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Supporting Information for

Efficient water-soluble surfactant-type palladium catalyst for Suzuki cross-coupling reactions in pure water at room temperature

Pei Qiu,[a] Jing-Yang Zhao,[a] Xu Shi[a] and Xin-Hong Duan[b,*]

[a]College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China.

[b]College of Science, Beijing Forestry University, Beijing 100083, China

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1 Experiment Details

1) General Methods

All reagents including aryl bromides/iodides and $PdCl_2$ were obtained from Sigma-Aldrich Chemical Co. or Alfa Aesar. ^{1}H-NMR spectra were recorded on a Bruker Avance DPX 400 (400 MHz) spectrometer at 400 MHz using $CDCl_3$, DMSO-*d6* or D_2O as the solvent. The chemical shifts are reported in δ (ppm) values. Coupling constants are reported in hertz (Hz). The following abbreviations are used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. ^{13}C-NMR spectra were recorded on a Bruker Avance DPX 400 (400 MHz) spectrometer at 100 MHz using $CDCl_3$, DMSO-*d6* or D_2O as the solvent. Elemental analyses were obtained on an Elementar Vario EI.

All known compounds were characterized by ^{1}H-NMR, ^{13}C-NMR and melting point determination (for solids); and all new compounds were characterized by ^{1}H-NMR, ^{13}C-NMR, elemental analysis and melting point determination (for solids). Melting points were uncorrected.

2) General procedures

(1) Procedure for ligand

$[(Ph_2PCH_2)_2N(CH_2CH_2SO_3Na)_2]Br$ (**L**)

$[Ph_2P(CH_2OH)_2]Cl$ (0.57 g, 2.00 mmol) and Et_3N (0.80 mL) were dissolved in EtOH/H_2O (2:1, 10 mL), $H_2NC_2H_4SO_3Na$ (0.14 g, 1.00 mmol) was then added and stirred under reflux for 3 h. After cooling and freezing overnight, $[(Ph_2PCH_2)_2NCH_2CH_2SO_3Na]$ [1] was obtain as white solid (89 % yield).This compound (0.54 g, 1 mmol) and $BrC_2H_4SO_3Na$ (0.23 g, 1.20 mmol) were added in EtOH/H_2O (2:1, 10 mL) and stirred at 50 ^{o}C for 24 h. Solvents were removed to give a viscous gum that was subsequently crystallized by washed with ethyl acetate, and **L** was then obtained as a white solid (84 % yield).

(2) General procedure for the cross-coupled biaryls

$PdCl_2$ (0.27 mg, 1.5 μmol, 0.15 mol %), **L** (4.6 mg, 6 μmol) and 3 mL H_2O were mixed and heated at 80 ^{o}C for 5 min. After cooling to room temperature, the bromine/iodine (1.0 mmol), the boronic acid (1.5 mmol) and Na_2CO_3 (212 mg, 2 mmol) were added. The reaction mixture was stirred at room temperature until the coupling reaction reached. Then, the reaction mixture was extracted with

EtOAc (3 x 15 mL), dried over Na_2SO_4, and concentrated in vacuo, the product was obtained by purification with silica gel flash chromatography.

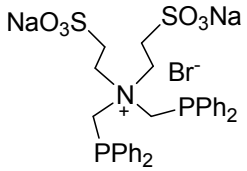
(3) Procedure for the double-coupled product

The Pd catalyst (0.30 mol %), 2,5-dibromopyridine (237 mg, 1.0 mmol), 4-methoxyphenylboronic acid (152 mg, 1.0 mmol) and Na_2CO_3 (318 mg, 3.0 mmol) were mixed and stirred at room temperature for 6h. Then, phenylboronic acid (122 mg, 1.0 mmol) was added and continued to be stirred at room temperature for 12h. After a routine workup including that the reaction mixture was extracted with EtOAc (3 x 20 mL), dried over Na_2SO_4, and concentrated in vacuo, the title product was obtained by purification with silica gel flash chromatography.

3) Characterization data

(1) Characterization data for ligands

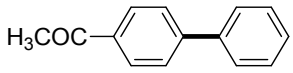
$[(Ph_2PCH_2)_2N(C_2H_4SO_3Na)_2]Br$ (L).



White solid, m.p. > 250 °C. ^{1}H-NMR (400 MHz, D_2O): δ 7.68-7.48 (m, 20H), 4.33 (q, J = 12.2 Hz, 2H), 3.16 (q, J = 8.4 Hz, 2H), 2.89 (t, J = 8.6 Hz, 4H), 2.83 (d, J = 13.8 Hz, 4H). ^{13}C-NMR (100 MHz, D_2O): δ 137.19, 133.11, 132.92, 130.92, 130.82, 130.65, 130.55, 129.46, 129.27, 129.14, 129.05, 128.93, 128.44, 128.36, 128.23, 122.51, 59.86, 49.40, 23.79. ^{31}P-NMR (162 MHz, D_2O): δ 39.49. Calculated for $C_{30}H_{32}BrNNa_2O_6P_2S_2$: C, 47.75; H, 4.27; N, 1.86. Found: C, 47.55; H, 4.33; N, 1.35.

(2) Characterization data for biaryls

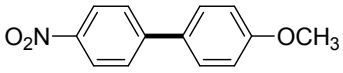
4-Acetylbiphenyl[2] **(1a)**



White solid, m.p. 120.1-120.7 °C (lit. 119-120 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.08 (q, J = 8.5 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.54-7.50 (m, 2H), 7.47-7.43 (m, 1H), 2.69 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 197.76, 145.77, 139.85, 135.82, 128.93, 128.89,

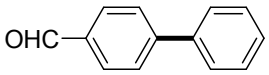
128.21, 127.25, 127.20, 26.65.

4-Methoxy-4'-nitrobiphenyl[3] (**1b**, Table 2, entry 1).



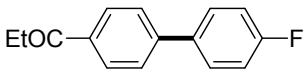
Pale yellow solid, m.p. 109.2-110.0 °C (lit. 108-110 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.58 (q, J = 8.8 Hz, 2H), 7.02 (t, J = 8.7 Hz, 2H), 3.87 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 160.42, 147.17, 146.49, 131.01, 128.54, 127.03, 124.11, 114.58, 55.40.

Biphenyl-4-carboxaldehyde[4] (**1c**, Table 2, entry 2)



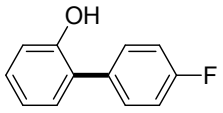
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.49 (t, J = 8.2 Hz, 2H), 7.47-7.42 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.94, 147.17, 139.68, 135.17, 130.26, 129.00, 128.47, 127.66, 127.35.

4'-Fluorobiphenyl-4-propan-1-one[5] (**1d**, Table 2, entry 3)



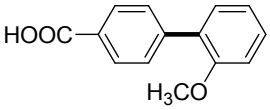
White solid, m.p. 86.2-86.6 °C (lit. 85-87 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.3 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.64-7.61 (t, 2H), 7.22-7.18 (t, 2H), 3.10-3.05 (m, 2H), 1.29 (t, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.36, 164.15, 161.68, 144.45, 136.02, 135.99, 135.54, 128.92, 128.84, 128.61, 127.02, 115.98, 115.77, 31.83, 8.26.

2-(4-Fluorophenyl)phenol[6] (**1e**, Table 2, entry 4).



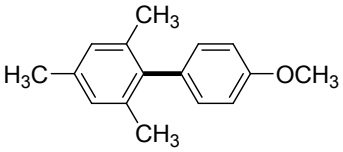
Colorless solid, m.p. 44.2-44.4 °C (lit. 45-46 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.52-7.48 (m, 2H), 7.33-7.28 (m, 2H), 7.26-7.20 (m, 2H), 7.06-7.01 (m, 2H), 5.08 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.62, 161.17, 152.33, 133.05, 130.92, 130.91, 130.85, 130.38, 129.22, 127.22, 120.99, 116.17, 115.93.

4-(2-Methoxyphenyl)benzoic acid[7] (**1f**, Table 2, entry 5)



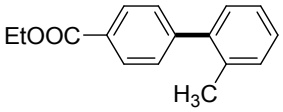
White solid, m.p. 251.1-252.9 °C (lit. 252-255 °C). ^{1}H-NMR (400 MHz, DMSO-*d6*): δ 13.0 (s, 1H), 7.99 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.43-7.39 (m, 1H), 7.37-7.34 (m, 1H), 7.16 (d, J = 8.2 Hz, 1H), 7.09-7.06 (m, 1H), 3.80 (s, 3H). ^{13}C-NMR (100 MHz, DMSO-*d6*): δ 167.65, 156.53, 143.09, 130.81, 130.03, 129.82, 129.49, 129.44, 129.12, 121.28, 112.25, 55.93.

4′-Methoxy-2,4,6-trimethylbiphenyl[8] (**1g**, Table 2, entry 6)



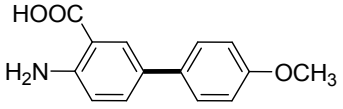
White solid, m.p. 75.1-76.0 °C (lit. 73-75 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.17 (q, J = 8.7 Hz, 2H), 7.08-7.05 (m, 4H), 3.96 (s, 3H), 2.44 (s, 3H), 2.13 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.23, 138.71, 136.44, 133.31, 130.34, 128.07, 113.79, 55.20, 21.06, 20.85.

Ethyl 2'-methylbiphenyl-4-carboxylate[9] (**1h,** Table 2, entry 7)



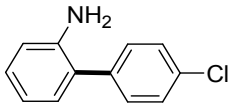
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 7.8 Hz, 2H), 7.95 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 10.4 Hz, 2H), 4.48-4.41 (m, 2H), 2.31 (s, 3H), 1.48-1.44 (t, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.54, 146.61, 140.88, 135.15, 131.64, 131.09, 130.49, 129.53, 129.39, 129.22, 128.91, 127.82, 125.91, 60.97, 20.41, 14.39.

4-Amino-4'-methoxybiphenyl-3-carboxylic acid[10] (**1i**, Table 2, entry 9)



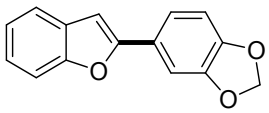
White solid, m.p. 260.6-262.0 °C (lit. 258.8 °C). ^{1}H-NMR (400 MHz, DMSO-*d6*): δ 7.96 (s, 1H), 7.82-7.78 (m, 1H), 7.60-7.54 (m, 2H), 7.48 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 7.8 Hz, 1H), 6.78 (d, J = 8.2 Hz, 1H), 4.32 (s, 2H), 3.78 (s, 3H). ^{13}C-NMR (400 MHz, DMSO-*d6*): δ 158.27, 150.58, 133.25, 132.16, 131.55, 131.48, 131.13, 129.03, 128.94, 126.90, 126.57, 117.15, 114.71, 55.55.

4'-Chlorobiphenyl-2-amine[11] (**1j**, Table 2, entry 10)



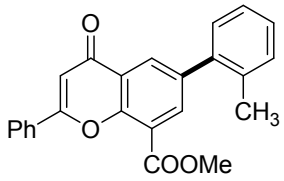
Light yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 4H), 7.18-7.14 (m, 1H), 7.08 (q, J = 9.0 Hz, 1H), 6.85-6.80 (m, 1H), 6.77 (d, J = 8.0 Hz, 1H), 3.73 (s, br, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.33, 137.89, 132.56, 130.45, 130.32, 128.97, 128.82, 128.32, 126.32, 119.39, 118.80, 115.73.

2-(4, 5-Methylenedioxyphenyl)benzofuran[12] (**2a**, Table 3, entry 1)



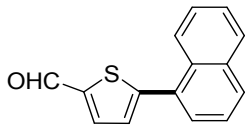
White solid, m.p. 102.6-103.1 ^{o}C (lit. 102-102.7 ^{o}C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.2 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.37 (s, 1H), 7.33-7.27 (m, 2H), 6.93 (d, J = 10.6 Hz, 2H), 6.06 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.74, 154.63, 148.09, 148.00, 129.33, 124.75, 123.95, 122.90, 120.66, 119.12, 111.02, 108.69, 105.45, 101.33, 100.16.

Methyl 4-oxo-2-phenyl-6-*o*-tolyl-4*H*-chromene-8-carboxylate (**2b**, Table 3, entry 2)



White solid, m.p. 128.6-129.3 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.31 (s, 1H), 7.89 (q, J = 7.9 Hz, 2H), 7.60 (d, J = 6.7 Hz, 2H), 7.35 (t, J = 7.0 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.17-7.10 (m, 1H), 6.90-6.83 (m, 1H), 4.01 (s, 3H), 2.35 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 178.55, 164.73, 161.15, 153.47, 139.25, 138.06, 137.14, 135.34, 133.01, 130.58, 129.84, 129.36, 128.48, 128.13, 126.92, 126.11, 122.99, 120.27, 117.62, 114.88, 52.52, 20.42. Calculated for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.55; H, 4.83.

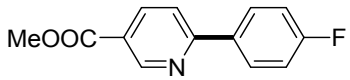
5-(Naphthalen-1-yl)thiophene-2-carbaldehyde[13] (**2c**, Table 3, entry 3)



Colorless solid, m.p. 56.7-56.9 °C (lit. 56-57 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H),

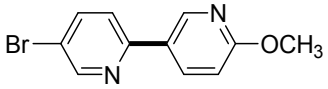
8.21 (d, J = 6. 1 Hz, 1H), 7.97 (d, J = 7.0 Hz, 2H), 7.89 (s, 1H), 7.65 (s, 1H), 7.65-7.59 (m, 3H), 7.41 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 183.01, 152.27, 143.49, 136.80, 133.82, 131.09, 131.06, 129.82, 128.69, 128.63, 128.37, 127.10, 126.45, 125.27, 125.08.

Methyl 6-(4-fluorophenyl)nicotinate[14] (**2d**, Table 3, entry 4)



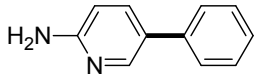
White solid, m.p. 130.1-130.9 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.30 (s, 1H), 8.39 (d, J = 8.2 Hz, 1H), 8.10 (t, J = 12.0 Hz, 2H), 7.81 (d, J = 8.2 Hz, 1H), 7.25-7.21 (t, 2H), 4.02 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 165.74, 165.28, 162.80, 159.69, 150.89, 137.92, 134.35, 129.29, 129.20, 124.06, 119.41, 115.96, 115.75, 52.35.

5-Bromo-6'-methoxy-2, 3'-bipyridine[15] (**2e**, Table 3, entry 5)



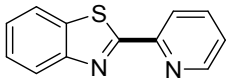
White solid, m.p.100.1-100.9 °C (lit. 100-100.5 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.72 (q, J = 8.5 Hz, 2H), 8.21 (q, J = 11.2 Hz, 1H), 7.87 (q, J = 10.8 Hz, 1H), 7.55 (d, J = 8.5 Hz, 1H), 6.83 (d, J = 8.7 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.85, 153.51, 150.85, 145.47, 139.33, 137.08, 127.48, 120.69, 119.04, 111.00, 53.68,

5-Phenylpyridin-2-amine[16] (**2f**, Table 3, entry 6)



Light yellow solid, m.p. 71.4-71.8 °C (lit. 72-73 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.75-7.72 (m, 1H), 7.55 (q, J = 8.4 Hz, 2H), 7.49-7.45 (m, 2H), 7.37 (q, J = 8.4 Hz, 1H), 6.65 (d, J = 8.5 Hz, 1H), 4.64 (s, br, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.44, 145.91, 138.17, 136.82, 128.93, 127.43, 126.98, 126.30, 108.69.

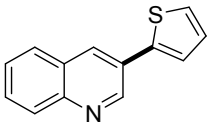
2-(Pyridin-2-yl)benzo[*d*]thiazole[17] (**2g**, Table 3, entry 7)



Light yellow solid, m.p. 138.2-139.1 °C (lit. 134 °C). ^{1}H-NMR (400 MHz, $CHCl_3$): δ 8.72 (d, J =

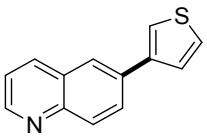
4.3 Hz, 1H), 8.68 (s, 1H), 8.39 (d, J = 7.9 Hz, 1H), 7.87-7.83 (m, 1H), 7.67 (q, J = 9.1 Hz, 1H), 7.43-7.39 (m, 1H), 7.24-7.20 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 160.26, 154.45, 149.61, 147.67, 136.76, 132.66, 127.80, 127.05, 125.87, 125.40, 122.13, 117.20.

3-(Thiophen-2-yl)quinoline[18] (**2h**, Table 3, entry 8)



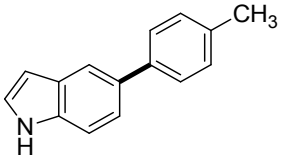
White solid, m.p.75.9-76.7 °C (lit. 70-70.3 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.22 (s, 1H), 8.28 (s, 1H), 8.12 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.72-7.68 (m, 1H), 7.58-7.54 (m, 1H), 7.50 (q, J = 5.0 Hz, 1H), 7.40 (q, J = 8.7 Hz, 1H), 7.17 (d, J = 8.7 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.55, 147.22, 140.68, 131.29, 129.30, 129.26, 128.41, 127.90, 127.82, 127.52, 127.22, 126.10, 124.40.

