

Supporting information for

Synthesis of a carbene transfer organometallic polymer and application to forming a recyclable heterogeneous catalyst for the Suzuki reactions of arylchlorides

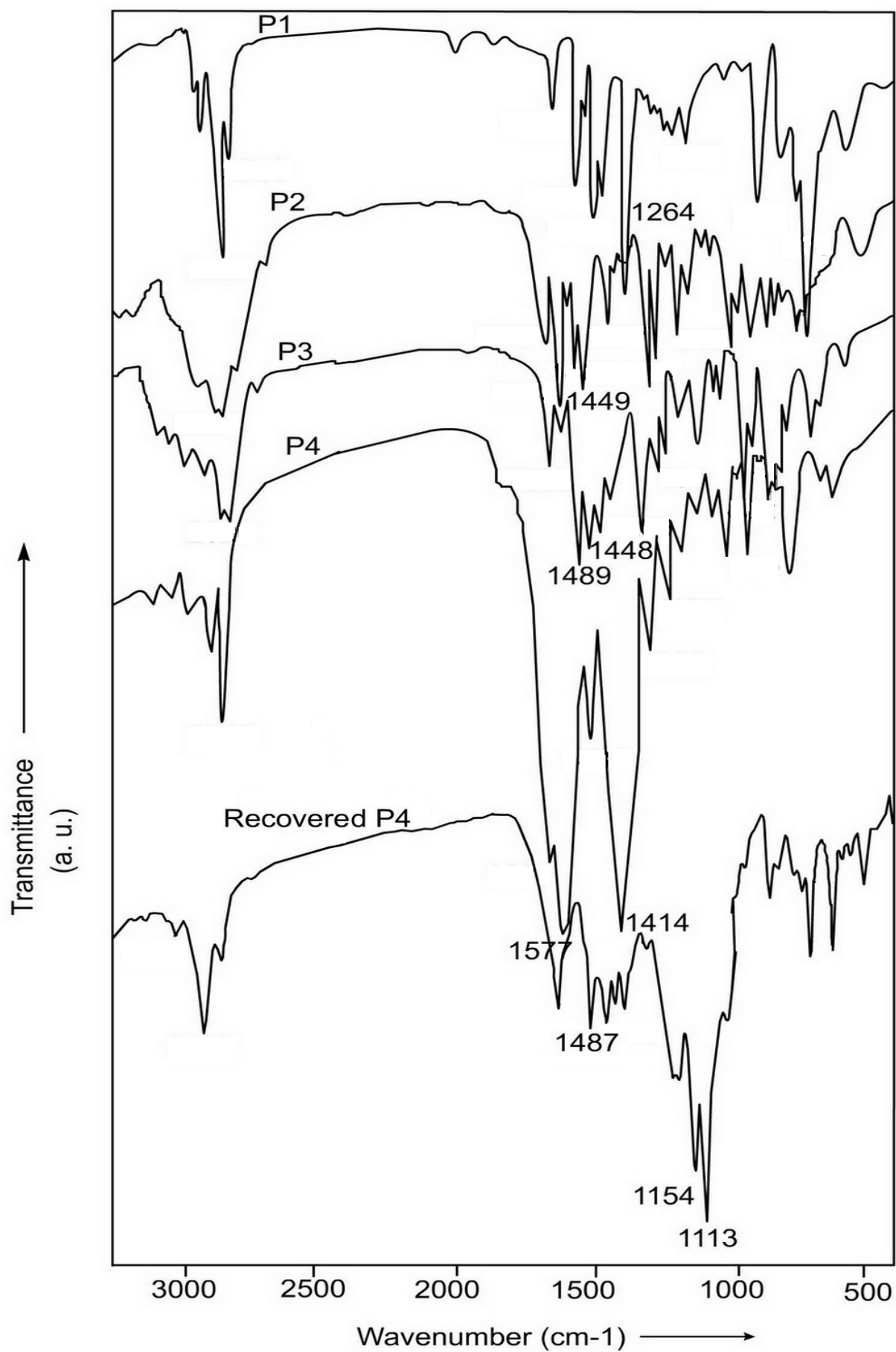
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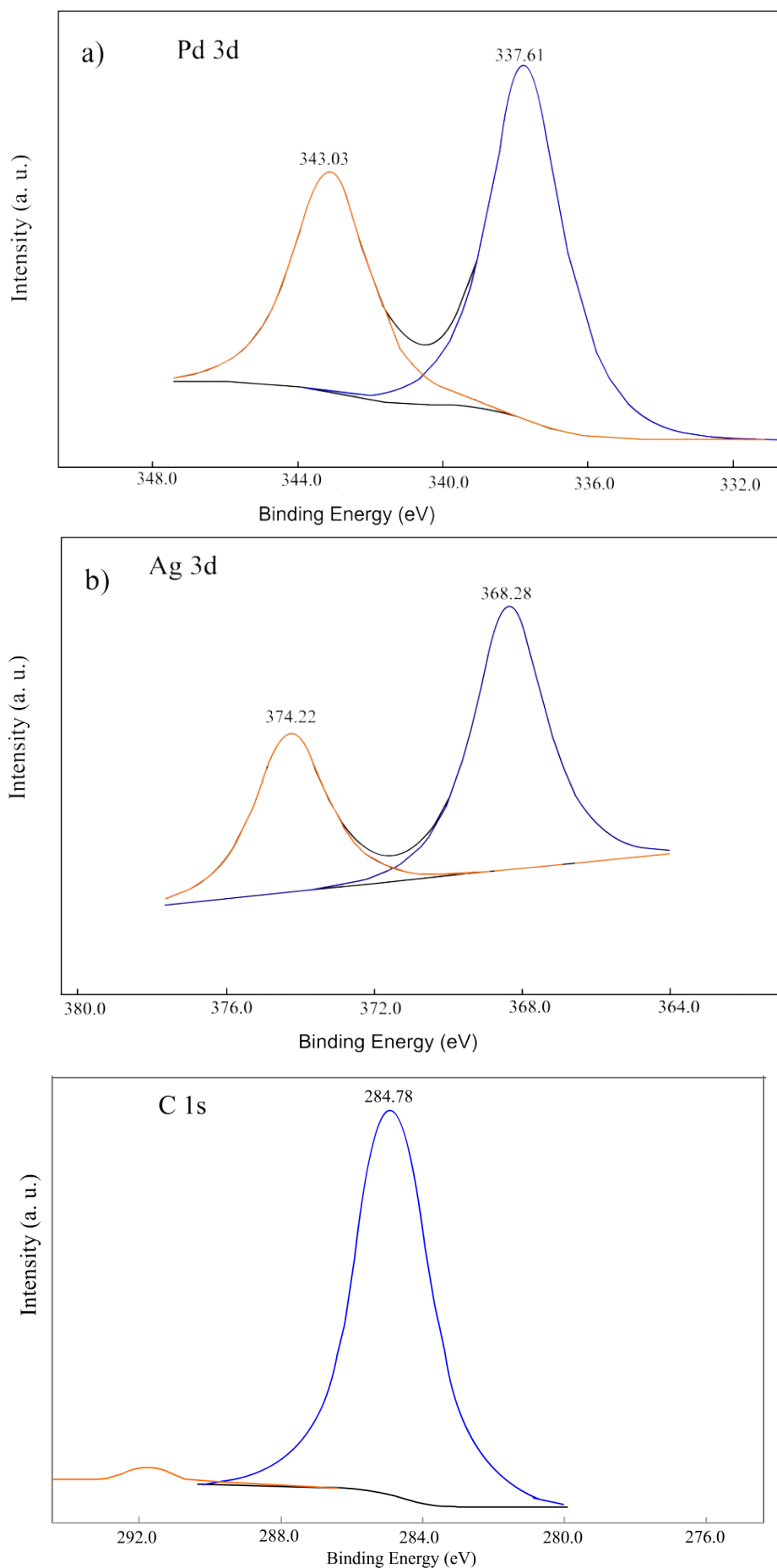
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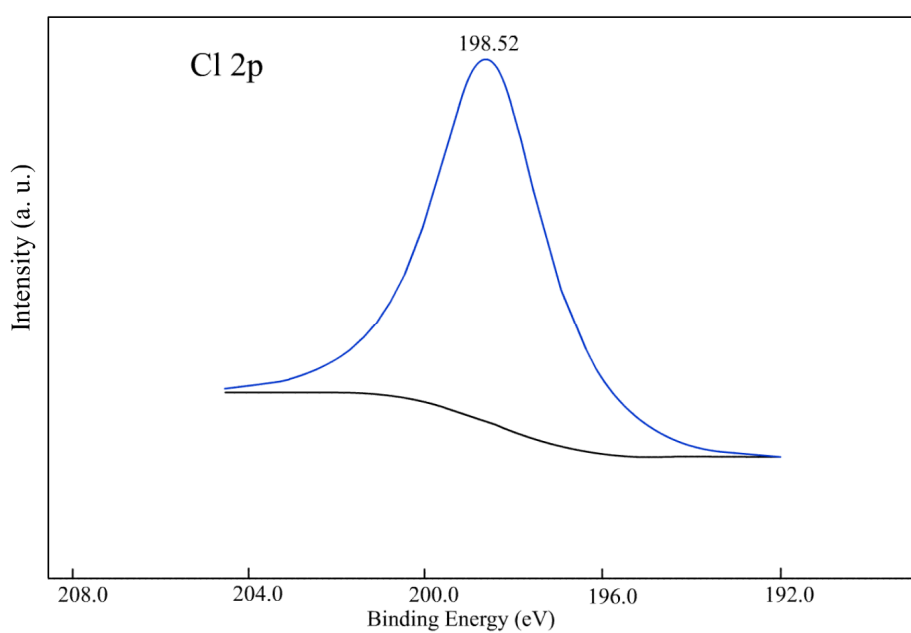
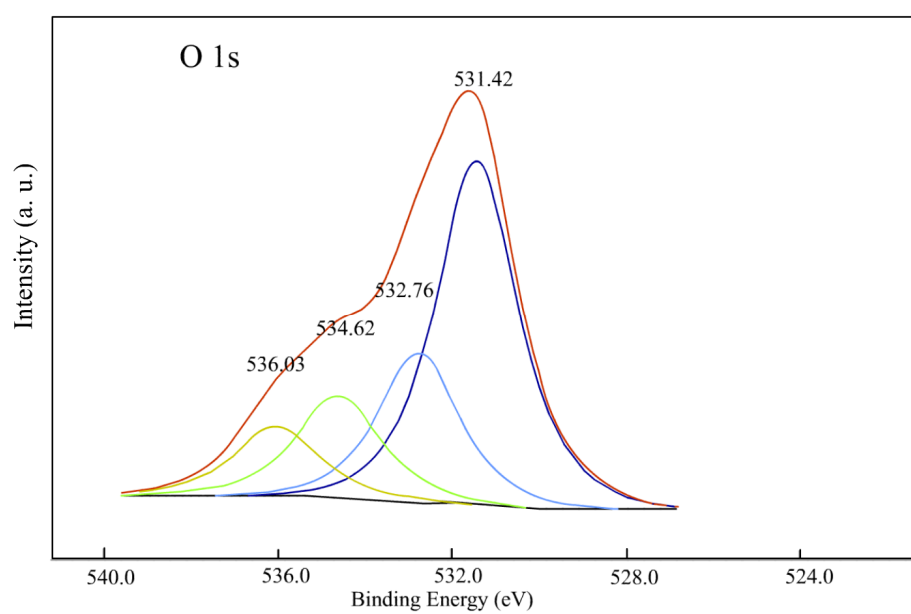
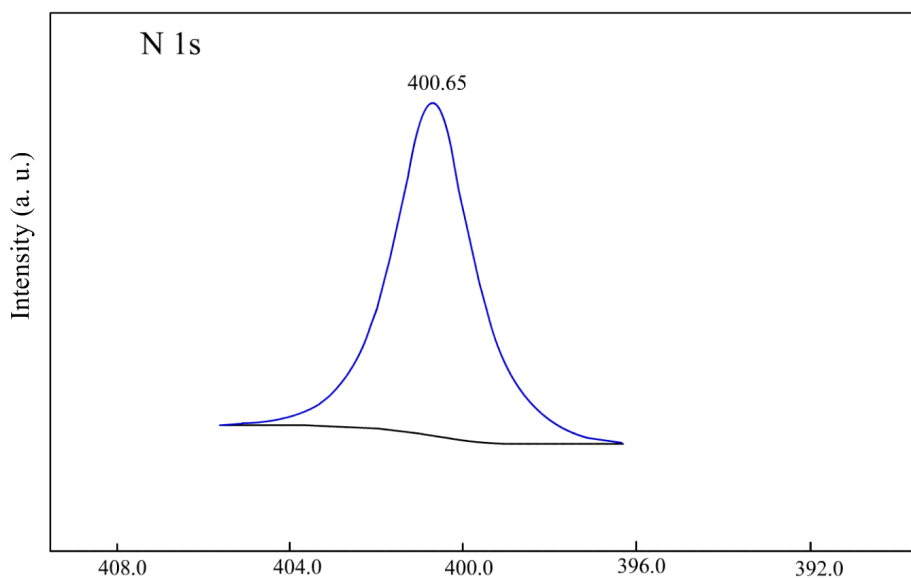
- I. Infrared spectra of **P1**, **P2**, **P3** and **P4**
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I. Infrared spectra of P1, P2, P3 and P4



