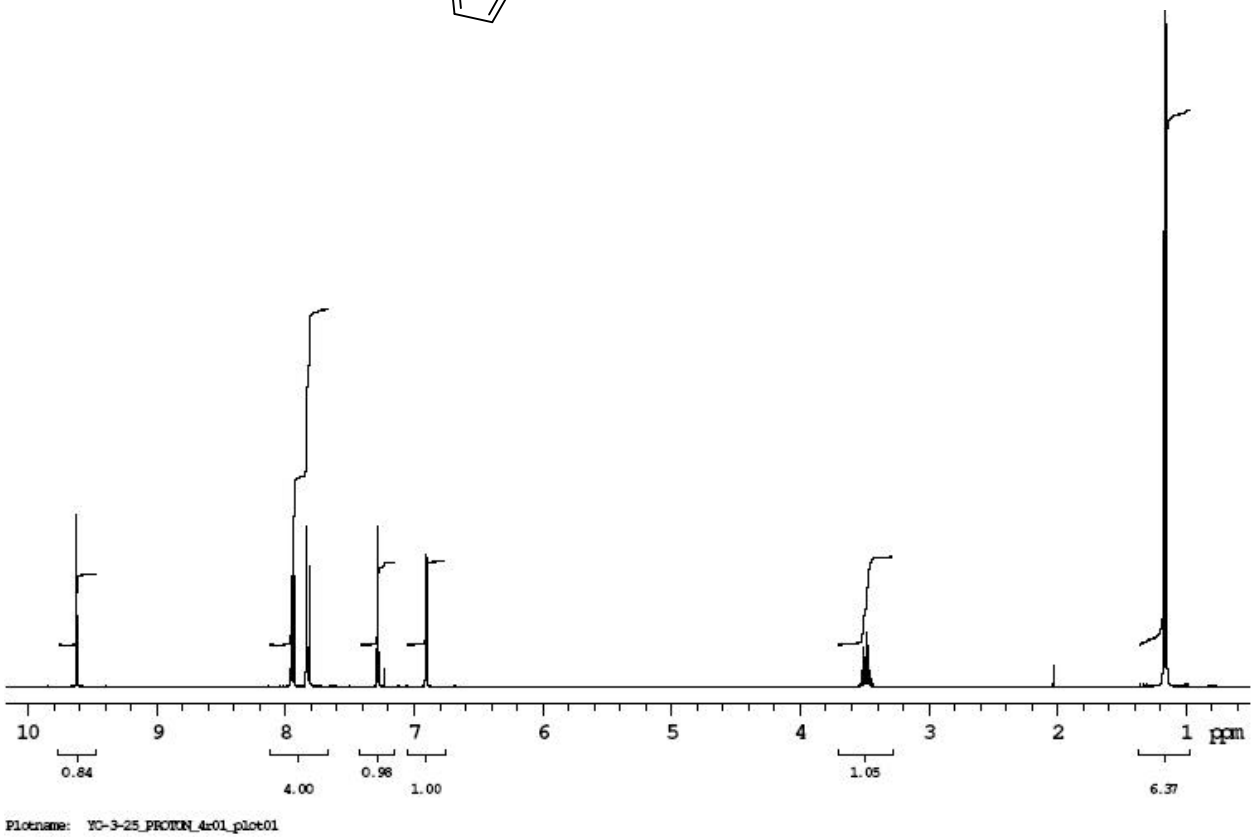
i-Pr
O
CHO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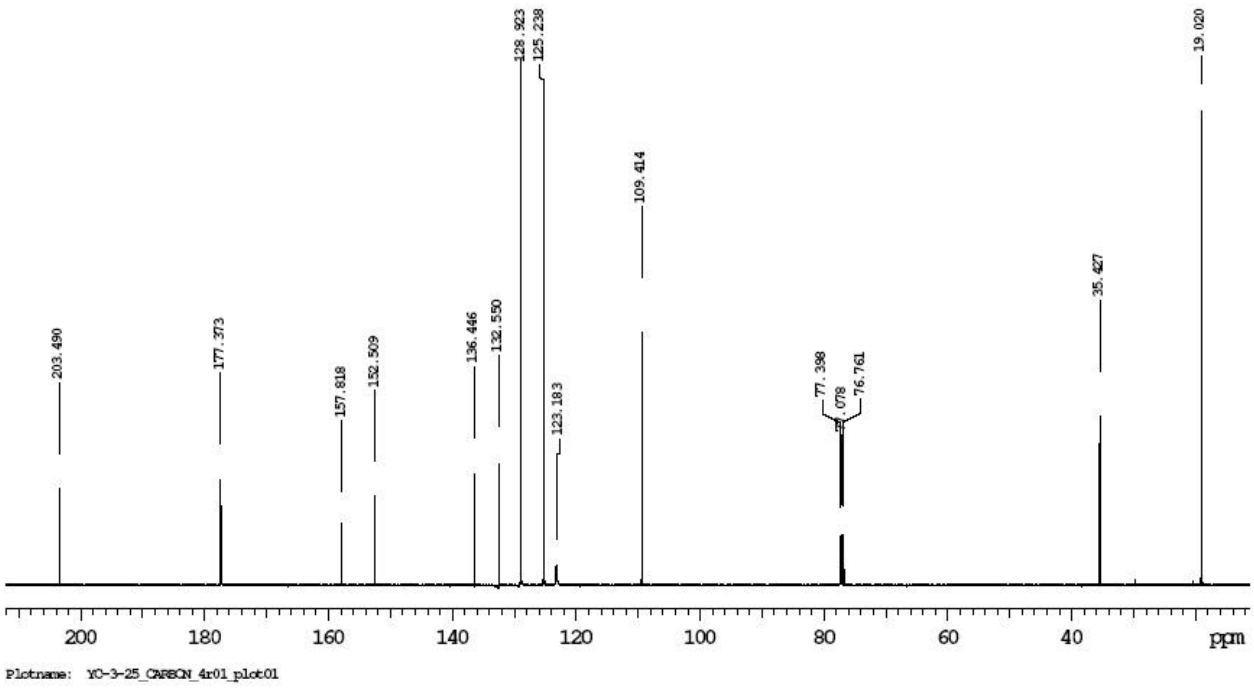
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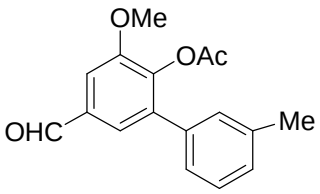
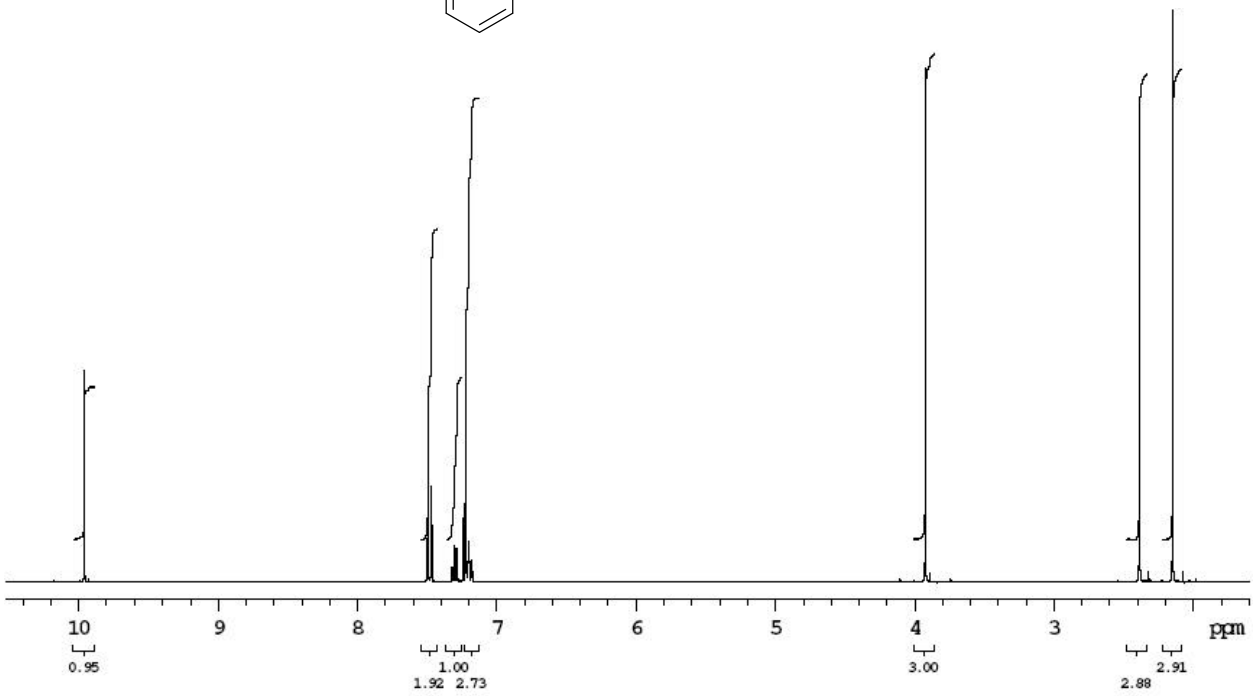
Compound 4c