6-(Thiophen-3-yl)quinoline[19] (**2i**, Table 3, entry 9)



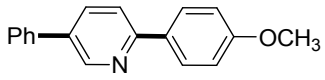
White solid, m.p. 95.2-96.0 °C (lit. 94-98 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.94 (t, J = 3.9 Hz, 1H), 8.23-8.19 (m, 2H), 8.01 (s, 2H), 7.63 (s, 1H), 7.55 (d, J = 4.8 Hz, 1H), 7.48 (s, 1H), 7.46-7.42 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.92, 147.16, 141.29, 136.43, 133.96, 129.63, 128.81, 128.59, 126.74, 126.29, 124.33, 121.52, 121.41.

5-(4-Tolyl)-1*H*-indole[20] (**2j**, Table 3, entry 10)



Light yellow solid, m.p. 130.7-131.1 °C (lit. 131-133 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.20 (s, br, 1H), 7.90 (s, 1H), 7.61 (d, J = 7.2 Hz, 2H), 7.50 (s, 2H), 7.31, (d, J = 6.7 Hz, 3H), 6.66 (s, 1H), 2.46 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 139.70, 136.06, 135.21, 133.35, 129.49, 128.41, 127.29, 124.94, 123.21, 121.84, 119.01, 112.54, 111.32, 102.93, 21.14.

2-(4-Methoxyphenyl)-5-phenylpyridine[21] (**3a**)



White solid, m.p. 210.5-211.4 °C (lit. 210-211 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.67 (d, J = 7.2 Hz, 1H), 7.56-7.52 (t, 1H), 7.27 (t, J = 8.4 Hz, 2H), 7.08-7.04 (t, 2H), 6.99-6.95 (t, 1H), 6.88 (t, J = 8.6 Hz, 2H), 3.93 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 160.56, 155.82, 147.64, 135.34, 129.58, 129.09, 128.30, 128.23, 127.99, 126.90, 120.42, 115.34, 114.23, 114.18, 55.36.

2. References

[1] O. Serindag, R. D. W. Kemmitt, J. Fawcett and D. R. Russell *Transition Met. Chem.*, 1995, **20**, 548-551.

[2] I. Hoffmann, B. Blumenröder, S. O. Thumann, S. Dommer and J. Schatz, *Green Chem.*, 2015, **17**, 3844-3857.

[3] A. Taher, D. Nandi, M. Choudhary and K. Mallick, *New J. Chem.*, 2015, **39**, 5589-5596.

[4] G. A. Molander and L. Iannazzo, *J Org. Chem.*, 2011, **76**, 9182-9187.

[5] J. Zeng, K. M. Liu and X. F. Duan, *Org. Lett.*, 2013, **15**, 5342-5345.

[6] K. Inamoto, J. Kadokawa and Y. Kondo, *Org. Lett.*, 2013, **15**, 3962-3965.

[7] D. N. Korolev and N. A. Bumagin, *Tetrahedron Lett.*, 2006, **47**, 4225-4229.

[8] L. S. Chen, H. Y. Lang, L. Fang, M. Y. Zhu, J. Q. Liu, J. J. Yu, L. M. Wang, *Eur. J. Org. Chem.*, 2014, 4953-4957.

[9] Q. Liang, P. Xing, Z. Huang, J. Dong, K. B. Sharpless, X. Li and B. Jiang, *Org. Lett.*, 2015, **17**, 1942-1945.

[10] A.-L. Gérard, V. Lisowski and S. Rault, *Tetrahedron*, 2005, **61**, 6082-6087.

[11] D. Cantillo, M. M. Moghaddam and C. O. Kappe, *J. Org. Chem.*, 2013, **78**, 4530-4542.

[12] X. F. Duan, J. Zeng, Z. B. Zhang and G. F. Zi, *J. Org. Chem.*, 2007, **72**, 10283-10286.

[13] T. E. Barder and S. L. Buchwald, *Org. Lett.*, 2004, **6**, 2649-2652.

[14] M. F. Brown, C. F. Donovan, E. L. Ellsworth, D. W. Hoyer, T. A. Johnson, M. S. Lall, C. Limberakis, S. T. Murphy, D. A. Sherry, C. B. Taylor and J. S. Warmus, WO 2010/032147 A2.

[15] X. Tan, Z. J. Zhou, J. X. Zhang and X. H. Duan, *Eur. J. Org. Chem.*, 2014, 5153-5157.

[16] S. Shi and Y. Zhang, *Green Chem.*, 2008, **10**, 868-872.

[17] J. Huang, J. Chan, Y. Chen, C. J. Borths, K. D. Baucom, R. D. Larsen and M. M. Faul, *J. Am. Chem. Soc.*, 2010, **132**, 3674-3675.

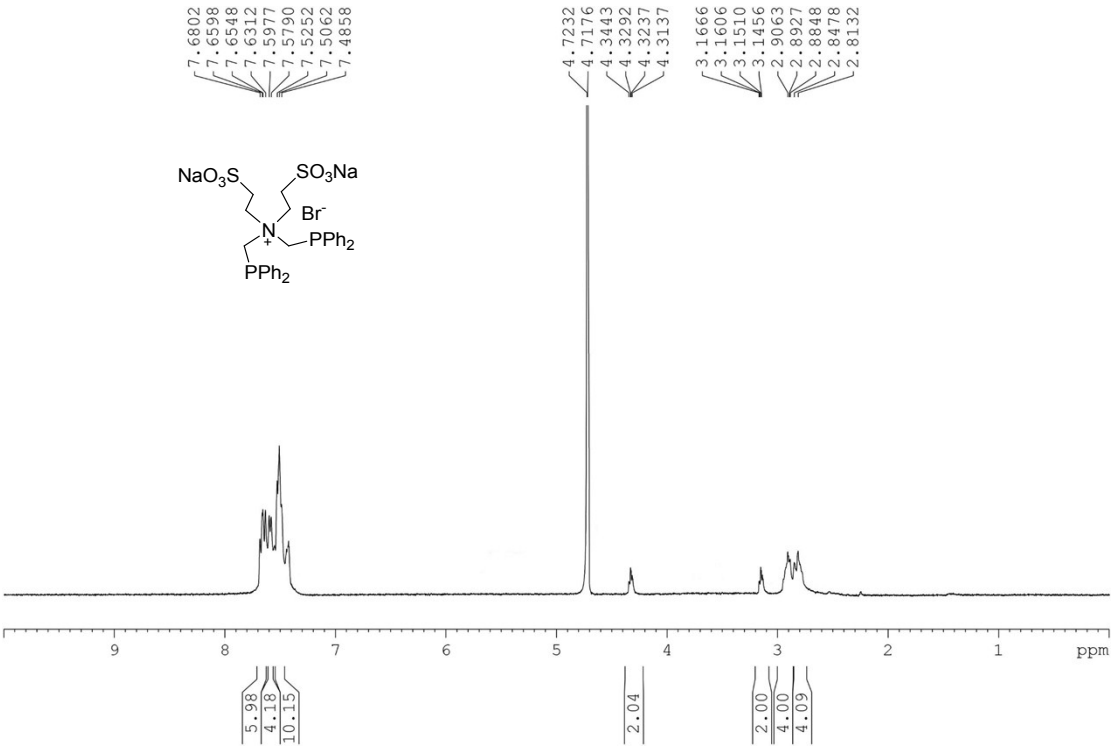
[18] W. Luo, Q. Mu, W. Qiu, T. Liu, F. Yang, X. Liu, J. Tang, *Tetrahedron*, 2011, **67**, 7090-7095.

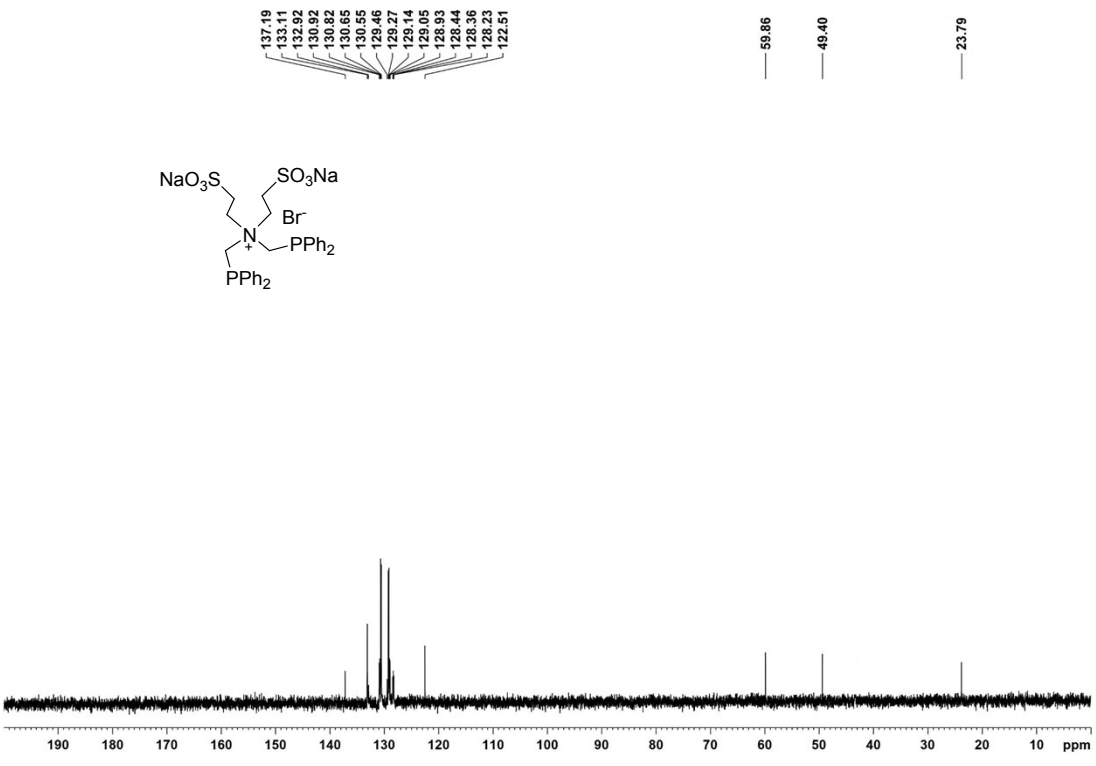
[19] T. Noël and A. J. Musacchio, *Org. Lett.*, 2011, **13**, 5180-5183.

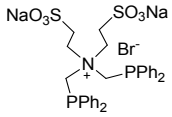
[20] A. K. Verma, A. K. Danodia, R. K. Saunthwal, M. Patel and D. Choudhary, *Org. Lett.*, 2015, **17**, 3658-3661.

[21] S. T. Handy, T. Wilson and A. Muth, *J. Org. Chem.*, 2007, **72**, 8496-8500.

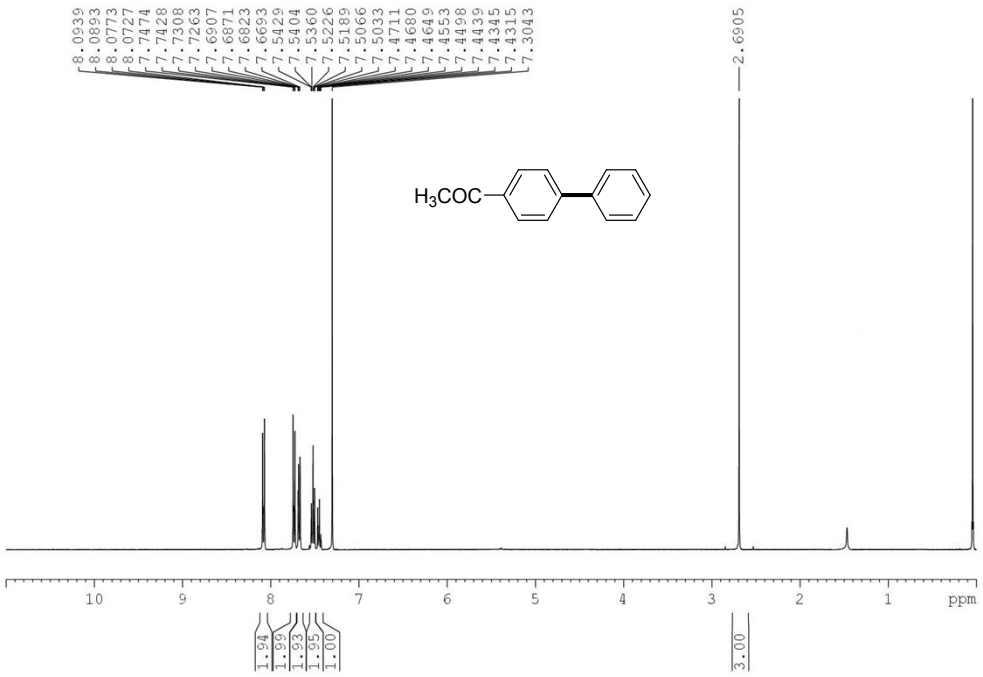
3. ^{1}H and ^{13}C NMR Spectra






NaO3S
SO3Na
Br-
N+
PPh2
PPh2

39.4911
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm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8.0893
8.0773
8.0727
7.7474
7.7428
7.7308
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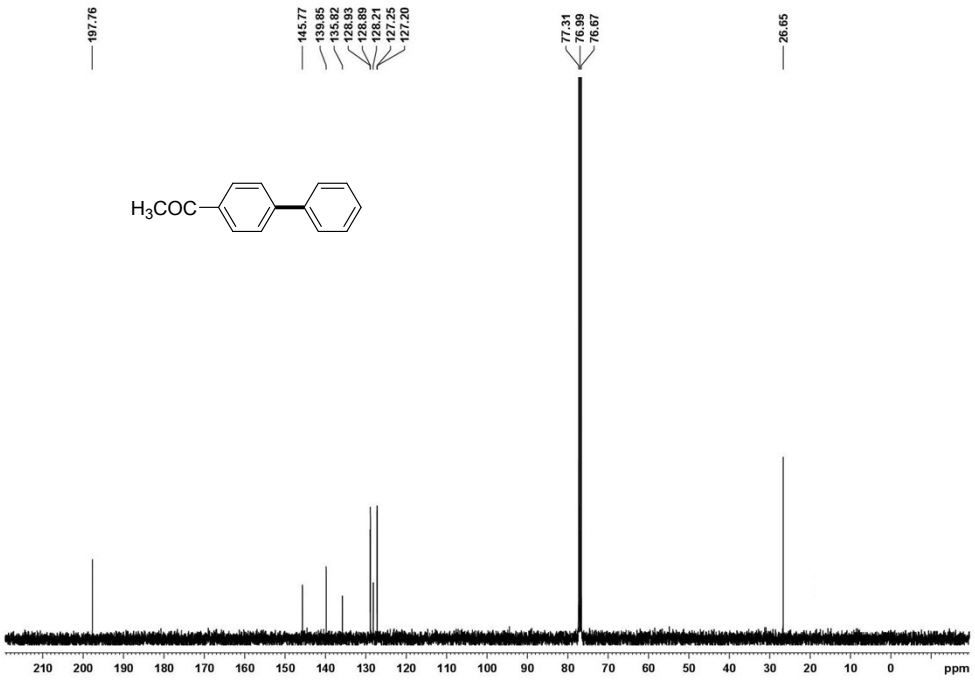
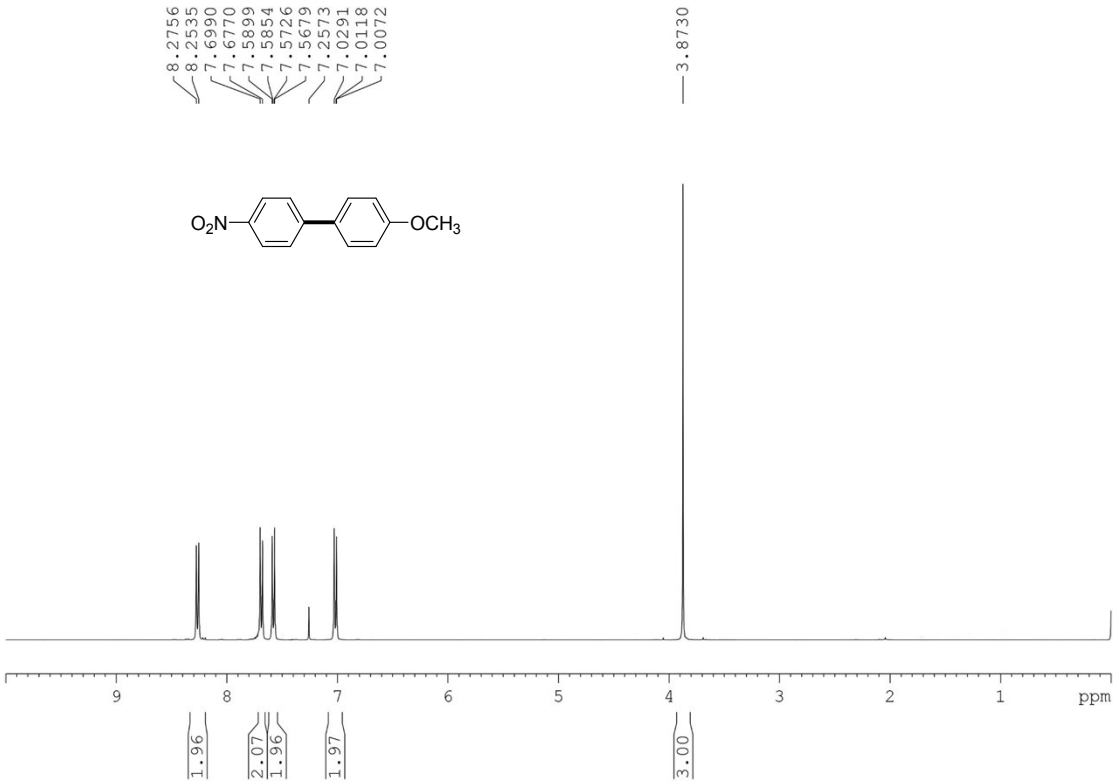
7.6907
7.6871
7.6823
7.6693
7.5429
7.5404
7.5360
7.5226
7.5189
7.5066
7.5033
7.4711
7.4680
7.4649
7.4553
7.4498
7.4439
7.4345
7.4315
7.3043
2.6905
H3COC
10 9 8 7 6 5 4 3 2 1 ppm
1.94
1.99
1.93
1.95
1.00
3.00