II. Pd_{3d}, Ag_{3d}, C 1s, N 1s, O 1s and Cl 2p XPS spectra of P4





III. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis.

P3 (50 mg) was treated with a muffle stove at 1000 °C for 5 h. After cooling to room temperature, a mixture (12 mL) of hydrochloric acid and nitric acid (3:1, v/v) was added and stirred for 30 min at 100 °C. The orange solution was filtered. The filtrate was diluted to 250 mL with distilled water and analyzed by ICP-AES. The filtered AgCl was completely dissolved with concentrated aqueous ammonia (5 mL). The solution was then diluted to 100 mL with distilled water and analyzed by ICP-AES.

The amount of palladium and silver in **P4** were similarly determined.

IV. Inductively coupled plasma mass spectrometry (ICP-MS) analysis.

When the reaction was completed, the catalyst was filtered and washed with ether (4 × 8 mL). The combined filtrate was evaporated under reduced pressure, and the residual solid were treated with muffle stove at 1000 °C for 5h, then stirred in a mixture (8 mL) of hydrochloric acid and nitric acid (3:1, v/v) at 100 °C for 4 h. After cooling to room temperature, the mixture was filtered. The filtrate was diluted to 50 mL with distilled water and analyzed by ICP-MS.

V. Analytical data for cross-coupling products.

4-Methoxybiphenyl^{1,2} (Table 1, entry 8; Table 3, entries 5 and 8): mp 89–90 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.52–7.55 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 3.84 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 140.8, 133.7, 128.7, 128.1, 127.7, 126.7, 126.6, 114.2, 114.1, 55.3 ppm.

4-Nitrobiphenyl³ (Table 3, entry 1): mp 114–115 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.29–8.32 (m, 2H), 7.72–7.76 (m, 2H), 7.61–7.64 (m, 2H), 7.43–7.52 ppm (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.6, 147.0, 138.7, 129.1, 128.9, 127.8, 127.4, 124.1 ppm.

2-Nitrobiphenyl⁴ (Table 3, entry 2): pale yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.40–7.51 (m, 5H), 7.31–7.34 ppm (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 137.4, 136.3, 132.3, 132.0, 128.7, 128.3, 128.2, 127.9, 124.1 ppm.

3-Nitrobiphenyl⁵ (Table 3, entries 3, 16): mp 59–60 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.46 (t, *J* = 2.0 Hz, 1H), 8.19–8.22 (m, 1H), 7.91–7.94 (m, 1H), 7.62–7.66 (m, 3H), 7.42–7.52 ppm (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 148.7, 142.8, 138.6, 133.0, 129.7, 129.2, 128.5, 127.1, 122.0, 121.9 ppm.

1, 4-Diphenylbenzene² (Table 3, entry 4): mp 209–210 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.68 (d, *J* = 4H), 7.64 (d, *J* = 7.92, 4H), 7.46 (t, *J* = 7.68 Hz, 4H), 7.36 (t, *J* = 7.38, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 140.1, 128.8, 127.5, 127.4, 127.1 ppm.

3-Methoxybiphenyl¹ (Table 3, entry 6): colorless liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32–7.36 (m, 2H), 7.12–7.21 (m, 2H), 6.89 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.84 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 142.9, 141.2, 129.9, 128.9, 127.5, 127.5, 119.8, 113.0, 112.8, 55.4 ppm.

2-Methoxybiphenyl² (Table 3, entry 7): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.22–7.25 (m, 3H), 6.89–6.96 (m, 2H), 3.76 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 155.4, 137.5, 129.9, 129.7, 128.5, 127.7, 126.9, 125.9, 119.8, 110.2, 54.5 ppm.

4-Methoxybiphenyl-4'-carbonitrile⁶ (Table 3, Entry 9): mp 103–104 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.86 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 144.2, 131.5, 130.5, 127.3, 126.1, 118.1, 113.5, 109.1, 54.4 ppm.

4-Methoxy-4'-methylbiphenyl² (Table 3, entries 10, 12): mp 108–109 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 2.38 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.6, 114.1, 55.3, 21.1 ppm.

4-Methoxy-2'-methylbiphenyl² (Table 3, entry 11): mp 51–52 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.20–7.26 (m, 6H), 6.93–6.96 (m, 2H), 3.84 (s, 3H), 2.27 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.5, 140.5, 134.4, 133.3, 129.3, 129.2, 128.9, 125.9, 124.7, 112.4, 54.2, 19.5 ppm.

3-Methoxy-4'-methylbiphenyl⁷ (Table 3, entry 13): mp 75–76 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.10 (t, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.83 (s, 3H), 2.38 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 142.8, 138.3, 137.3, 129.8, 129.5, 127.1, 119.6, 112.8, 112.4, 55.3, 21.2 ppm.

2-Methoxy-4'-methylbiphenyl⁸ (Table 3, entry 14): mp 80–81 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.48–7.50 (m, 2H), 7.36–7.38 (m, 2H), 7.27–7.29 (m, 2H), 7.02–7.08 (m, 2H), 3.86 (s, 3H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 21.3, 55.6, 111.2, 120.8, 128.8, 129.4, 129.5, 130.7, 130.8, 135.6, 136.6, 156.6 ppm.

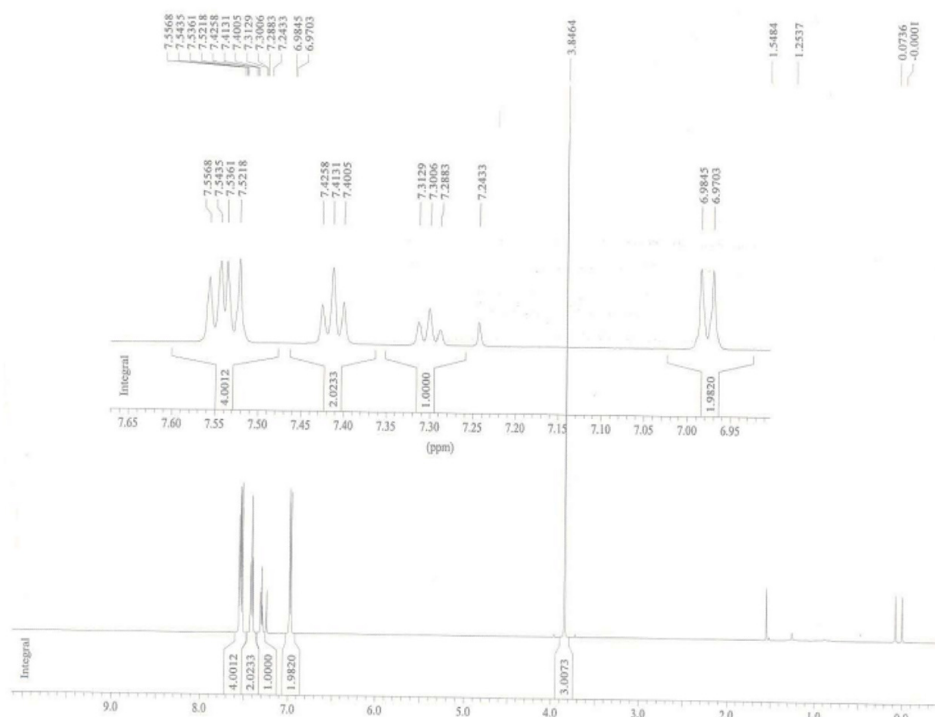
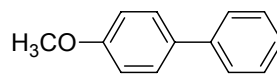
3-Nitro-4'-methyl-biphenyl⁹ (Table 3, entry 15): mp 75–76 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.44 (s, 1H), 8.15–8.19 (d, *J* = 16 Hz 1H), 7.88–7.92 (d, *J* = 15.5 Hz 1H), 7.51–7.62 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.42 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 148.7, 142.8, 138.5, 135.7, 132.8, 129.9, 129.6, 129.4, 126.9, 126.8, 121.7, 121.6, 21.2 ppm.