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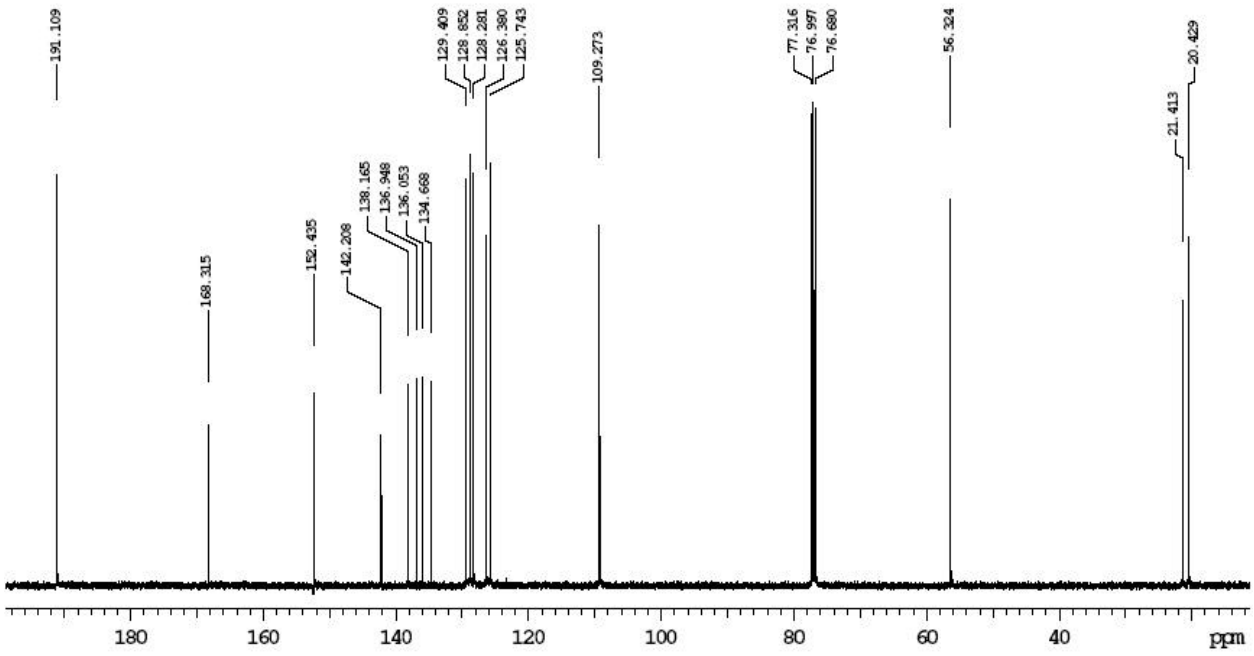

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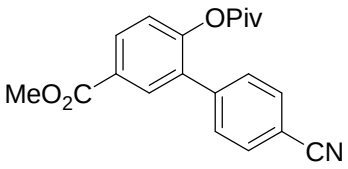

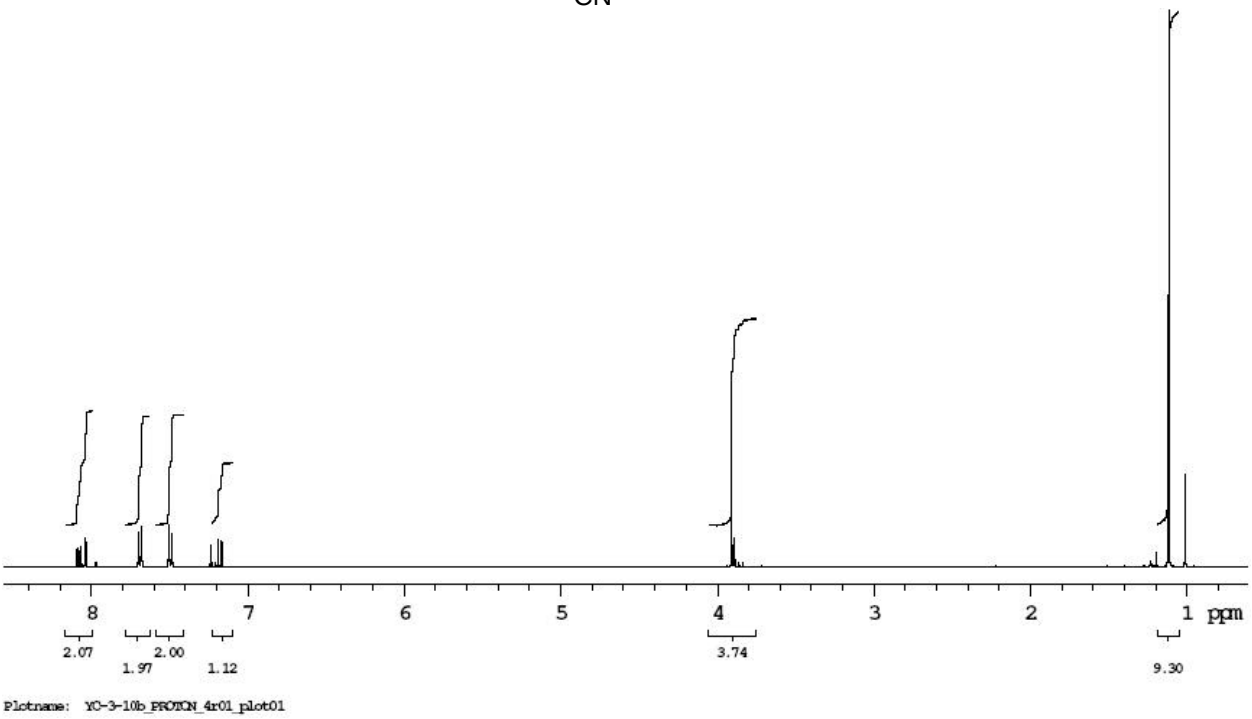

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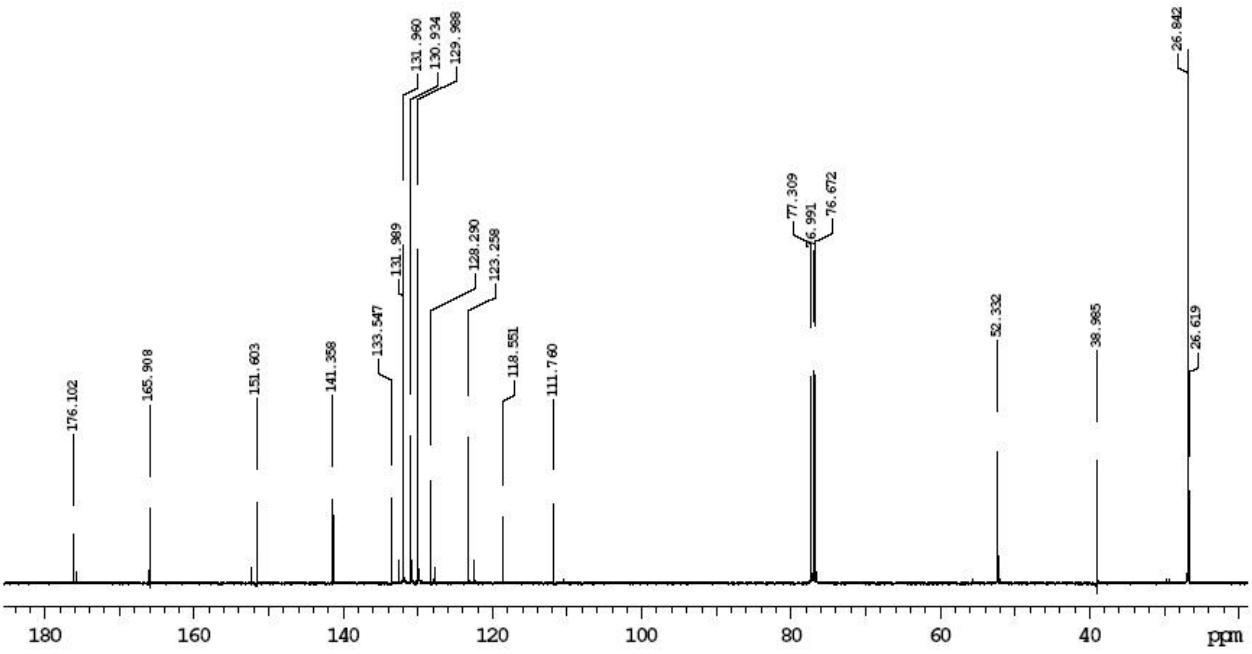

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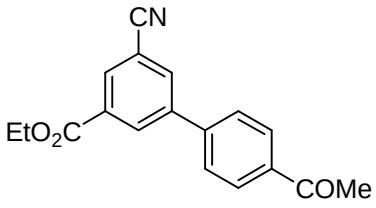