197.76
145.77
139.85
135.82
128.93
128.89
128.21
127.25
127.20
77.31
76.99
76.67
26.65
H3COC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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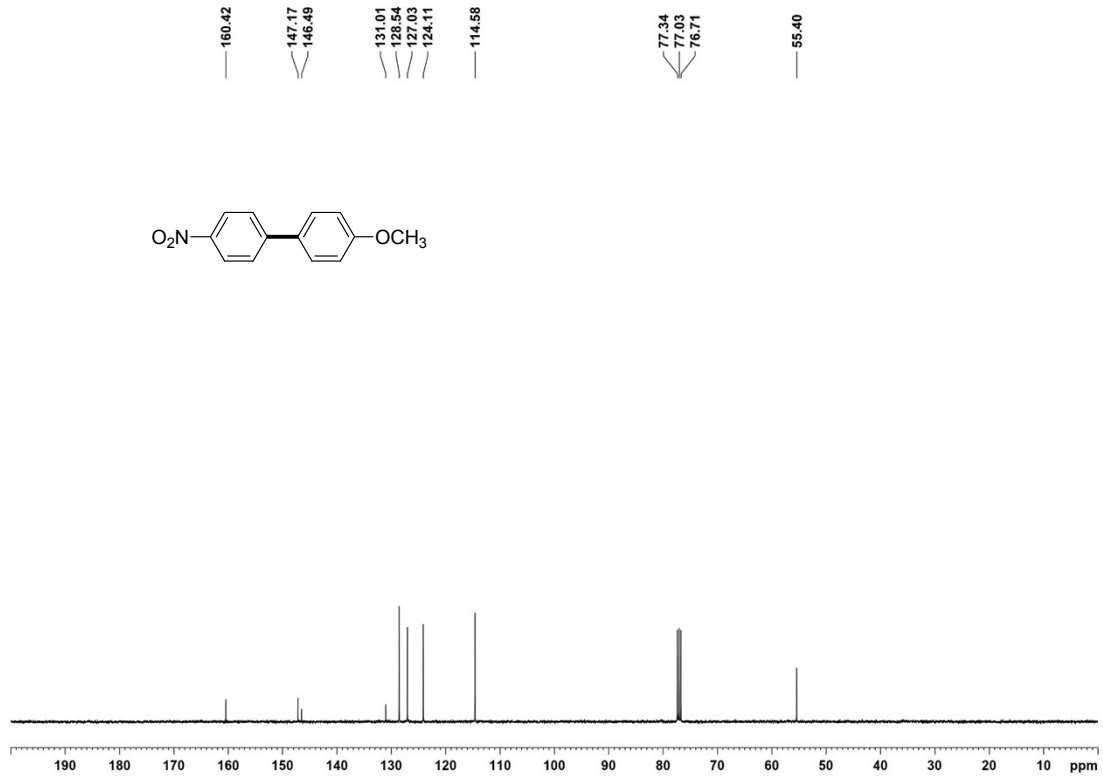
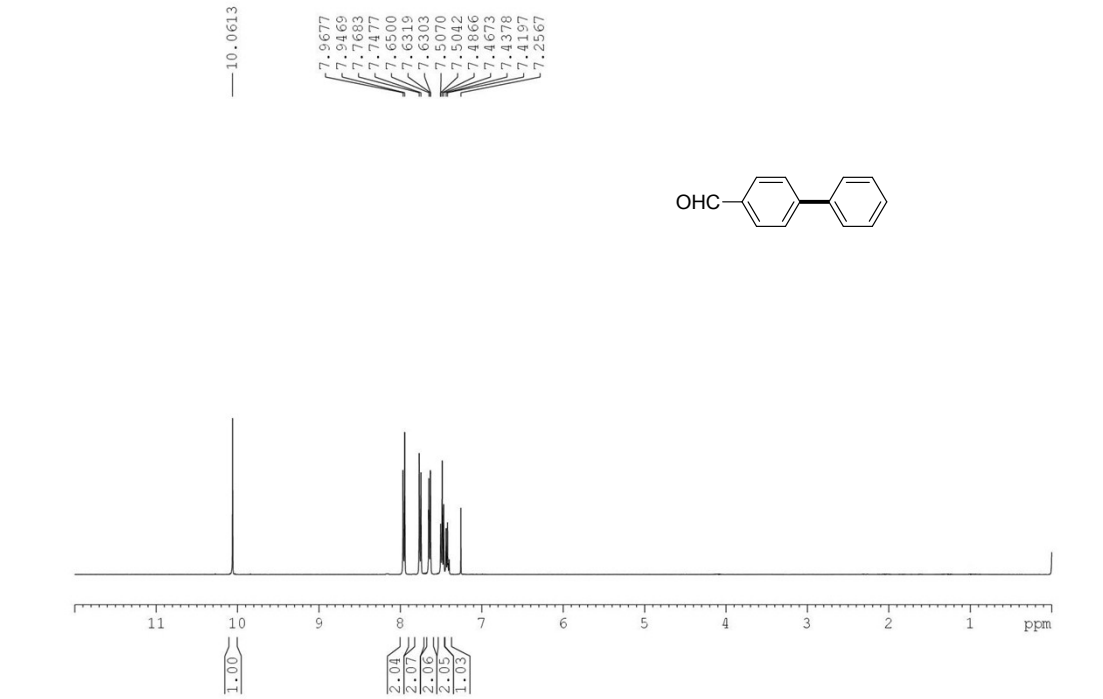
8.2535
7.6990
7.6770
7.5899
7.5854
7.5726
7.5679
7.2573
7.0291
7.0118
7.0072
3.8730
O2N
OCH3
9 8 7 6 5 4 3 2 1 ppm
1.96
2.07
1.96
1.97
3.00


160.42
147.17
146.49
131.01
128.54
127.03
124.11
114.58
77.34
77.03
76.71
55.40
O2N
OCH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.9469
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7.5042
7.4866
7.4673
7.4378
7.4197
7.2567
OHC
11
10
9
8
7
6
5
4
3
2
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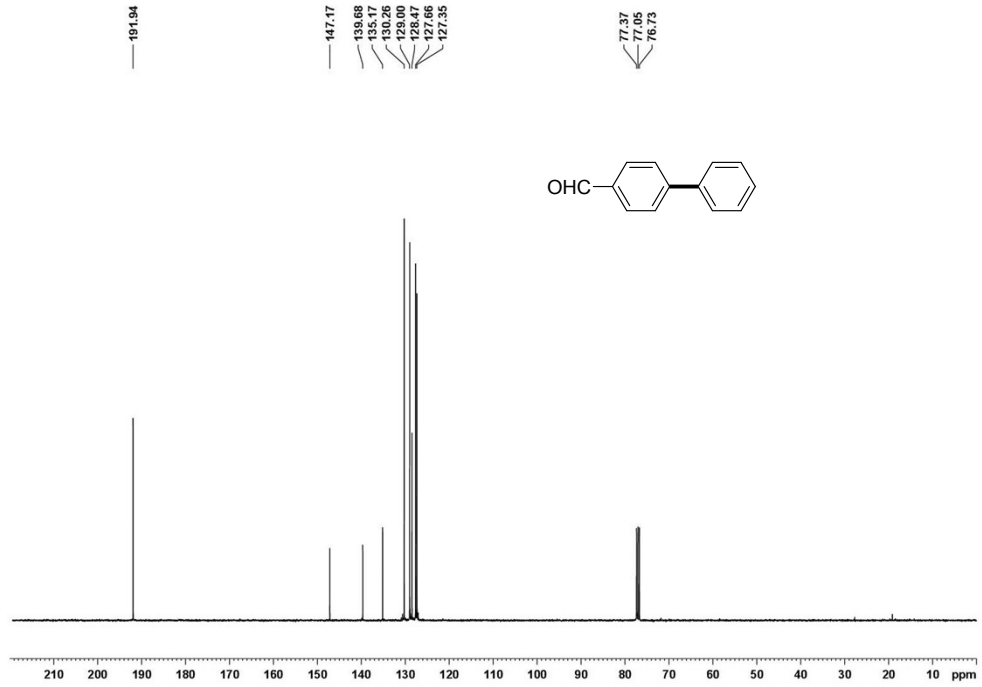
1.00
2.04
2.07
2.06
2.05
1.03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139.68
135.17
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128.47
127.66
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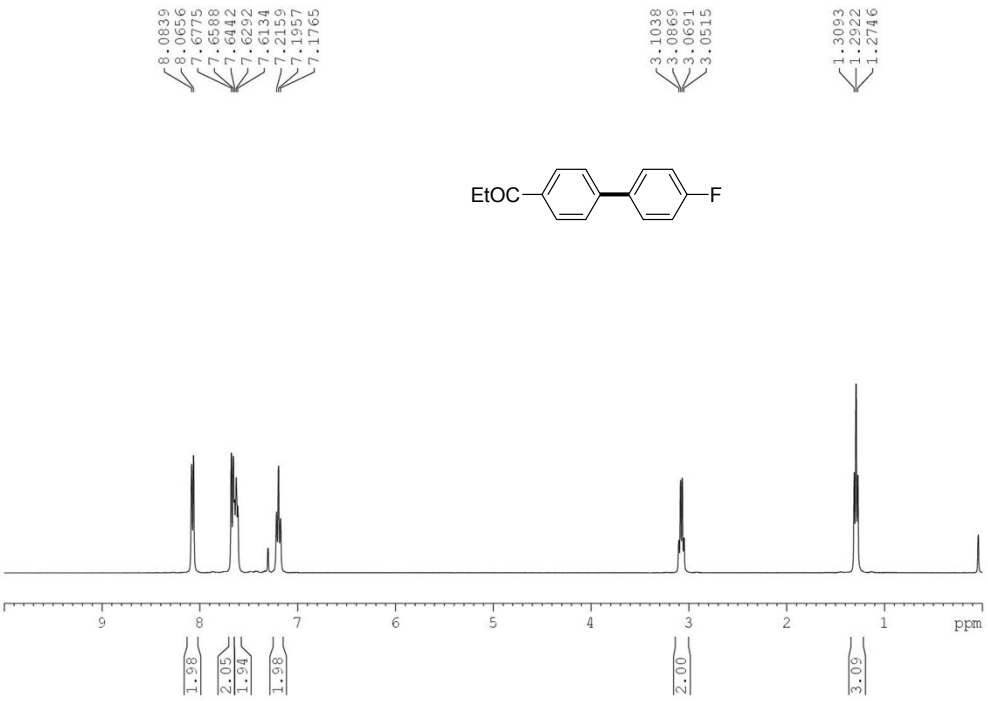
77.37
77.05
76.73
OHC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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8.0656
7.6775
7.6588
7.6442
7.6292
7.6134
7.2159
7.1957
7.1765
3.1038
3.0869
3.0691
3.0515
1.3093
1.2922
1.2746
EtOC
F
9 8 7 6 5 4 3 2 1 ppm
1.98
2.05
1.94
1.98
2.00
3.09


200.36
164.15
161.68
144.45
136.02
135.99
135.54
128.92
128.84
128.61
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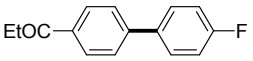
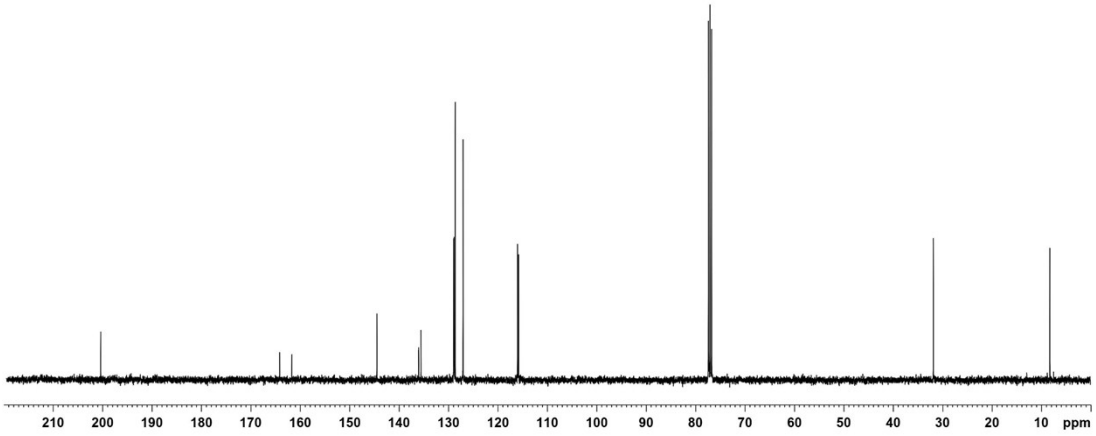
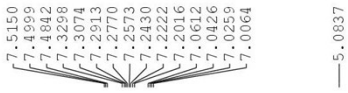
115.98
115.77
77.35
77.03
76.71
31.83
8.26


EtOC
F


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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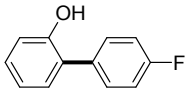
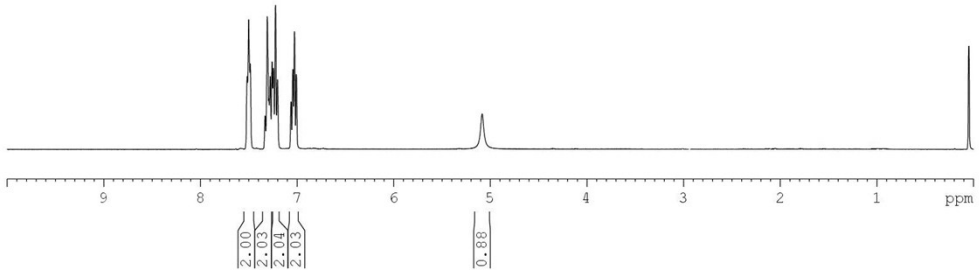
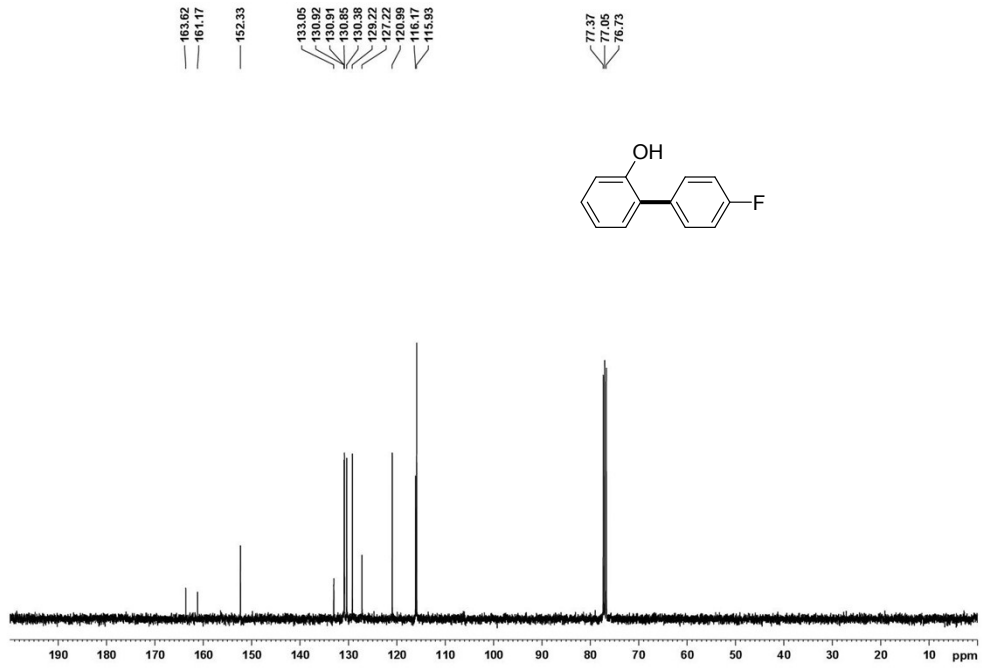
7.0064
5.0837