VI. References

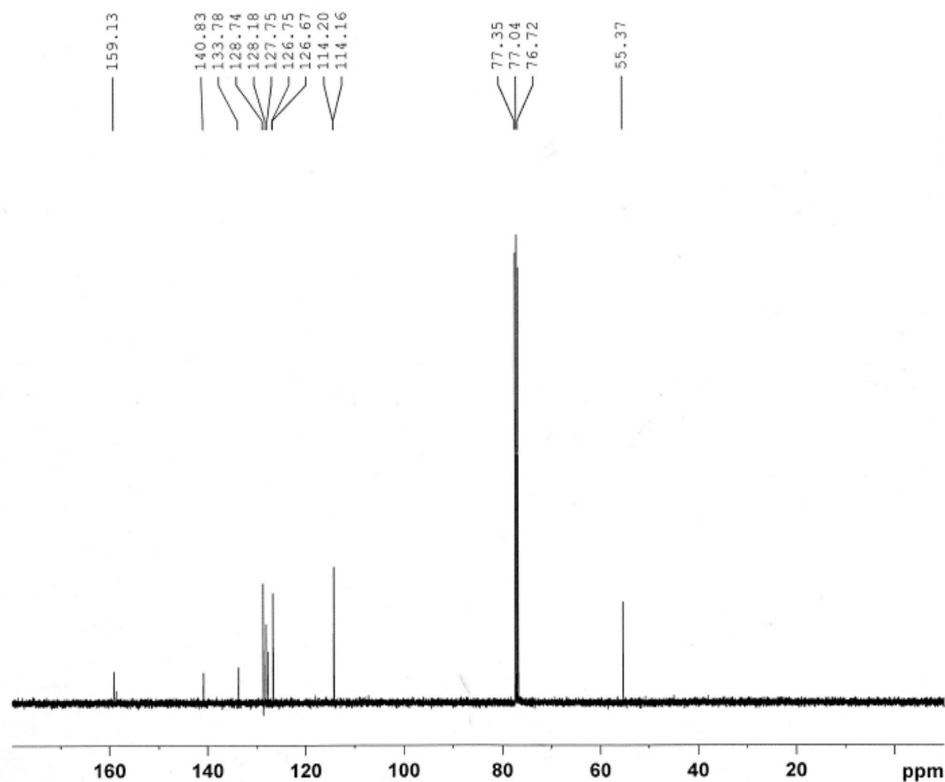
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- [6] G. A. Molander, B. Biolatto, *Org. Lett.* **2002**, *4*, 1867.
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VII. ^1H NMR and ^{13}C NMR Spectra for cross-coupling products

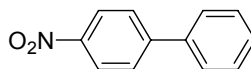
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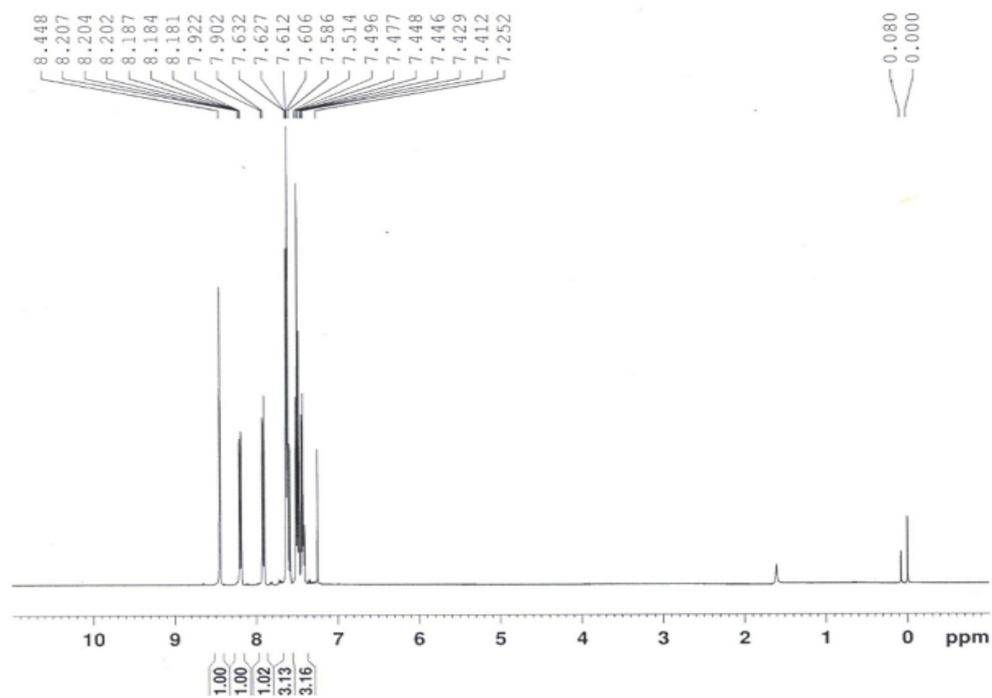
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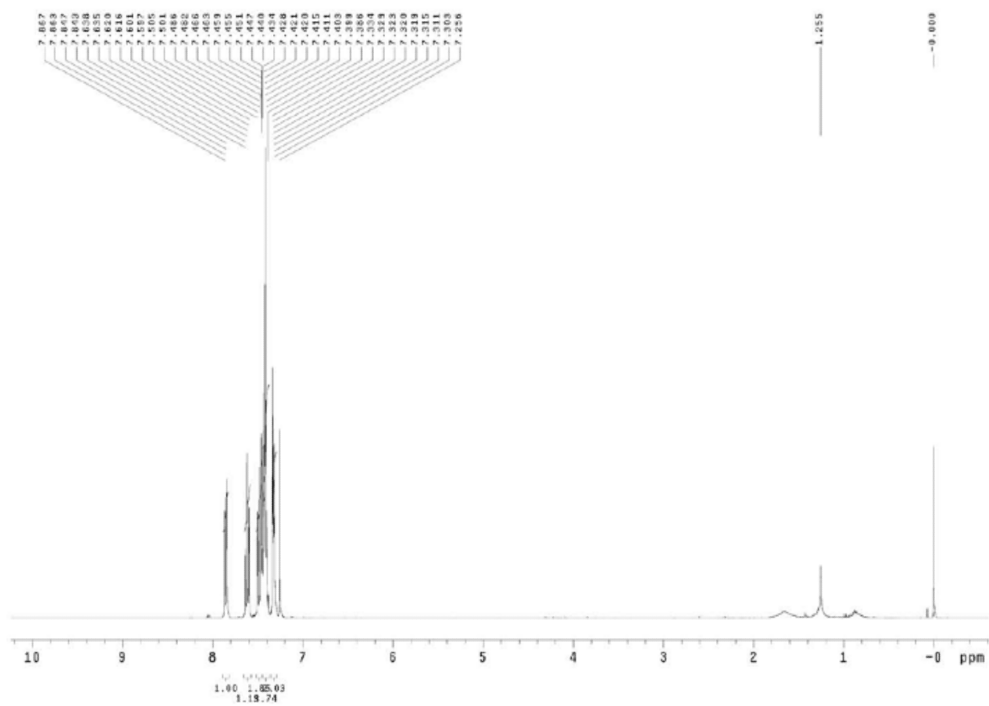
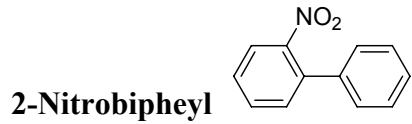
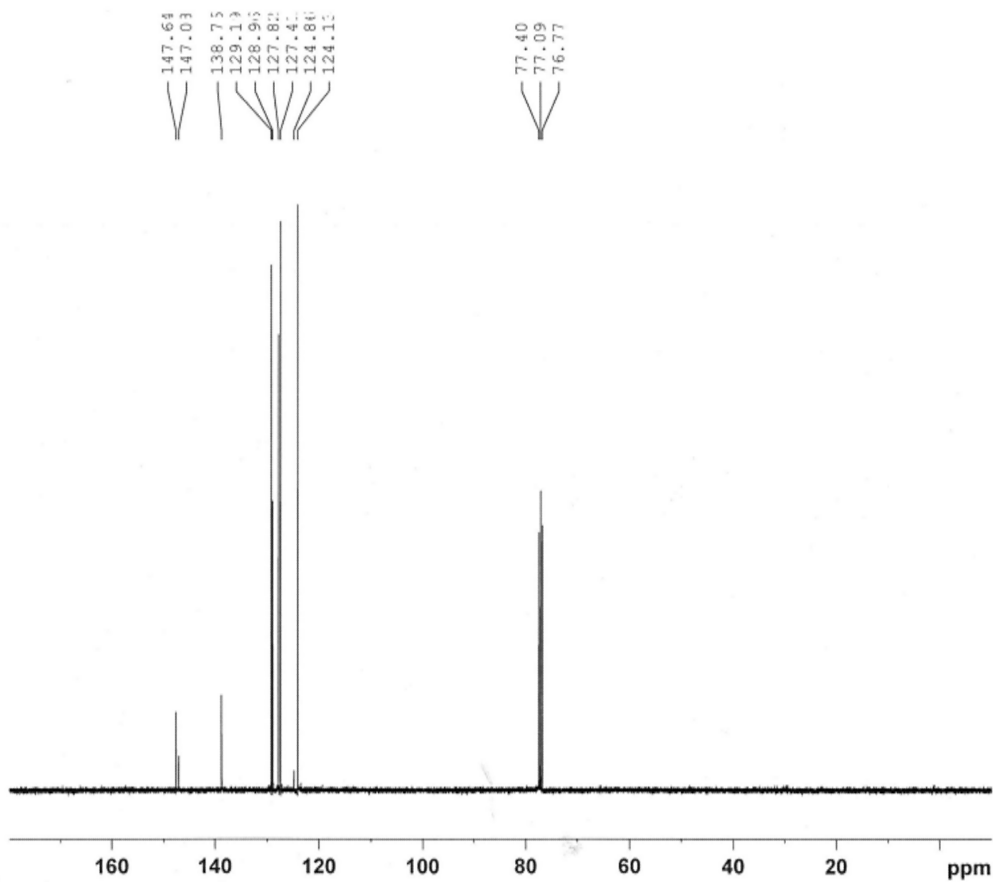
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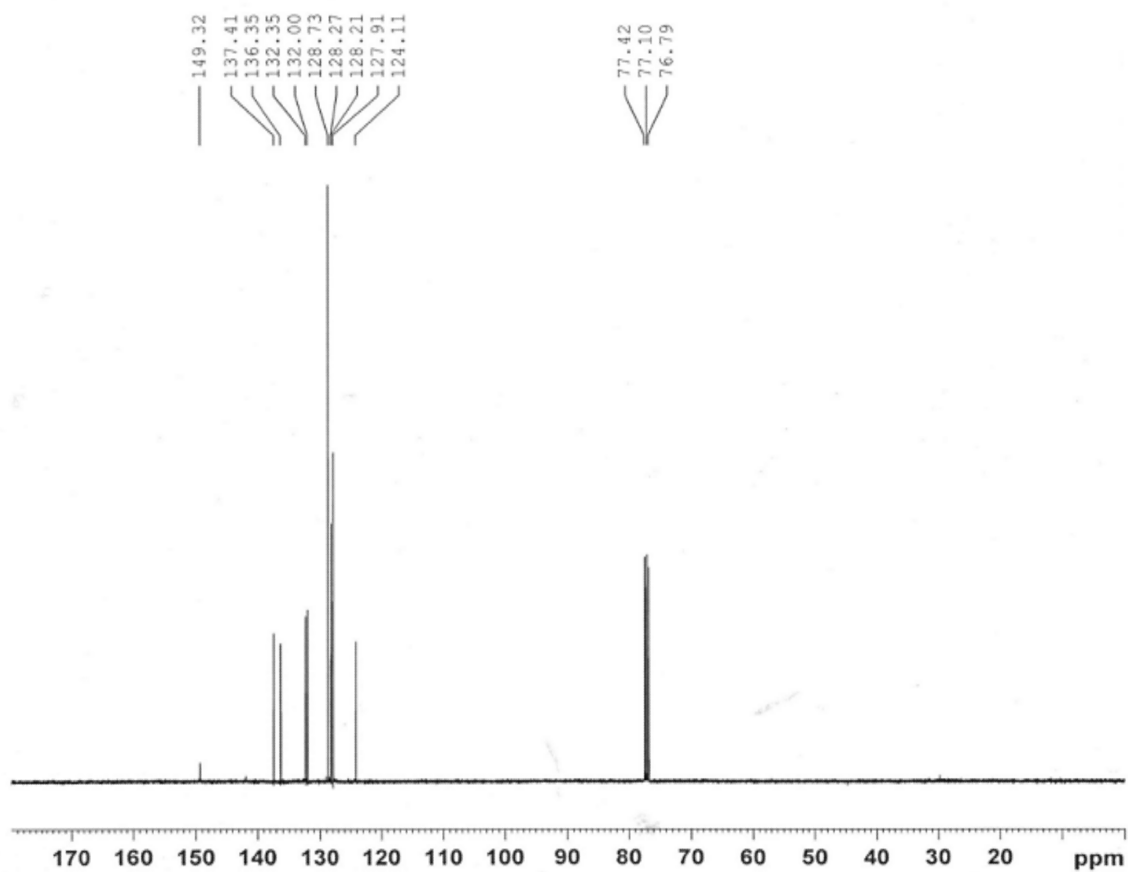
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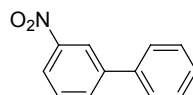
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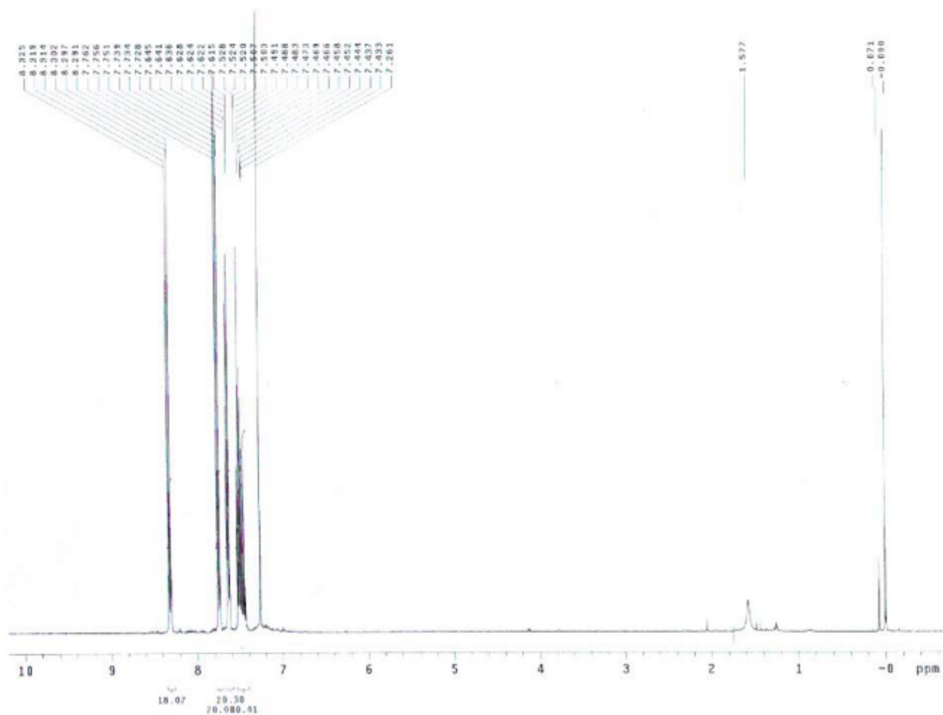