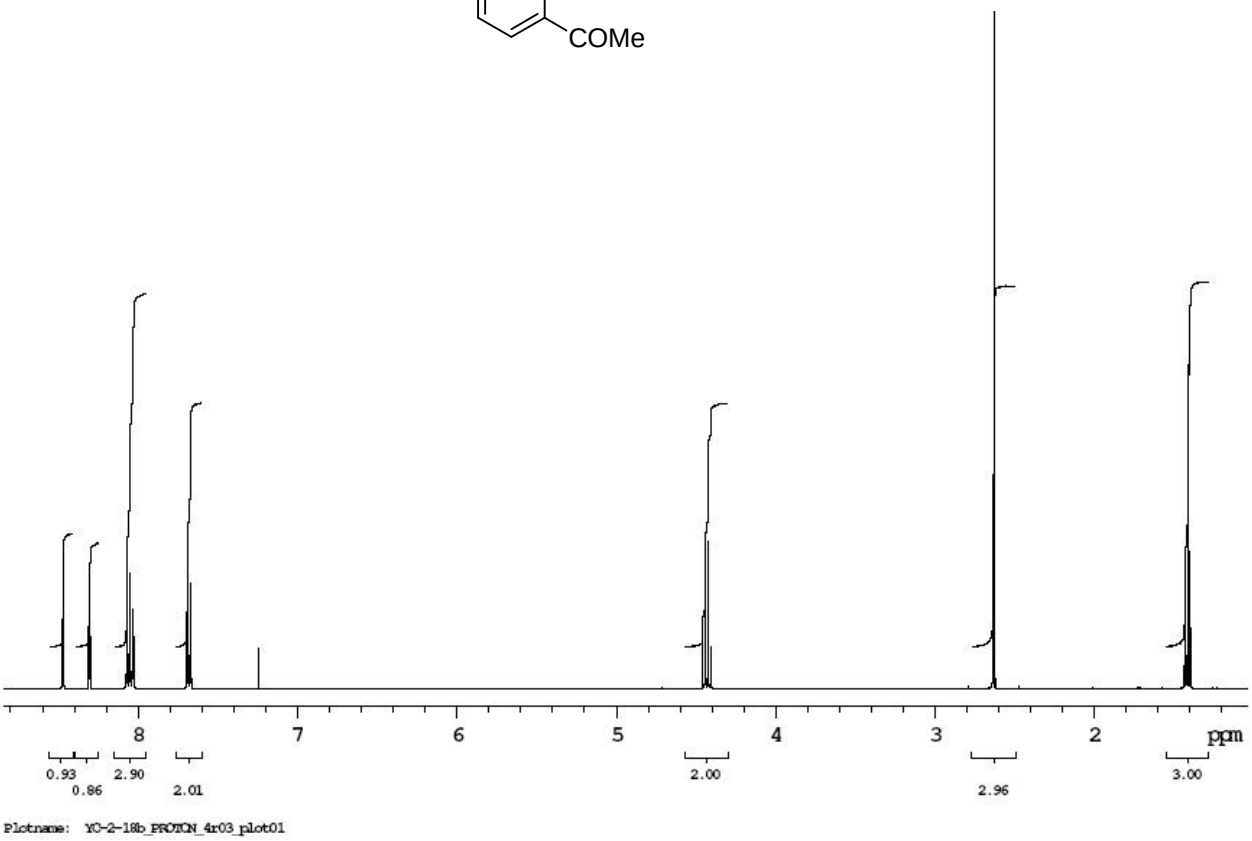

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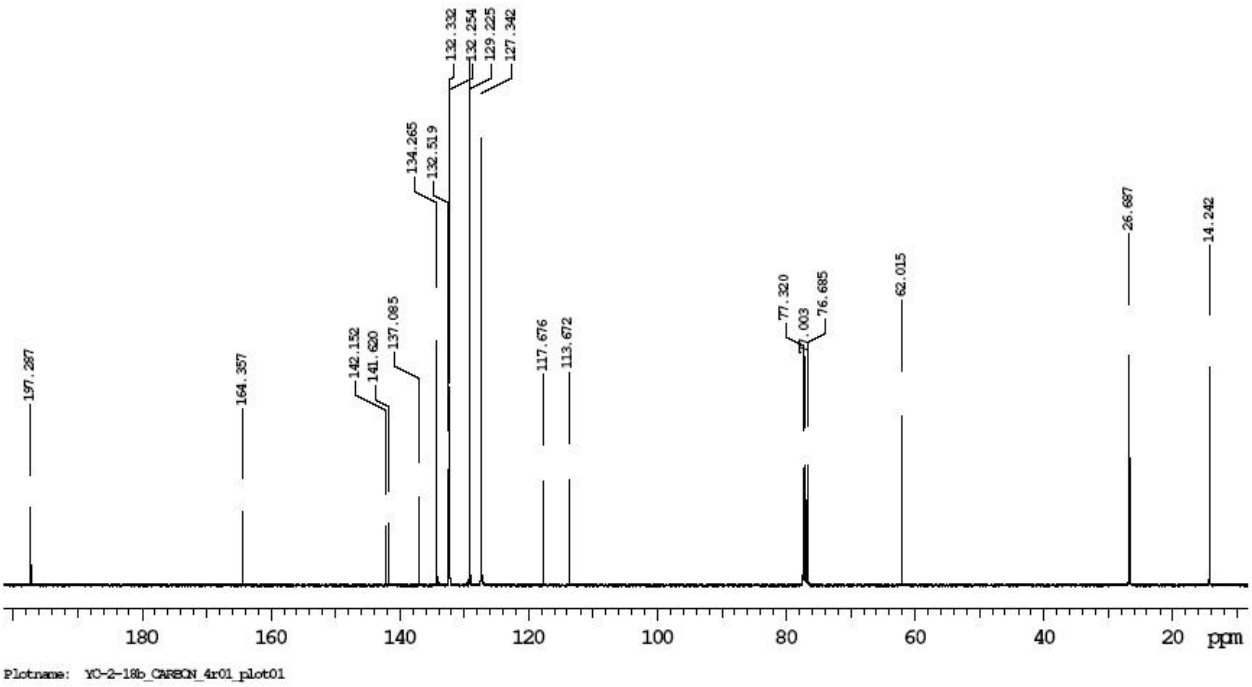

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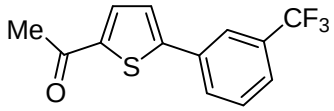
Compound 4f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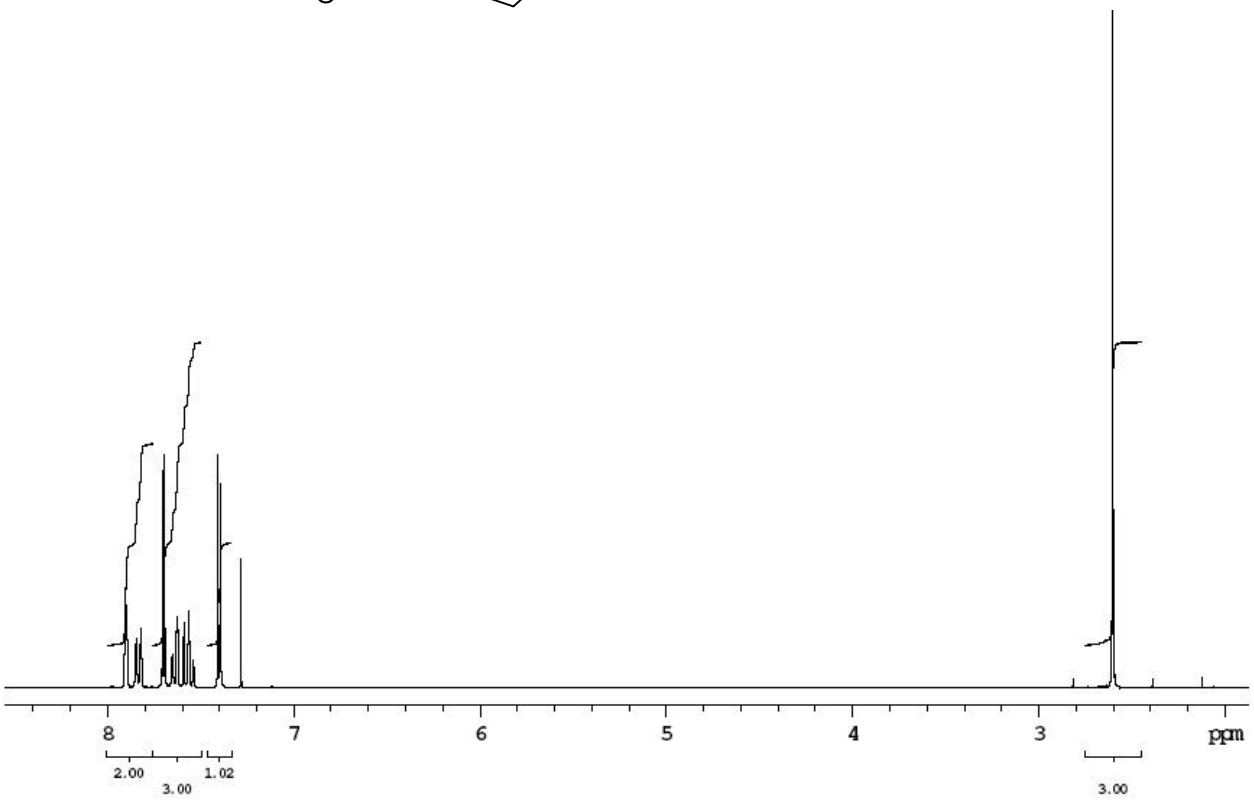
CF3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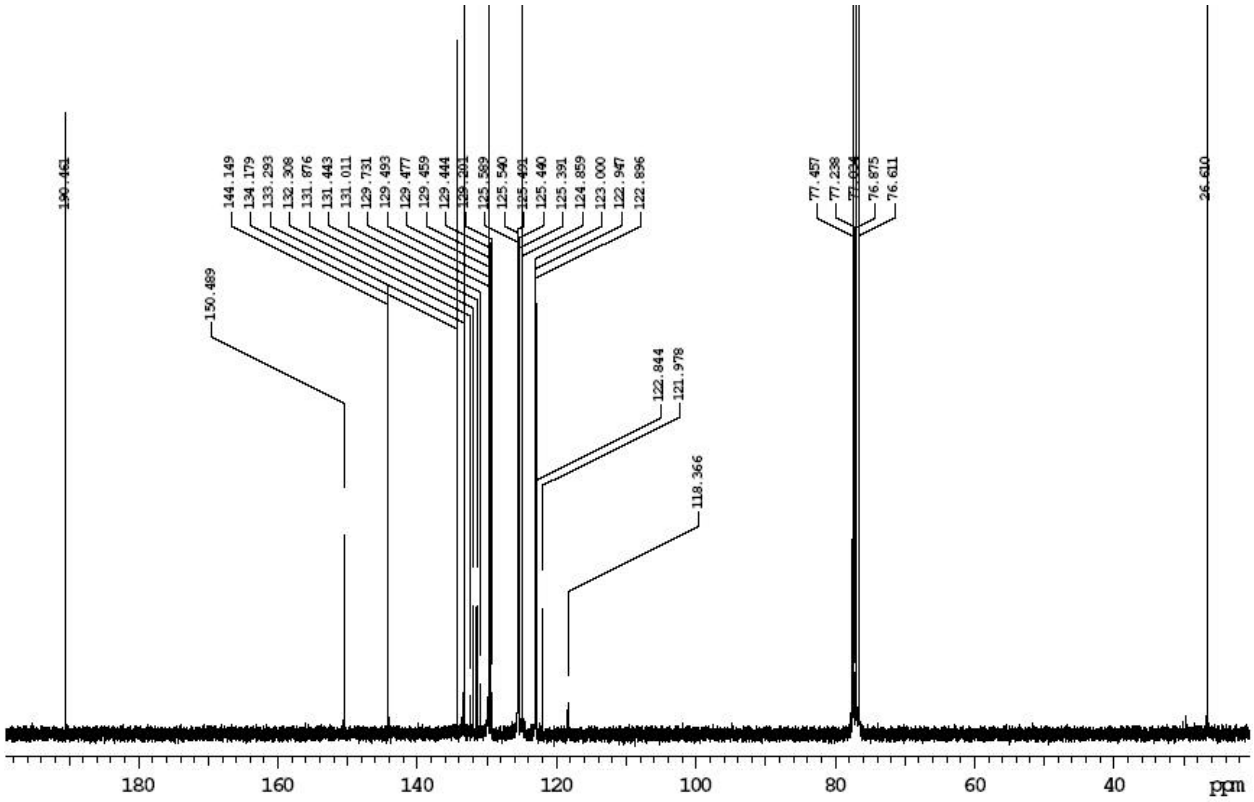
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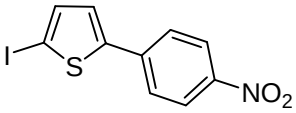