OH
F


9
8
7
6
5
4
3
2
1
ppm
2.00
2.03
2.04
2.03
0.88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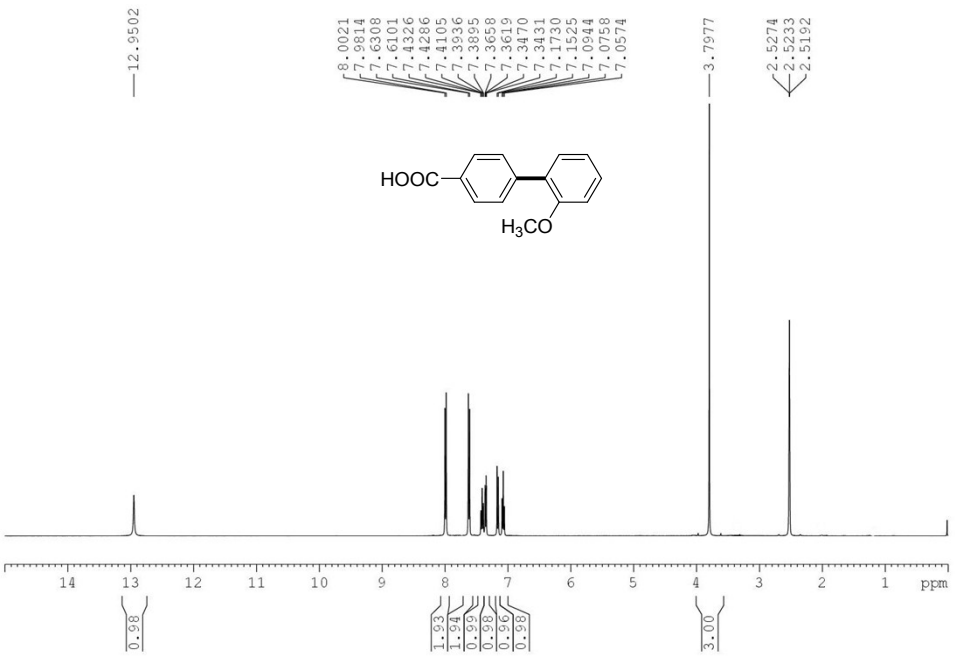
161.17
152.33
133.05
130.92
130.91
130.85
130.38
129.22
127.22
120.99
116.17
115.93
77.37
77.05
76.73
OH
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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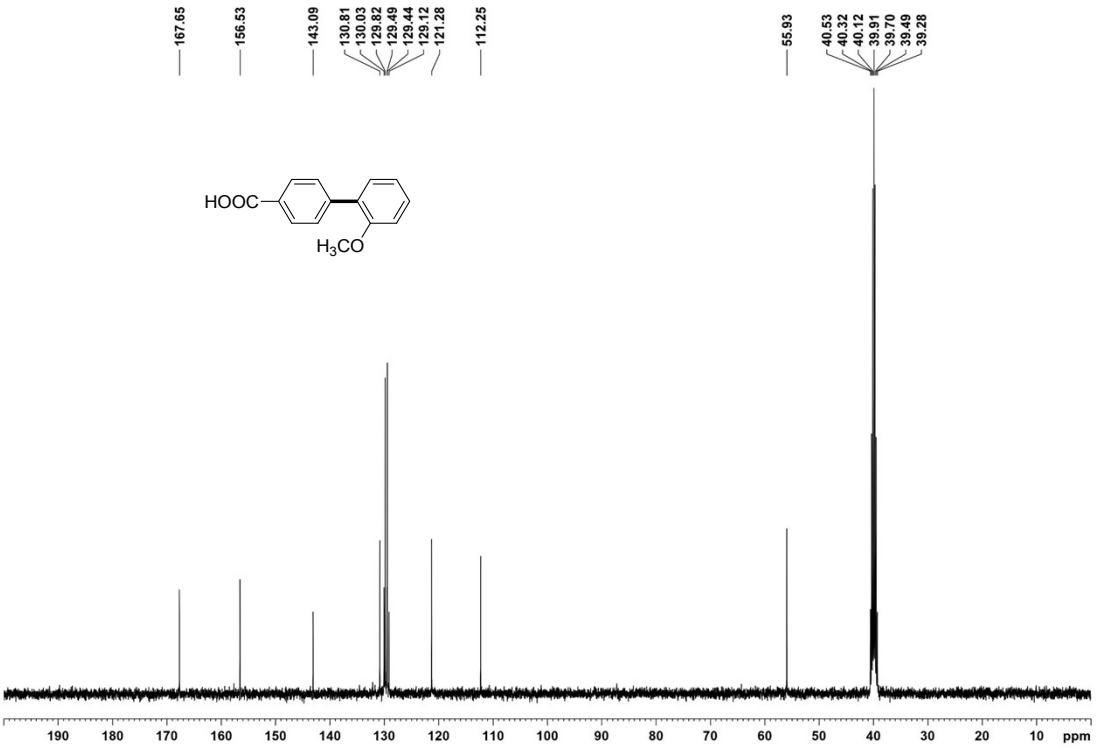
7.3936
7.3895
7.3658
7.3619
7.3470
7.3431
7.1730
7.1525
7.0944
7.0758
7.0574
3.7977
2.5274
2.5233
2.5192
HOOC
H3CO
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.98
1.93
1.94
0.99
0.98
0.96
0.98
3.00


167.65
156.53
143.09
130.81
130.03
129.82
129.49
129.44
129.12
121.28
112.25
55.93
40.53
40.32
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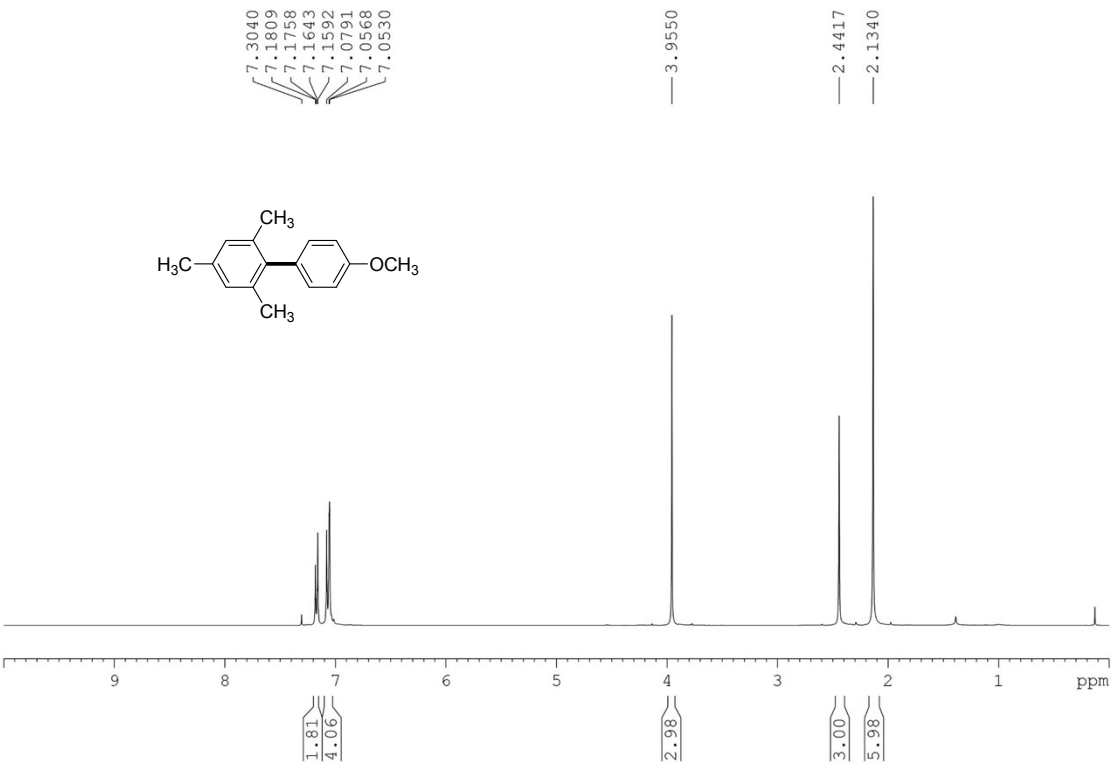
39.70
39.49
39.28
HOOC
H3CO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.0530
3.9550
2.4417
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CH3
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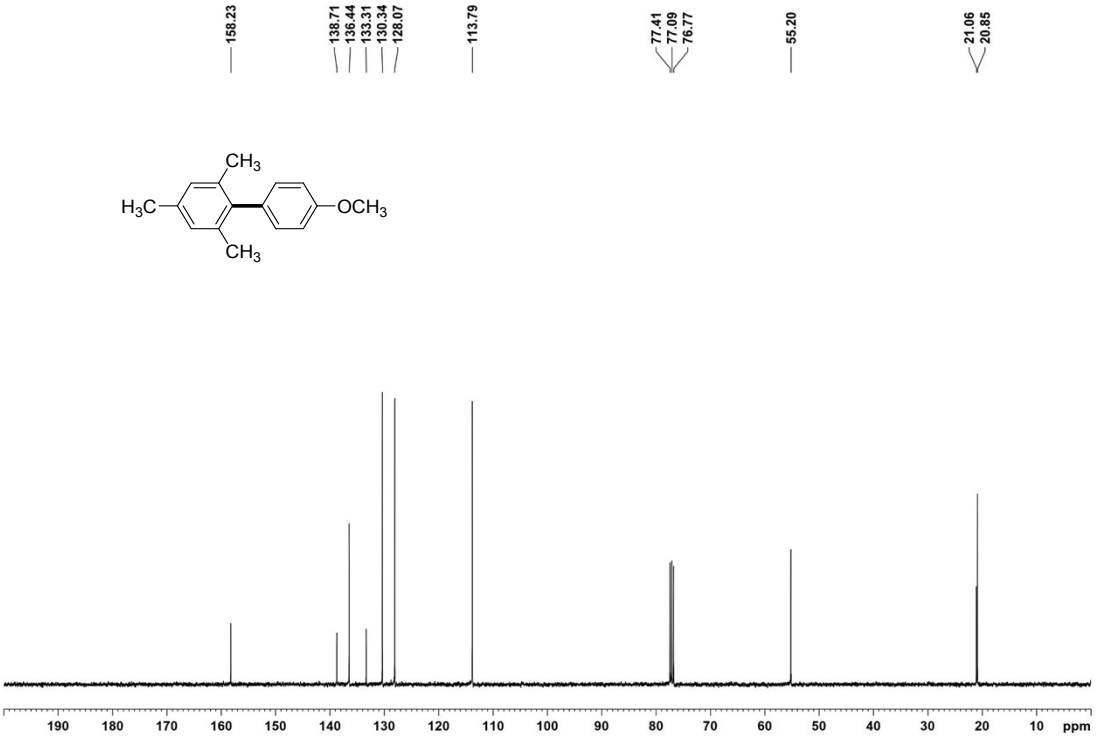
OCH3
CH3
9 8 7 6 5 4 3 2 1 ppm
1.81
4.06
2.98
3.00
5.98