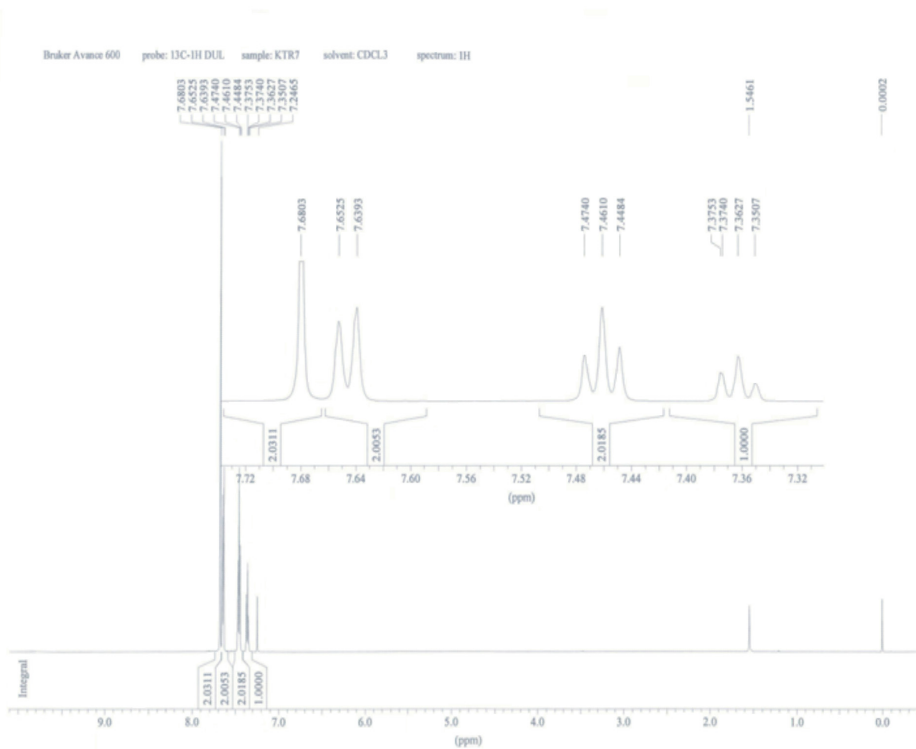
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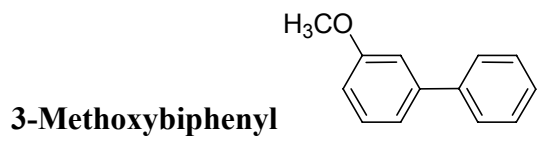
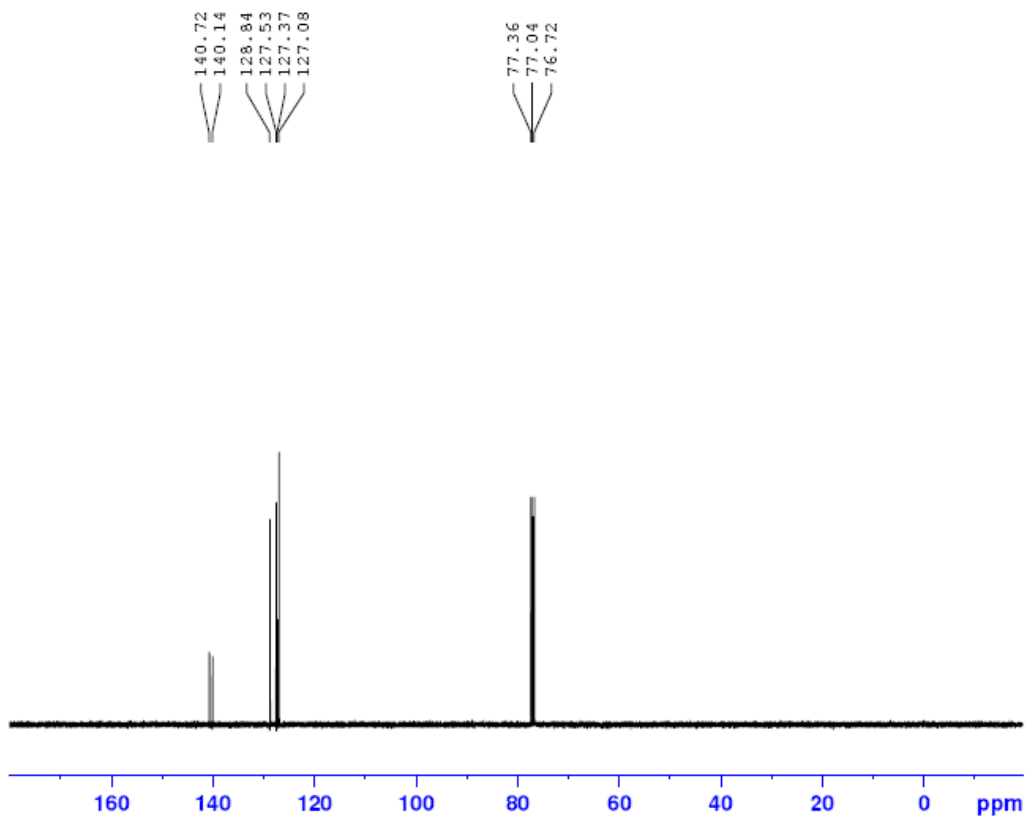
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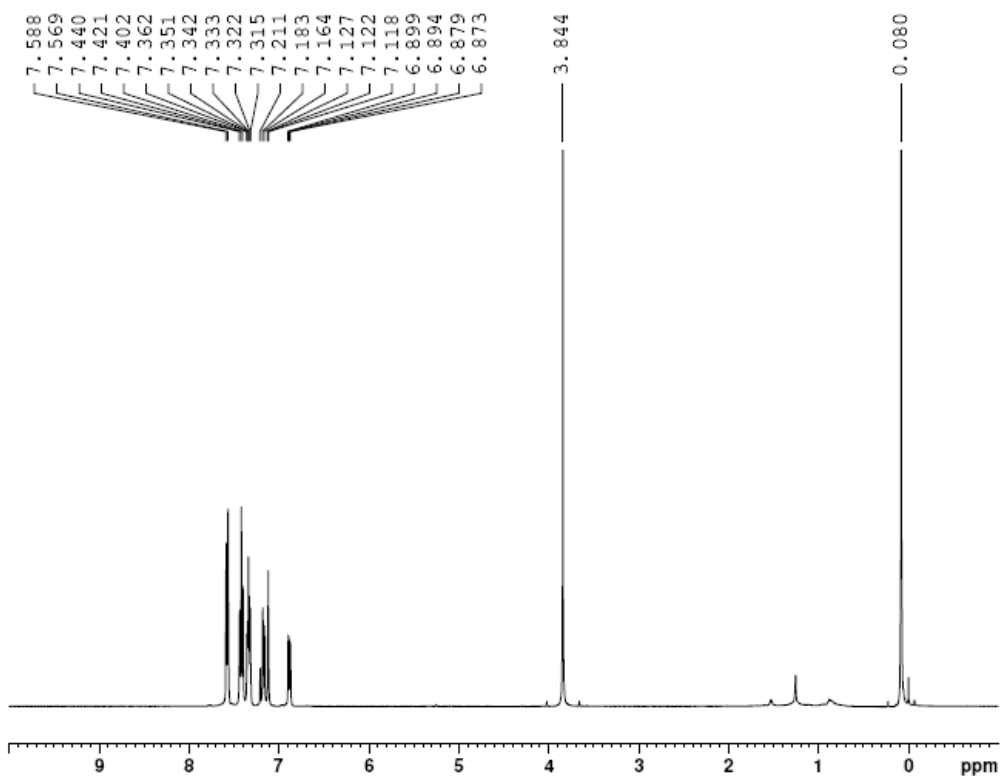