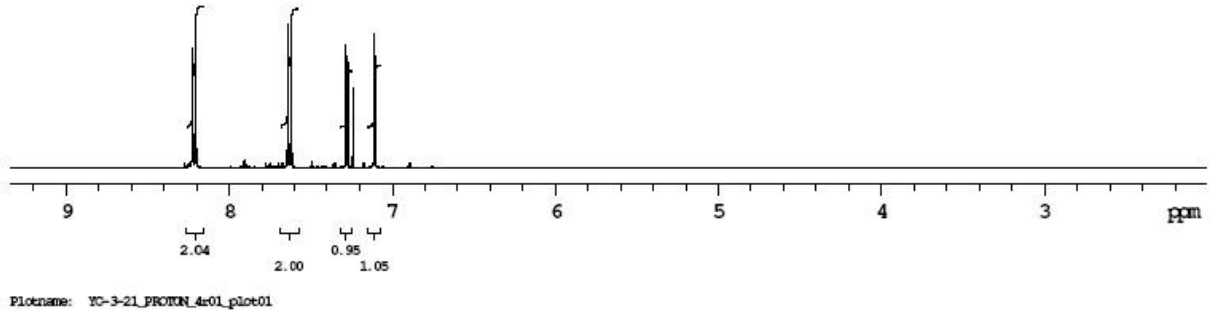

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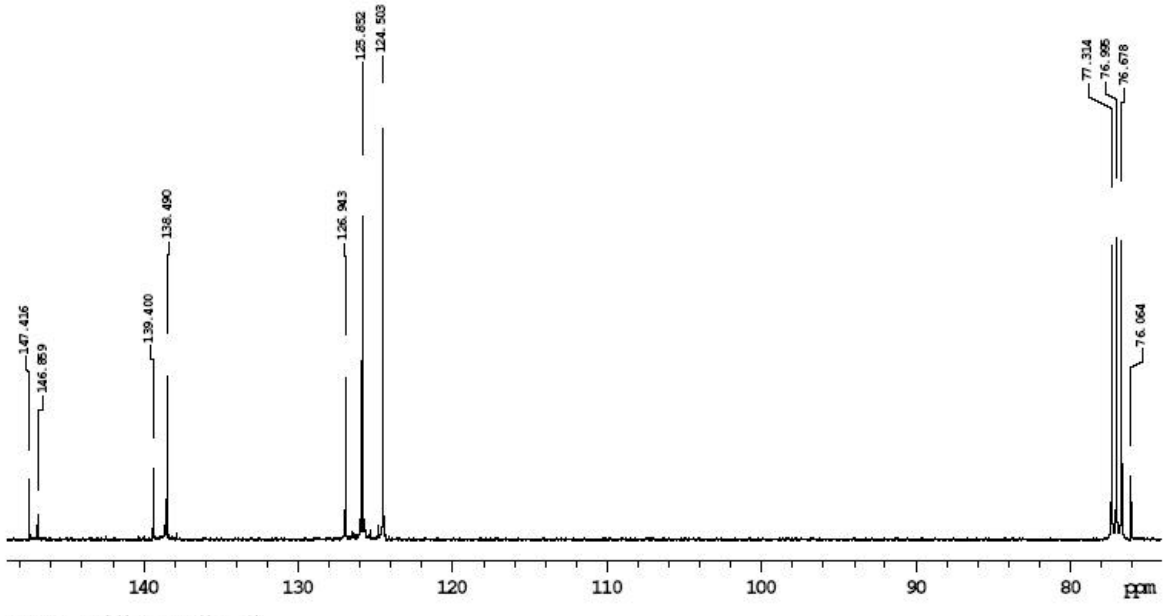

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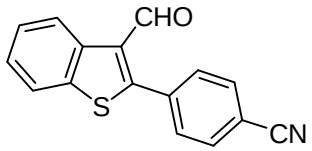
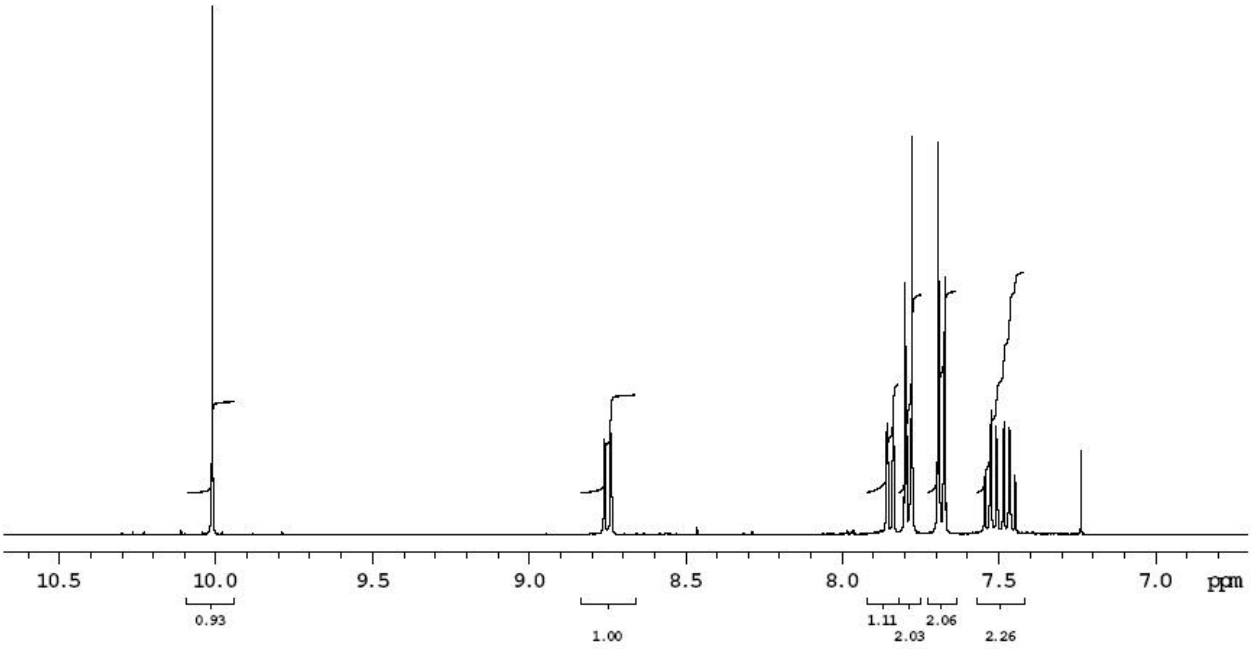
Compound 4h