158.23
138.71
136.44
133.31
130.34
128.07
113.79
77.41
77.09
76.77
55.20
21.06
20.85
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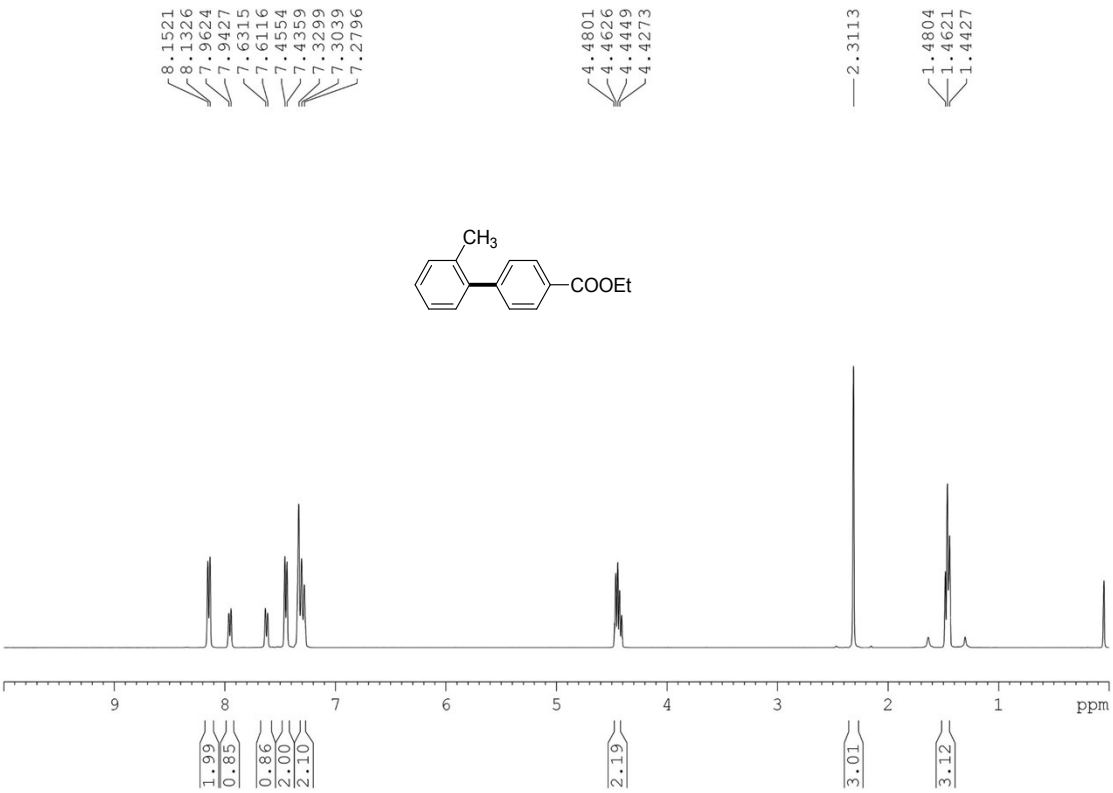
OCH3
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.6315
7.6116
7.4554
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7.3299
7.3039
7.2796
4.4801
4.4626
4.4449
4.4273
2.3113
1.4804
1.4621
1.4427
CH3
COOEt
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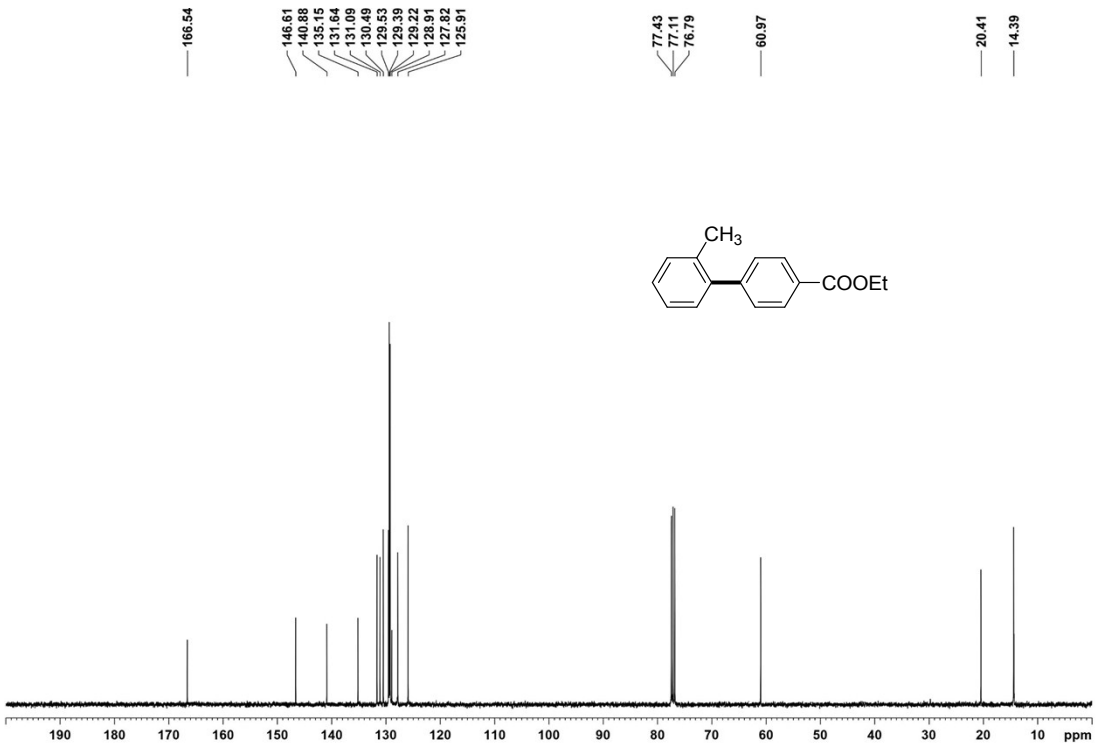
0.85
0.86
2.00
2.10
2.19
3.01
3.12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129.53
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125.91
77.43
77.11
76.79
60.97
20.41
14.39
CH3
COOEt
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150
140
130
120
110
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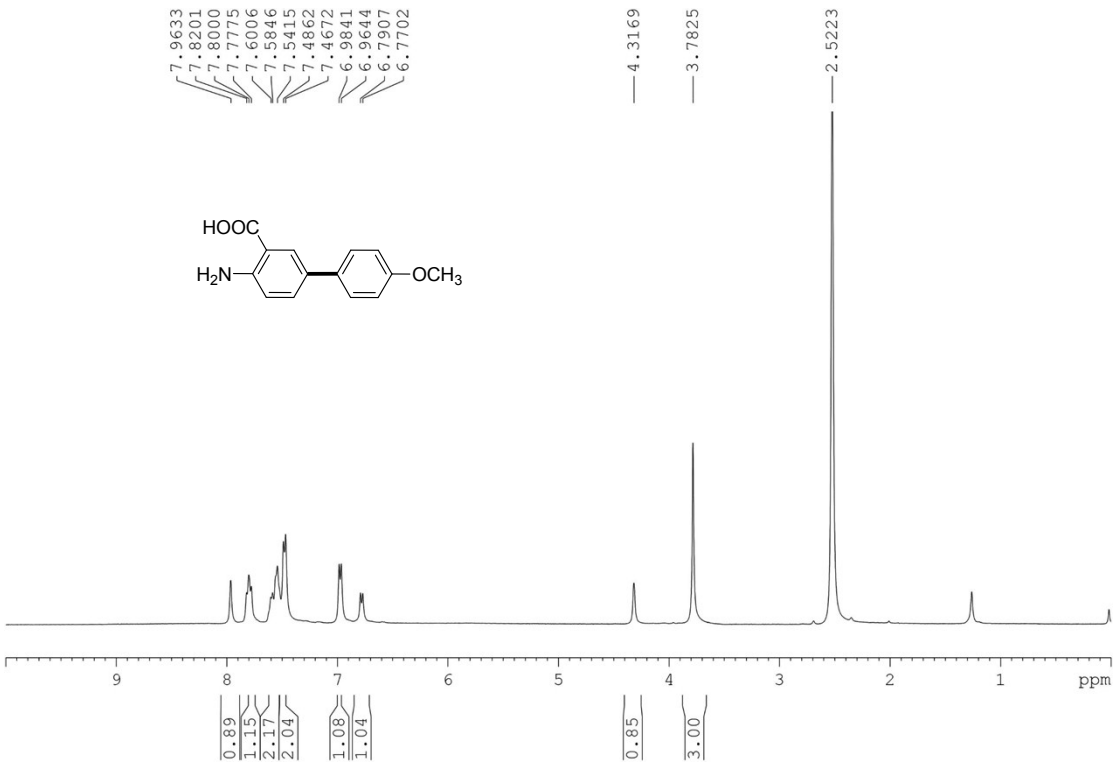
70
60
50
40
30
20
10
ppm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7.5415
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7.4672
6.9841
6.9644
6.7907
6.7702
4.3169
3.7825
2.5223
HOOC
H2N
OCH3
9
8
7
6
5
4
3
2
1
ppm
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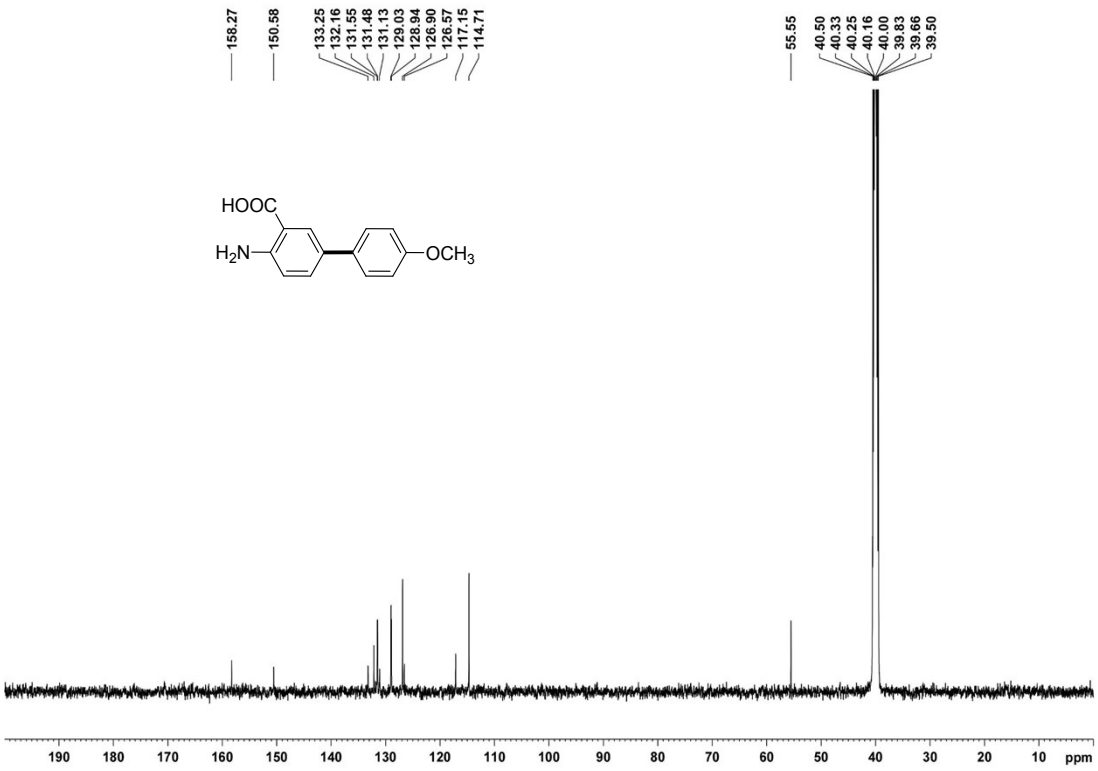
2.17
2.04
1.08
1.04
0.85
3.00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131.13
129.03
128.94
126.90
126.57
117.15
114.71
55.55
40.50
40.33
40.25
40.16
40.00
39.83
39.66
39.50
HOOC
H2N
OCH3
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150
140
130
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90
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70
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30
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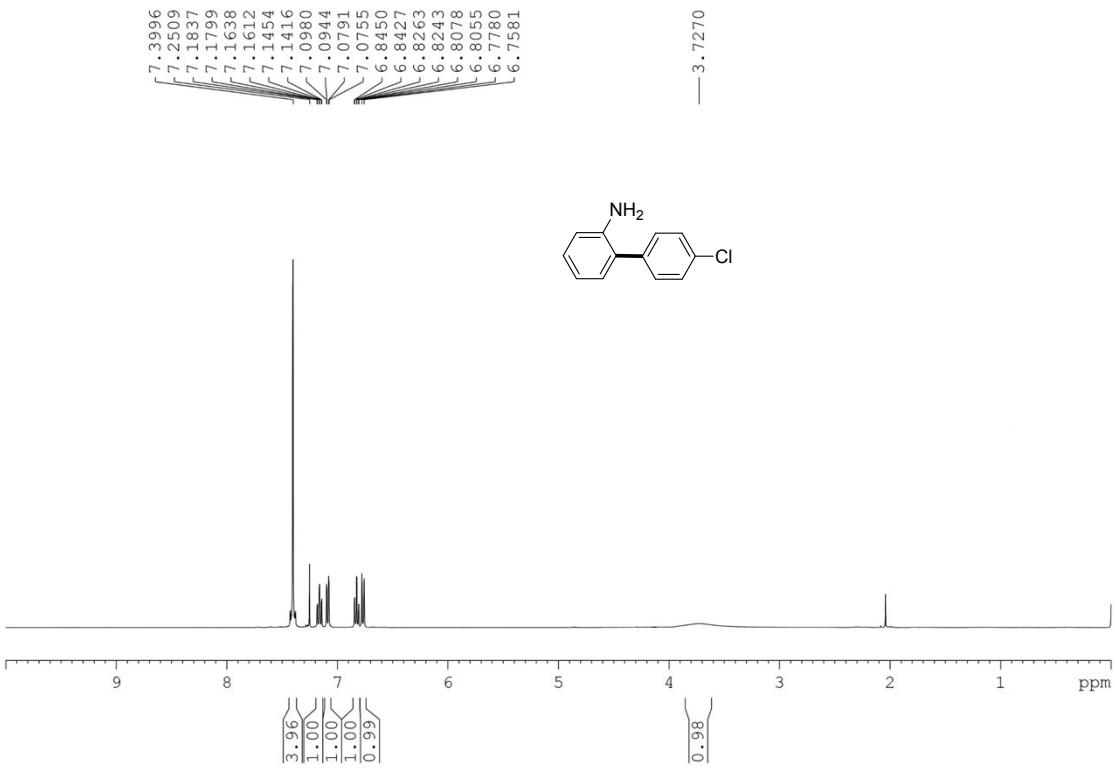
10
ppm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7.1454
7.1416
7.0980
7.0944
7.0791
7.0755
6.8450
6.8427
6.8263
6.8243
6.8078
6.8055
6.7780
6.7581
3.7270
NH2
Cl
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5
4
3
2
1
ppm
3.96
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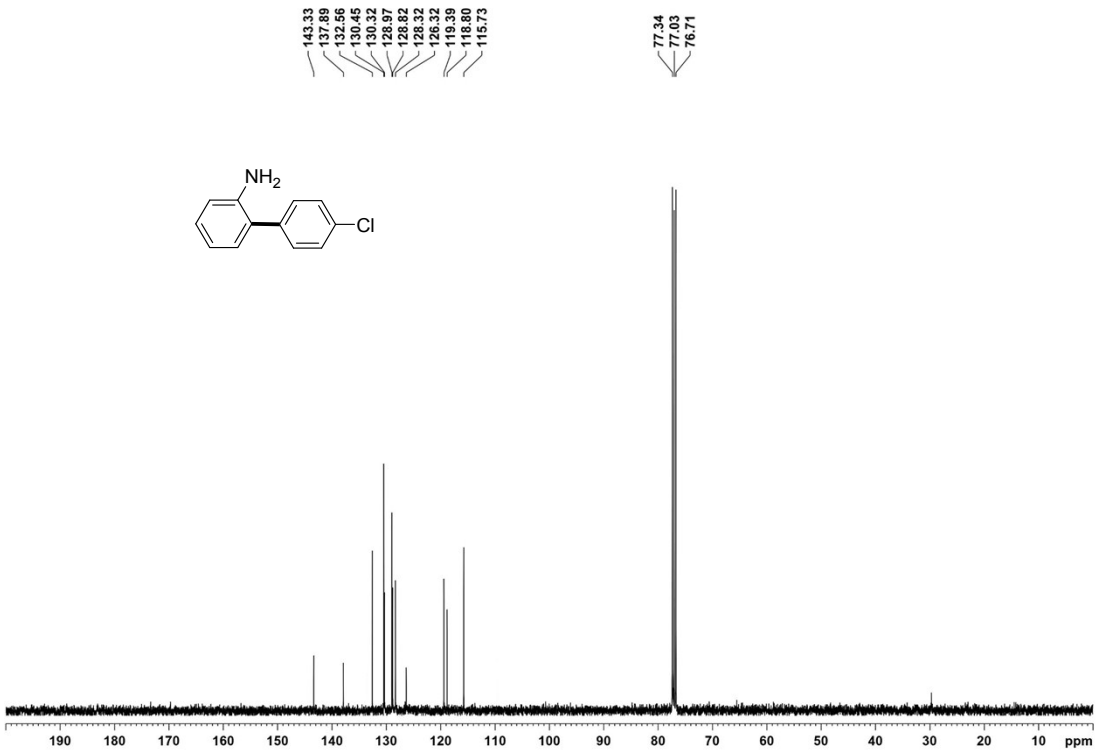
0.98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137.89
132.56
130.45
130.32
128.97
128.82
128.32
126.32
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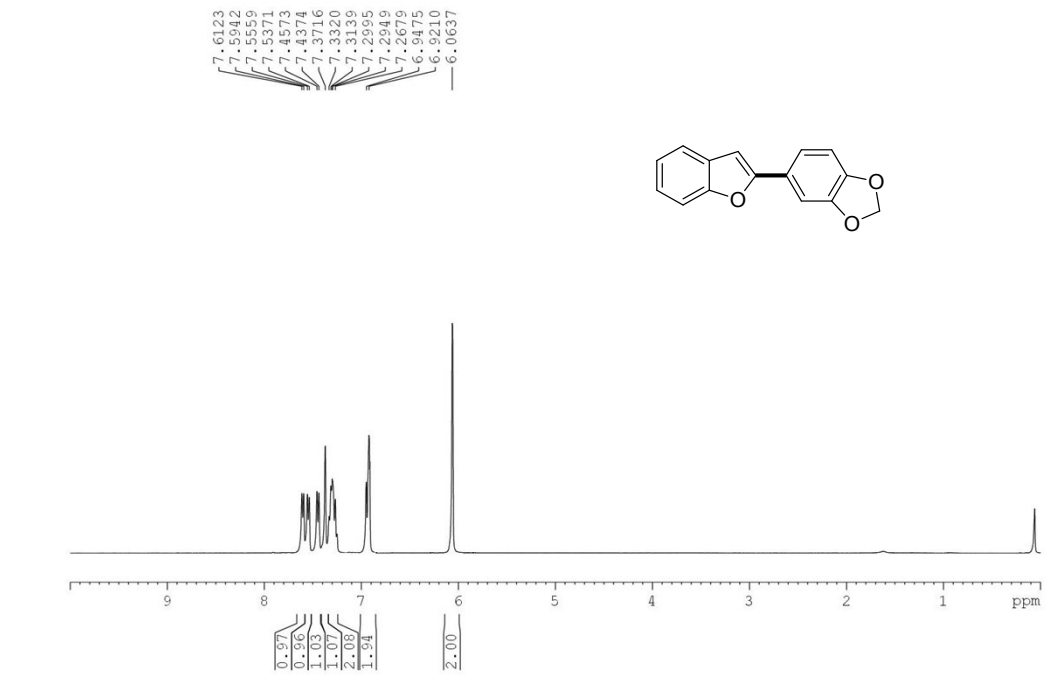
115.73
77.34
77.03
76.71
NH2
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.3716
7.3320
7.3139
7.2995
7.2949
7.2679
6.9475
6.9210
6.0637
O
O
O
9 8 7 6 5 4 3 2 1 ppm
0.97
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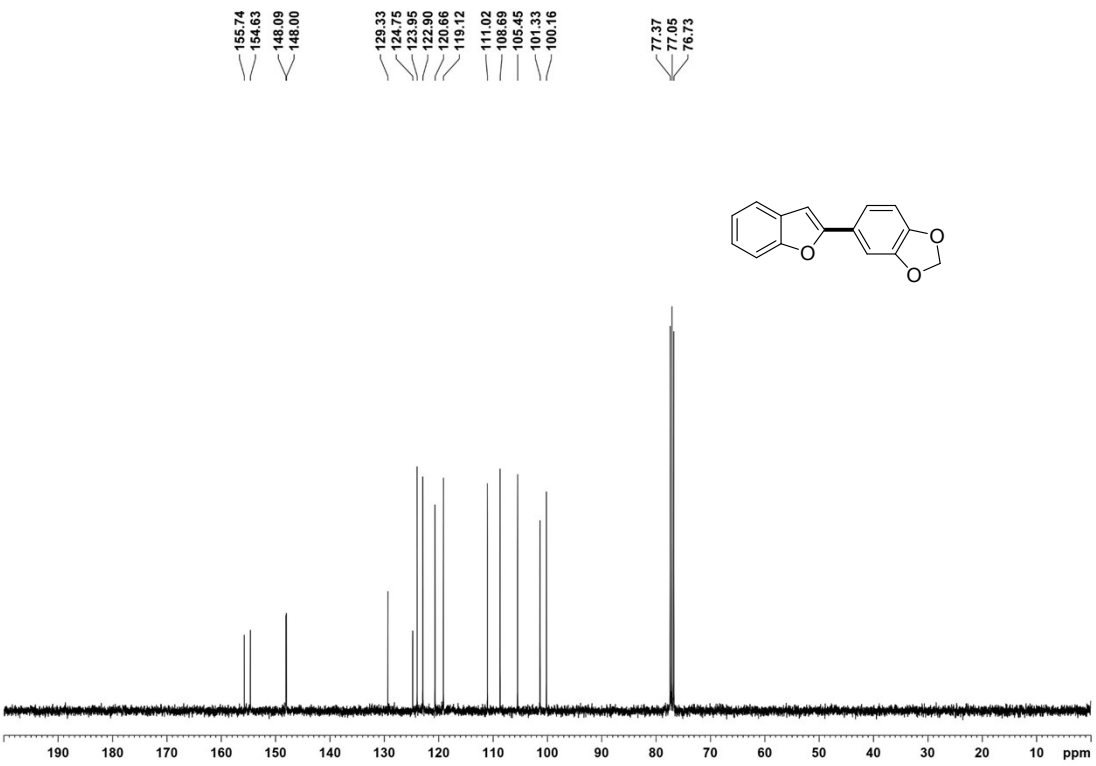
1.03
1.07
2.08
1.94
2.00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154.63
148.09
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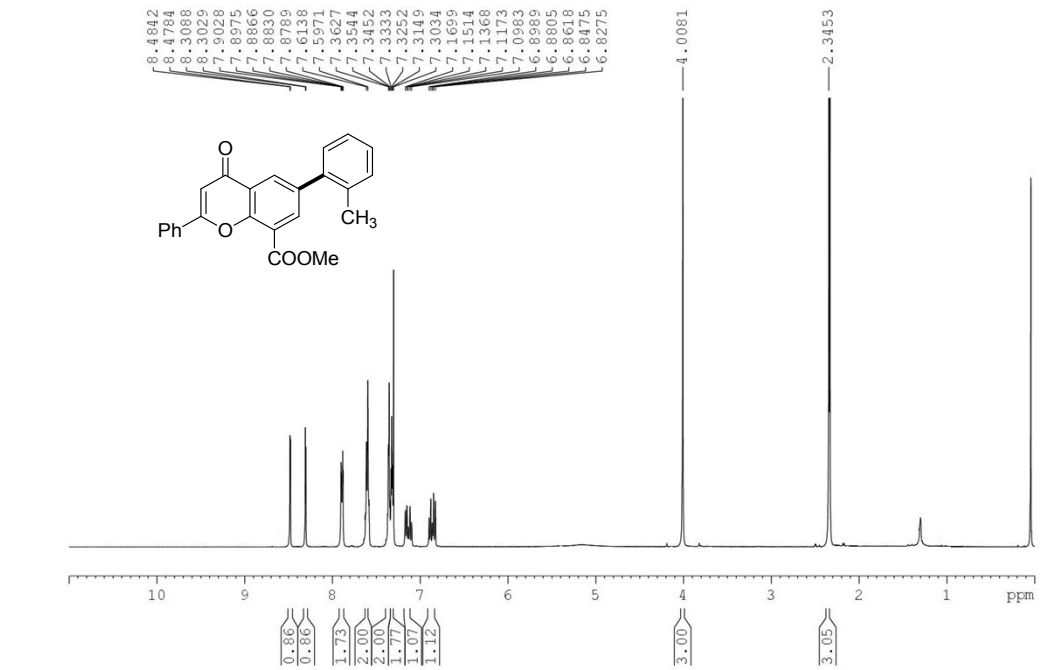
124.75
123.95