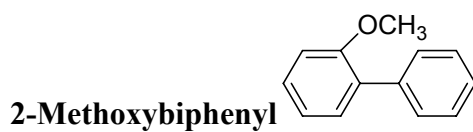
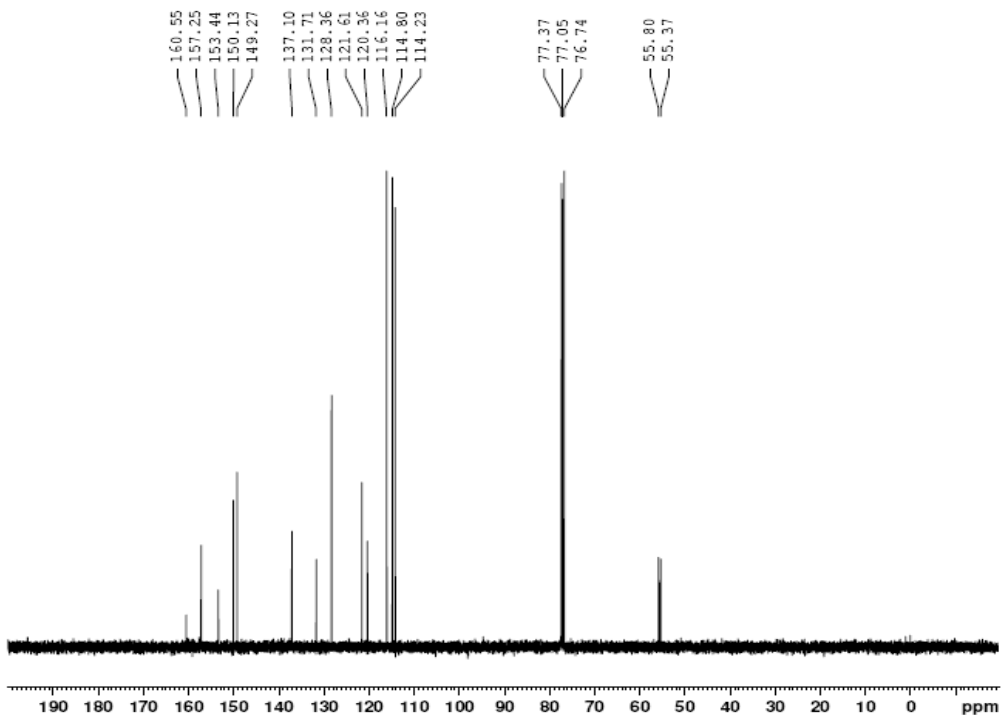
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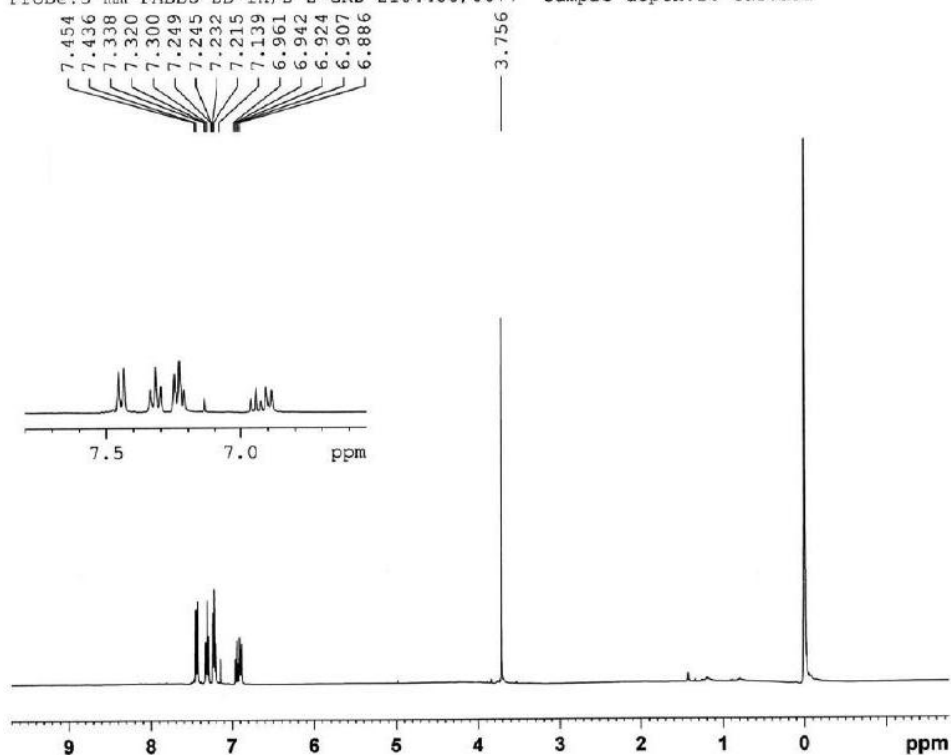
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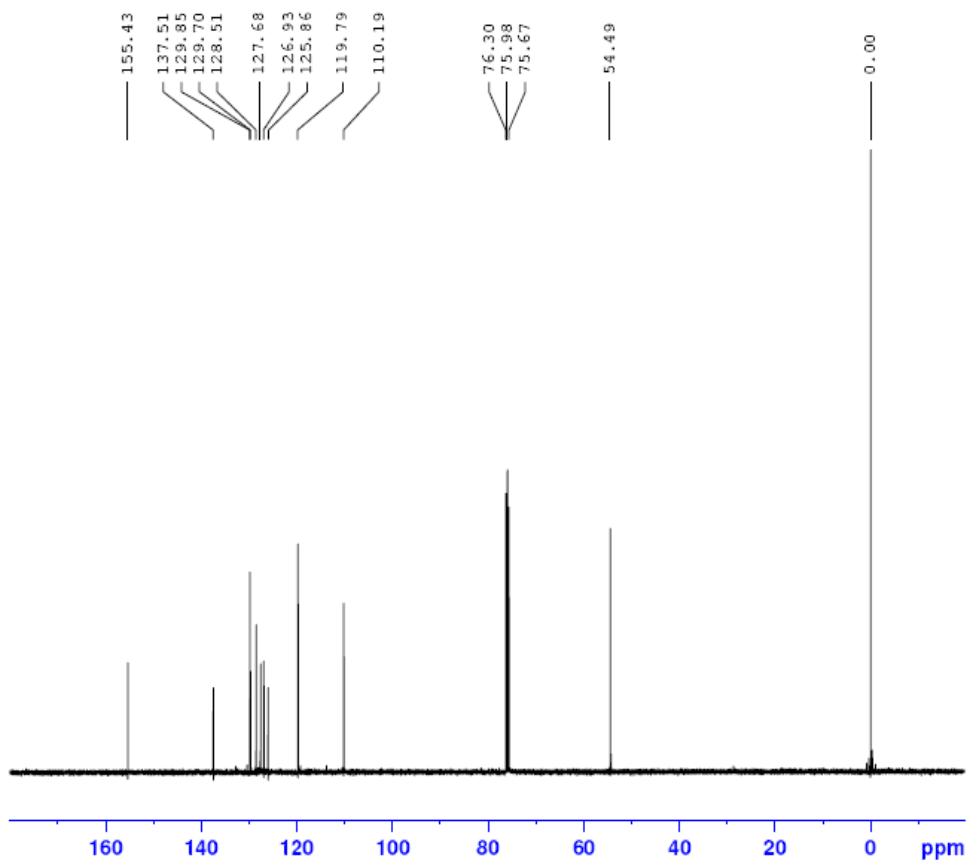
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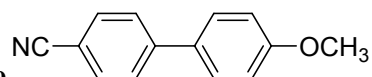
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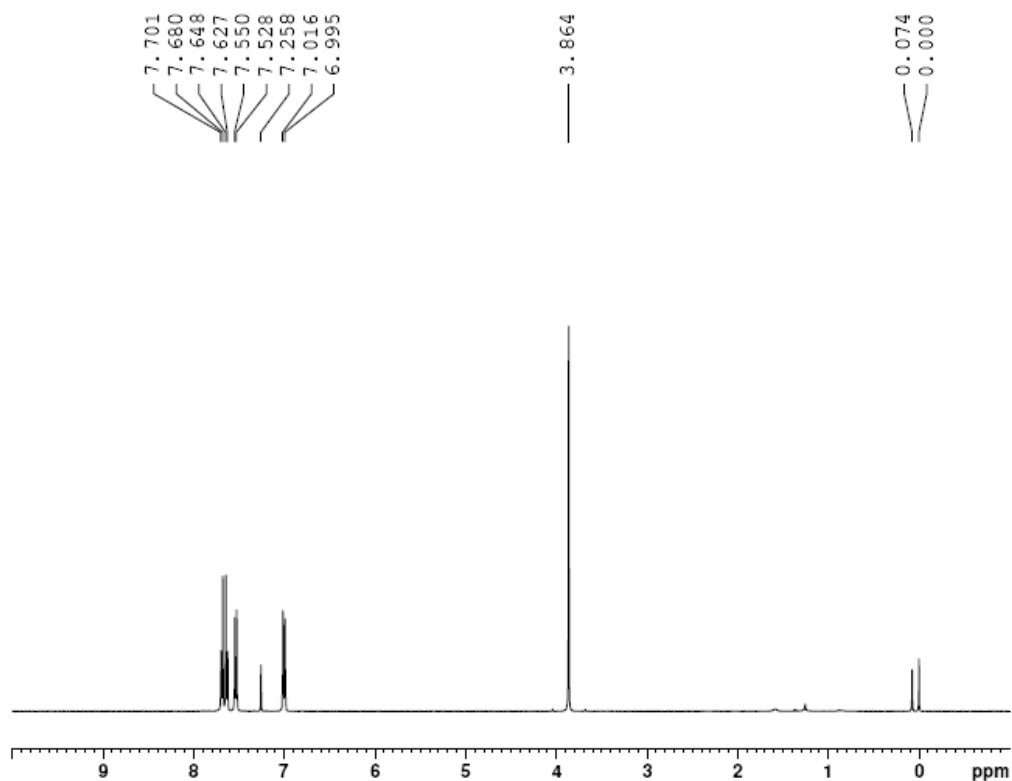
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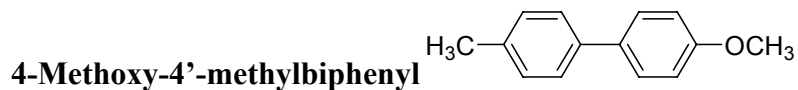
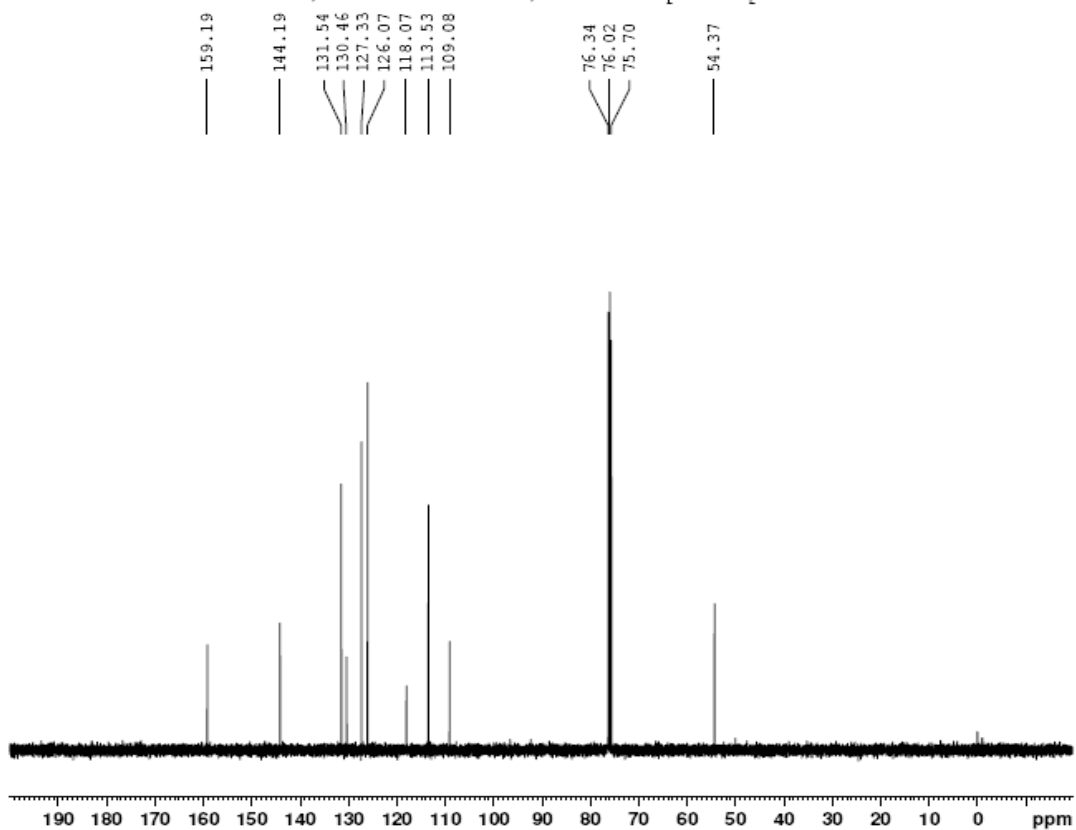
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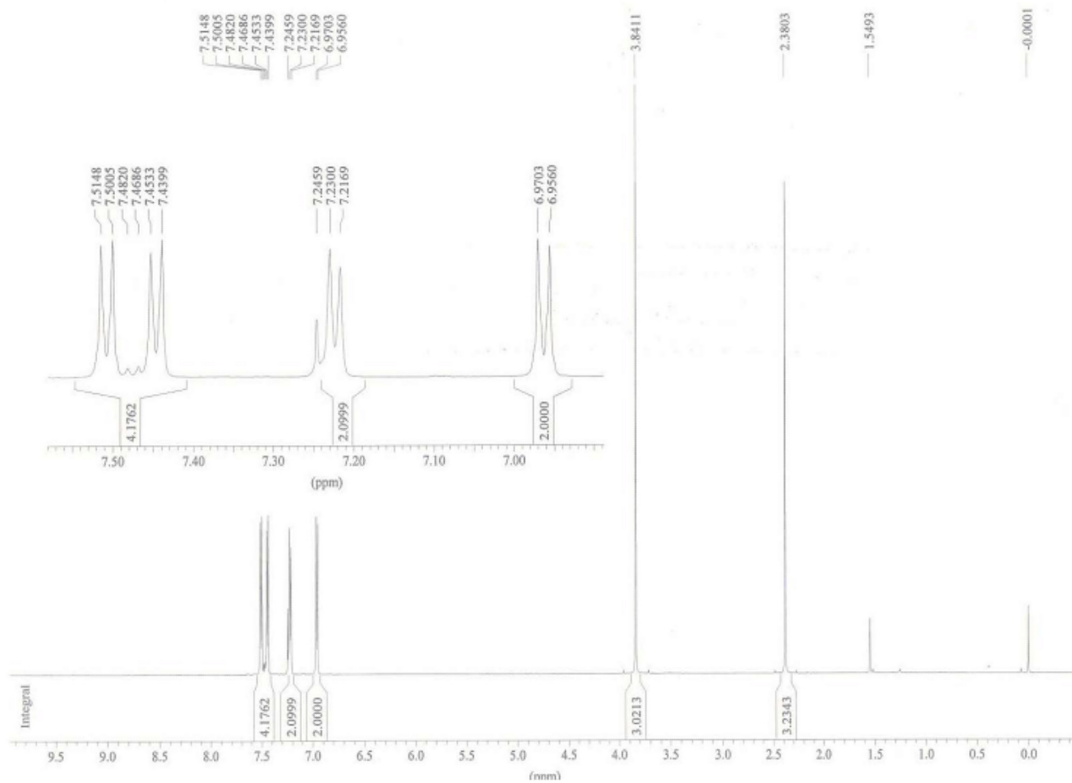


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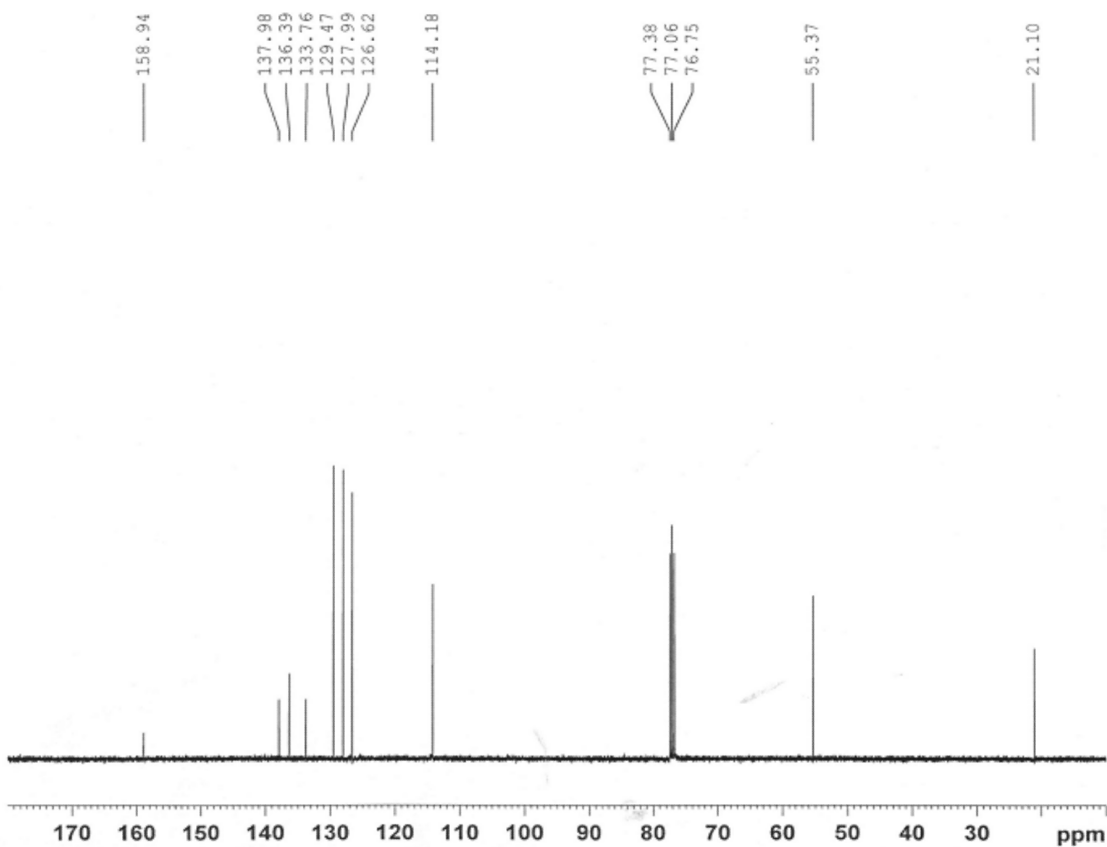