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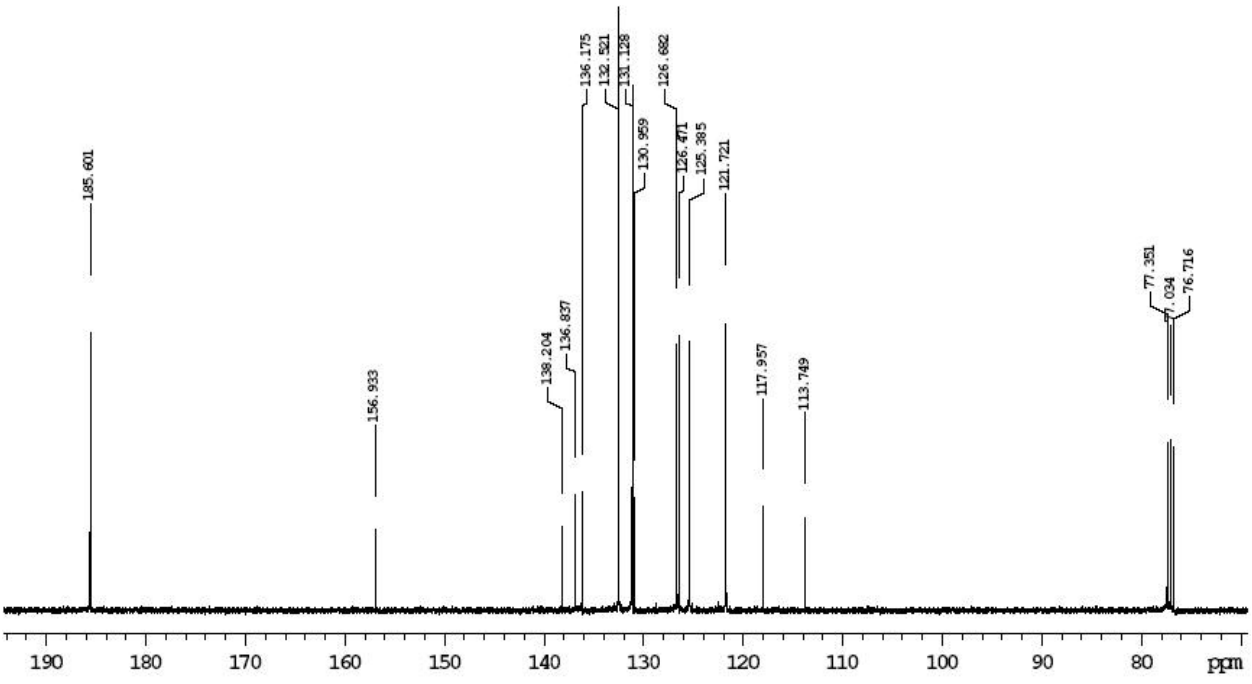

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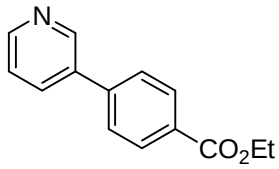
Compound 4i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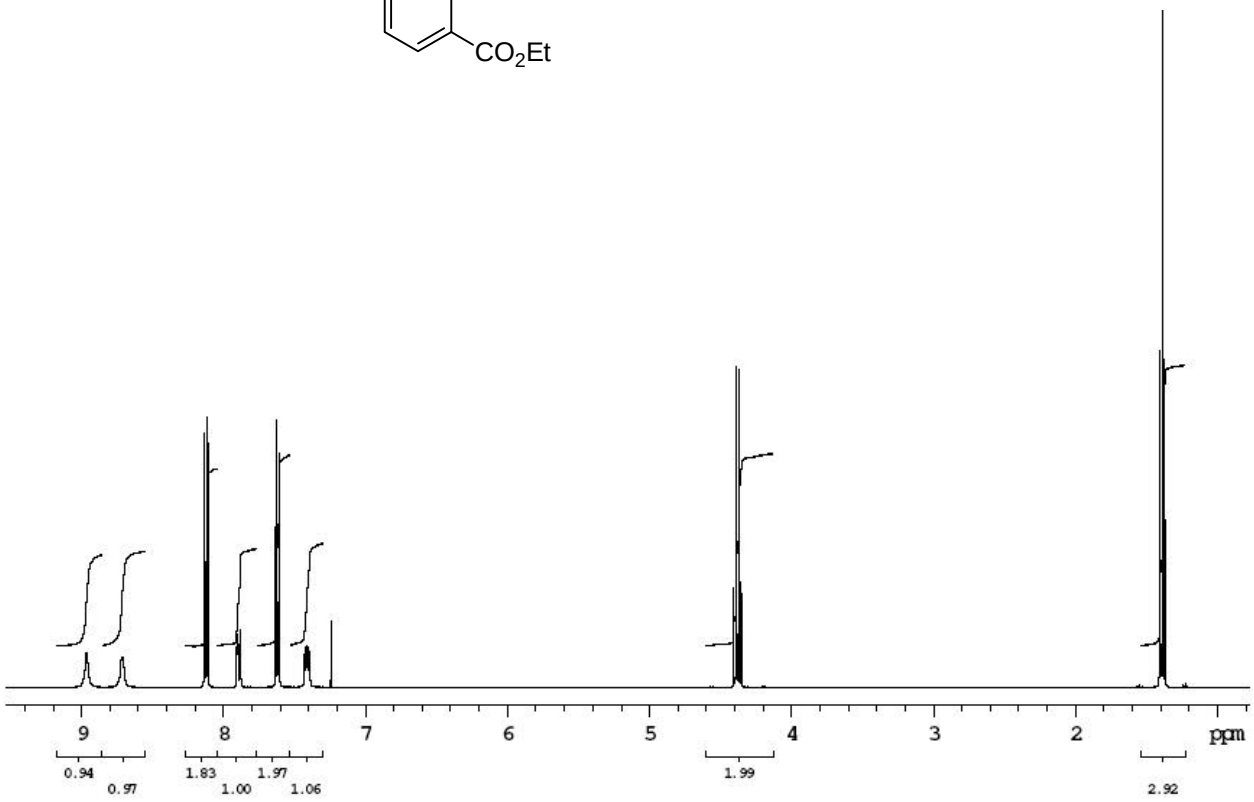
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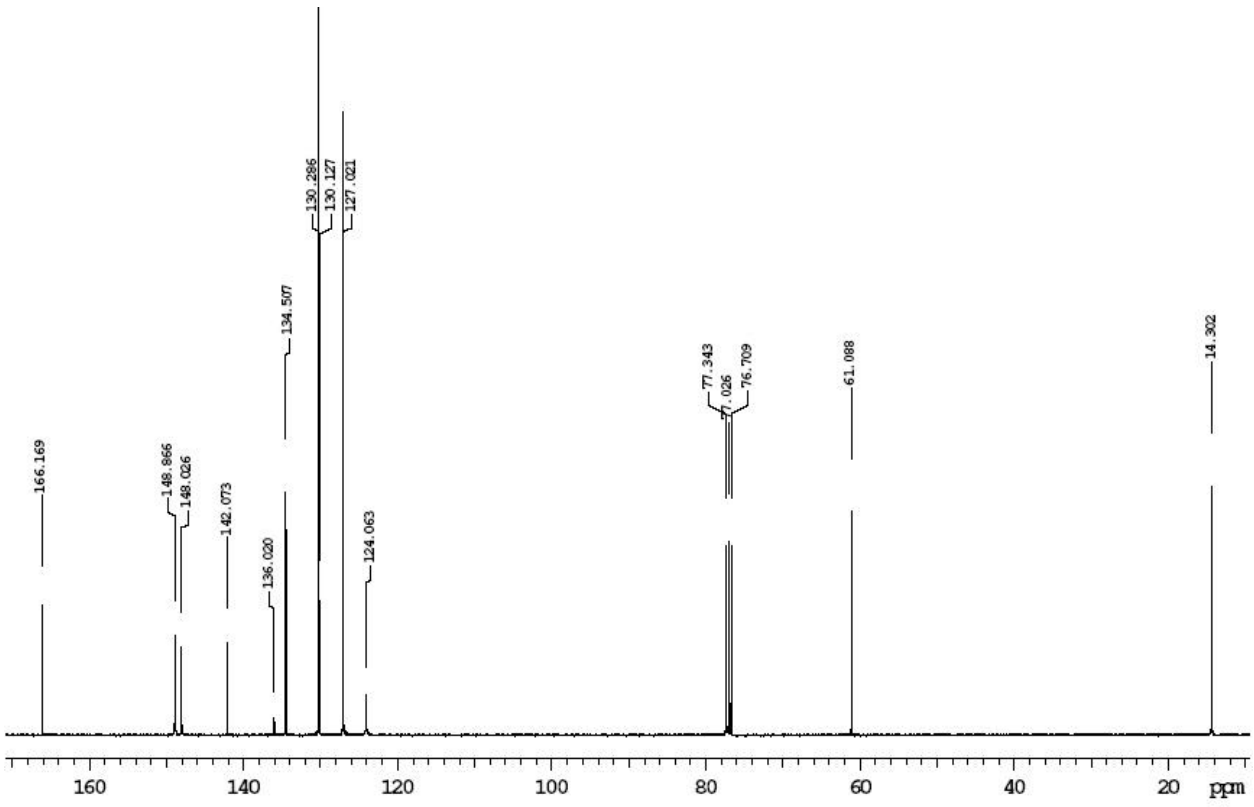
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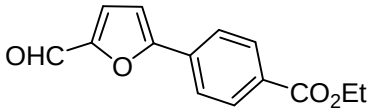
ppm