122.90
120.66
119.12
111.02
108.69
105.45
101.33
100.16
77.37
77.05
76.73
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.3088
8.3029
7.9028
7.8975
7.8866
7.8830
7.8789
7.6138
7.5971
7.3627
7.3544
7.3452
7.3333
7.3252
7.3149
7.3034
7.1699
7.1514
7.1368
7.1173
7.0983
6.8989
6.8805
6.8618
6.8475
6.8275
4.0081
2.3453
O
Ph
O
CH3
COOMe
10
9
8
7
6
5
4
3
2
1
ppm
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0.86
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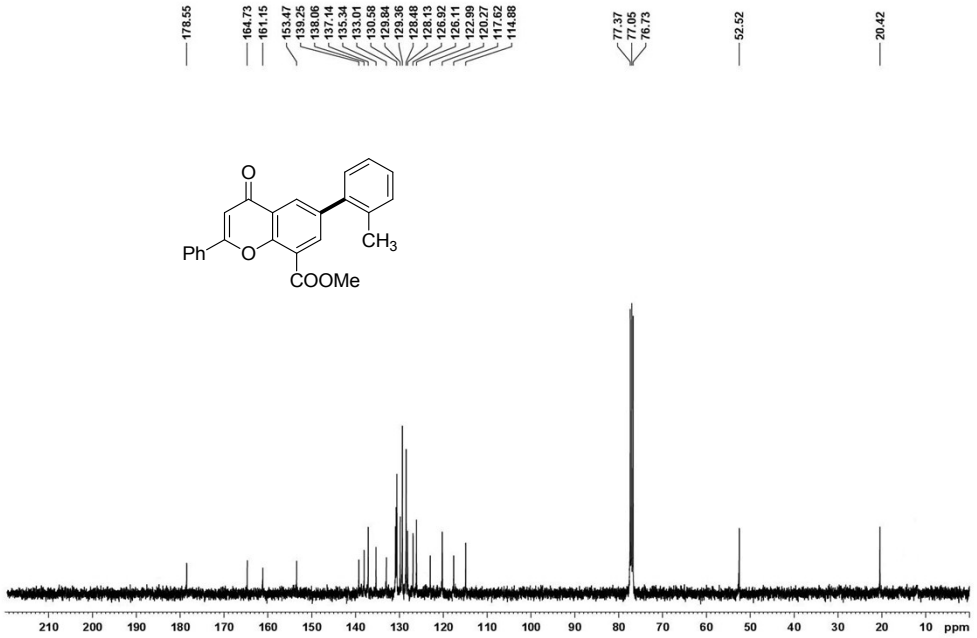
2.00
2.00
1.77
1.07
1.12
3.00
3.05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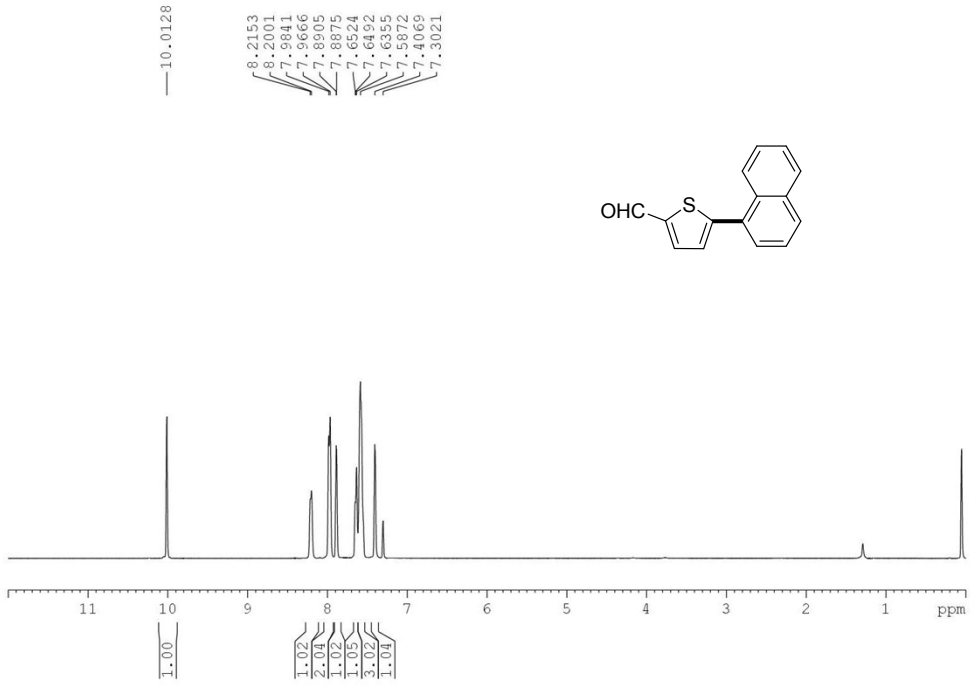
161.15
153.47
139.25
138.06
137.14
135.34
133.01
130.58
129.84
129.36
128.48
128.13
126.92
126.11
122.99
120.27
117.62
114.88
77.37
77.05
76.73
52.52
20.42
O
Ph
O
CH3
COOMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.2001
7.9841
7.9666
7.8905
7.8875
7.6524
7.6492
7.6355
7.5872
7.4069
7.3021
OHC
S
11
10
9
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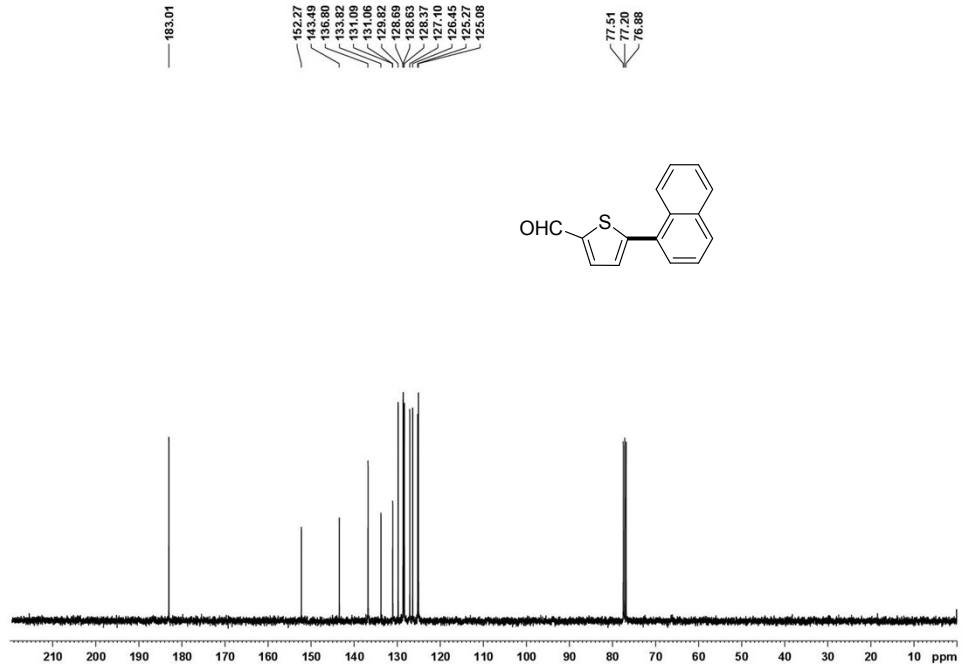
1.02
2.04
1.02
1.05
3.02
1.04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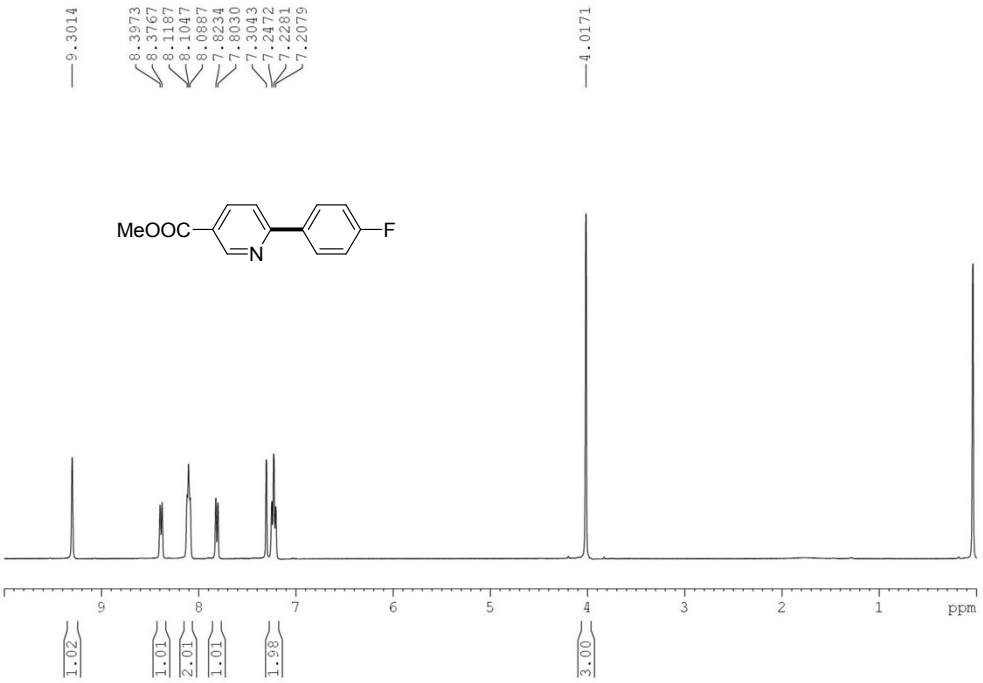
152.27
143.49
136.80
133.82
131.09
131.06
129.82
128.69
128.63
128.37
127.10
126.45
125.27
125.08
77.51
77.20
76.88
OHC
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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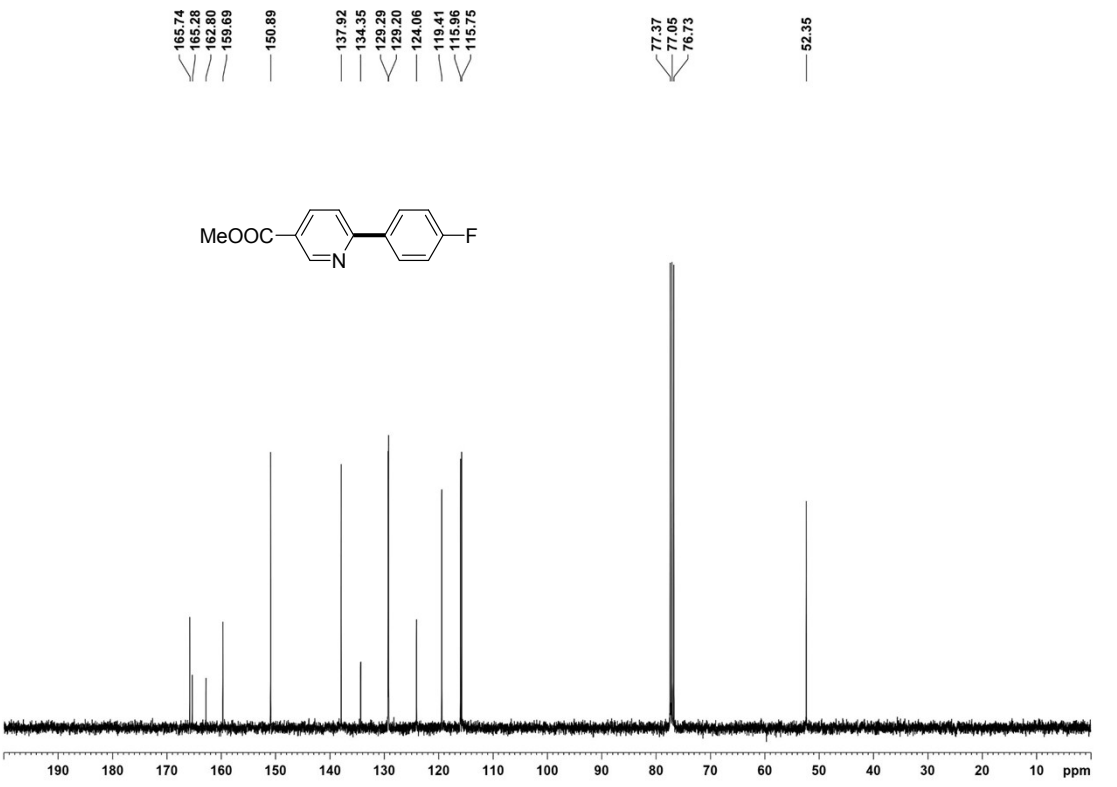
8.3767
8.1187
8.1047
8.0887
7.8234
7.8030
7.3043
7.2472
7.2281
7.2079
4.0171
MeOOC
N
F
9 8 7 6 5 4 3 2 1 ppm
1.02
1.01
2.01
1.01
1.98
3.00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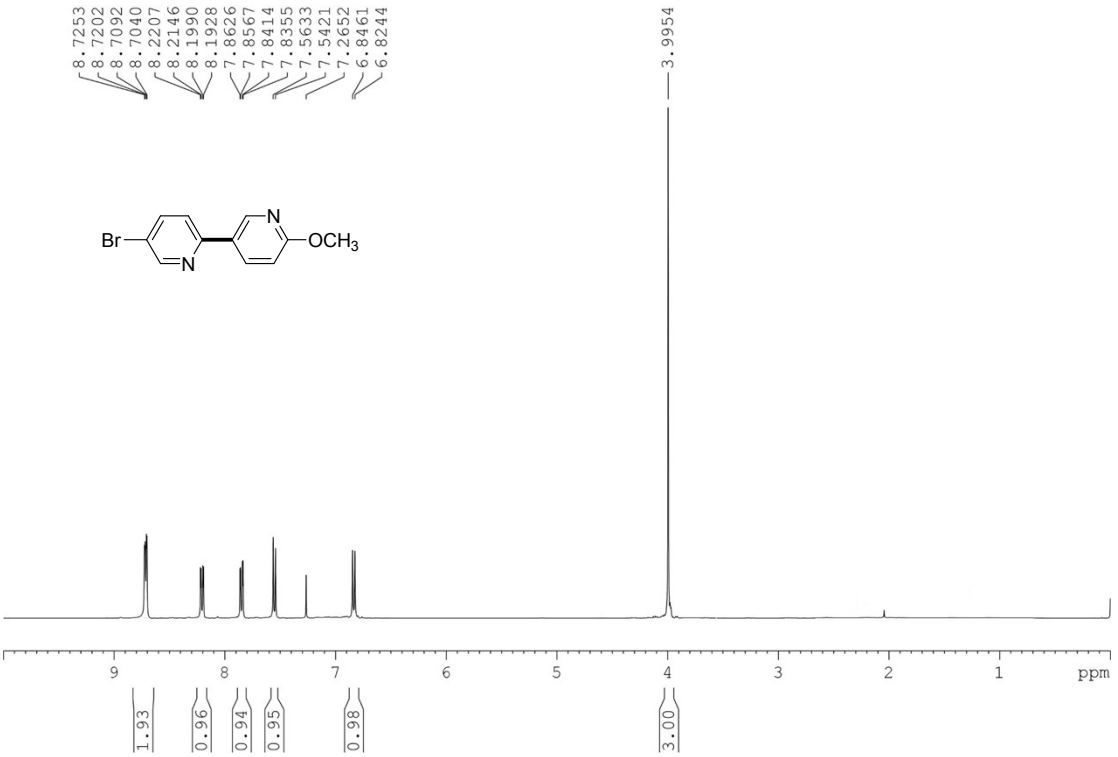
165.28
162.80
159.69
150.89
137.92
134.35
129.29
129.20
124.06
119.41
115.96
115.75
77.37
77.05
76.73
52.35
MeOOC
N
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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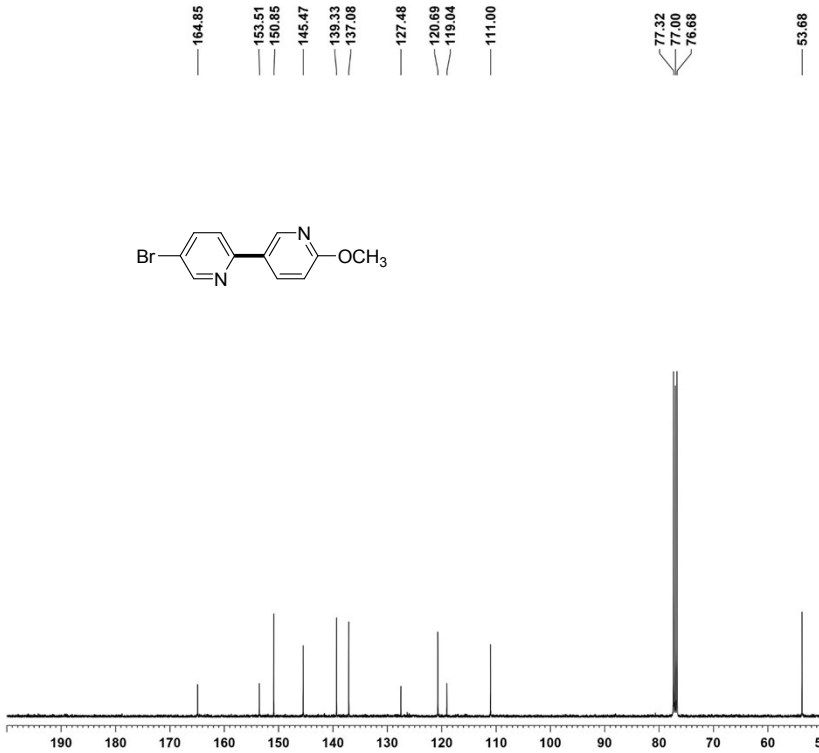
8.7202
8.7092
8.7040
8.2207
8.2146
8.1990
8.1928
7.8626
7.8567
7.8414
7.8355
7.5633
7.5421
7.2652
6.8461
6.8244
3.9954
Br
N
N
OCH3
9
8
7
6
5
4
3
2
1
ppm
1.93
0.96
0.94
0.95
0.98
3.00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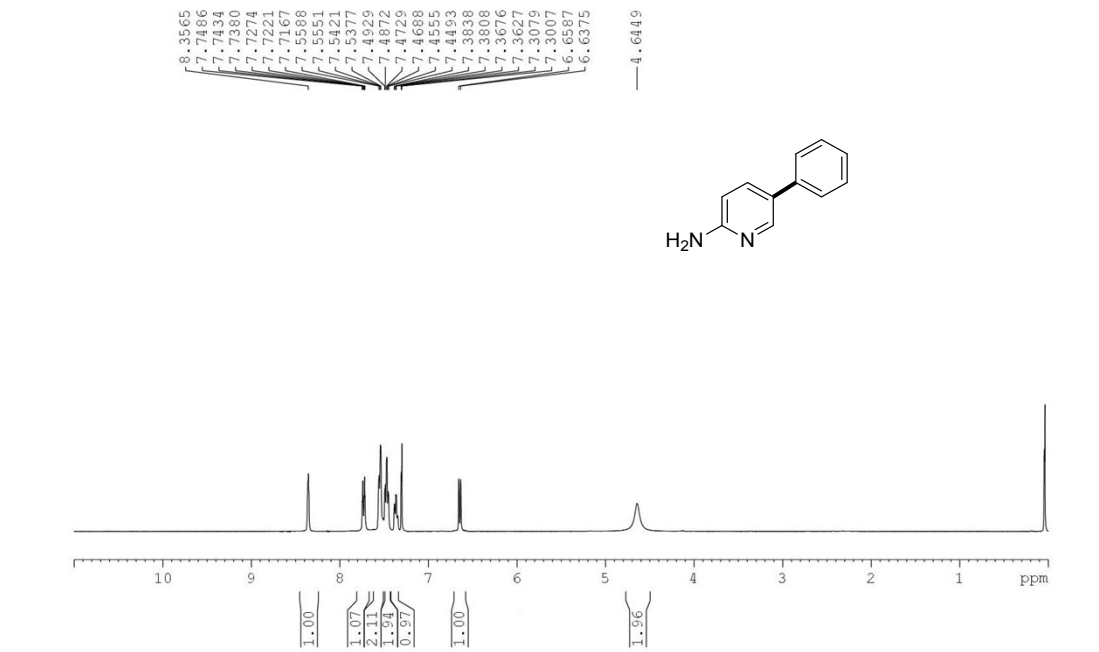
150.85
145.47
139.33
137.08
127.48
120.69
119.04
111.00
77.32
77.00
76.68
53.68
Br
N
N
OCH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.7274
7.7221
7.7167
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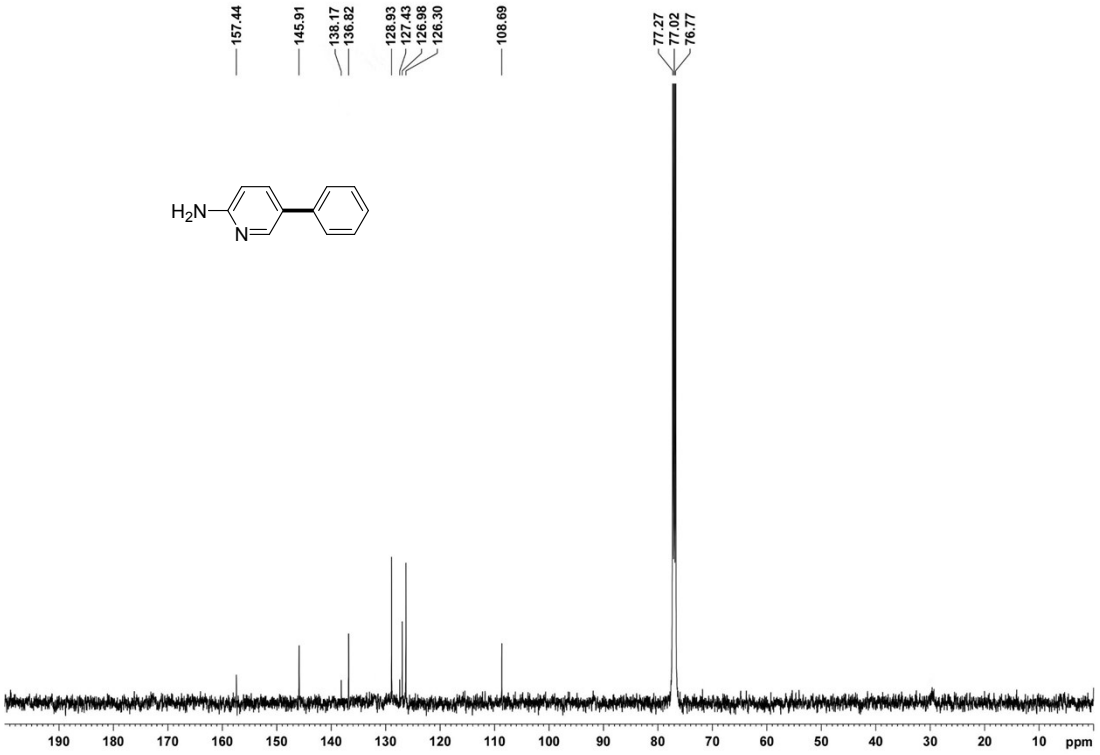
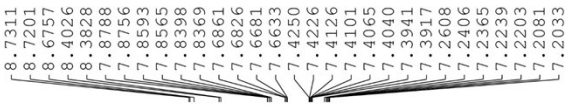
7.5551
7.5421
7.5377
7.4929
7.4872
7.4729
7.4688
7.4555
7.4493
7.3838
7.3808
7.3676
7.3627
7.3079
7.3007
6.6587
6.6375
4.6449
H2N
N
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.07
2.11
1.94
0.97
1.00
1.96