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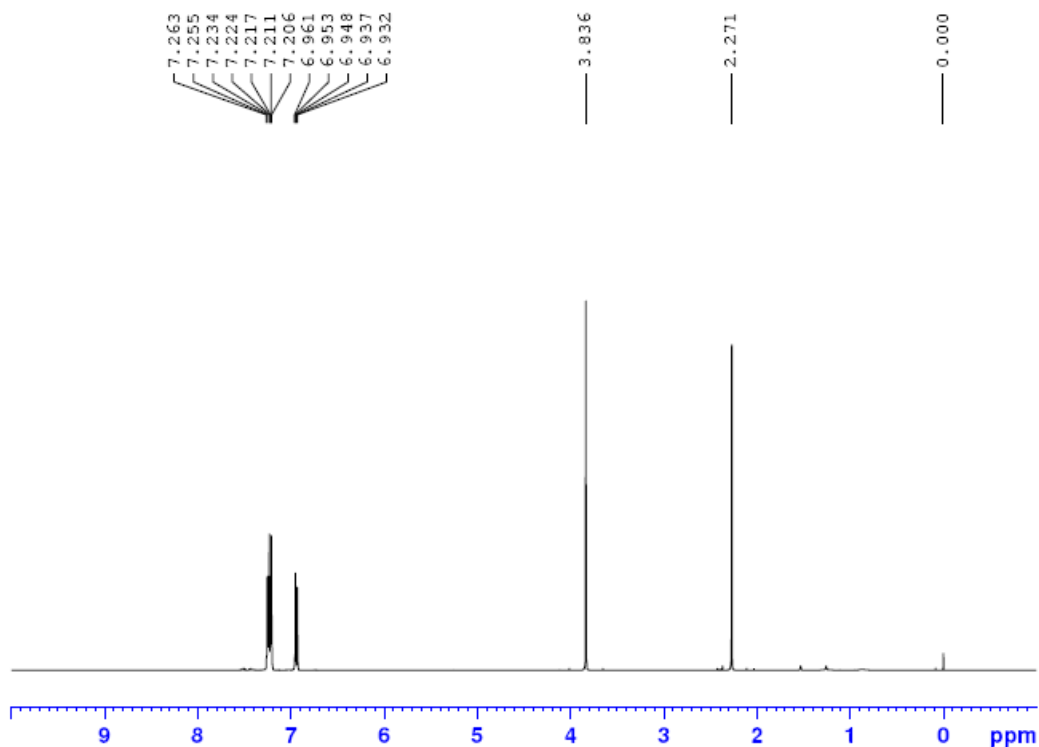




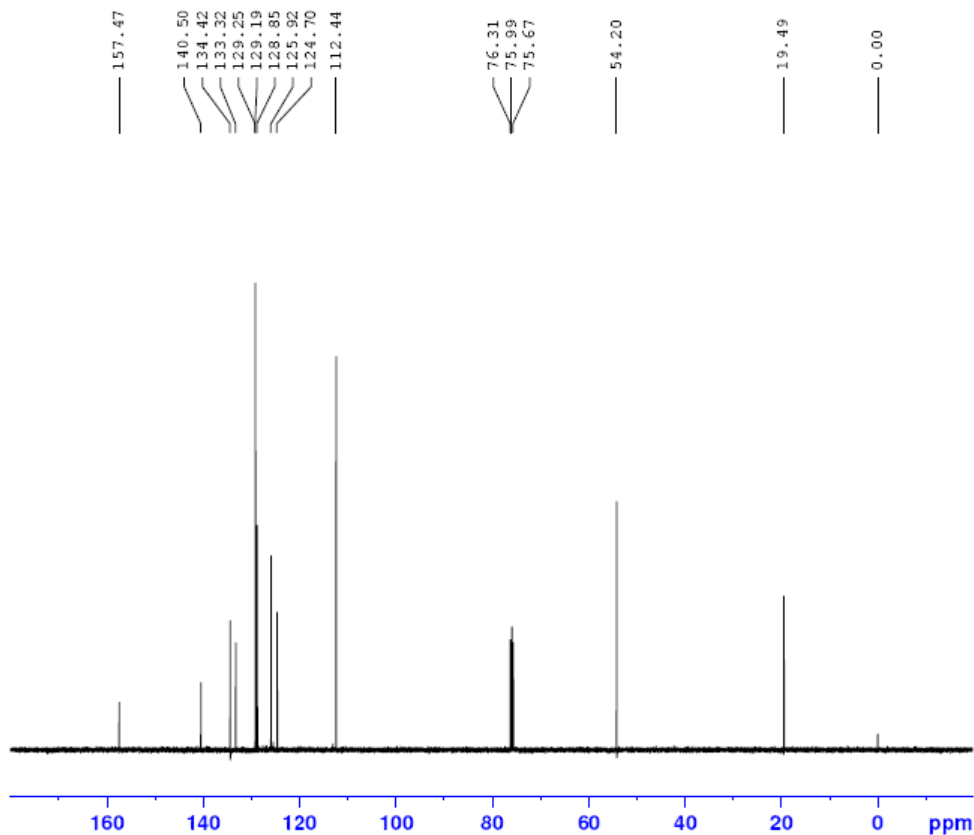
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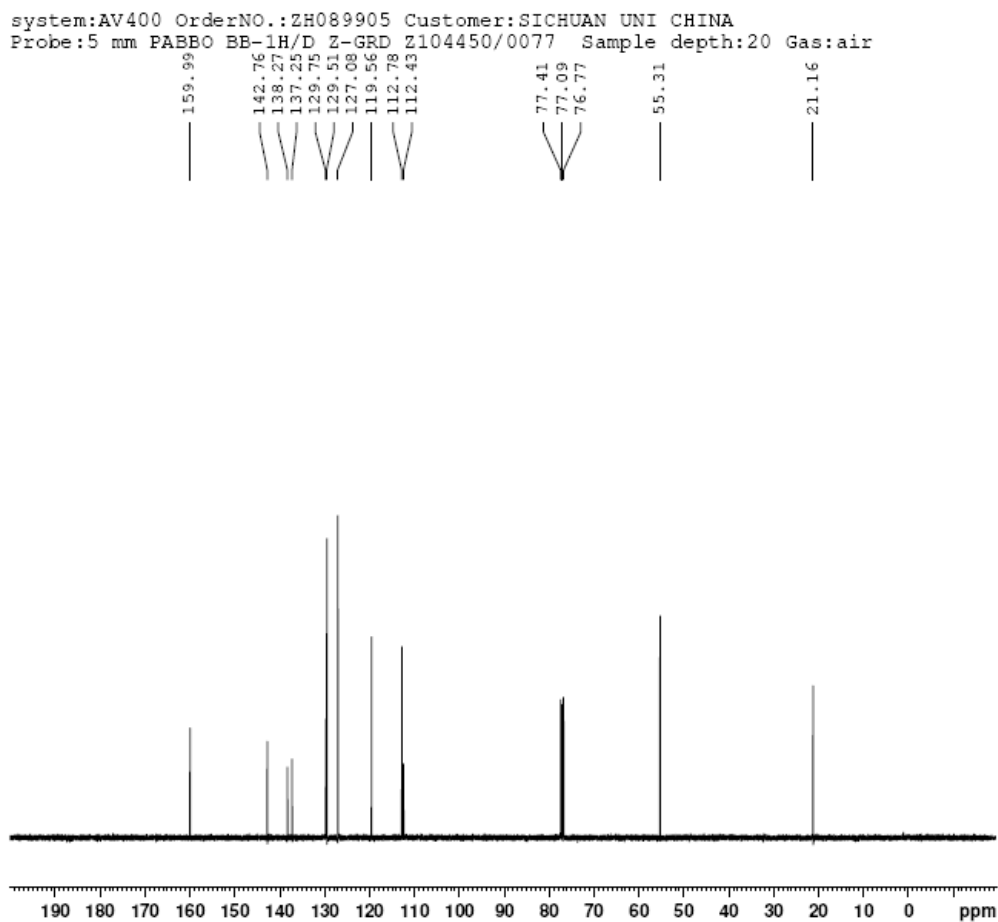
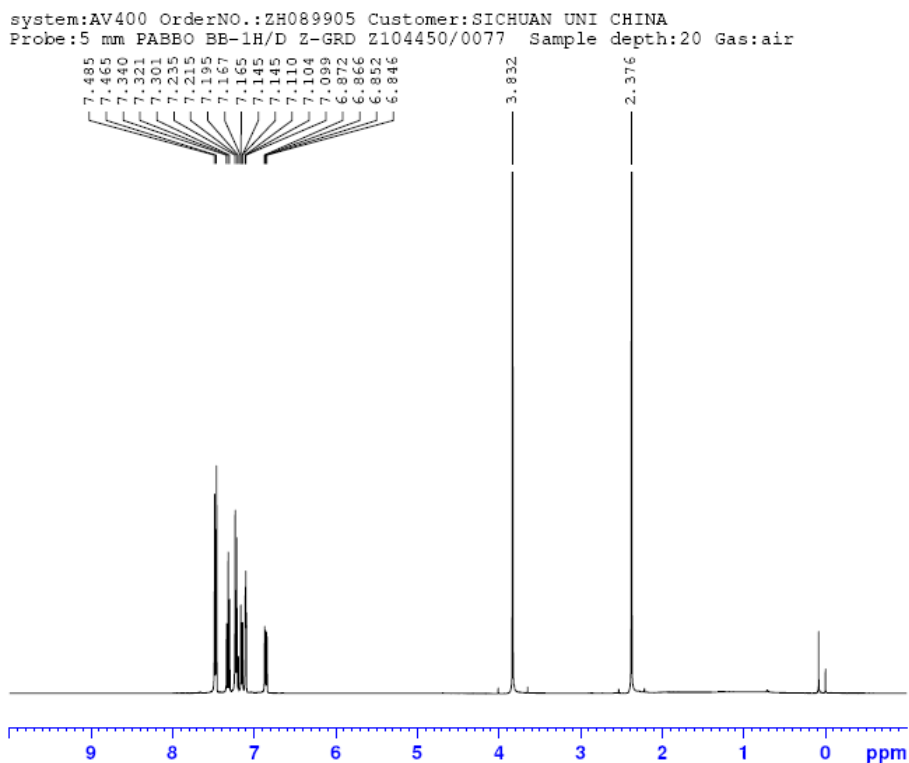
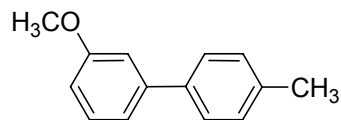
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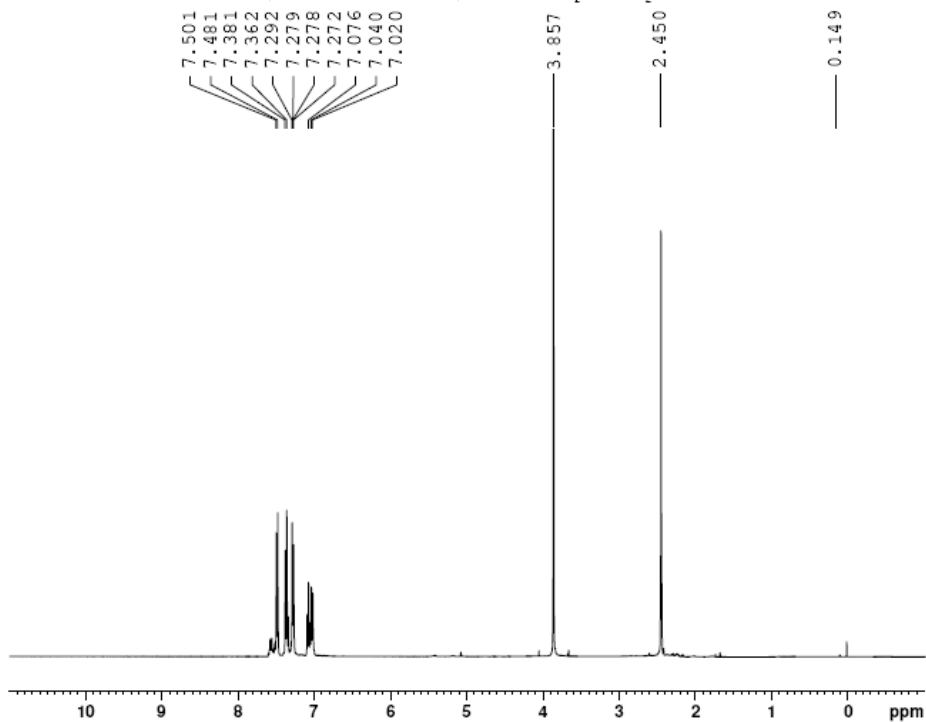