Compound 4j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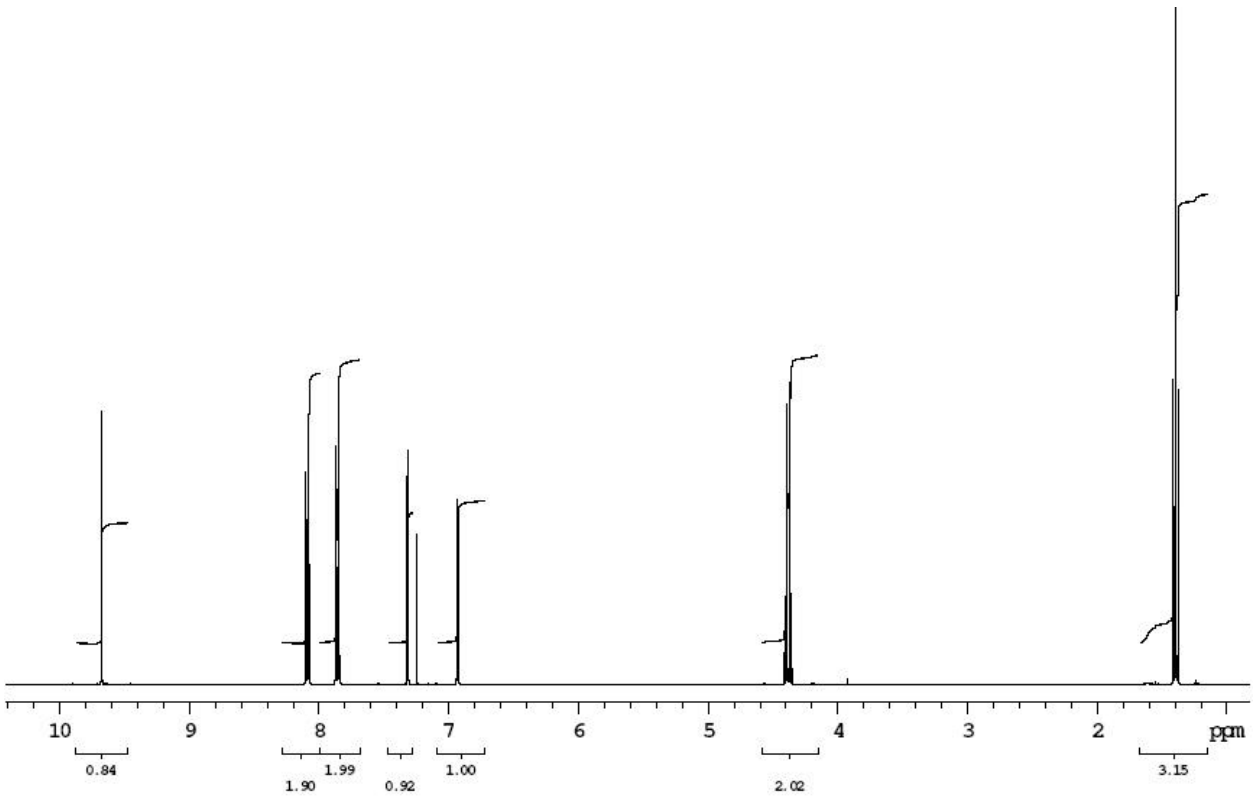
O
CO2Et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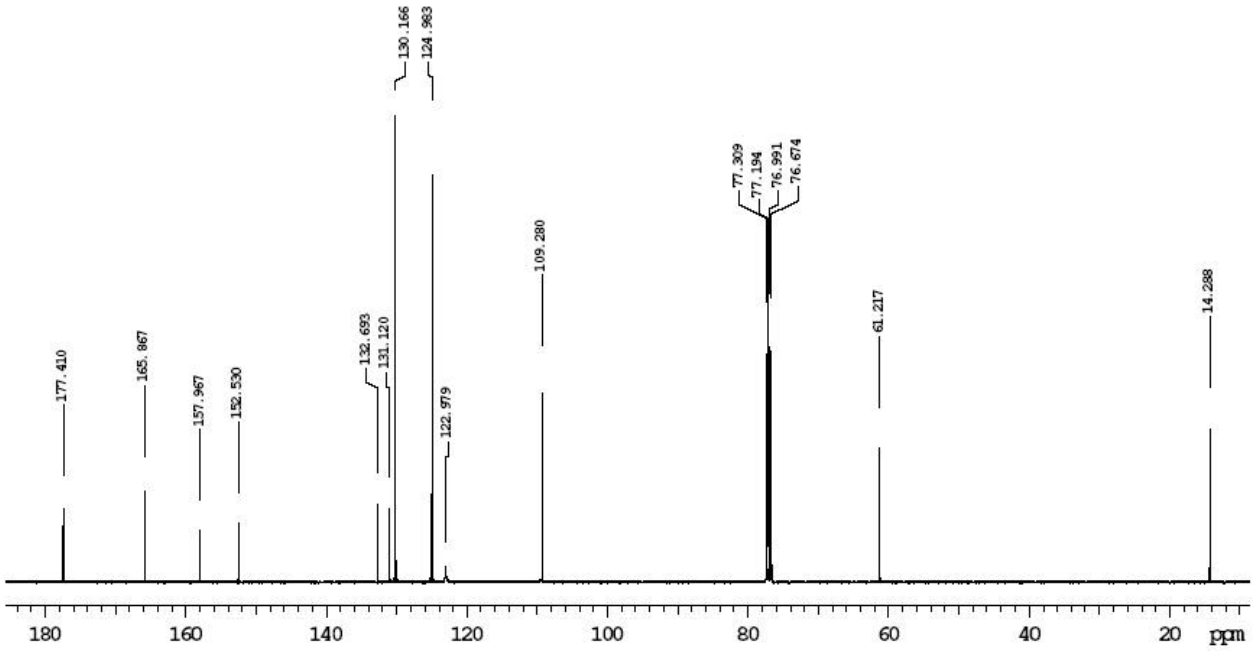
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100
80
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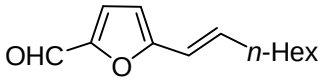
40
20
ppm

