Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Supplementary materials

$NiFe_2O_4@SiO_2@ZrO_2/SO_4^{2-}/Cu/Co$ Nanoparticles: A Novel Efficient, Magnetically Recyclable and Bimetallic Catalyst for Pd-Free Suzuki, Heck and C-N Cross-Coupling Reactions in aqueous media

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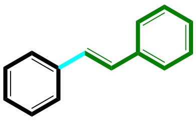
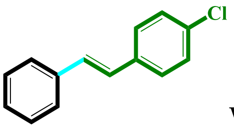
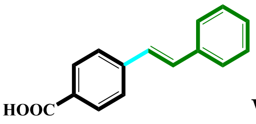
^{1}H NMR and ^{13}C NMR characterization data of the C-C and C-N cross-coupling products:



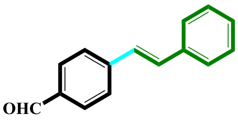
white solid, m.p. 124°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.13 (d, 2H), 7.31 – 7.42 (m, 6H), 7.52 – 7.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 137.4, 128.8, 128.7, 127.6, 126.6. MS (m/e)= 180 [M$^+$].[1].



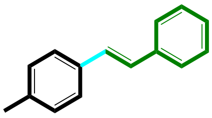
White solid, m.p. 128°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.06 (d, J = 16.2 Hz, 1H), 7.09 (d, J = 16.2 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H),), 7.41 – 7.35 (m, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 137.0, 135.8, 133.1, 129.3, 128.8, 128.7, 127.8, 127.6, 127.3, 126.5. MS (m/e)= 214 [M$^+$].[2].



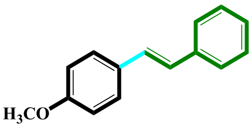
White solid, m.p. 251°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.15 (d, 2H), 7.31 – 7.63 (m, 5H), 7.73 (d, 2H), 7.95 (d, 2H), 12.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 169.6, 141.4, 136.6, 130.9, 129.7, 129.4, 128.7, 128.2, 127.4, 126.8, 126.4. MS (m/e)= 224 [M$^+$].[3].



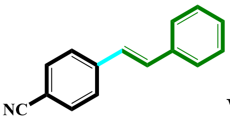
White solid, m.p. 112°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.10 (d, 2H), 7.23 – 7.59 (m, 5H), 7.68 (d, 2H), 7.87 (d, 2H), 10.89 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 193.2, 136.2, 133.5, 129.7, 128.7, 127.9, 126.6, 125.7, 124.9, 124.6, 124.1. MS (m/e)= 208 [M^+].[3].



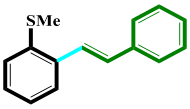
White solid, m.p. 118°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 2.26 (s, 3H), 6.91 – 7.64 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 137.5, 137.4, 134.5, 129.5, 128.62, 128.60, 127.8, 127.4, 126.4, 21.3. MS (m/e)= 194 [M^+].[2].



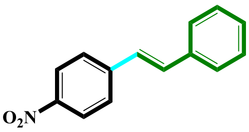
White solid, m.p. 133°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 3.77 (s, 3H), 6.80 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 16.5 Hz, 1H), 6.99 (d, J = 16.0 Hz, 1H), 7.18 (t, J = 6.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 160.5, 138.8, 130.8, 128.9, 128.0, 127.6, 127.3, 126.6, 126.3, 117.0, 57.4. MS (m/e)= 210 [M^+].[3].



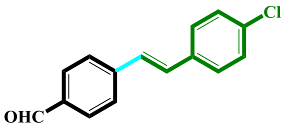
White solid, m.p. 116°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.02 (d, J = 16.5 Hz, 1H), 7.45 – 7.60 (m, 6H), 7.49 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.45 Hz, 1H), 7.20 (d, J = 16.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 139.3, 136.8, 134.6, 120.2, 129.4, 128.9, 126.6, 127.9, 127.1, 126.4. MS (m/e)= 205 [M^+].[4].



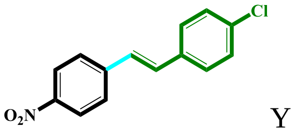
White solid, m.p. 132°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 3.70 (s, 3H), 6.78 (d, J = 8.7 Hz, 1H), 6.90 (d, J = 10.7 Hz, 1H), 7.00 – 7.38 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 159.3, 137.8, 130.3, 128.5, 128.1, 127.6, 127.4, 126.6, 126.4, 115.2, 54.9. MS (m/e)= 226 [M^+].[5].



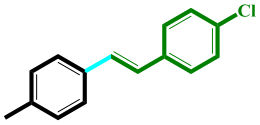
Yellow solid, m.p. 158°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.23 (d, J = 16.5 Hz, 1H), 7.37 (d, J= 16 Hz, 1H), 7.45 – 7.55 (m, 3H), 7.71 (d, J = 7.3 Hz, 2H), 7.80 (d, J = 9.3 Hz, 2H), 8.40 (d, J = 9.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 152.2, 149.9, 140.7, 135.8, 130.4, 129.4, 128.8, 127.2, 125.9. MS (m/e)= 225 [M$^+$].[2].



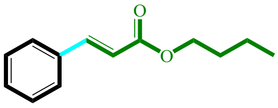
White solid, m.p. 110°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.15 (s, 2H), 7.34 – 7.25 (m, 2H), 7.37 – 7.43 (m, 1H), 7.52 – 7.59 (m, 2H), 7.71 – 7.83 (m, 2H), 8.03 – 8.01 (m, 1H), 10.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 192.2, 138.6, 137.9, 136.9, 134.8, 132.5, 130.0, 129.5, 129.3, 129.1, 128.5 128.1, 127.3, 126.5, 125.0. MS (m/e)= 242 [M$^+$].[1].



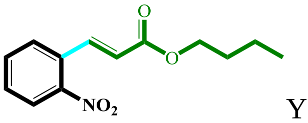
Yellow solid, m.p. 122°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.24 (d, 1H), 7.21 – 7.37 (m, 3H), 7.55 (d, J = 7.3 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 8.21 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 146.8, 143.9, 136.2, 133.3, 128.9, 128.9, 127.1, 126.9, 126.3, 124.2. MS (m/e)= 259 [M$^+$].[1].



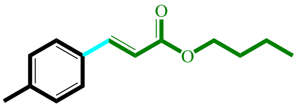
White solid, m.p. 59°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.42 (t, J = 5.6 Hz, 2H), 7.31 – 7.43 (m, 2H), 7.23 – 7.31 (m, 2H), 7.18 (t, J = 10.0 Hz, 2H), 7.06 (d, J = 16.3 Hz, 1H), 7.00 (d, J = 16.3 Hz, 1H), 2.37 (d, J = 4.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 137.8, 136.0, 134.2, 132.9, 129.4, 129.2, 128.8, 127.5, 126.4, 126.3, 21.3. MS (m/e)= 228 [M$^+$].[1].



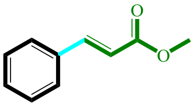
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 0.90 (t, J = 7.5 Hz, 3H), 1.37 – 1.42 (m, 2H), 1.65 – 1.69 (m, 2H), 4.17 (t, J = 6.7 Hz, 2H), 6.53 (d, J = 16 Hz, 1H), 7.60 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 16.2 Hz, 1H), 8.18 (d, J= 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 166.0, 141.5, 140.5, 128.5, 124.1, 122.6, 64.8, 30.6, 19.1, 13.7. MS (m/e)= 204 [M$^+$].[6].



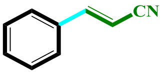
Yellow solid, m.p. 62°C, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 0.88 (t, J = 7.5 Hz, 3H), 1.35 – 1.40 (m, 2H), 1.62 – 1.66 (m, 2H), 4.14 (t, J = 7.5 Hz, 2H), 6.29 (d, J = 17.5 Hz, 1H), 7.42 – 7.57 (m, 2H), 7.94 – 7.97 (m, 2H), 8.02 (d, J = 17.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 165.9, 148.2, 139.7, 133.5, 130.3, 130.2, 129.2, 124.6, 123.3, 64.7, 30.6, 19.1, 13.9. MS (m/e)= 249 [M$^+$].[6].



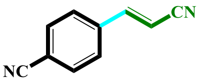
Colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 0.85 (t, J = 4.7 Hz, 3H), 1.32 – 1.36 (m, 2H), 1.56 – 1.59 (m, 2H), 2.24 (s, 3H), 4.09 (t, J = 5.0 Hz, 2H), 6.30 (dd, J = 16.0 Hz, J'= 5.9 Hz, 1H), 7.06 – 7.1 (m, 2H), 7.29 – 7.31 (m, 2H), 7.52 (dd, J= 18.2 Hz, J'= 5.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 167.2, 144.5, 140.5, 131.7, 129.5, 128.3, 117.1, 64.2, 30.8, 21.4, 19.2, 13.7. MS (m/e)= 218 [M$^+$].[6].



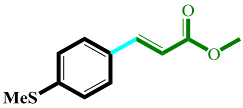
White solid, m.p. 38°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 3.84 – 3.71 (m, 3H), 6.45 (dd, J = 25.2, 16.6 Hz, 1H), 7.39 (d, J = 22.4 Hz, 3H), 7.53 (d, 2H, J = 20.8 Hz), 7.71 (dd, J = 25.2, 16.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 166.9, 144.7, 131.2, 131.4, 131.9, 117.8, 53.4. MS (m/e)= 162 [M$^+$].[7].



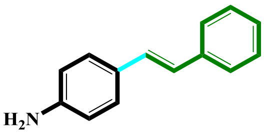
Clear colorless liquid, m.p. 17°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 5.88 (d, 1H, J = 16.8 Hz), 7.26 (s, 1H), 7.36 – 7.44 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 151.7, 129.4, 128.6, 128.4, 135.5, 117.6, 96.3. MS (m/e)= 129[M$^+$].[1].



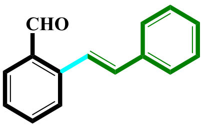
Light brown solid, m.p. 74°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 7.10-7.16 (d, J = 16.3 Hz, 1H), 7.23-7.28 (d, J = 16.3 Hz, 1H), 7.30- 7.36 (t, 2H), 7.52-7.55 (d, 2H), 7.53-7.62 (q, 4H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 141.9, 136.3, 132.5, 132.4, 128.9 128.7, 126.9, 126.9, 126.8, 119.0, 110.6. MS (m/e)= 154[M$^+$].[1].



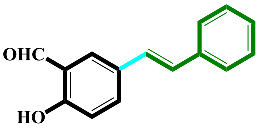
Yellow solid, m.p. 49°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 3.30 (s, 3H), 3.82 (s, 3H), 6.41 (d, J = 16.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 16.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 168.2, 145.7, 141.6, 132.4, 130.5, 128.6, 118.4, 52.8, 21.9. MS (m/e)= 208 [M$^+$].[7].



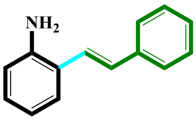
White solid, m.p. 153°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 3.74 (s, 2H), 6.68 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 16.4 Hz, 1H), 7.03 (d, J = 16.4 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.35 (s, 2H), 7.48 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 146.1, 137.9, 128.7, 128.6, 128.0, 127.7, 126.9, 126.1, 125.1, 115.2. MS (m/e)= 195[M$^+$].[9].



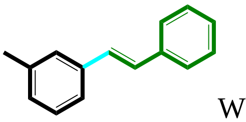
White solid, m.p. 77°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 7.15 (d, J = 16.3 Hz, 1H), 7.28 (d, J = 16.3 Hz, 1H), 7.32 – 7.42 (m, 3H), 7.56 (d, J = 7.2 Hz, 2H), 7.66 (d, J = 7.7 Hz, 2H), 7.88 (d, J = 7.7 Hz, 2H), 10.0 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 191.7, 143.7, 135.8, 135.3, 132.4, 130.5, 128.6, 128.1, 127.2, 126.4. MS (m/e)= 208[M$^+$].[9].



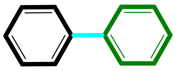
White solid, m.p. 188°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 7.09 (d, J = 16.3 Hz, 1H), 7.23 (d, J = 16.3 Hz, 1H), 7.26 – 7.42 (m, 3H), 7.53-7.66 (m, 5H), 10.9 (s, 1H), 15.8 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 192.4, 163.2, 144.1, 135.9, 135.6, 1332.2, 130.9, 129.1, 128.7, 127.8, 126.8. MS (m/e)= 224[M$^+$].[6].



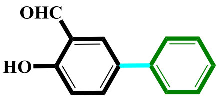
Pale pink solid, m.p. 107°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 3.65 (s, 2H), 6.20 – 6.33 (m, 1H), 6.71 – 6.81 (m, 1H), 6.95 (t, J = 14.4 Hz, 1H), 7.02 – 7.14 (m, 2H), 7.13 (dd, J = 15.6, 7.6 Hz, 1H), 7.26 – 7.32 (m, 1H), 7.35 (dd, J = 7.2, 1.6 Hz, 2H), 8.38 – 7.49 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 146.6, 138.4, 137.4, 129.6, 128.9, 128.6, 128.5, 127.5, 126.5, 117.3, 114.7, 112.9. MS (m/e)= 195[M$^+$].[1].



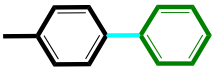
White solid, m.p. 42°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 2.35 (s, 3H), 7.07 (d, 2H), 7.13 – 7.15 (d, J = 7.9 Hz, 2H), 7.22 – 7.26 (t, J = 7.3 Hz, 1H), 7.36 – 7.39 (t, J = 7.6 Hz, 2H), 7.40 – 7.46 (d, J = 7.5 Hz, 2H), 7.42 – 7.44 (d, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 137.6, 137.5, 134.6, 129.4, 128.7, 127.7, 127.4, 126.5, 126.4, 21.3. MS (m/e)= 194[M$^+$].[1].



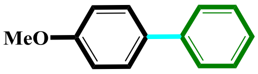
Colorless solid, m.p. 70°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 7.34 – 7.60 (m, 10H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 141.3, 129.0, 127.3, 127.23. MS (m/e)= 154[M$^+$].[12].



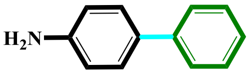
White solid, m.p. 100°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 7.31 – 7.36 (m, 3H), 7.57 (dd, J = 4.4, 2.5 Hz, 2H), 7.68 (d, J = 6.8 Hz, 2H), 7.87 (d, J = 6.8 Hz, 2H), 10.03 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 198.3, 161.5, 145.5, 136.6, 134.8, 133.1, 132.5, 127.5, 127.3, 130.3, 127.8, 121.3. MS (m/e)= 198[M$^+$].[12].