3-Methoxy-4'-methylbiphenyl

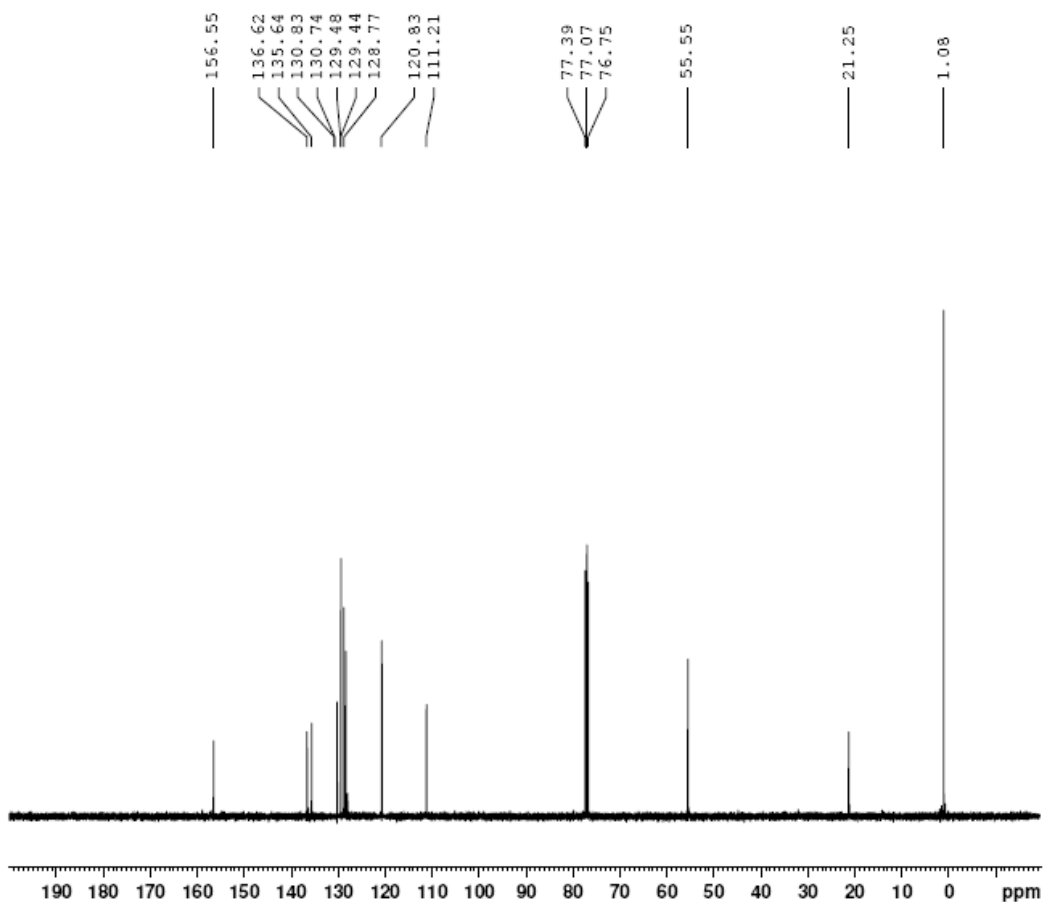


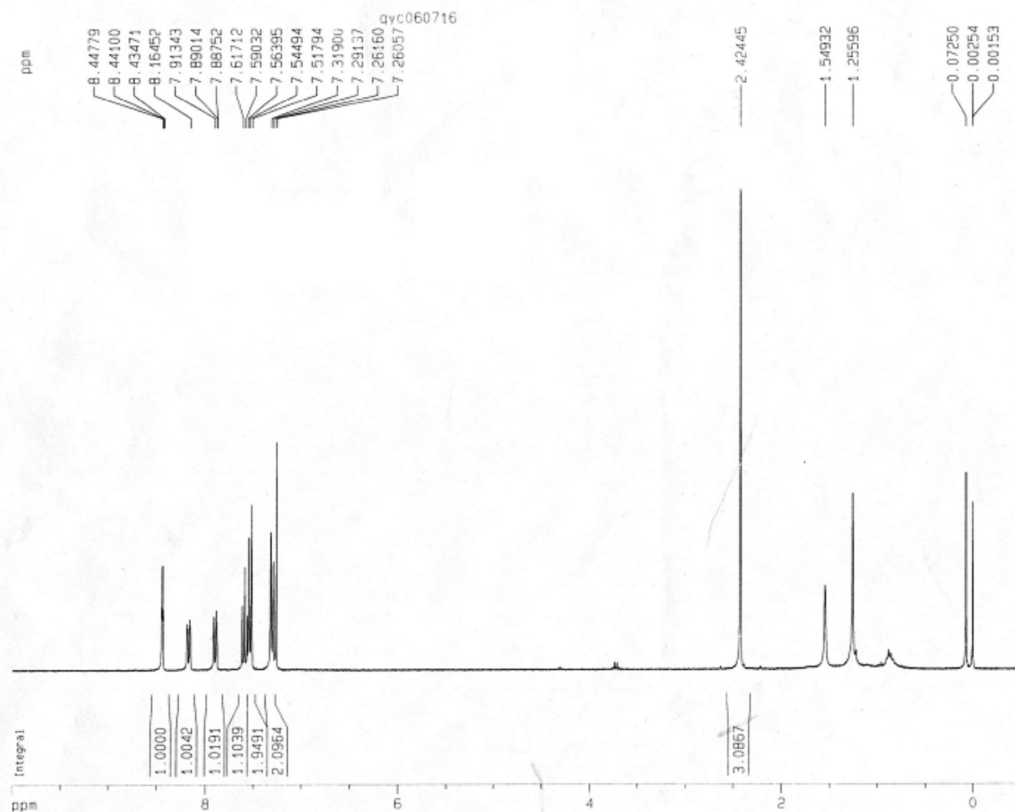
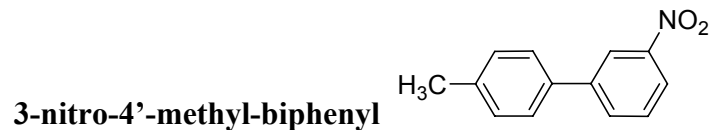


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