Compound 4k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O
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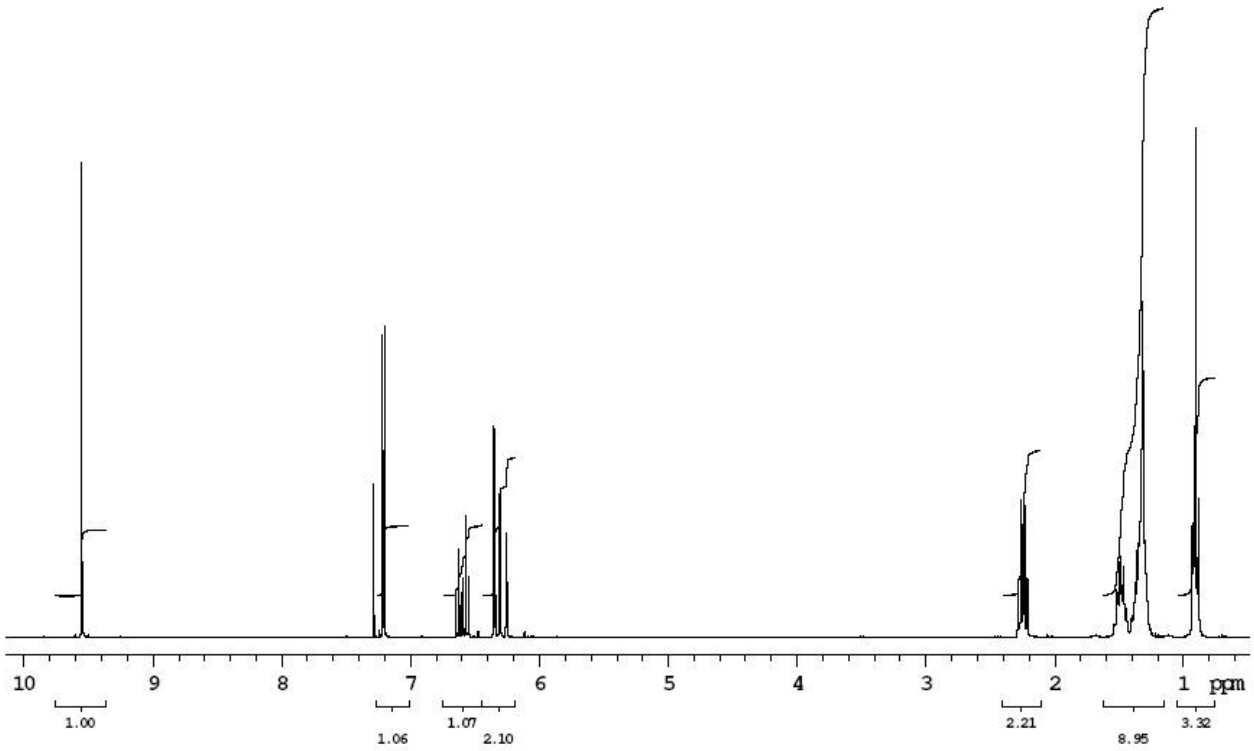
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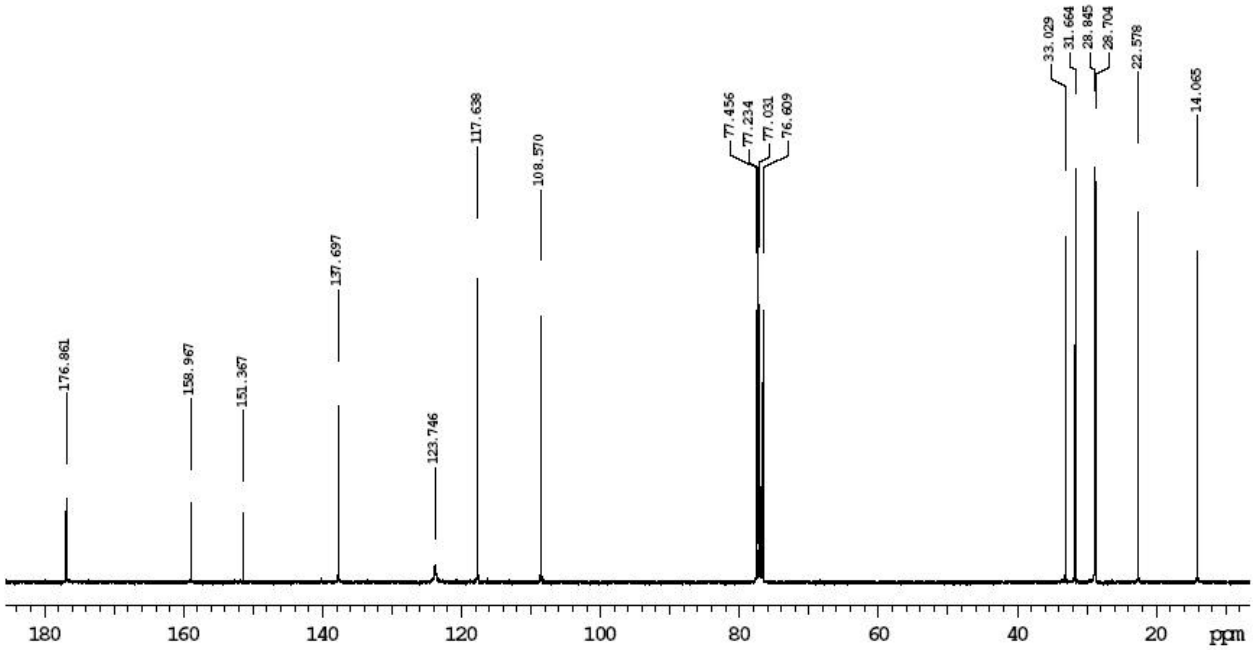
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20
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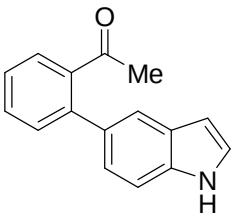
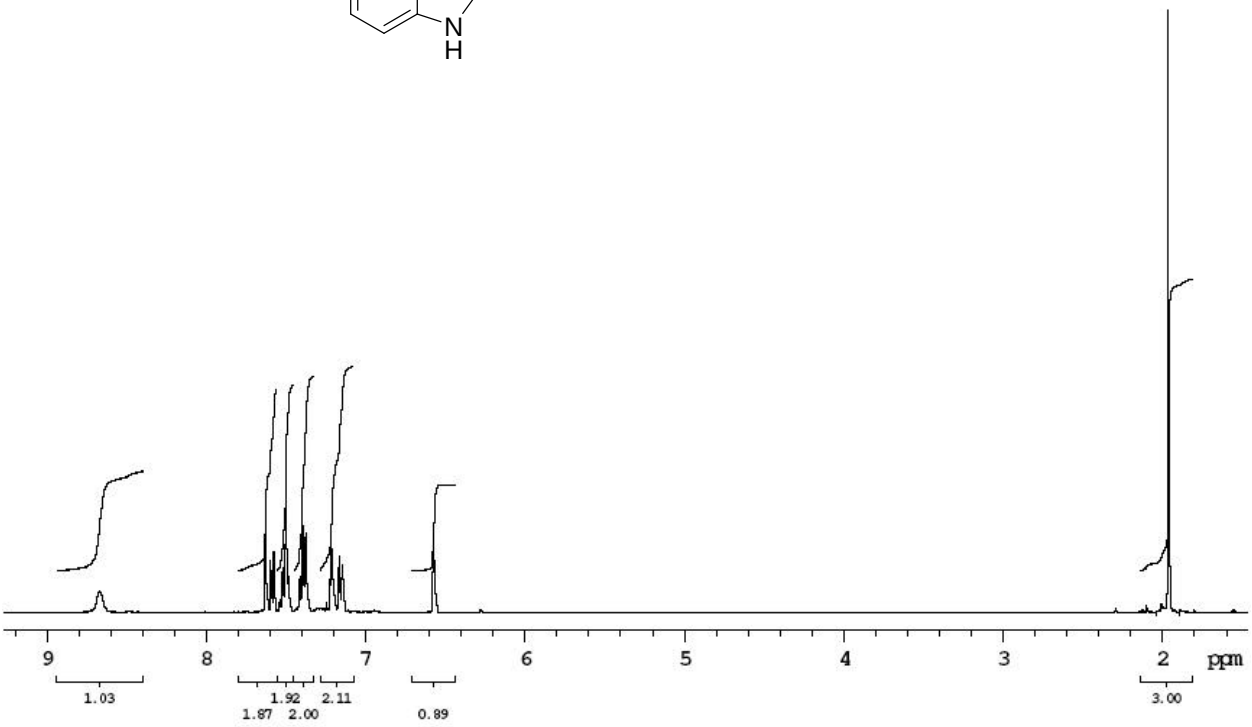
Compound 4l





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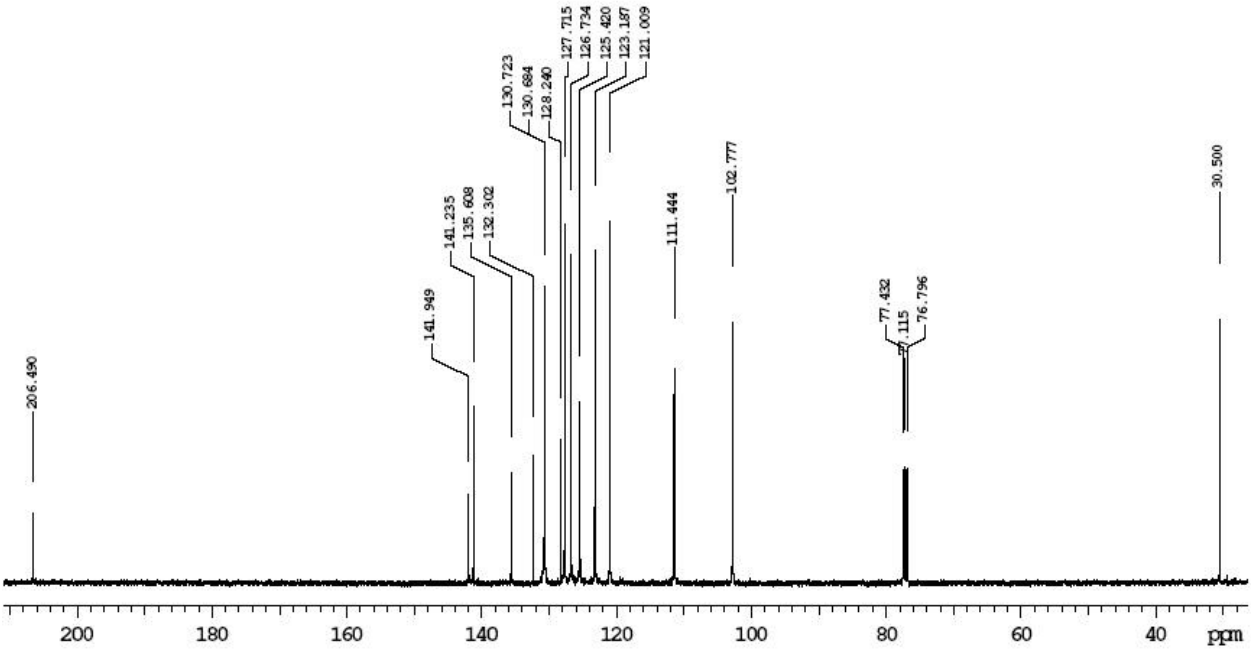