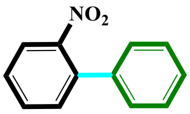
White solid, m.p. 49°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 2.44 (s, 3H), 7.27 – 7.55 (m, 7H), 7.62 – 7.74 (m, 2H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 141.2, 138.6, 137.1, 129.6, 129.0, 127.4, 127.1, 127.0, 21.1. MS (m/e)= 168[M$^+$].[10].



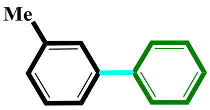
Light yellow solid, m.p. 86°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 3.85 (s, 3H), 6.98 (d, J = 7.5 Hz, 2H), 7.28 (t, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 2H), 7.51 – 7.57 (m, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 160.1, 142.9, 141.2, 129.9, 128.9, 127.5, 127.3, 119.8, 113.6, 112. 3, 100.0, 55.4. MS (m/e)= 184[M$^+$].[8].



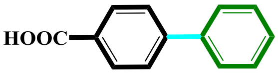
Brown solid, m.p. 103°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 3.54 (s, 2H), 6.66 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.1 Hz, 1H), 7.42 (d, J = 8.7 Hz, 2H), 7.46 (s, 2H), 7.59 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 146.7, 133.4, 131.3, 127.7, 124.0, 114.8, 112.7, 90.1 87.4. MS (m/e)= 169[M$^+$].[10].



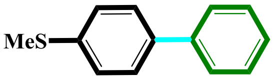
Yellow solid, m.p. 37°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 7.45 – 7.76 (m, 7H), 8.31 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 150.0, 148.8, 140.2, 133.2, 130.2, 128.1, 124.4, 123.5, 122.3. MS (m/e)= 199[M$^+$].[11].



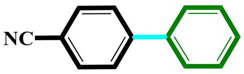
Colorless liquid, m.p. 4°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm): 2.40 (s, 3H), 7.27 (d, J = 8 Hz, 2H), 7.35 (t, J = 8 Hz, 1H), 7.42 (d, J = 8 Hz, 2H), 7.45 (t, J = 8 Hz, 2H), 7.60 (d, J = 8 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ(ppm): 148.9, 140.3, 138.9, 133.0, 130.3, 130.1, 129.0, 128.3, 123.3, 122.1, 22.7. MS (m/e)= 168[M$^+$].[11].



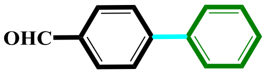
White solid, m.p. 220°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.43 – 7.55 (m, 5H), 7.60 – 7.68 (m, 1H), 7.75 – 7.85 (m, 2H), 8.56 – 8.58 (m, 1H), 13.65 (broad, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 167.5, 141.9, 137.2, 132.9, 130.5, 129.6, 122.1. MS (m/e)= 198[M^+].[11].



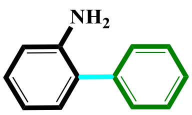
White solid, m.p. 72°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 3.85 (s, 3H), 6.98 (d, J = 8 Hz, 2H), 7.33 (t, J = 8 Hz, 1H), 7.44 (t, J = 8 Hz, 2H), 7.51 – 7.57 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 148.0, 136.7, 131.8, 128.6, 127.9, 121.4, 116.8, 112.8, 107.9, 105.6, 19.9. MS (m/e)= 200[M^+].[12].



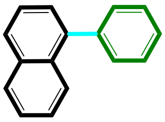
Light yellow solid, m.p. 80°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.53 – 7.42 (m, 3H), 7.59 (d, J = 6.8 Hz, 2H), 7.70 (s, 2H), 7.73 (d, J = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 146.2, 139.6, 133.1, 129.6, 129.1, 128.9, 127.4, 127.1, 118.8, 111.0. MS (m/e)= 179[M^+].[13].



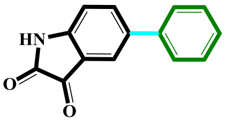
Colorless solid, m.p. 55°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.28 – 7.34 (m, 3H), 7.52 – 7.59 (m, 2H), 7.65 – 7.69 (m, 2H), 7.98 – 8.04 (m, 2H), 10.08 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 191.6, 192.0, 147.2, 140.0, 135.3, 130.2, 130.0, 128.5, 127.7, 127.3. MS (m/e)= 182[M^+].[14].



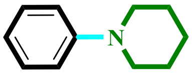
Light brown color solid, m.p. 50°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 5.00 (s, br, 2H), 6.73 – 6.82 (m, 2H), 7.28 – 7.50 (m, 5H), 7.50 – 7.66 (m, 2H), 8.59 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 145.7, 132.0, 131.1, 129.4, 128.0, 127.9, 119.6, 122.9, 118.9, 115.1, 94.8, 85.2. MS (m/e)= 169[M^+].[13].



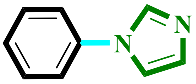
White solid, m.p. 47°C ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.40 (t, J = 7.3 Hz, 1H), 7.48 – 7.56 (m, 3H), 7.74 – 7.79 (m, 3H), 7.87 – 8.00 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 141.0, 138.4, 128.4, 133.4, 132.6, 128.5, 128.4, 128.1, 128.0, 127.3, 127.1, 127.0, 126.6, 125.9, 125.7, 125.3. MS (m/e)= 204 [M^+].[15].



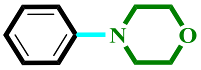
Orange solid; m.p. 153°C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm): 7.46 – 7.86 (m, 5H), 8.03 (d, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 8.62 (s, 1H), 11.21 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ*(ppm): 189.7, 162.4, 149.6, 142.6, 139.3, 137.6, 133.5, 129.4, 129.1, 127.6, 127.4, 126.1, 122.9, 118.7. MS (m/e)= 223 [M$^+$].[16].



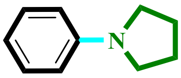
Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 1.62 (m, 6H), 3.73 (d, *J* = 5.0 Hz, 4H), 6.73–6.80 (m, 3H), 7.07 – 7.17 (m, 2H), 6.93 (m, 2H), 7.22 – 7.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 150.5, 129.1, 123.6, 114.4, 54.1, 26.5, 24.6. MS (m/e)= 161 [M$^+$].[17].



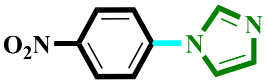
Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm): 7.15 – 7.45 (m, 5H), 7.42 – 7.49 (m, 2H), 7.80 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ*(ppm): 137.3, 135.6, 130.5, 29.9, 127.6, 121.5, 118.3. MS (m/e)= 144 [M$^+$].[18].



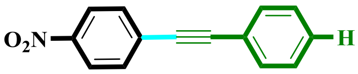
Purple solid. m.p. 52°C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm): 3.14 (t, *J* = 4.9 Hz, 4H), 3.30 (t, *J* = 4.9 Hz, 4H), 6.60 – 6.67 (m, 3H), 7.27 – 7.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ*(ppm): 151.2, 129.1, 119.9, 119.9, 115.6, 66.6, 49.2. MS (m/e)= 163 [M$^+$].[19].



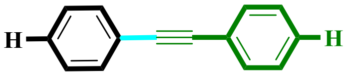
Pale yellow oil. m.p. 5°C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm): 2.05 (t, *J* = 12.9 Hz, 4H), 3.27 (t, *J* = 10.2 Hz, 4H), 6.55 (d, *J* =8.1 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 7.20 – 7.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ*(ppm): 150.7, 130.0, 121.8, 114.7, 51.3, 25.0. MS (m/e)= 147 [M$^+$].[20].



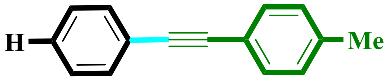
Light brown solid, m.p. 201°C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm): 7.21 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.93 (s, 1H), 8.30 – 8.34 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ*(ppm): 147.4, 143.7, 136.2, 130.2, 126.0, 118.6. MS (m/e)= 189 [M$^+$].[21].



Yellow solid, m.p. 111°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 6.66 – 7.41 (m, 3H), 7.54 – 7.69 (m, 4H), 8.22 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 147.0, 132.3, 132.0, 132.2, 129.7, 128.6, 123.8, 122.0, 94.8, 87.5. MS (m/e)= 223 [M$^+$].[22].



White solid, m.p. 59°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 6.93 – 7.28 (m, 5H), 7.44 – 7.98 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 131.5, 129.3, 128.8, 128.5, 128.3, 127.7, 126.5, 123.4, 89.5. MS (m/e)= 178 [M$^+$].[23].



Colorless solid, m.p. 71°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 2.22 (s, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.42 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm): 138.4. 131.6, 131.5, 129.4, 128.6, 128.1, 123.5, 120.2, 89.5, 88.7, 21.5. MS (m/e)= 192 [M$^+$].[23].

REFERENCES

[1] Zhang, J. Q., Cao, J., Li, W., Li, S. M., Li, Y. K., Wang, J. T., & Tang, L. (2017). Palladium/copper-catalyzed arylation of alkenes with N′-acyl arylhydrazines. *New Journal of Chemistry*, *41*(2), 437-441.

[2] Puthiaraj, P., & Pitchumani, K. (2014). Palladium nanoparticles supported on triazine functionalised mesoporous covalent organic polymers as efficient catalysts for Mizoroki–Heck cross coupling reaction. *Green Chemistry*, *16*(9), 4223-4233.

[3] Shen, C., Shen, H., Yang, M., Xia, C., & Zhang, P. (2015). A novel D-glucosamine-derived pyridyl-triazole@ palladium catalyst for solvent-free Mizoroki–Heck reactions and its application in the synthesis of Axitinib. *Green Chemistry*, *17*(1), 225-230.

[4] Sun, P., Zhu, Y., Yang, H., Yan, H., Lu, L., Zhang, X., & Mao, J. (2012). The ligand and base-free Pd-catalyzed oxidative Heck reaction of arylboronic acids and olefins. *Organic & biomolecular chemistry*, *10*(23), 4512-4515.

[5] Liu, X., Zhao, X., Zhu, J., & Xu, J. (2016). One-pot synthesis of magnetic palladium–NiFe2O4–graphene oxide composite: an efficient and recyclable catalyst for Heck reaction. *Applied Organometallic Chemistry*, *30*(5), 354-359.

[6] Kazemnejadi, M., Alavi, S. A., Rezazadeh, Z., Nasseri, M. A., Allahresani, A., & Esmaeilpour, M. (2019). Imidazolium chloride-Co (iii) complex immobilized on Fe 3 O 4@ SiO 2 as a highly active bifunctional nanocatalyst for the copper-, phosphine-, and base-free Heck and Sonogashira reactions. *Green Chemistry*, *21*(7), 1718-1734.

[7] Wang, Y., & Zhang, M. (2019). Schiff Base/CuI as a Novel Efficient Catalyst System for Cu–Catalyzed Heck Reaction in Water. *ChemistrySelect*, *4*(33), 9673-9676.

[8] Mao, S. L., Sun, Y., Yu, G. A., Zhao, C., Han, Z. J., Yuan, J., ... & Liu, S. H. (2012). A highly active catalytic system for Suzuki–Miyaura cross-coupling reactions of aryl and heteroaryl chlorides in water. *Organic & biomolecular chemistry*, *10*(47), 9410-9417.

[9] Liu, X., Mao, Y., & Lu, M. (2012). Complex of [BMIm] PF6 with PEG1000: a high efficient and recycle system for palladium-catalyzed Suzuki cross-coupling and Heck reaction. *Applied Organometallic Chemistry*, *26*(6), 305-309.

[10] Cheng, S., Wei, W., Zhang, X., Yu, H., Huang, M., & Kazemnejadi, M. (2020). A new approach to large scale production of dimethyl sulfone: a promising and strong recyclable solvent for ligand-free Cu-catalyzed C–C cross-coupling reactions. *Green Chemistry*, *22*(6), 2069-2076.

[11] Liu, K. M., Zhang, R., & Duan, X. F. (2016). Room-temperature cobalt-catalyzed arylation of aromatic acids: overriding the ortho-selectivity via the oxidative assembly of carboxylate and aryl titanate reagents using oxygen. *Organic & biomolecular chemistry*, *14*(5), 1593-1598.

[12] Keesara, S., & Parvathaneni, S. (2016). A 2-((4-Arylpiperazin-1-yl) methyl) phenol ligated Pd (ii) complex: an efficient, versatile catalyst for Suzuki–Miyaura cross-coupling reactions. *New Journal of Chemistry*, *40*(9), 7596-7603.

[13] Kohzadi, H., & Soleiman-Beigi, M. (2020). A recyclable heterogeneous nanocatalyst of copper-grafted natural asphalt sulfonate (NAS@ Cu): characterization, synthesis and application in the Suzuki–Miyaura coupling reaction. *New Journal of Chemistry*, *44*(28), 12134-12142.

[14] Zhang, Y., Jiang, X., Wang, J. M., Chen, J. L., & Zhu, Y. M. (2015). Palladium-catalyzed synthesis of aldehydes from aryl halides and tert-butyl isocyanide using formate salts as hydride donors. *RSC Advances*, *5*(22), 17060-17063.

[15] Taherpour, A. A., Taban, S., & Yari, A. (2015). One-pot Solvent-free Catalytic Dimerization Reaction of Phenylacetylene to 1-Phenylnaphthalene. *Journal of Chemical Sciences*, *127*(9), 1523-1530.

[16] Zhao, D., Wang, P., Xu, T., Wu, J., Wang, J., & Xu, S. (2016, March). Synthesis of 5-Substituted Indole-2, 3-dione. In *2016 4th International Conference on Machinery, Materials and Computing Technology* (pp. 776-779). Atlantis Press.

[17] Kumar, Atul, and Ajay Kumar Bishnoi. "Application of nanoparticle mediated N-arylation of amines for the synthesis of pharmaceutical entities using vit-E analogues as amphiphiles in water." *RSC advances* 5.26 (2015): 20516-20520.

[18] Nasseri, M. A., Rezazadeh, Z., Kazemnejadi, M., & Allahresani, A. (2020). A Co–Cu bimetallic magnetic nanocatalyst with synergistic and bifunctional performance for the base-free Suzuki, Sonogashira, and C–N cross-coupling reactions in water. *Dalton Transactions*, *49*(30), 10645-10660.