157.44
145.91
138.17
136.82
128.93
127.43
126.98
126.30
108.69
77.27
77.02
76.77
H2N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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8.3828
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7.8756
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7.8565
7.8398
7.8369
7.6861
7.6826
7.6681
7.6633
7.4250
7.4226
7.4126
7.4101
7.4065
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7.3917
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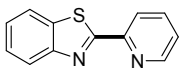
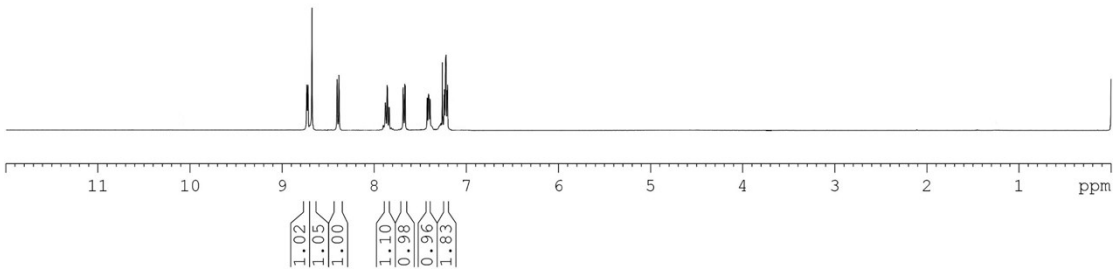
7.2406
7.2365
7.2239
7.2203
7.2081
7.2033