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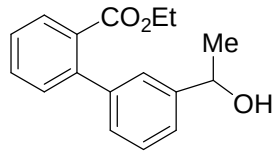
Compound 4m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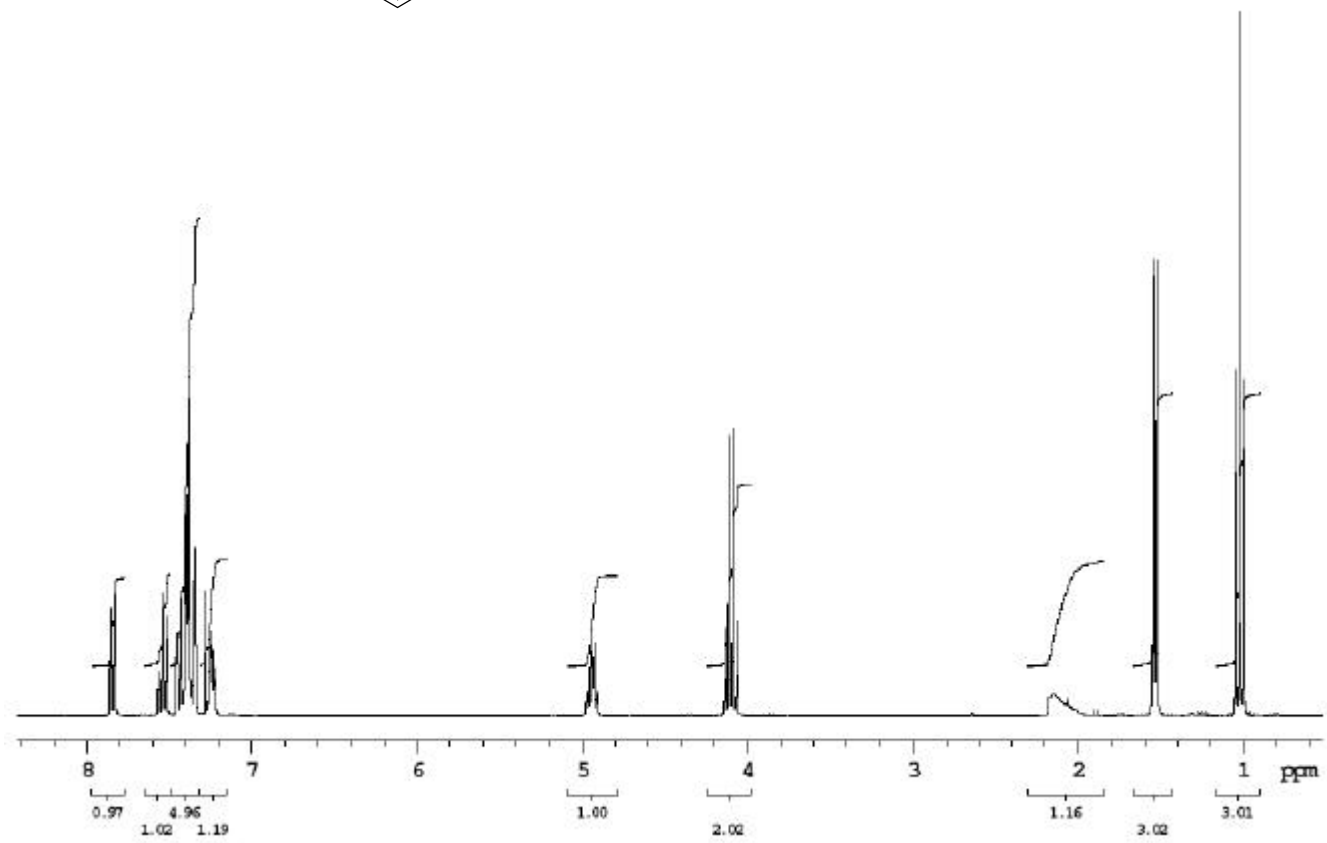
Me
OH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6
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2
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ppm
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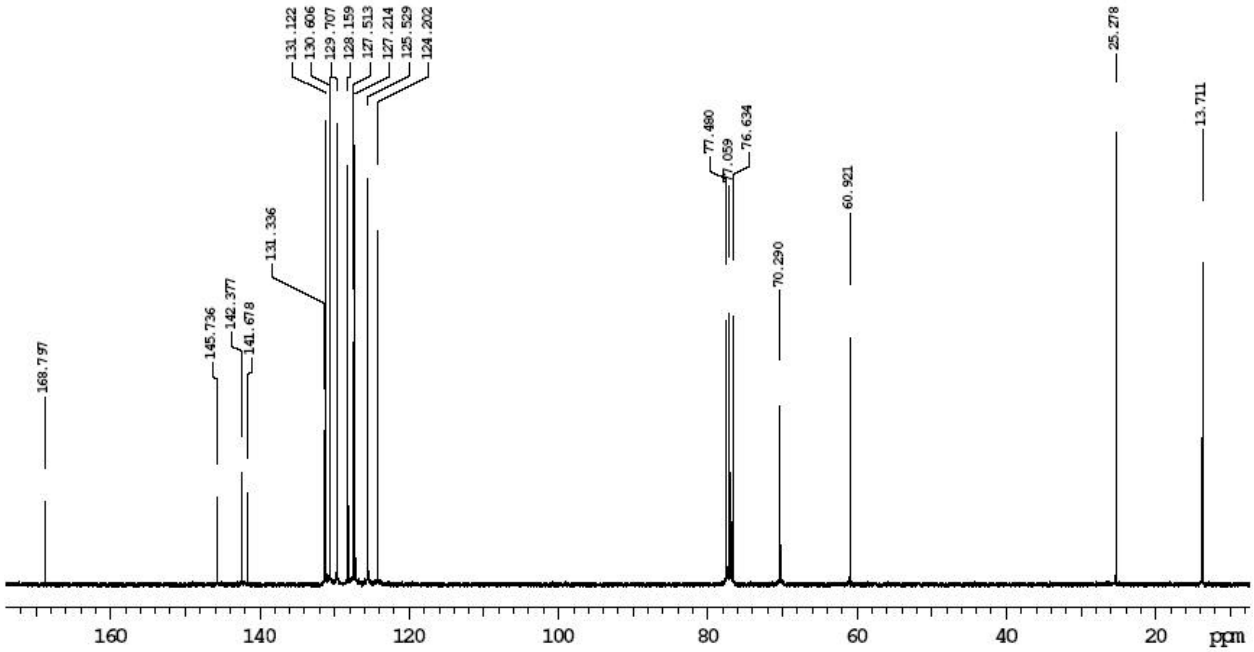
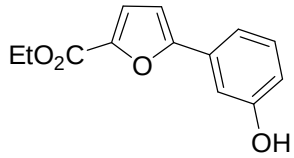
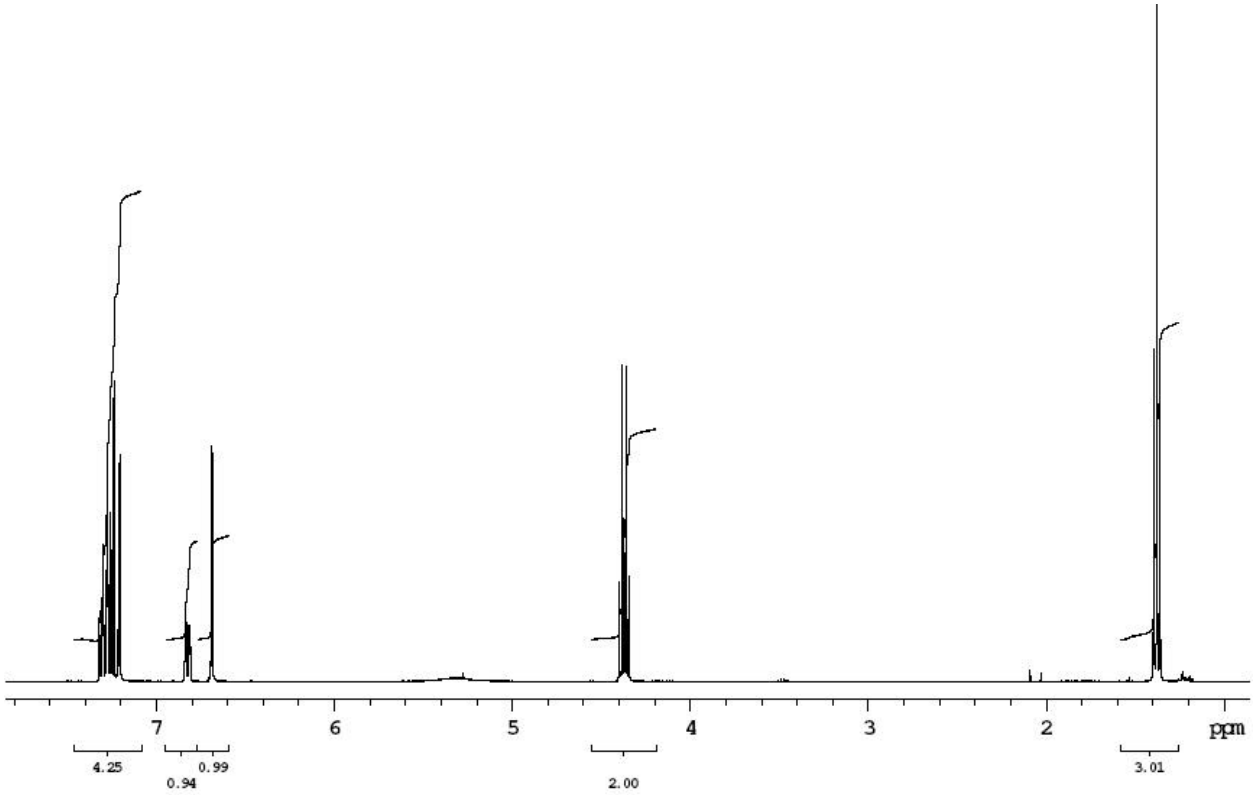
1.02
1.19
1.00
2.02
1.16
3.02
3.01


168.797
145.736
142.377
141.678
131.336
131.122
130.606
129.707
128.159
127.513
127.214
125.529
124.202
77.480
77.059
76.634
70.290
60.921
25.278
13.711
160
140
120
100
80
60
40
20
ppm

Compound 4n





Plotname: YC-3-Z7_PROTON_4r01_plot01