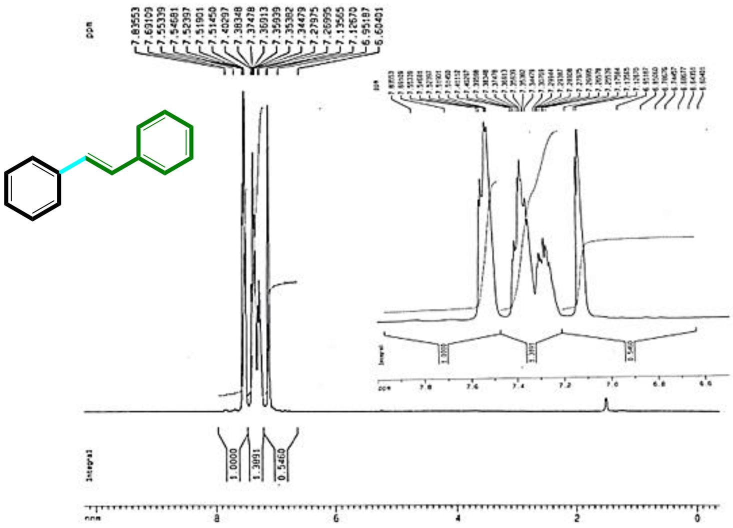
[19] Yong, F. F., & Teo, Y. C. (2010). Manganese-catalyzed cross-coupling reactions of aliphatic amines with aryl halides. *Tetrahedron Letters*, *51*(30), 3910-3912.

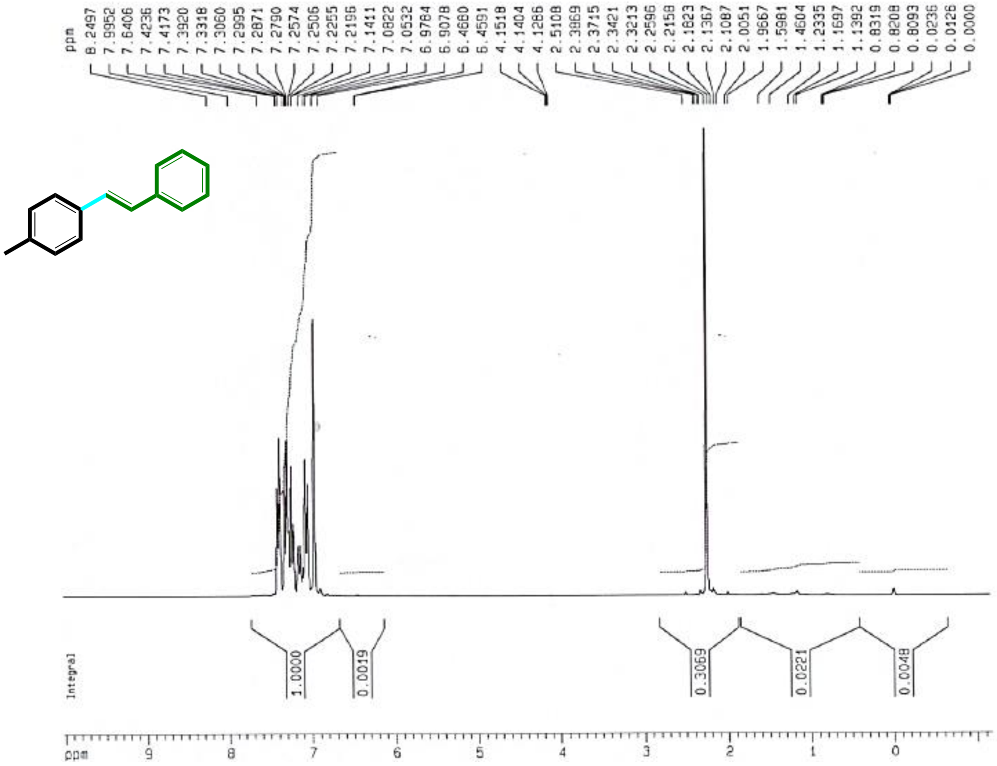
[20] Wang, D., Zhang, F., Kuang, D., Yu, J., & Li, J. (2012). A highly efficient Cu-catalyst system for N-arylation of azoles in water. *Green Chemistry*, *14*(5), 1268-1271.

[21] Nasseri, M. A., Alavi, S. A., Kazemnejadi, M., & Allahresani, A. (2020). Chiral Mn (III) Salen Complex Immobilized on CuFe2O4@ SiO2-NH2 NPs: A Cheap and Efficient Catalyst for N-arylation of Aryl Halides and Phenylboronic Acid Under Mild Conditions. *Letters in Organic Chemistry*, *17*(11), 857-863.

[22] Boyarskii, V. P. (2017). Sonogashira reaction catalyzed by palladium isocyanide complex modified in situ. *Russian Journal of General Chemistry*, *87*(8), 1663-1666.

[23] Nasseri, M. A., Alavi, S. A., Kazemnejadi, M., & Allahresani, A. (2019). The CuFe 2 O 4@ SiO 2@ ZrO 2/SO 4 2−/Cu nanoparticles: an efficient magnetically recyclable multifunctional Lewis/Brønsted acid nanocatalyst for the ligand-and Pd-free Sonogashira cross-coupling reaction in water. *RSC Advances*, *9*(36), 20749-20759.

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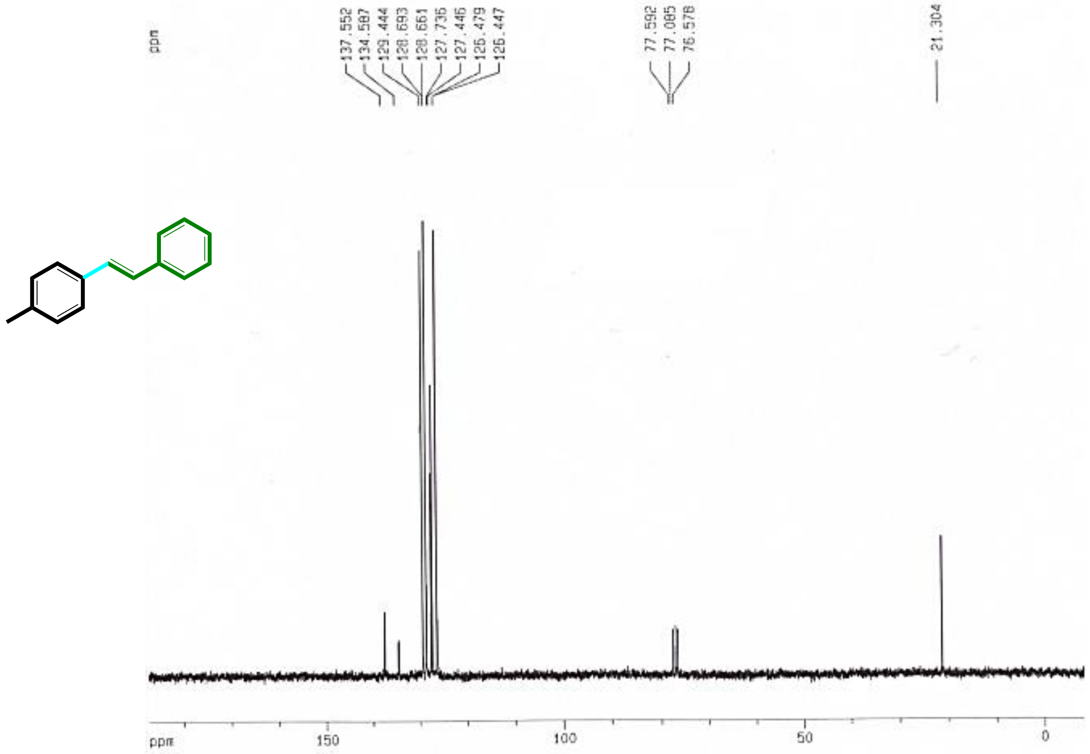
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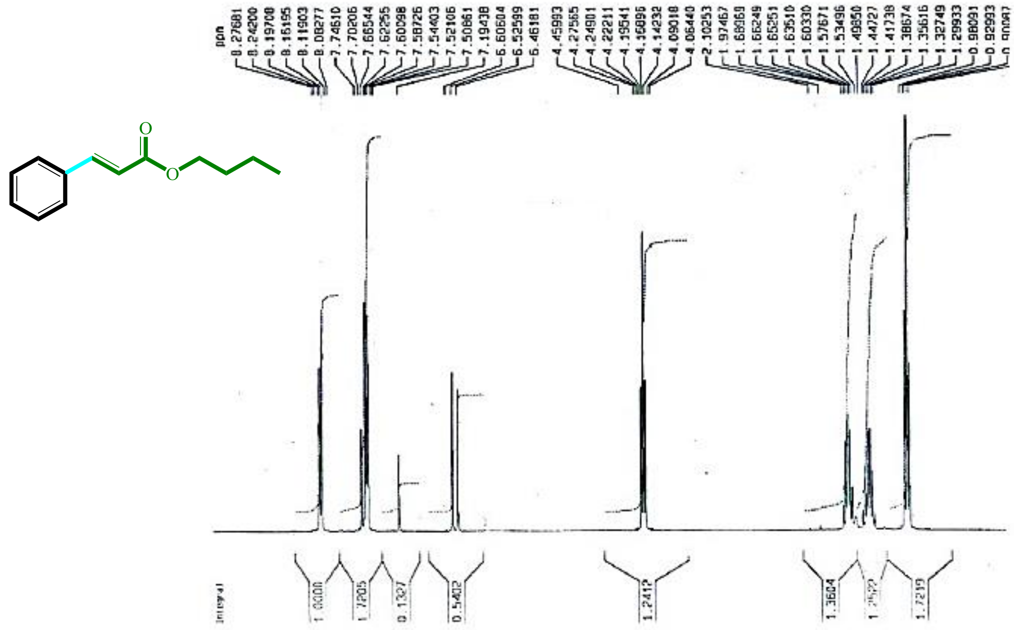
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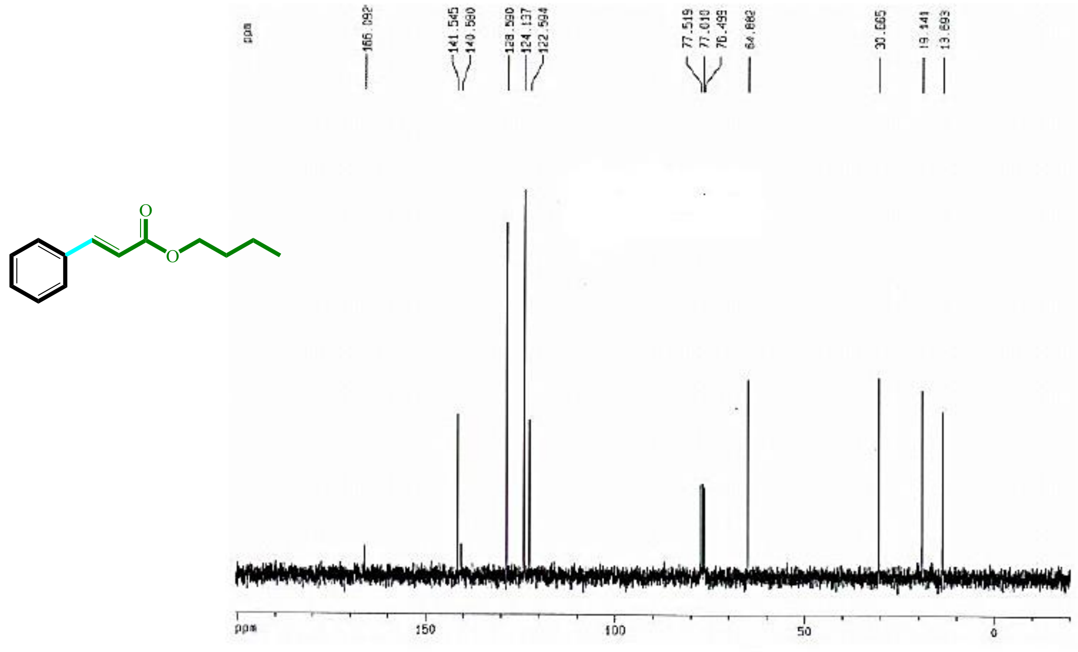
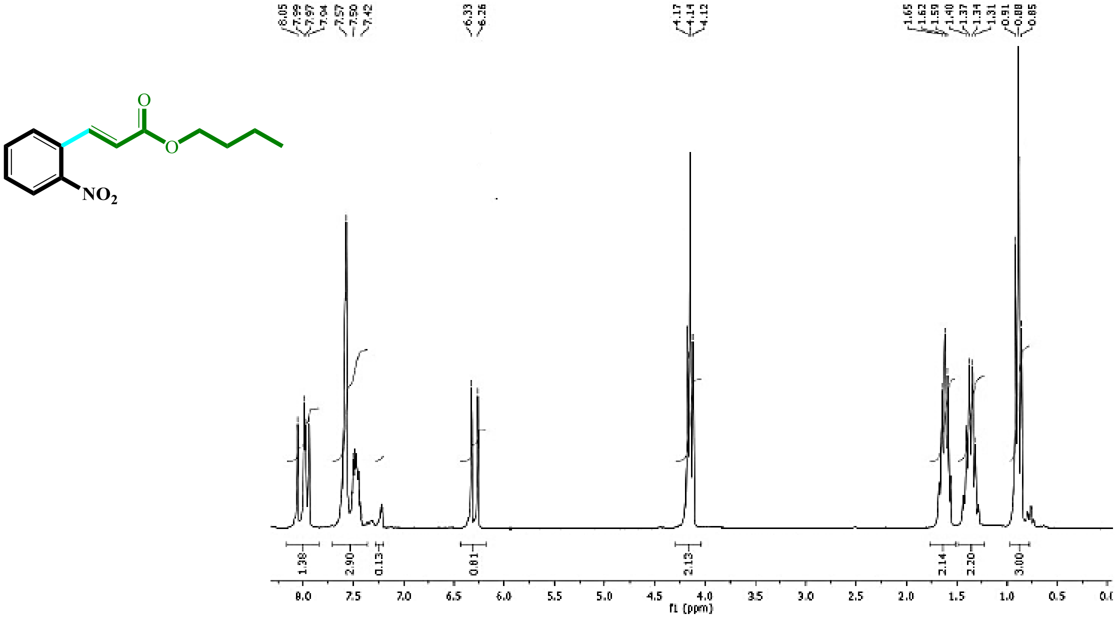
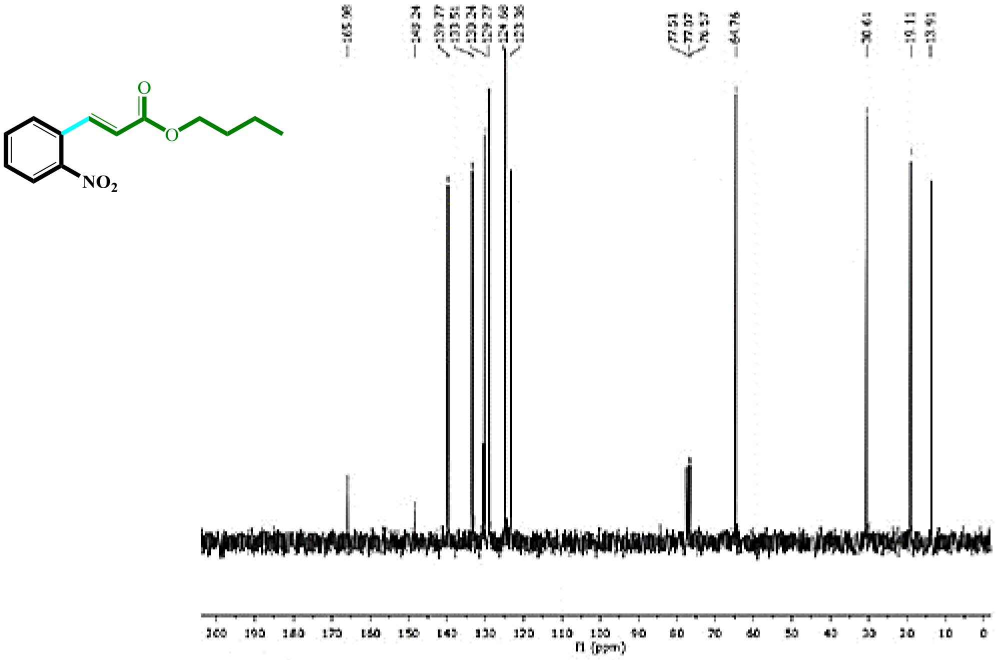
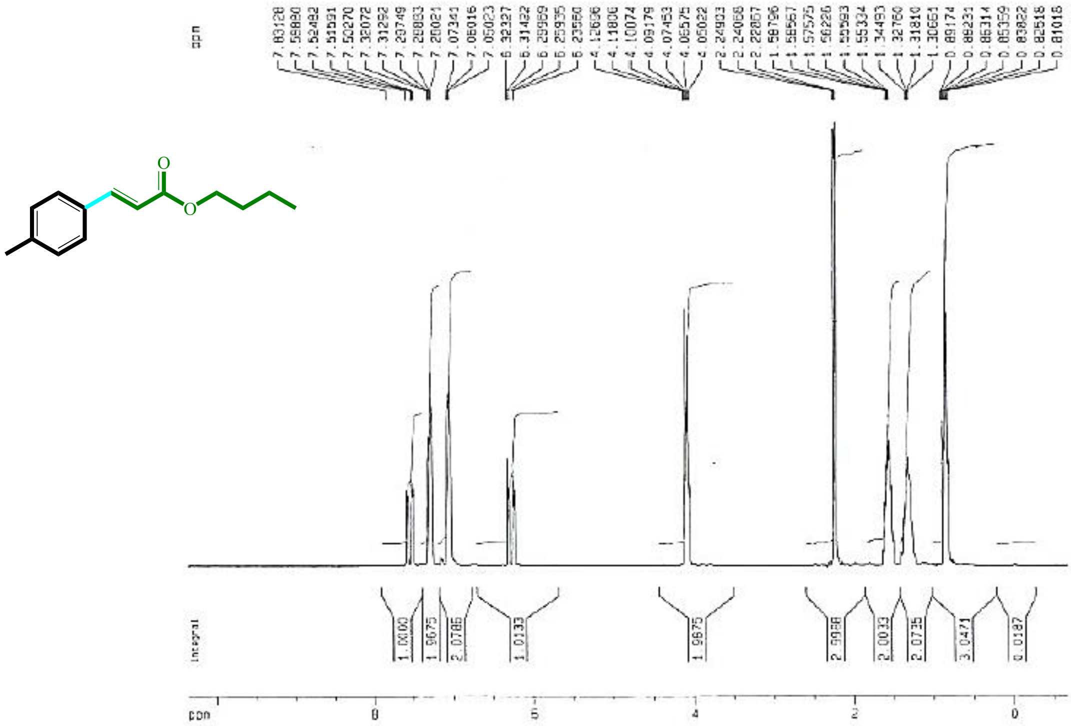
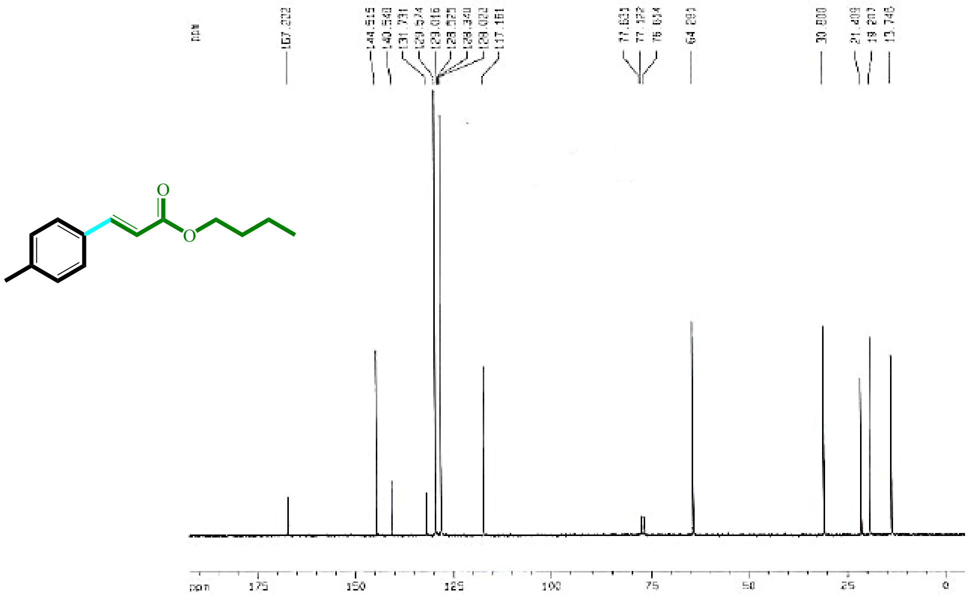
7.19438
6.60504
6.52599
6.46181
4.45993
4.27565
4.24901
4.22211
4.19541
4.16896
4.14232
4.09018
4.06440
2.10253
1.97467
1.68969
1.66249
1.65251
1.63510
1.60330
1.57671
1.53496
1.49850
1.44727
1.41738
1.38674
1.35616
1.32749
1.29933
0.98091
0.92993
Integral
1.0000
1.7205
0.1327
0.5402
1.2412
1.3604
1.2522
1.7219

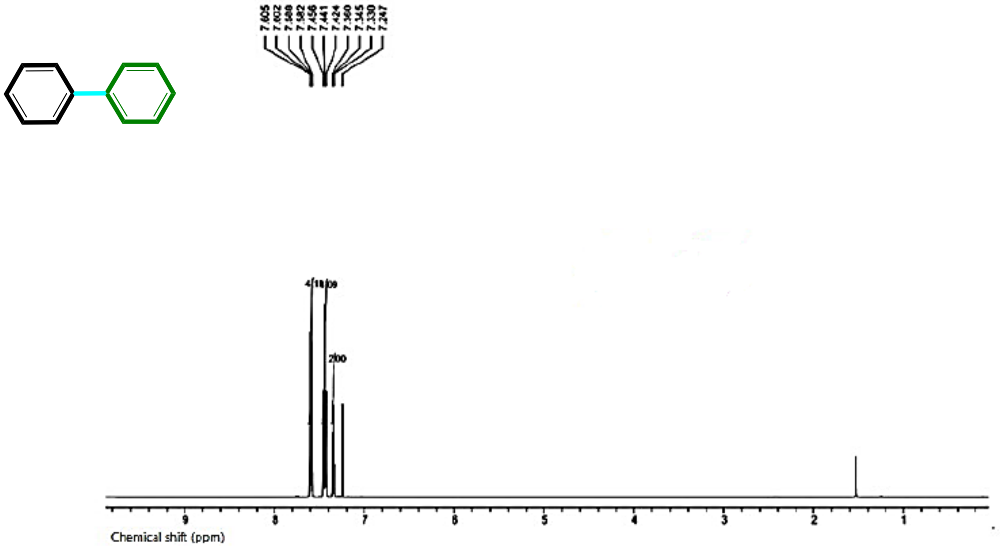

O
O
ppm
166.092
141.545
140.580
128.590
124.137
122.594
77.519
77.010
76.499
64.882
30.665
19.141
13.693
ppm
150
100
50
0

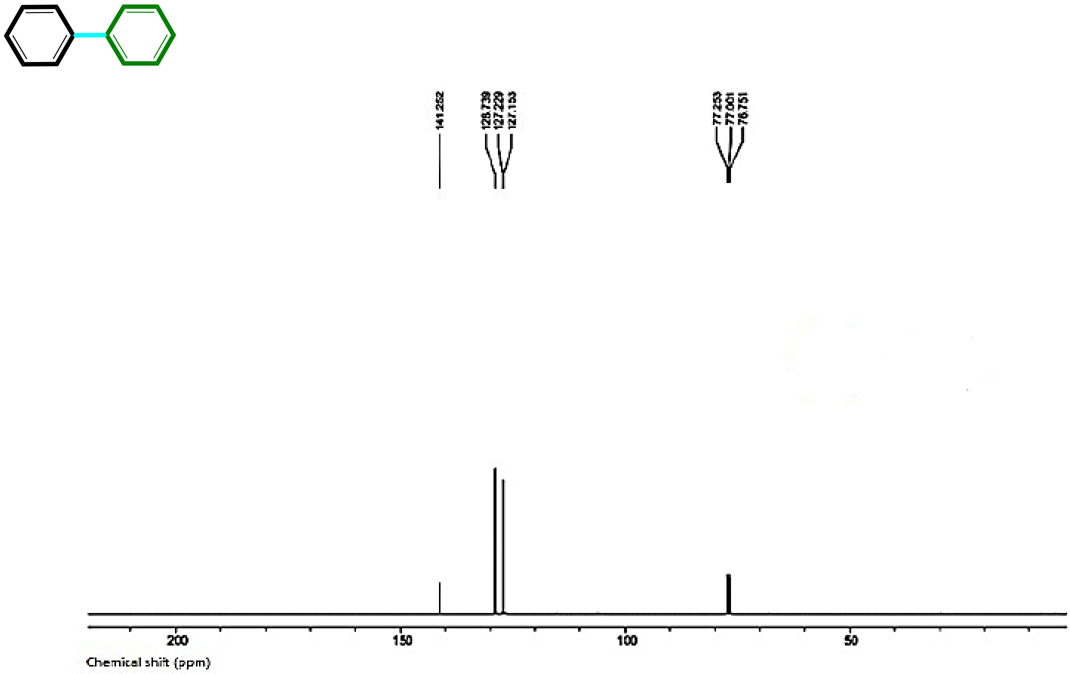

O
O
NO2
8.05
7.99
7.97
7.94
7.57
7.50
7.42
6.33
6.26
4.17
4.14
4.12
1.65
1.62
1.59
1.40
1.37
1.34
1.31
0.91
0.88
0.85
1.38
2.90
0.13
0.81
2.13
2.14
2.20
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

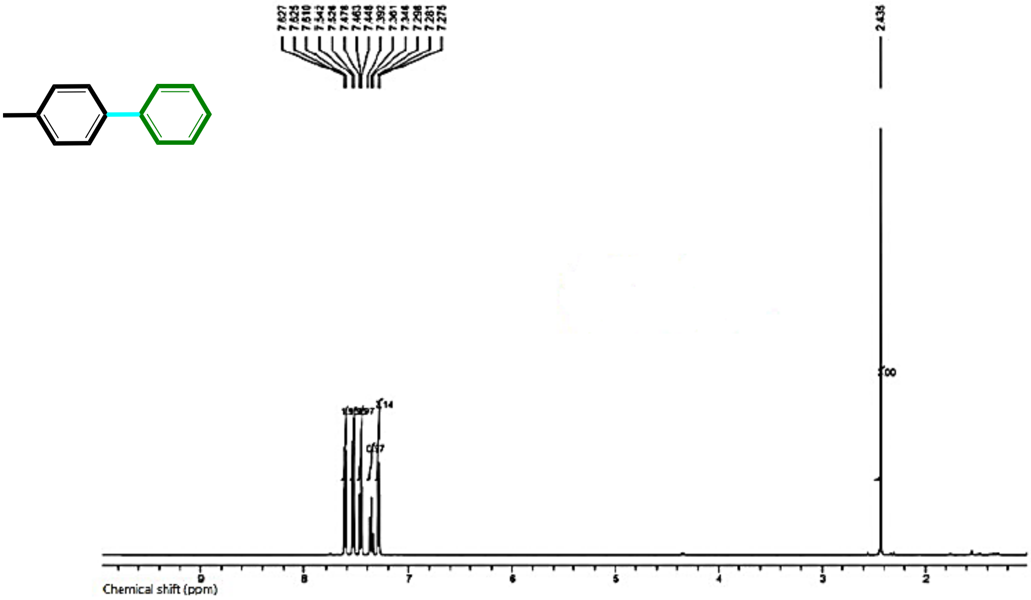

O
O
NO2
165.98
148.24
139.77
133.51
130.24
129.27
124.68
123.36
77.51
77.07
76.57
64.76
30.61
19.11
13.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


ppm
7.63128
7.59880
7.52492
7.51591
7.50270
7.32072
7.31292
7.29749
7.26883
7.28021
7.07341
7.05016
7.05023
6.32327
6.31432
6.29959
6.25935
6.23550
4.12606
4.11806
4.10074
4.09179
4.07453
4.06575
4.05022
2.24903
2.24068
2.22857
1.58796
1.58567
1.57575
1.56226
1.55593
1.55334
1.34493
1.32760
1.31810
1.30661
0.89174
0.88231
0.86314
0.85359
0.83822
0.82516
0.81016
O
O
Integral
1.0000
1.9675
2.0786
1.0133
1.9875
2.9958
2.0033
2.0735
3.0471
0.0187
ppm
8
6
4
2
0

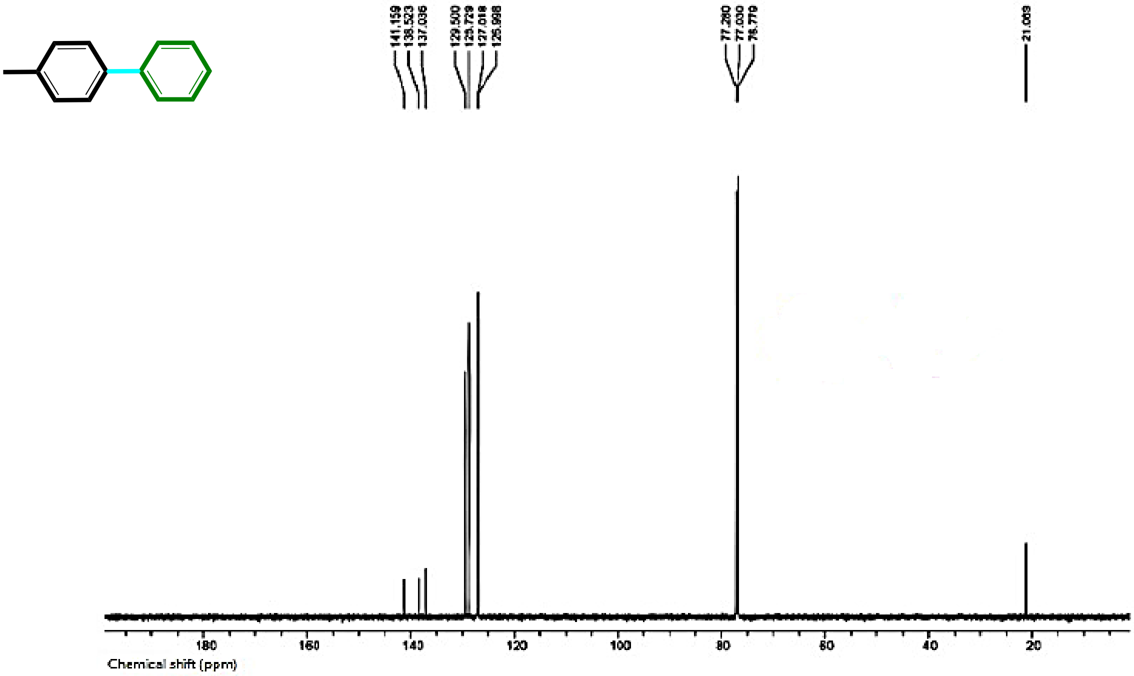

ppm
167.222
144.515
140.548
131.791
129.574
129.016
128.525
128.340
128.022
117.181
77.631
77.372
76.654
64.283
30.808
21.409
19.203
13.748
O
O
ppm
175
150
125
100
75
50
25
0


7.605
7.602
7.589
7.582
7.456
7.441
7.424
7.360
7.345
7.330
7.247
4.18
4.09
2.00
9
8
7
6
5
4
3
2
1
Chemical shift (ppm)

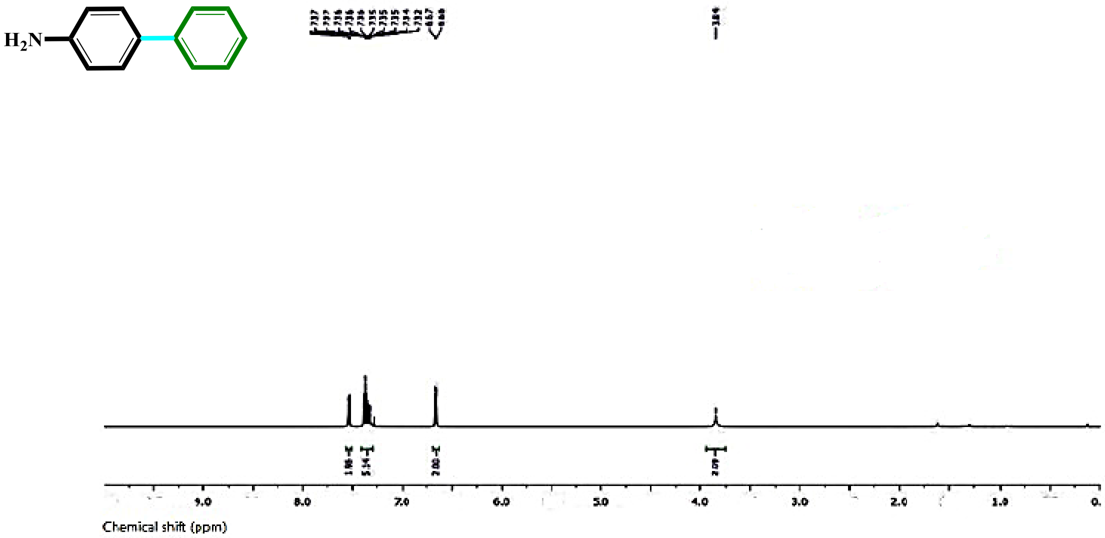

141.252
128.739
127.229
127.153
77.253
77.001
76.751
200
150
100
50
Chemical shift (ppm)

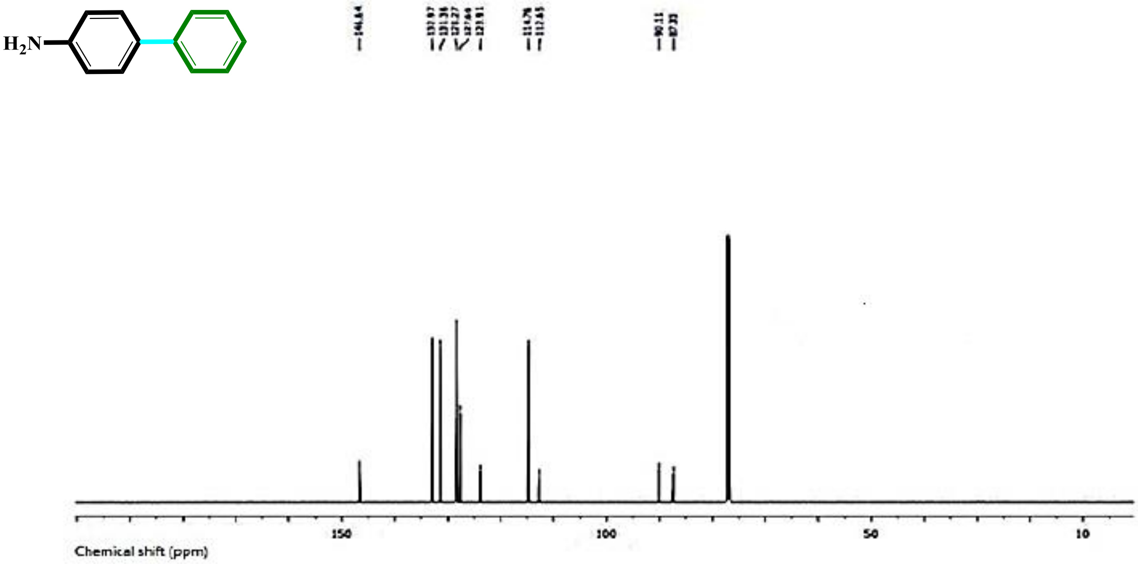


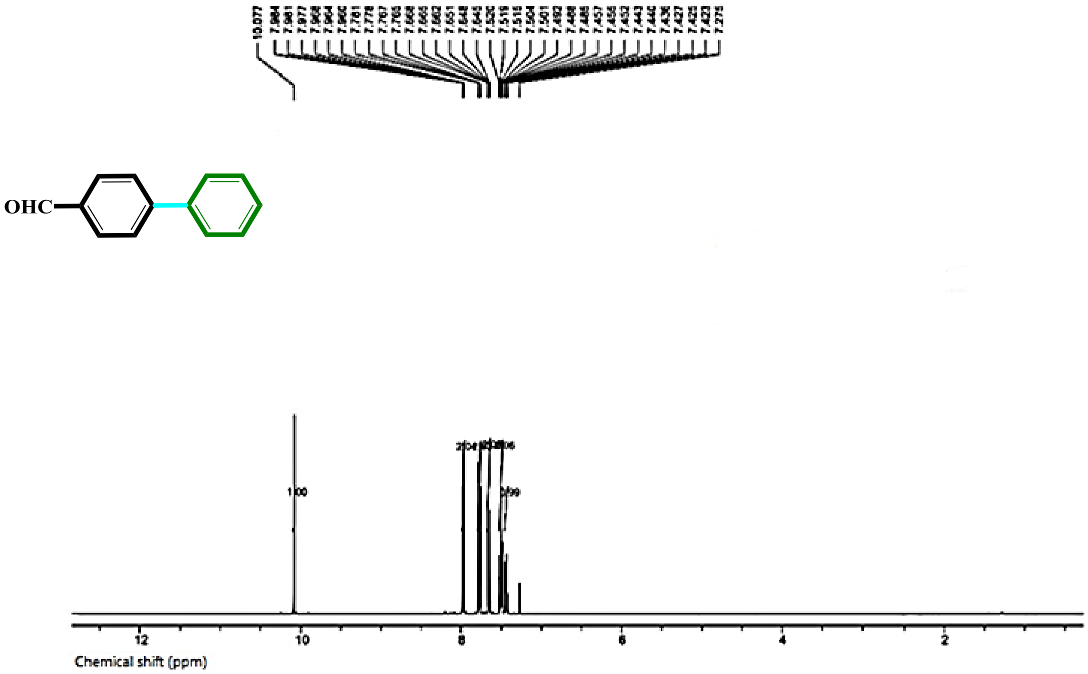
7.627
7.625
7.610
7.542
7.524
7.478
7.463
7.448
7.392
7.361
7.344
7.298
7.281
7.275
2.435
1.95
0.97
3.14
3.00
9
8
7
6
5
4
3
2
Chemical shift (ppm)

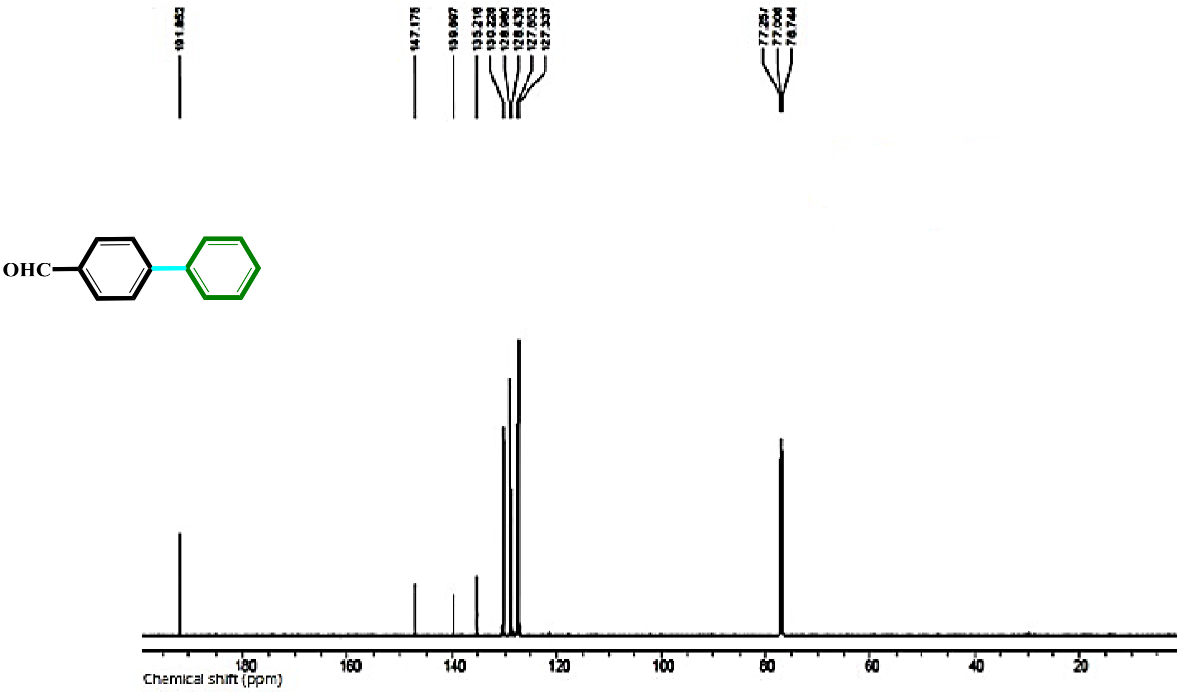


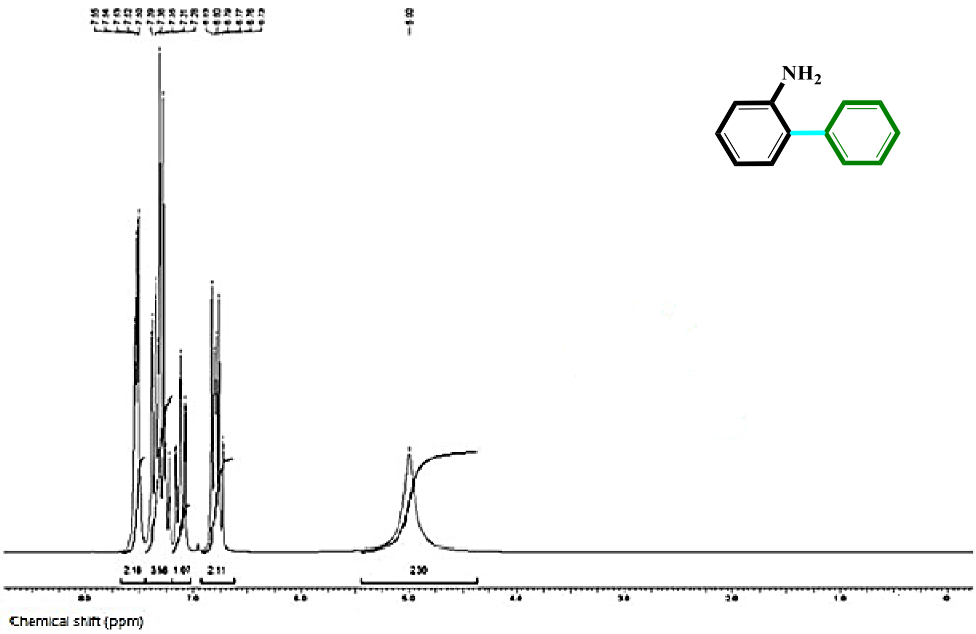
141.159
138.523
137.036
129.500
128.729
127.018
126.998
77.280
77.030
76.779
21.089
180
160
140
120
100
80
60
40
20
Chemical shift (ppm)

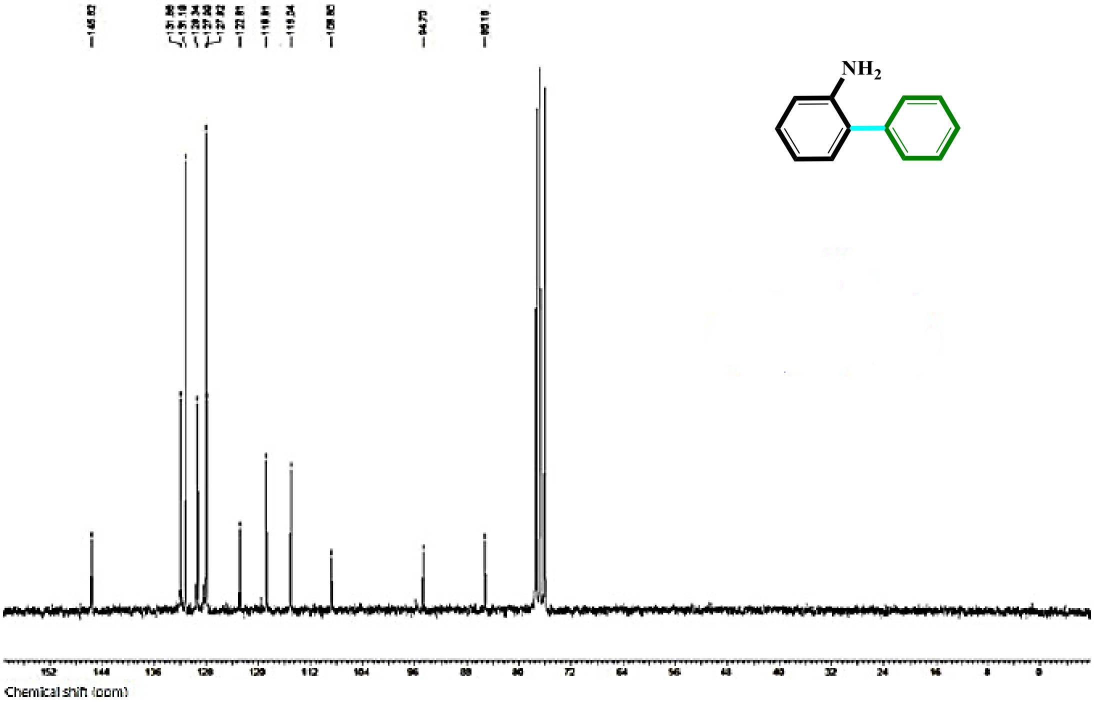

H$_2$N
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.32
6.67
6.66
3.84
1.98
5.14
2.00
2.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.
Chemical shift (ppm)

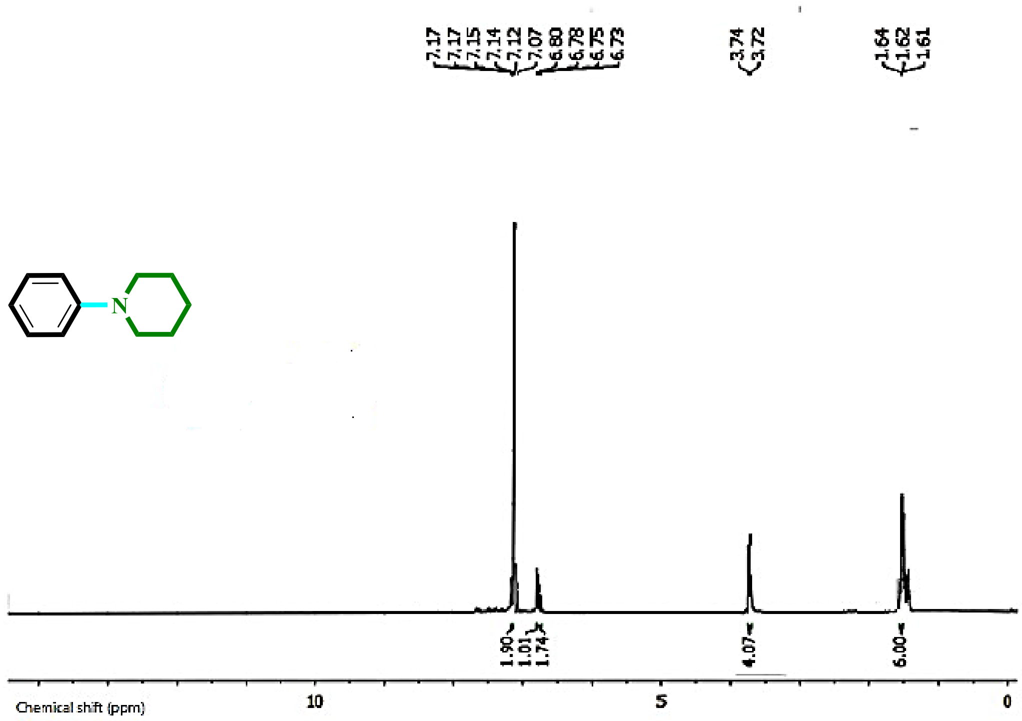

H$_2$N
146.84
132.97
131.36
129.27
127.66
123.91
114.76
112.65
90.11
87.32
150
100
50
10
Chemical shift (ppm)

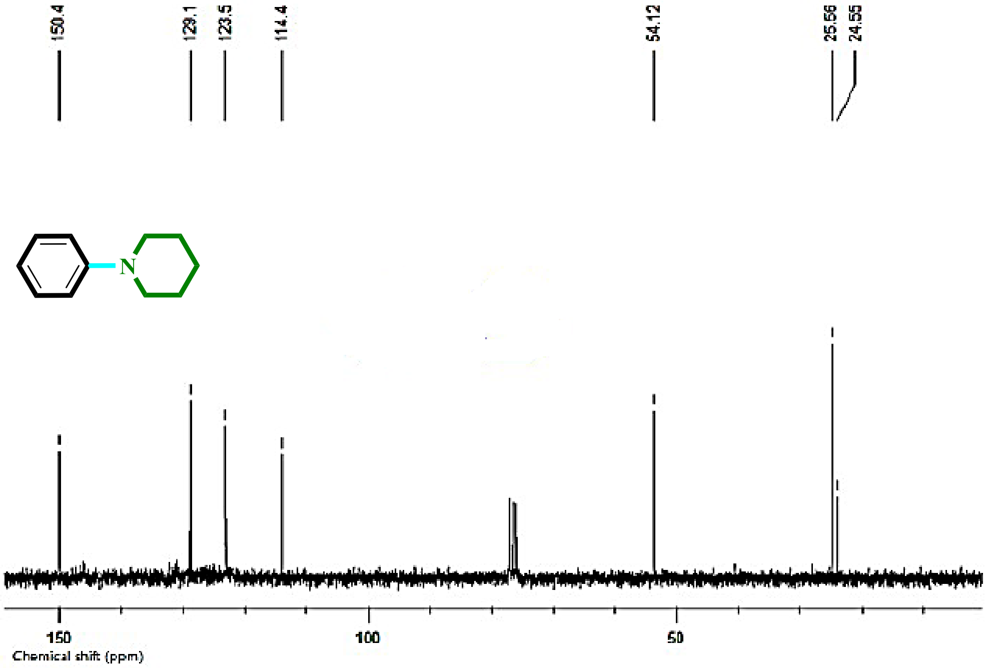

10.077
7.984
7.981
7.977
7.968
7.964
7.960
7.781
7.778
7.767
7.765
7.668
7.665
7.662
7.651
7.648
7.645
7.520
7.518
7.515
7.504
7.501
7.492
7.488
7.485
7.457
7.455
7.453
7.443
7.440
7.436
7.427
7.425
7.423
7.275
OHC
1.00
12
10
8
6
4
2
Chemical shift (ppm)

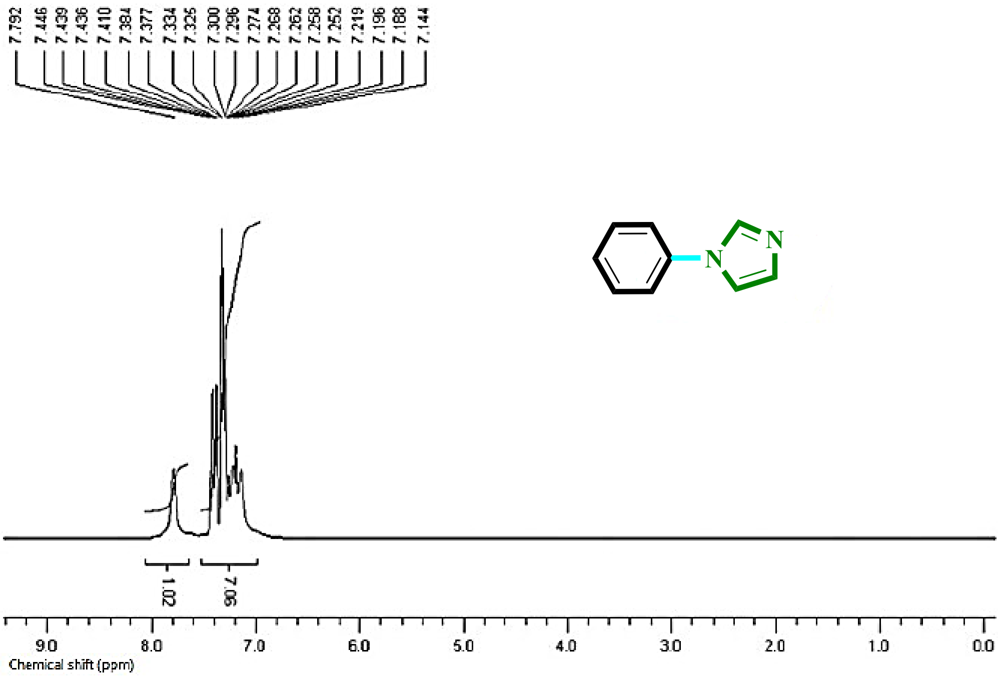

191.852
147.176
139.667
135.216
130.226
129.060
128.439
127.663
127.337
77.257
77.006
76.744
OHC
180
160
140
120
100
80
60
40
20
Chemical shift (ppm)

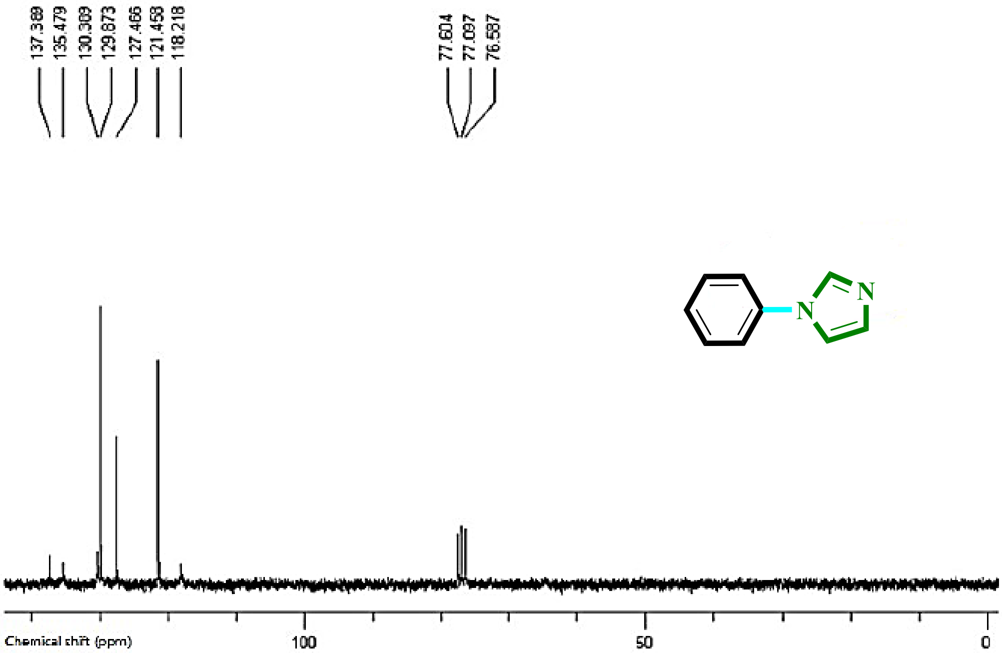

7.55
7.54
7.53
7.52
7.50
7.39
7.38
7.36
7.31
7.29
6.83
6.82
6.79
6.77
6.76
6.73
5.02
NH2
2.19
3.50
1.07
2.11
2.30
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
Chemical shift (ppm)

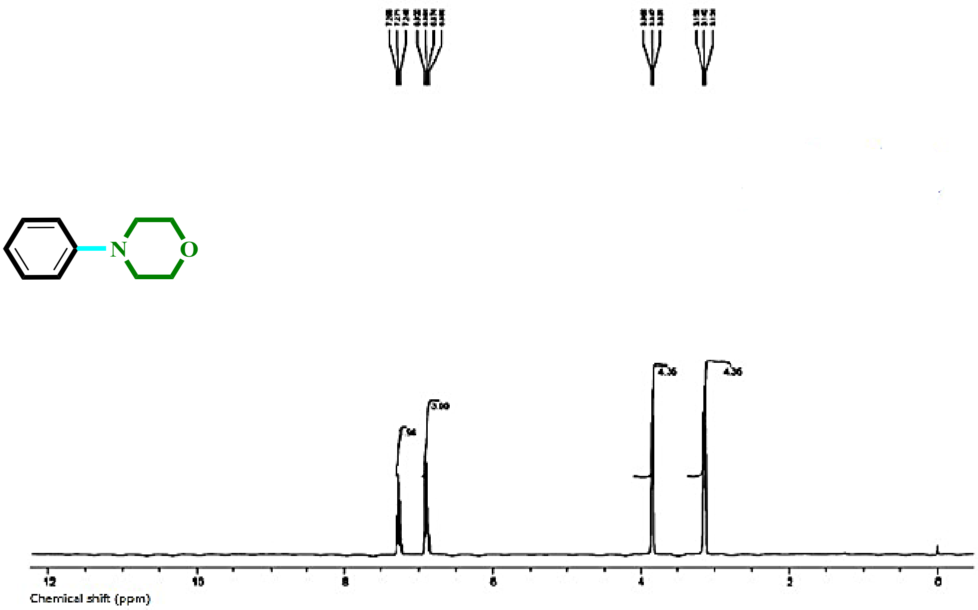

145.62
131.86
131.19
129.34
127.88
127.62
122.61
118.61
115.34
108.80
94.70
85.19
NH2
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical shift (ppm)

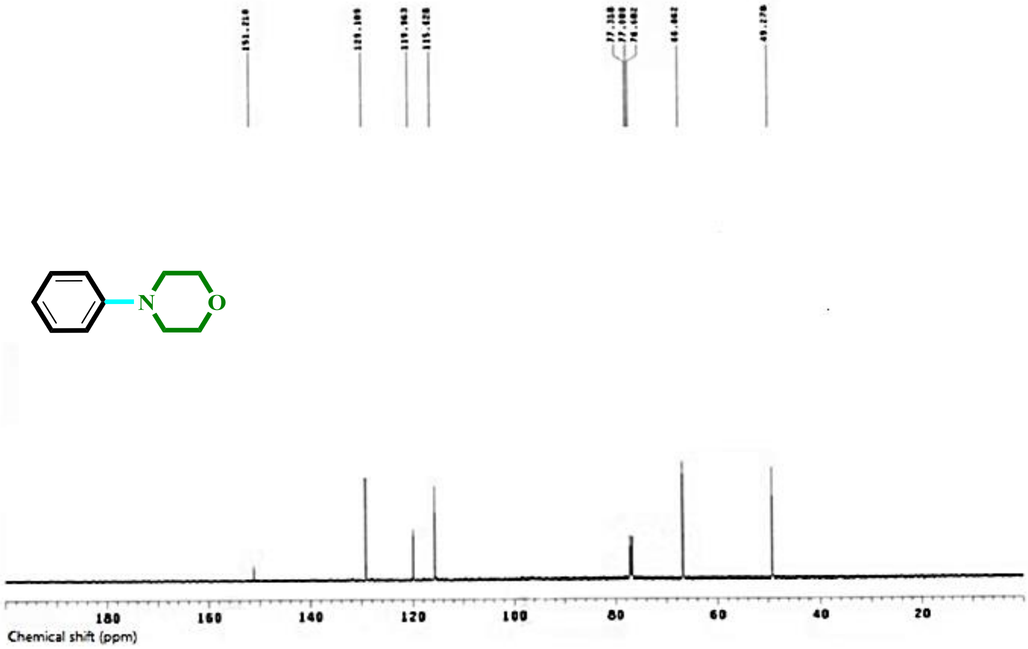

7.17
7.17
7.15
7.14
7.12
7.07
6.80
6.78
6.75
6.73
3.74
3.72
1.64
1.62
1.61
N
1.90
1.01
1.74
4.07
6.00
Chemical shift (ppm)
10
5
0

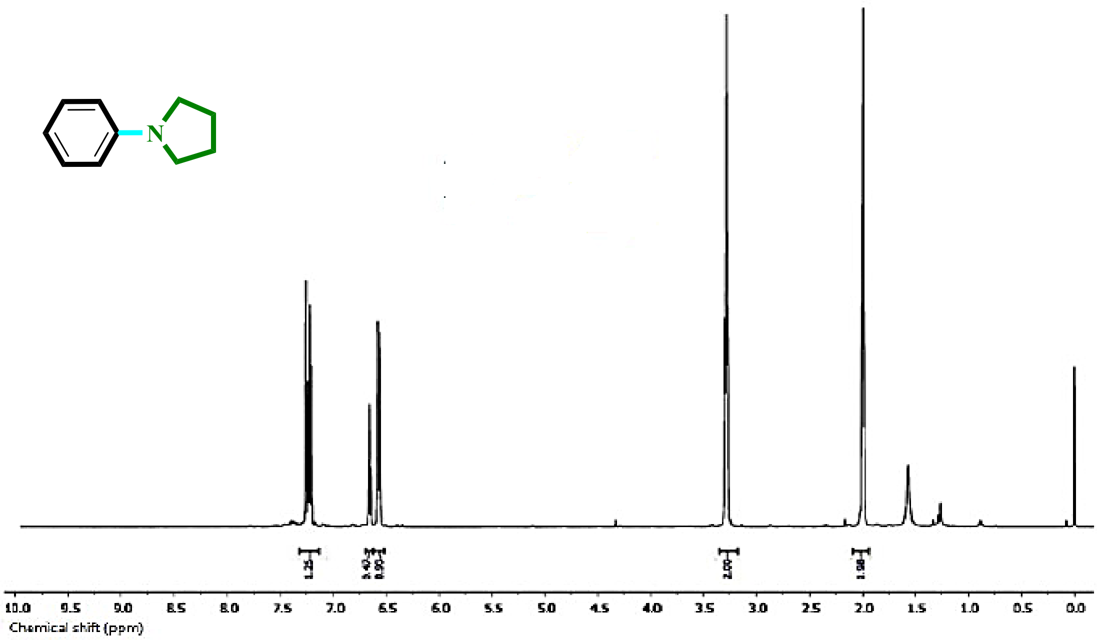

150.4
129.1
123.5
114.4
54.12
25.56
24.55
N
150
100
50
Chemical shift (ppm)

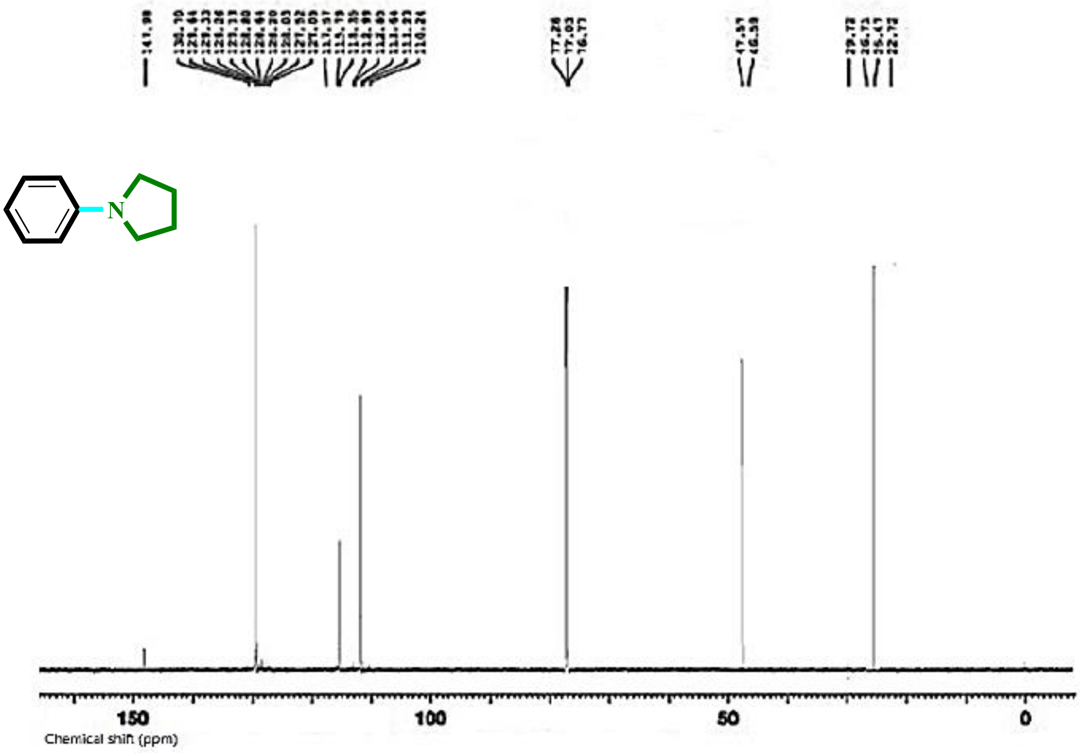

7.792
7.446
7.439
7.436
7.410
7.384
7.377
7.334
7.325
7.300
7.296
7.274
7.268
7.262
7.258
7.252
7.219
7.196
7.188
7.144
N
N
1.02
7.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)

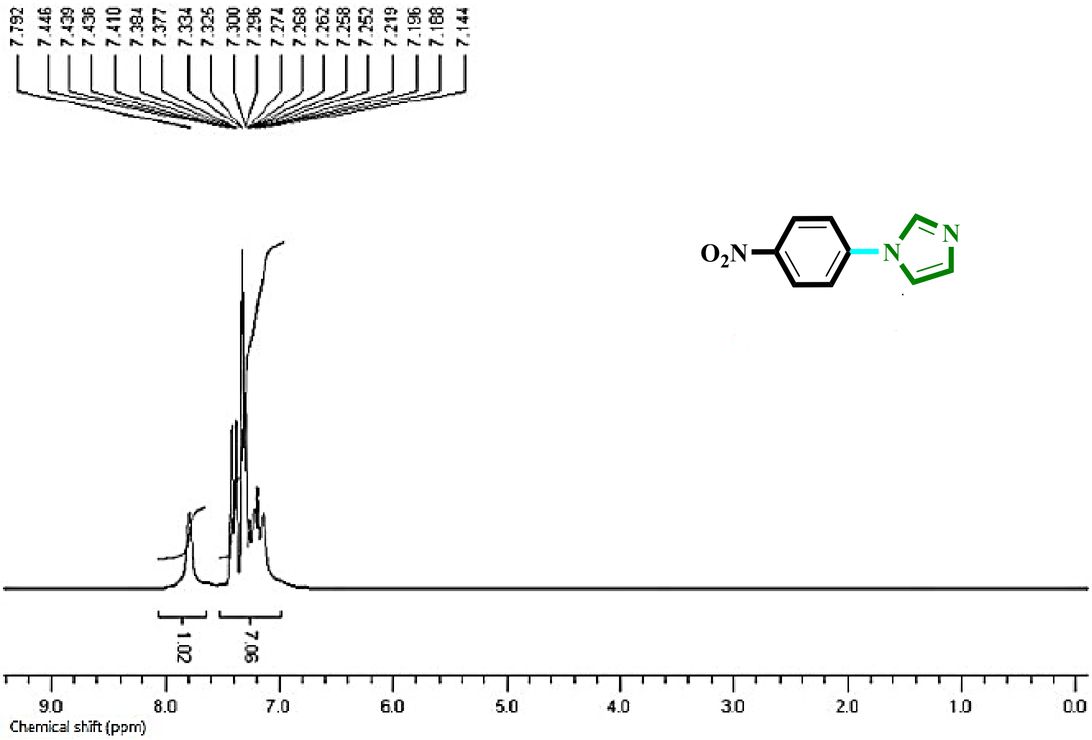

137.389
135.479
130.309
129.873
127.466
121.458
118.218
77.604
77.097
76.587
N
N
Chemical shift (ppm)
100
50
0

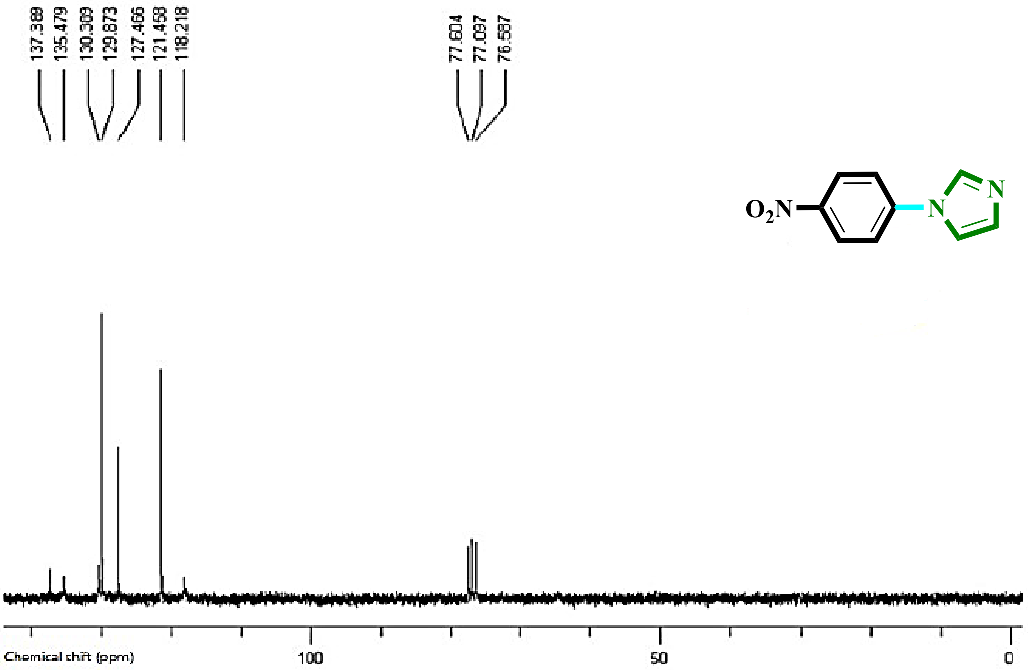

N
O
3.00
4.36
4.36
12
10
8
6
4
2
0
Chemical shift (ppm)

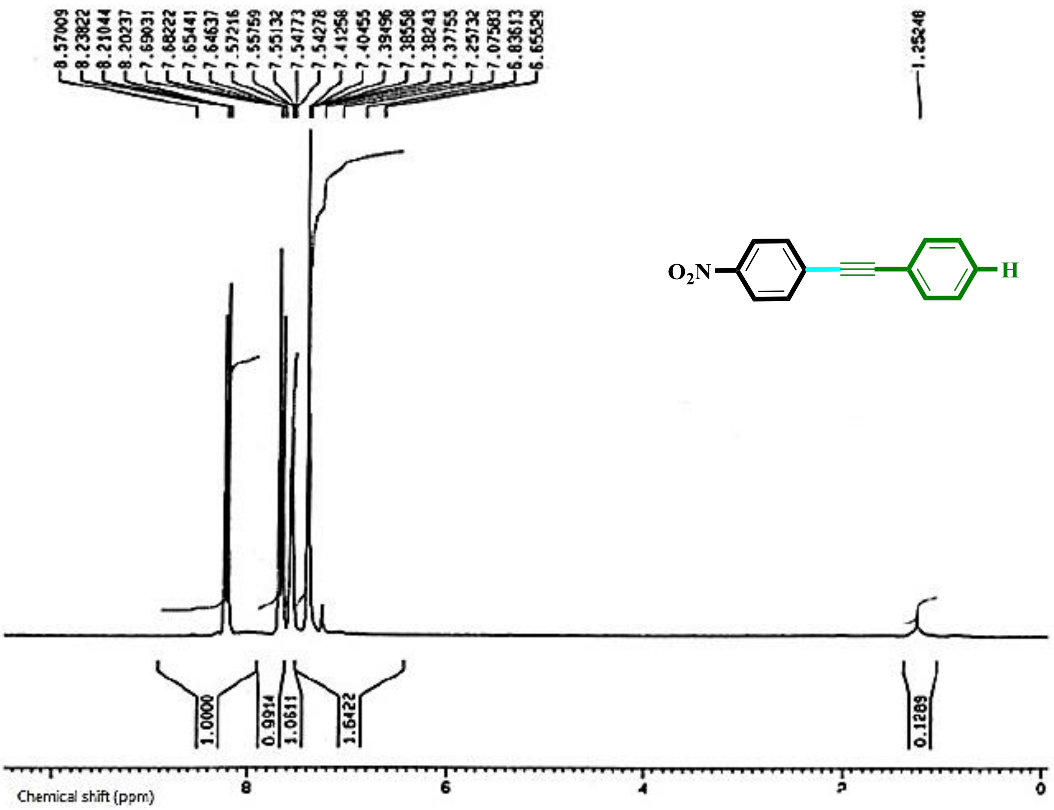

151.218
129.105
119.963
115.628
77.318
77.000
76.682
66.862
49.270
N
O
180
160
140
120
100
80
60
40
20
Chemical shift (ppm)

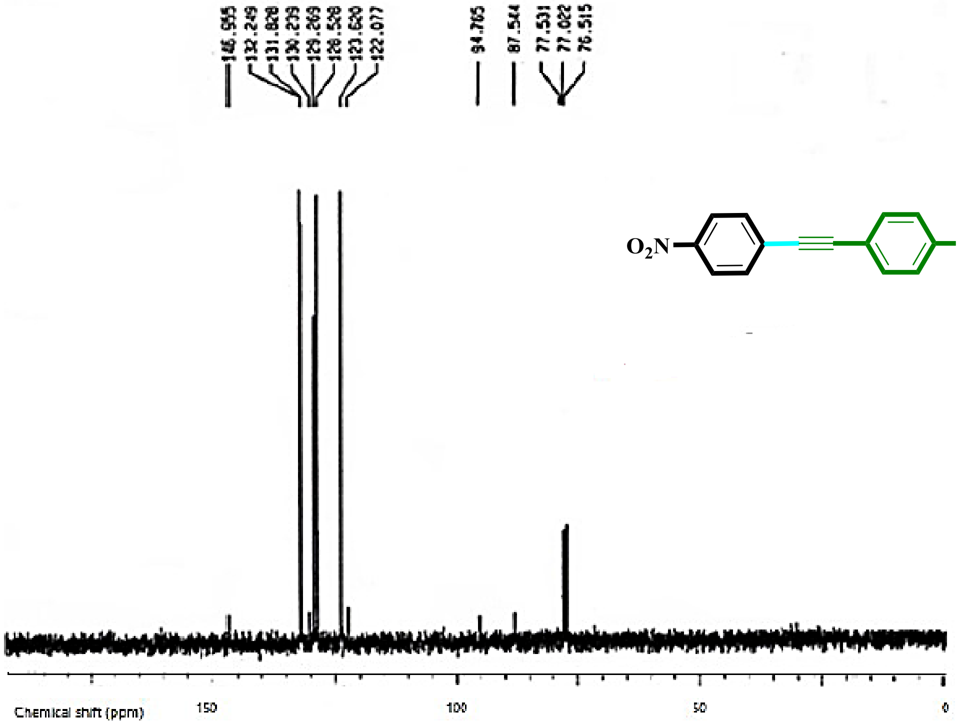
N
1.25
1.40
0.90
2.00
1.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)

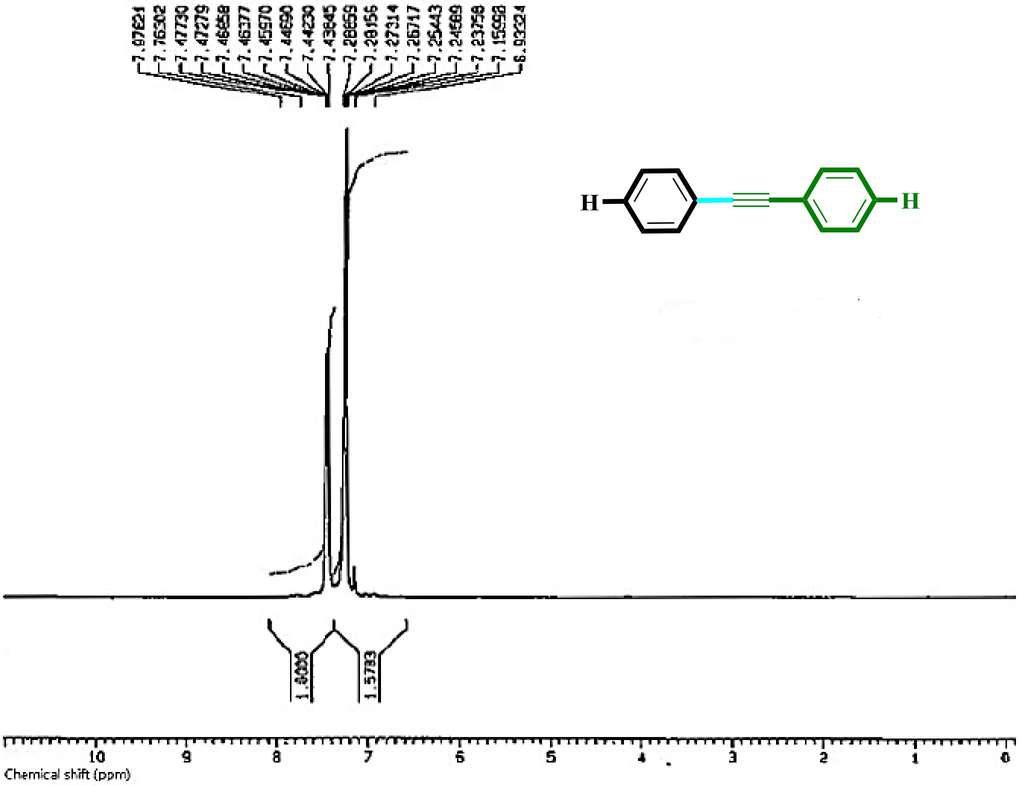
141.98
130.10
129.64
129.32
129.26
129.13
128.80
128.61
128.20
128.03
127.52
127.09
117.97
115.79
115.35
112.99
112.60
111.64
111.23
110.24
77.28
77.03
76.77
47.57
46.59
29.72
26.73
25.47
22.72
N
150
100
50
0
Chemical shift (ppm)

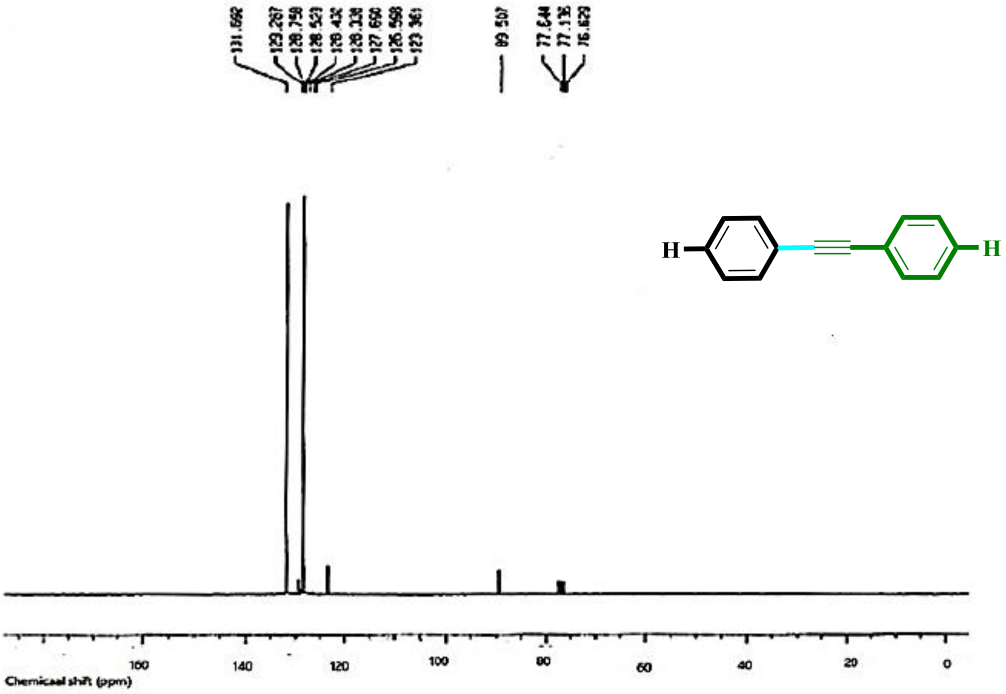

7.792
7.446
7.439
7.436
7.410
7.384
7.377
7.334
7.325
7.300
7.296
7.274
7.268
7.262
7.258
7.252
7.219
7.196
7.188
7.144
O_2N
N
N
1.02
7.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)

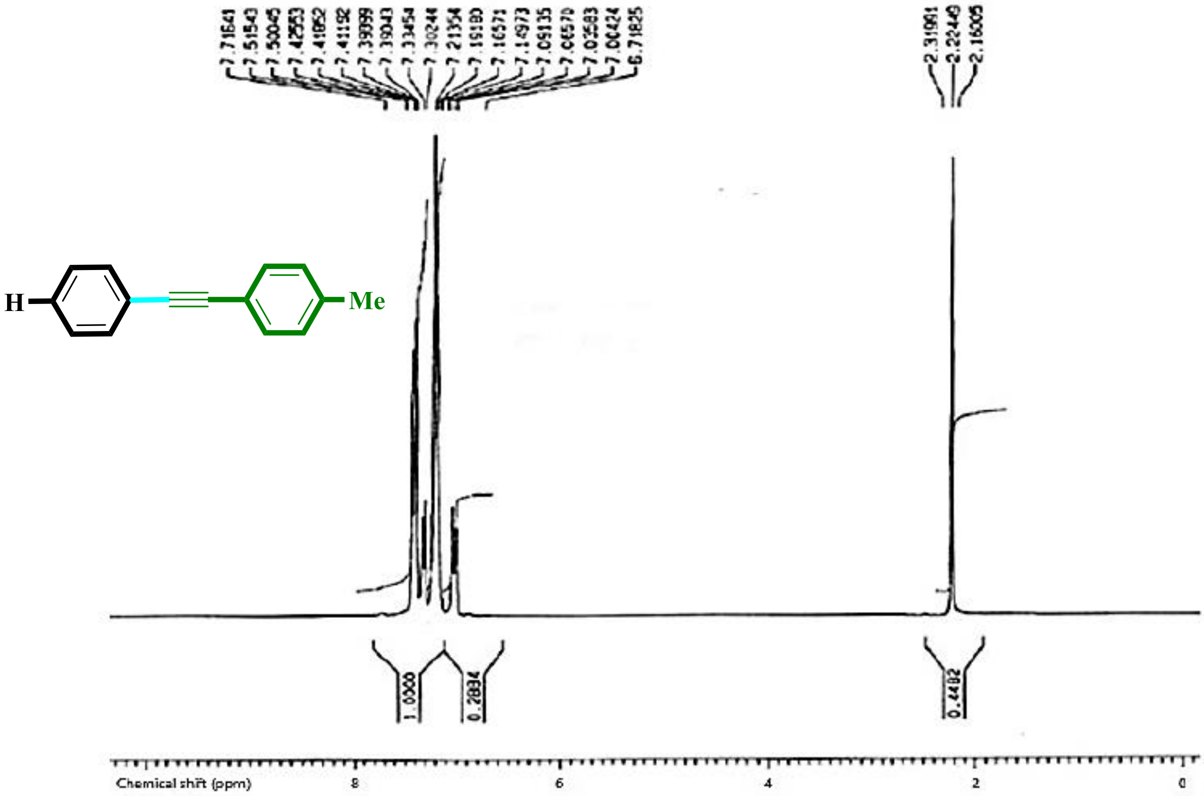

137.389
135.479
130.309
129.873
127.466
121.458
118.218
77.604
77.097
76.587
O_2N
N
N
Chemical shift (ppm)
100
50
0

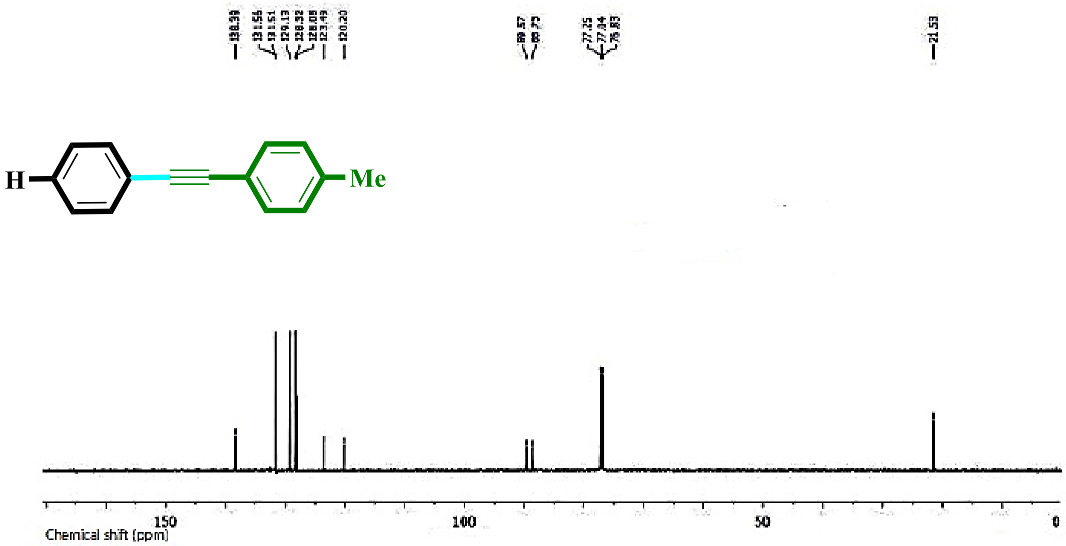

8.57009
8.23822
8.21044
8.20237
7.69031
7.68222
7.65441
7.64637
7.57216
7.55759
7.55132
7.54773
7.54278
7.41258
7.40455
7.39496
7.38558
7.38243
7.37755
7.25732
7.07583
6.83613
6.65529
1.25248
O_2N
H
1.0000
0.9914
1.0611
1.6422
0.1289
Chemical shift (ppm)
8
6
4
2
0


146.955
132.249
131.828
130.239
129.269
128.528
123.630
122.077
94.705
87.544
77.531
77.022
76.515
O_2N
H
Chemical shift (ppm)
150
100
50
0


7.97621
7.76302
7.47730
7.47279
7.46858
7.46377
7.45570
7.44690
7.44230
7.43645
7.28659
7.28156
7.27314
7.26717
7.25443
7.24589
7.23758
7.15698
6.93324
H
H
1.0000
1.5783
10
9
8
7
6
5
4
3
2
1
0
Chemical shift (ppm)


131.692
129.287
128.759
128.523
128.432
128.338
127.690
125.598
123.361
89.507
77.644
77.136
76.629
H
H
160
140
120
100
80
60
40
20
0
Chemicaal shift (ppm)


7.71641
7.51543
7.50045
7.42553
7.41852
7.41192
7.39399
7.39043
7.33454
7.30244
7.21354
7.19180
7.16571
7.14973
7.09135
7.06570
7.03583
7.00424
6.71825
2.31991
2.22445
2.16005
H
Me
1.0000
0.2894
0.4482
Chemical shift (ppm)
8
6
4
2
0


138.39
131.56
131.51
129.13
128.32
128.05
123.49
120.20
89.57
88.75
77.25
77.04
76.83
21.53
H
Me
150
100
50
0
Chemical shift (ppm)