S
N
N


11 10 9 8 7 6 5 4 3 2 1 ppm
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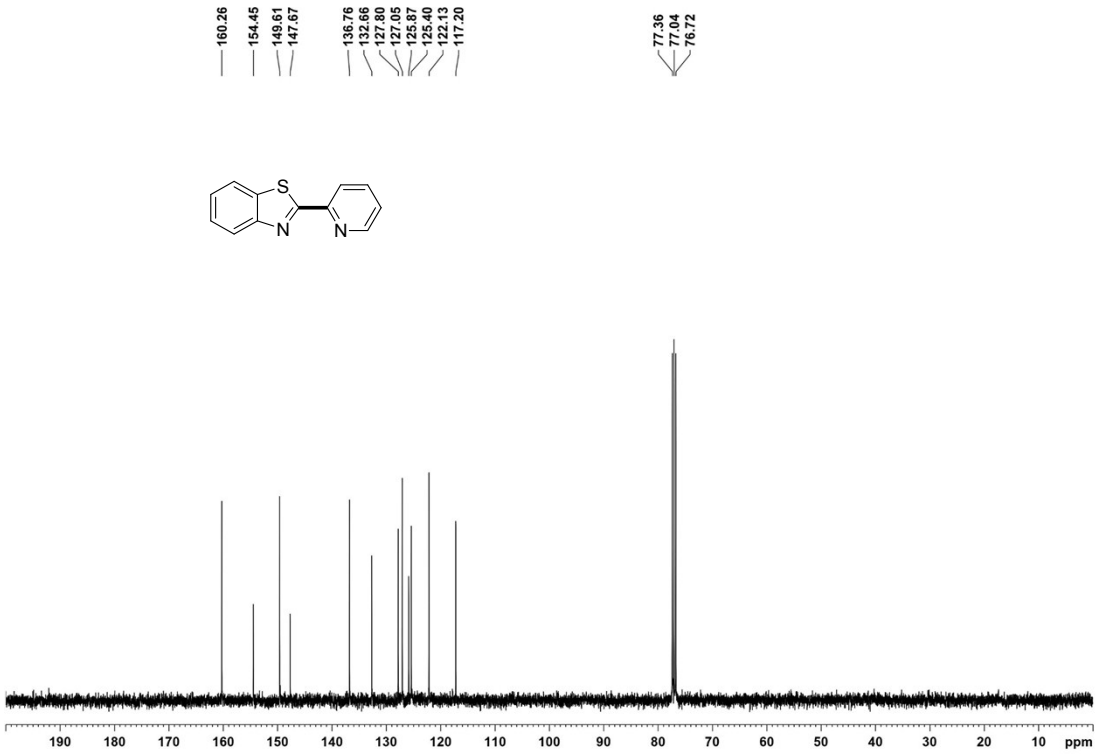
1.05
1.00
1.10
0.98
0.96
1.83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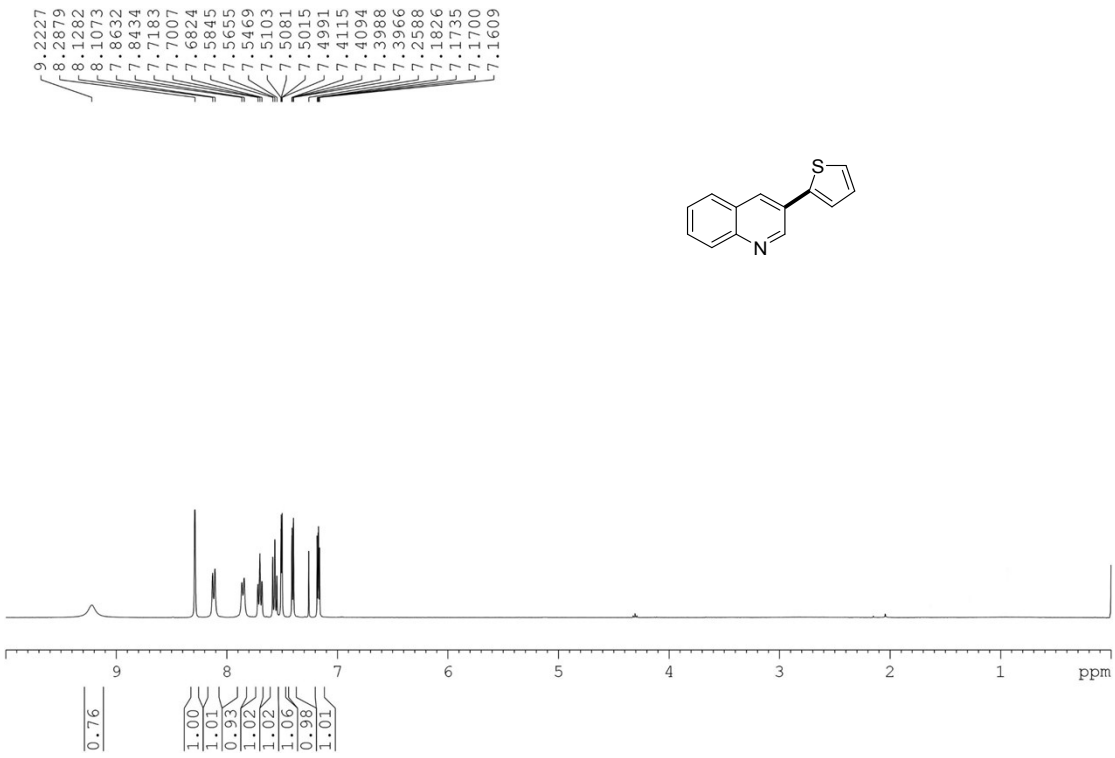
154.45
149.61
147.67
136.76
132.66
127.80
127.05
125.87
125.40
122.13
117.20
77.36
77.04
76.72
S
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.1282
8.1073
7.8632
7.8434
7.7183
7.7007
7.6824
7.5845
7.5655
7.5469
7.5103
7.5081
7.5015
7.4991
7.4115
7.4094
7.3988
7.3966
7.2588
7.1826
7.1735
7.1700
7.1609
S
N
9
8
7
6
5
4
3
2
1
ppm
0.76
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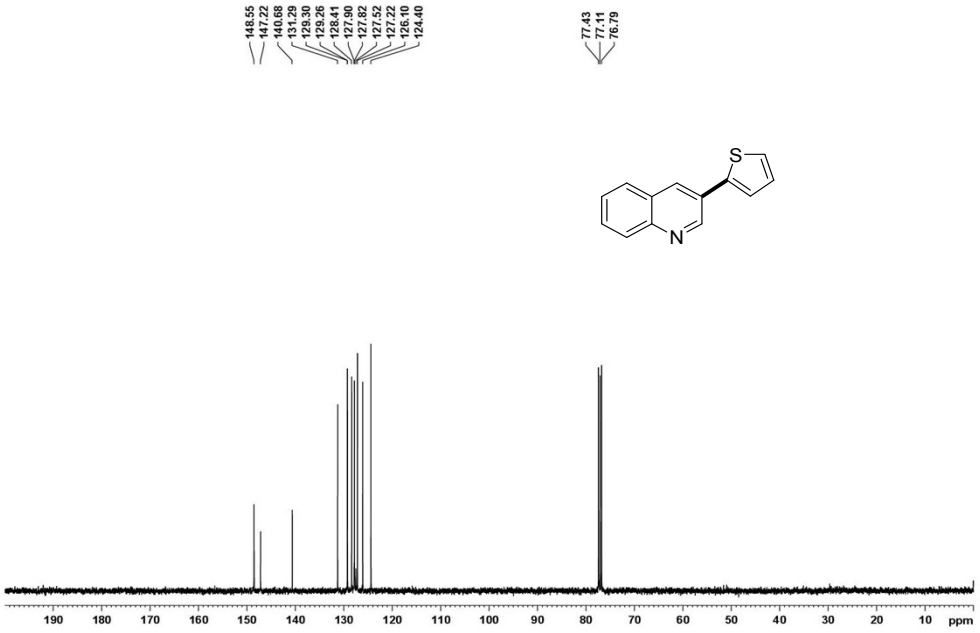
1.02
1.02
1.06
0.98
1.01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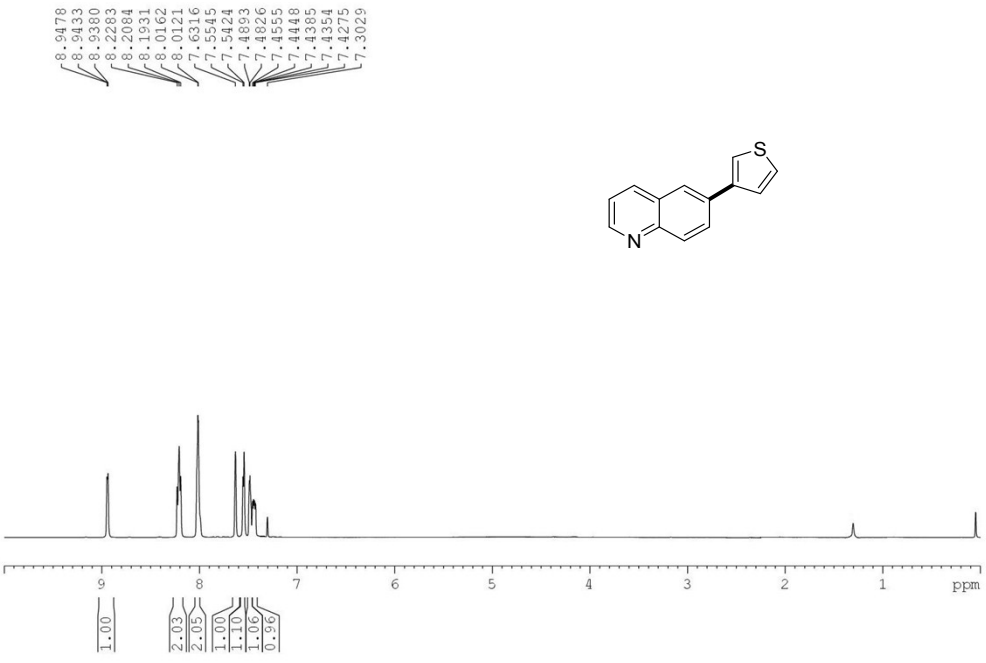
129.26
128.41
127.90
127.82
127.52
127.22
126.10
124.40
77.43
77.11
76.79
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.0162
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7.6316
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7.5424
7.4893
7.4826
7.4555
7.4448
7.4385
7.4354
7.4275
7.3029
S
N
9
8
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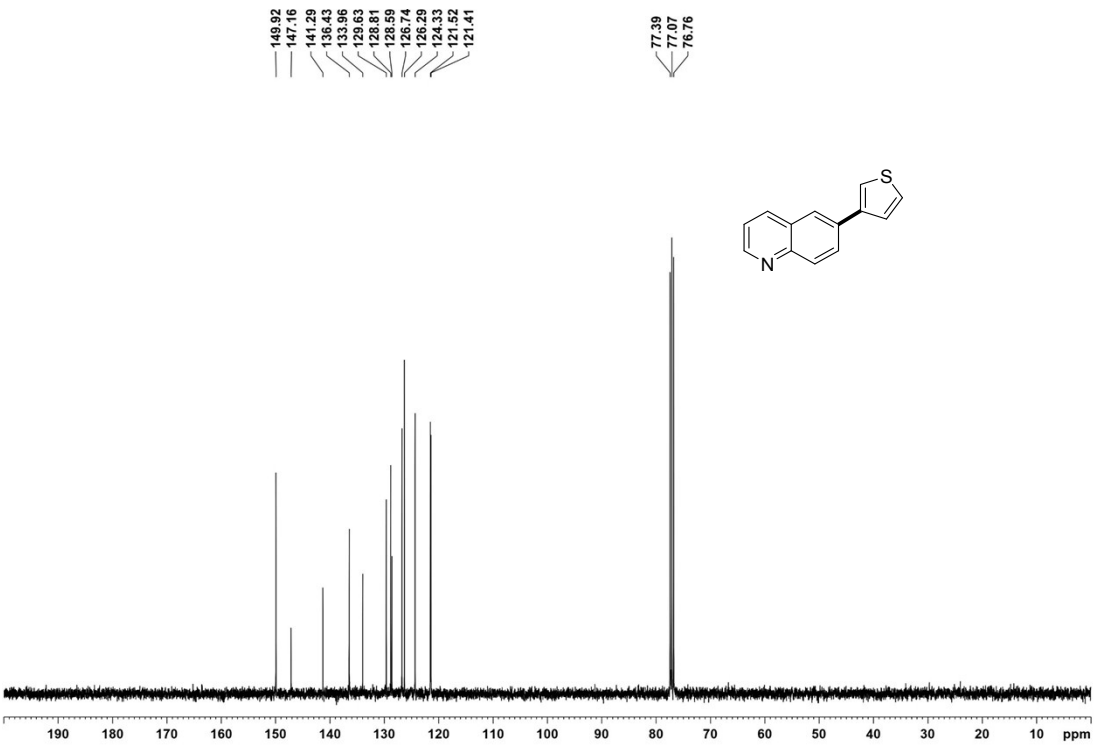
2.05
1.00
1.10
1.06
0.96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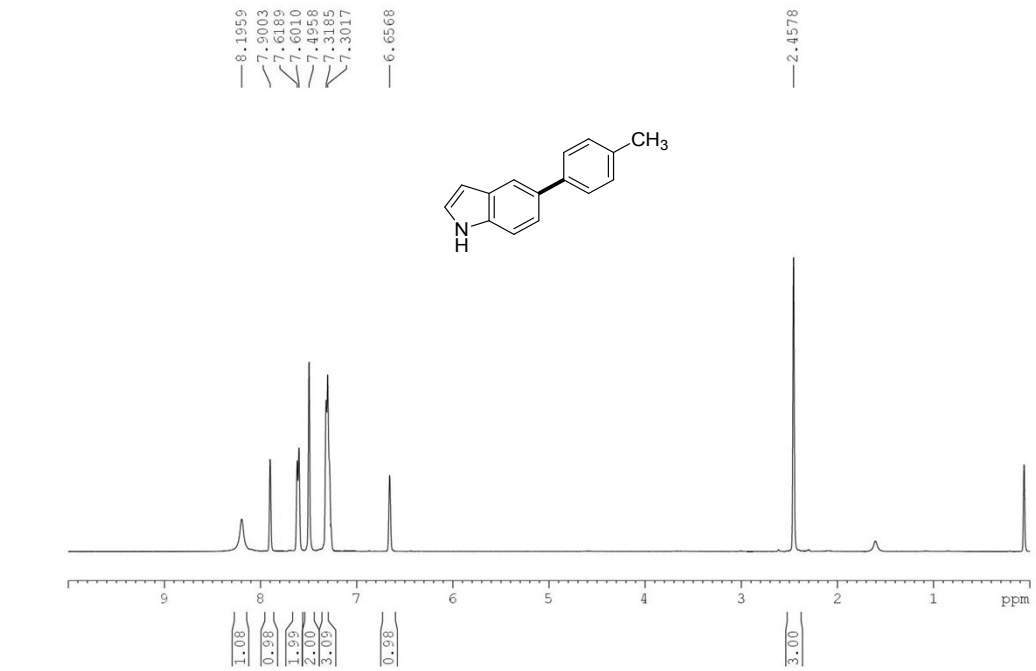
147.16
141.29
136.43
133.96
129.63
128.81
128.59
126.74
126.29
124.33
121.52
121.41
77.39
77.07
76.76
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.4958
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7.3017
6.6568
2.4578
CH3
N
H
9
8
7
6
5
4
3
2
1
ppm
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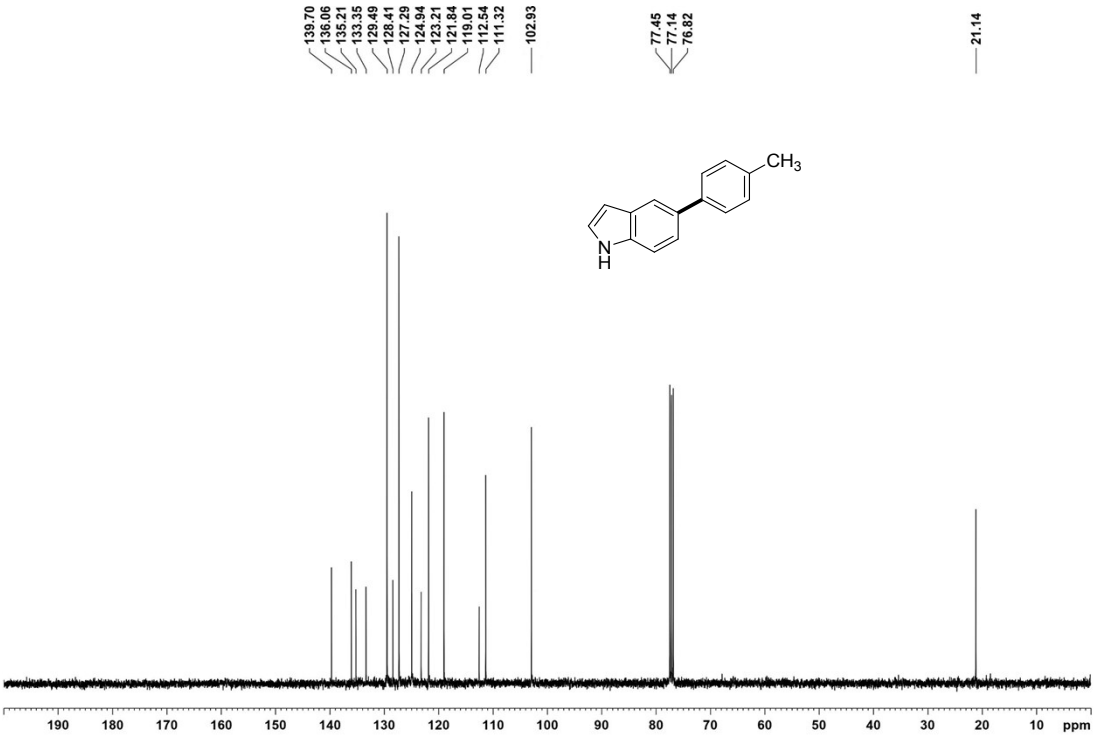
0.98
1.99
2.00
3.09
0.98
3.00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124.94
123.21
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119.01
112.54
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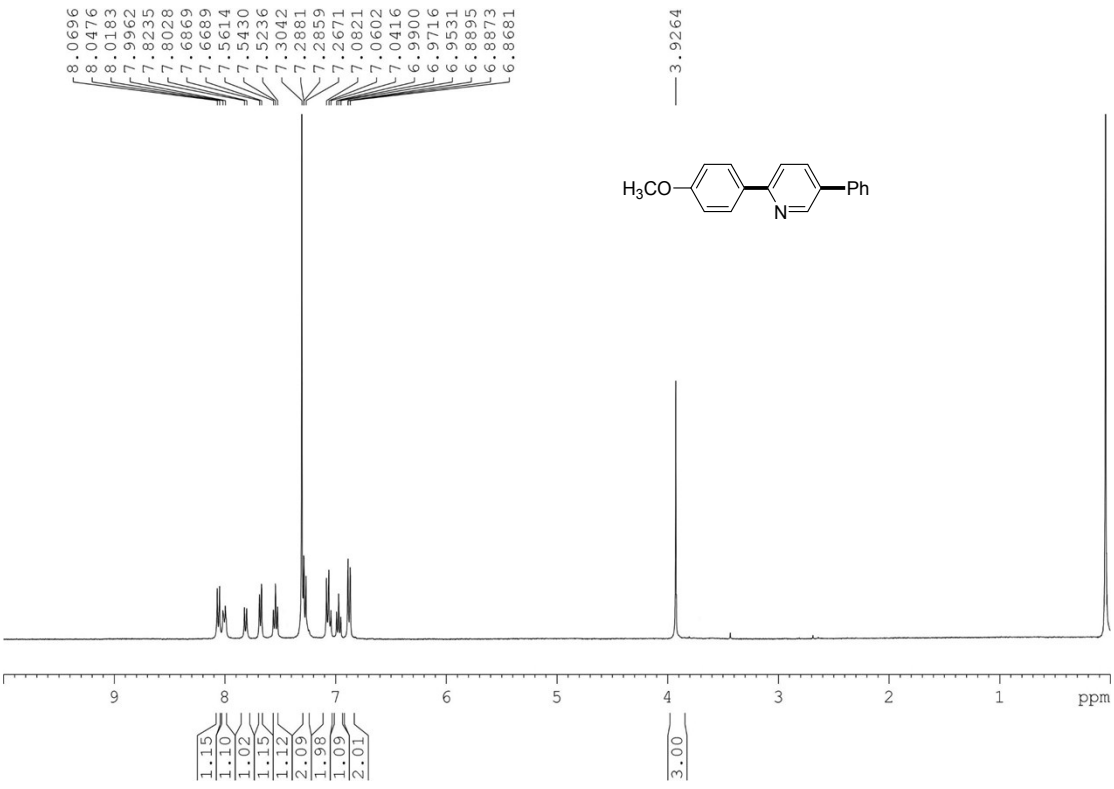
77.14
76.82
21.14
CH3
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.3042
7.2881
7.2859
7.2671
7.0821
7.0602
7.0416
6.9900
6.9716
6.9531
6.8895
6.8873
6.8681
3.9264
H3CO
Ph
N
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1.10
1.02
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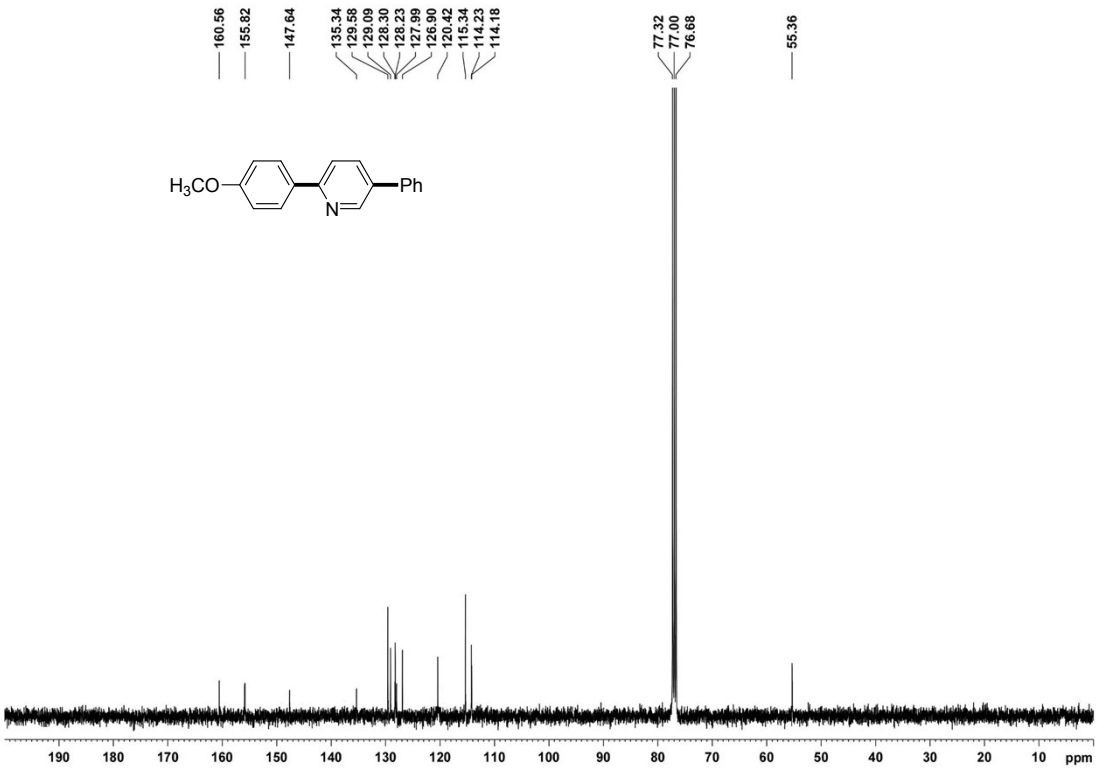
1.12
2.09
1.98
1.09
2.01
3.00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128.30
128.23
127.99
126.90
120.42
115.34
114.23
114.18
77.32
77.00
76.68
55.36
H3CO
N
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm