Synthesis of indole-fused heteroacenes by cascade cyclisation involving rhodium(II)-catalysed intramolecular C–H amination

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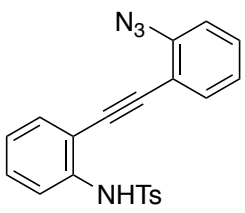
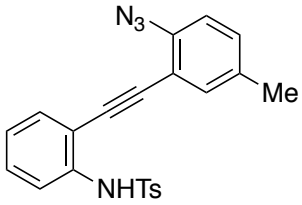
General. All reactions were carried out with standard Schlenk techniques under a nitrogen atmosphere. Column chromatography was carried out on Wakogel® C-200 (75–150 μm). Preparative thin-layer chromatography (TLC) was performed on Wakogel® B-5F. Proton chemical shifts (δ) were referenced to residual $CHCl_3$ (at 7.26 ppm), THF-d_8 (at 1.72 and 3.57 ppm) or acetone-d_6 (at 2.09 ppm). Carbon chemical shifts (δ) were referenced to $CDCl_3$ (at 77.0 ppm), THF-d_8 (at 25.3 and 67.5 ppm) or acetone-d_6 (at 29.9 and 206.3 ppm).

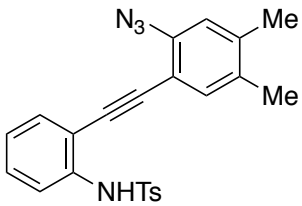
Materials. 2-[(2-Azidophenyl)ethynyl]anilines **1**, 2-[(2-azidophenyl)ethynyl]phenols **4**, and 2-[(2-azidophenyl)ethynyl]biphenyl **6** were prepared by the literature methods (Refer to pages 25–27 for the procedures and references). All other reagents and solvents were obtained from commercial sources and used without further purification.



2-[(2-Azidophenyl)ethynyl]-*N*-tosylaniline (1a).[1] Brown solid, mp 122–125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 7.00 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.14–7.19 (m, 3H), 7.24–7.29 (m, 2H), 7.34 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.41–7.47 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 8.55 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 90.5, 92.8, 112.8, 113.9, 117.7, 118.0, 123.5, 124.6, 127.2, 129.5, 129.7, 130.0, 130.6, 131.6, 136.2, 138.7, 141.9, 143.7; HRMS (ESI) calcd for $C_{21}H_{16}N_4NaO_2S$ $[M + Na]^+$ 411.0886, found 411.0889; IR (ν/cm^{-1}): 3233, 2163, 1480, 1291, 1158, 919.

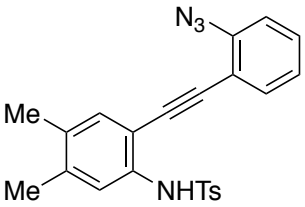


2-[(2-Azido-5-methylphenyl)ethynyl]-*N*-tosylaniline (1b). Pale yellow solid, mp 183–184 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.34 (s, 3H), 6.97–7.02 (m, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.20–7.29 (m, 3H), 7.31–7.35 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 8.59 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.5, 21.4, 90.0, 92.9, 112.8, 113.6, 117.5, 117.9, 123.4, 127.1, 129.5, 129.6, 130.5, 130.8, 131.8, 134.5, 136.2, 138.6, 139.2, 143.7; HRMS (ESI) calcd for $C_{22}H_{18}N_4NaO_2S$ $[M + Na]^+$ 425.1043, found 425.1045; IR (ν/cm^{-1}): 3233, 2163, 1480, 1291, 1158, 919.

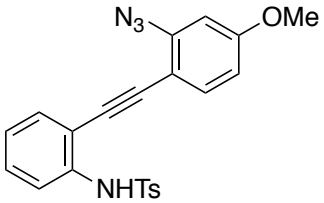


2-[(2-Azido-4,5-dimethylphenyl)ethynyl]-*N*-tosylaniline (1c). Pale yellow solid, mp 173–176 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.32 (s, 3H), 2.32 (s, 3H), 6.96–7.01 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.21 (s, 1H), 7.21–7.26 (m, 1H), 7.31 (dd, *J* = 7.7, 1.2 Hz,

1H), 7.67 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 8.52 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.0, 20.1, 21.5, 89.6, 93.1, 111.2, 113.2, 118.1, 118.8, 123.5, 127.2, 129.46, 129.51, 130.4, 132.3, 133.4, 136.3, 138.5, 139.4, 139.6, 143.7; HRMS (ESI) calcd for $C_{23}H_{20}N_4NaO_2S$ $[M + Na]^+$ 439.1199, found 439.1201; IR (ν/cm^{-1}): 3250, 2119, 1485, 1340, 1270, 1158.

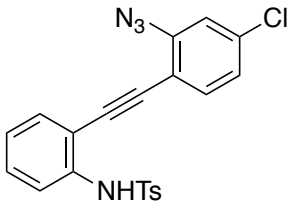


2-[(2-Azidophenyl)ethynyl]-4,5-dimethyl-*N*-tosylaniline (1d). Pale yellow solid, mp 171–174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H), 2.23 (s, 3H), 2.31 (s, 3H), 7.09 (s, 1H), 7.11–7.17 (m, 3H), 7.23 (d, J = 8.5 Hz, 1H), 7.37–7.43 (m, 2H), 7.47 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 8.33 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.0, 20.3, 21.5, 90.9, 91.8, 110.4, 114.3, 117.7, 119.9, 124.6, 127.2, 129.5, 129.7, 131.2, 131.5, 132.3, 136.3, 136.5, 139.2, 141.7, 143.5; HRMS (ESI) calcd for $C_{23}H_{20}N_4NaO_2S$ $[M + Na]^+$ 439.1199, found 439.1198; IR (ν/cm^{-1}): 3258, 2123, 1483, 1155.

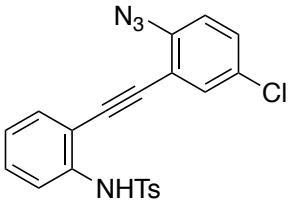


2-[(2-Azido-4-methoxyphenyl)ethynyl]-*N*-tosylaniline (1e). Yellow solid, mp 150–152 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.88 (s, 3H), 6.70 (dd, J = 8.8, 2.3 Hz, 1H), 6.75–6.77 (m, 1H), 6.96–7.01 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.21–7.26 (m, 1H), 7.29–7.32 (m, 1H), 7.37 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 8.49 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5, 55.6, 89.1, 92.9, 103.8, 106.5, 110.7, 113.3, 118.1, 123.5, 127.2, 129.3, 129.5, 130.2, 132.7, 136.3, 138.3, 143.4, 143.7, 161.1; HRMS (ESI) calcd

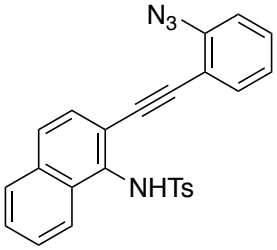
for $C_{22}H_{18}N_4NaO_3S$ $[M + Na]^+$ 441.0992, found 441.0995; IR (ν/cm^{-1}): 3242, 2109, 1333, 1233, 1157.



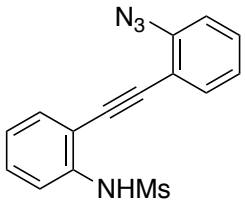
2-[(2-Azido-4-chlorophenyl)ethynyl]-*N*-tosylaniline (1f). Yellow solid, mp 150–153 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 7.00 (dt, J = 1.5, 7.5 Hz, 1H), 7.14 (dd, J = 8.3, 2.2 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.23–7.30 (m, 2H), 7.33 (dd, J = 7.8, 1.3 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.72–7.76 (m, 2H), 8.47 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5, 91.4, 91.8, 112.5, 112.6, 118.0, 118.1, 123.6, 125.1, 127.2, 129.6, 130.1, 130.6, 132.4, 135.7, 136.3, 138.8, 143.2, 143.9; HRMS (ESI) calcd for $C_{21}H_{15}ClN_4NaO_2S$ $[M + Na]^+$ 445.0496, found 445.0495; IR (ν/cm^{-1}): 3245, 2107, 1478, 1402, 1335, 1156.



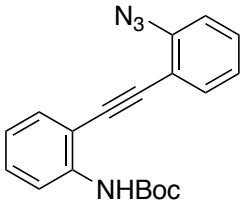
2-[(2-Azido-5-chlorophenyl)ethynyl]-*N*-tosylaniline (1g). Brown solid, mp 152–155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.95–7.04 (m, 1H), 7.16–7.20 (m, 3H), 7.26–7.31 (m, 1H), 7.34 (dd, J = 7.2, 1.2 Hz, 1H), 7.38 (dd, J = 8.5, 3.0 Hz, 1H), 7.42 (d, J = 2.5 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H), 8.47 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5, 91.4, 91.7, 112.3, 115.4, 118.1, 118.8, 123.6, 127.2, 129.6, 129.85, 129.91, 130.2, 130.8, 131.1, 136.2, 138.9, 140.6, 143.9; HRMS (ESI) calcd for $C_{21}H_{15}ClN_4NaO_2S$ $[M + Na]^+$ 445.0496, found 445.0496; IR (ν/cm^{-1}): 3240, 2134, 1478, 1286, 1156, 1090.



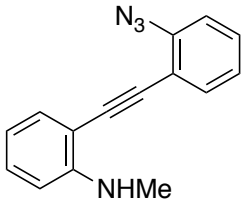
2-[(2-Azidophenyl)ethynyl]-*N*-tosyl-1-naphthylamine (1h). Black solid, mp 94–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.22 (s, 3H), 6.89 (d, *J* = 8.0 Hz, 2H), 7.11–7.16 (m, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.28 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.33–7.38 (m, 3H), 7.39–7.45 (m, 2H), 7.54–7.58 (m, 1H), 7.60–7.65 (m, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 8.67 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 91.5, 91.7, 114.5, 117.2, 118.2, 124.6, 126.3, 126.7, 126.8, 127.49, 127.52, 127.58, 127.61, 129.0, 130.0, 130.8, 132.3, 134.3, 134.8, 135.6, 141.2, 143.5; HRMS (ESI) calcd for $C_{25}H_{18}N_4NaO_2S$ $[M + Na]^+$ 461.1043, found 461.1037; IR (ν/cm^{-1}): 3266, 2124, 2102, 1330, 1290, 1162.



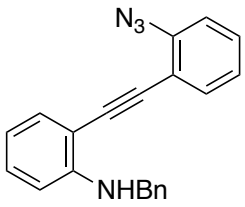
2-[(2-Azidophenyl)ethynyl]-*N*-mesylaniline (1i). Pale yellow solid, mp 109–110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.05 (s, 3H), 7.12–7.18 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.35–7.44 (m, 2H), 7.47–7.51 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 8.22 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.4, 90.4, 93.0, 113.3, 113.8, 117.7, 118.8, 124.2, 124.7, 130.1, 130.2, 130.9, 131.7, 138.8, 142.1; HRMS (ESI) calcd for $C_{15}H_{12}N_4NaO_2S$ $[M + Na]^+$ 335.0573, found 335.0574; IR (ν/cm^{-1}): 3249, 2132, 2097, 1482, 1294, 1147.



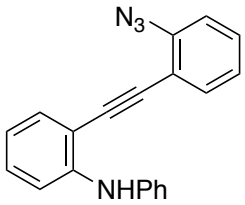
2-[(2-Azidophenyl)ethynyl]-*N*-Boc-aniline (1j). Brown solid, mp 40–43 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58 (s, 9H), 6.99 (dt, *J* = 1.3, 7.4 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.31–7.42 (m, 2H), 7.44 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.96 (s, 1H), 8.26 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 28.4, 80.7, 90.9, 91.8, 110.6, 114.8, 117.6, 117.9, 121.9, 124.7, 129.7, 129.9, 131.0, 132.2, 140.2, 141.3, 152.8; HRMS (ESI) calcd for $C_{19}H_{18}N_4NaO_2$ $[M + Na]^+$ 357.1322, found 357.1322; IR (ν/cm^{-1}): 3361, 2978, 2122, 2090, 1724, 1519, 1153.



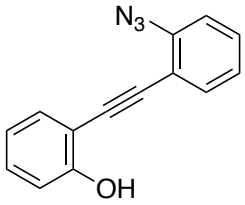
2-[(2-Azidophenyl)ethynyl]-*N*-methylaniline (1k). Black solid, mp 87–89 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.97 (d, *J* = 5.0 Hz, 3H), 5.17 (s, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 7.11–7.16 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.23–7.28 (m, 1H), 7.32–7.38 (m, 2H), 7.50 (dd, *J* = 7.7, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 30.0, 90.6, 92.2, 106.5, 108.5, 115.3, 115.6, 118.0, 124.4, 128.8, 130.1, 131.2, 132.3, 140.2, 149.9; HRMS (ESI) calcd for $C_{15}H_{13}N_4$ $[M + H]^+$ 249.1135, found 249.1135; IR (ν/cm^{-1}): 3412, 2122, 2085, 1571, 1300, 1288.



2-[(2-Azidophenyl)ethynyl]-*N*-benzylaniline (1l). Greenish solid, mp 72–73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.49 (s, 2H), 5.62 (s, 1H), 6.65–6.73 (m, 2H), 7.09–7.15 (m, 2H), 7.20–7.25 (m, 1H), 7.30–7.35 (m, 2H), 7.38–7.45 (m, 3H), 7.46–7.51 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 48.1, 91.4, 92.5, 107.3, 109.9, 115.6, 116.6, 118.2, 124.8, 127.6, 127.7, 128.9, 129.3, 130.5, 131.8, 132.7, 139.0, 140.9, 149.3; HRMS (ESI) calcd for $C_{21}H_{17}N_4$ $[M + H]^+$ 325.1448, found 325.1448; IR (ν/cm^{-1}): 3371, 2122, 1487, 1284, 1264.

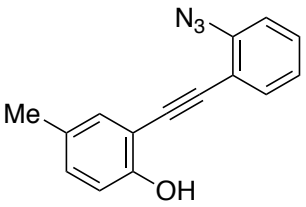


2-[(2-Azidophenyl)ethynyl]-*N*-phenylaniline (1m). Black solid, mp 69–71 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 7.12–7.20 (m, 2H), 7.21–7.31 (m, 4H), 7.331–7.40 (m, 4H), 7.46–7.53 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 91.8, 92.1, 109.4, 112.8, 115.1, 118.1, 118.7, 119.8, 122.3, 124.7, 129.3, 129.4, 129.7, 131.6, 132.2, 140.8, 141.7, 145.2; HRMS (ESI) calcd for $C_{20}H_{14}N_4Na$ $[M + Na]^+$ 333.1111, found 333.1112; IR (ν/cm^{-1}): 3338, 2121, 2090, 1286.

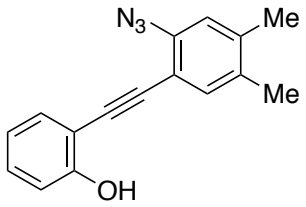


2-[(2-azidophenyl)ethynyl]phenol (4a). Brown solid, mp 45–47 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (br s, 1H), 6.91 (dt, J = 1.2, 7.4 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 7.13–7.18 (m, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.29 (dt, J = 1.8, 7.7 Hz, 1H), 7.37–7.42 (m, 2H), 7.50 (dd, J = 7.5, 1.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 89.9, 92.5, 109.2, 114.5, 114.7, 117.9, 120.1,

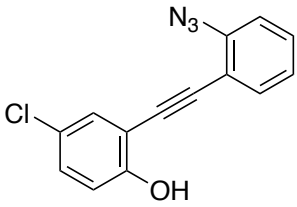
124.8, 129.7, 130.5, 130.7, 132.0, 141.0, 157.3; HRMS (ESI) calcd for $C_{14}H_9N_3NaO$ $[M + Na]^+$ 258.0638, found 258.0638; IR (ν/cm^{-1}): 3512, 3433, 2122, 1287.



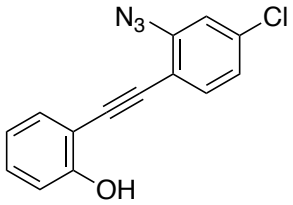
2-[(2-Azidophenyl)ethynyl]-4-methylphenol (4b). Brown solid, mp 52–53 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 3H), 6.54 (br s, 1H), 6.91 (d, J = 8.0 Hz, 1H), 7.09 (dd, J = 8.5, 2.0 Hz, 1H), 7.12–7.22 (m, 3H), 7.35–7.41 (m, 1H), 7.48 (dd, J = 7.5, 1.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.3, 90.2, 92.2, 108.8, 114.4, 114.6, 117.9, 124.8, 129.4, 129.6, 130.5, 131.6, 132.0, 141.0, 155.3; HRMS (ESI) calcd for $C_{15}H_{11}N_3NaO$ $[M + Na]^+$ 272.0794, found 272.0793; IR (ν/cm^{-1}): 3382, 2129, 2089, 1482, 1285.



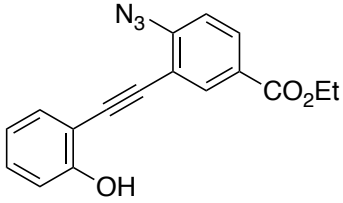
2-[(2-Azido-4,5-dimethylphenyl)ethynyl]phenol (4c). Brown solid, mp 108–109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.30 (s, 3H), 6.68 (s, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.95 (s, 1H), 7.00 (d, J = 9.0 Hz, 1H), 7.24–7.29 (m, 2H), 7.38 (dd, J = 7.5, 1.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.0, 20.1, 88.9, 92.8, 109.5, 111.6, 114.6, 119.1, 120.1, 130.4, 130.5, 132.7, 133.6, 138.4, 139.3, 157.2 HRMS (ESI) calcd for $C_{16}H_{13}N_3NaO$ $[M + Na]^+$ 286.0951, found 286.0951; IR (ν/cm^{-1}): 3435, 2111, 2090, 1480, 1270, 1221.



2-[(2-Azidophenyl)ethynyl]-4-chlorophenol (4d). Brown solid, mp 88–91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72 (s, 1H), 6.94 (d, J = 8.5 Hz, 1H), 7.14–7.25 (m, 3H), 7.36 (d, J = 2.0 Hz, 1H), 7.39–7.44 (m, 1H), 7.49 (dd, J = 7.8, 1.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 88.7, 93.5, 110.6, 114.0, 116.0, 117.9, 124.8, 124.9, 129.7, 130.1, 130.7, 132.1, 141.3, 156.0; HRMS (ESI) calcd for $C_{14}H_8ClN_3NaO$ $[M + Na]^+$ 292.0248, found 292.0244; IR (ν/cm^{-1}): 3437, 2114, 2080, 1474.

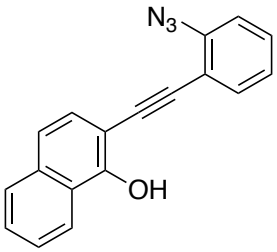


2-[(2-Azido-4-chlorophenyl)ethynyl]phenol (4e). Black solid, mp 70–72 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (br s, 1H), 6.88–6.93 (m, 1H), 6.99–7.03 (m, 1H), 7.08–7.14 (m, 2H), 7.27–7.32 (m, 1H), 7.36–7.40 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 90.8, 91.4, 108.9, 113.0, 114.8, 118.2, 120.2, 125.1, 130.5, 130.9, 132.7, 135.3, 142.1, 157.2; HRMS (ESI) calcd for $C_{14}H_8ClN_3NaO$ $[M + Na]^+$ 292.0248, found 292.0246; IR (ν/cm^{-1}): 3424, 2109, 1474, 1283, 1268.

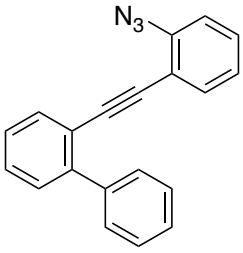


2-{[2-Azido-5-(ethoxycarbonyl)phenyl]ethynyl}phenol (4f). Brown solid, mp 83–85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41 (t, J = 7.2 Hz, 3H), 4.38 (q, J = 7.2 Hz, 2H), 6.57–

6.61 (m, 1H), 6.91 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 7.19–7.24 (m, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 8.16 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2, 61.3, 90.6, 91.4, 108.8, 114.5, 114.8, 117.7, 120.2, 127.0, 130.67, 130.72, 130.9, 133.4, 145.0, 157.3, 165.0; HRMS (ESI) calcd for $C_{17}H_{13}N_3NaO_3$ $[M + Na]^+$ 330.0849, found 330.0846; IR (ν/cm^{-1}): 3413, 2132, 1714, 1705, 1273, 1254.



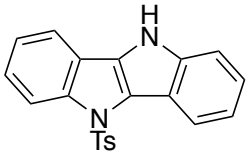
2-[(2-Azidophenyl)ethynyl]-1-naphthol (4g). Black solid, mp 118–120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16–7.20 (m, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.36–7.43 (m, 3H), 7.50–7.5 (m, 3H), 7.76–7.81 (m, 1H), 8.27–8.32 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 91.0, 92.8, 102.3, 114.7, 117.9, 119.9, 122.4, 123.3, 124.8, 125.8, 126.1, 127.4, 127.6, 129.5, 131.8, 134.6, 140.8, 154.9; HRMS (ESI) calcd for $C_{18}H_{12}N_3O$ $[M + H]^+$ 286.0975, found 286.0973; IR (ν/cm^{-1}): 3402, 2124, 2104, 1258.



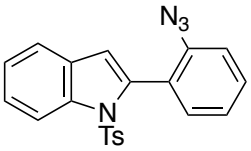
2-[(2-Azidophenyl)ethynyl]biphenyl (6).[1] Brown solid, mp 55–58 °C (lit. 97.0–98.0 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04–7.11 (m, 2H), 7.27–7.33 (m, 2H), 7.35–7.52 (m, 6H), 7.71–7.75 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 87.8, 95.1, 115.6, 118.7, 121.2, 124.5, 127.0, 127.4, 127.8, 128.8, 129.3, 129.45, 129.47, 133.0, 133.3, 140.3, 140.7, 143.8; HRMS

(ESI) calcd for $C_{20}H_{13}N_3Na$ $[M + Na]^+$ 318.1002, found 318.1001; IR (ν/cm^{-1}): 2127, 2092, 1306.

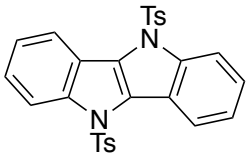
General Procedure for the Gold(I)/Rhodium(II)-Catalysed Cascade Cyclisation of 2-[(2-Azidophenyl)ethynyl]anilines 1 (GP-1). A Schlenk tube containing a magnetic stirring bar was charged with 2-[(2-azidophenyl)ethynyl]aniline **1** (0.100 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 2.0 mol%) and $Rh_2(esp)_2$ (2.3 mg, 3.0 μmol, 3.0 mol%) under nitrogen atmosphere. Toluene (1.0 mL) was added via a syringe through the septum, and the mixture was stirred at 80 °C or 100 °C for the indicated period of time. After completion, the reaction mixture was filtered through a plug of Florisil® eluting with hexane–AcOEt (1:1~3:1). The filtrate was concentrated, and the residue was purified by preparative TLC (hexane–AcOEt) to give 5,10-dihydroindolo[3,2-*b*]indole **2**.



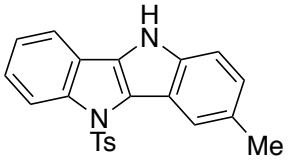
5-Tosyl-5,10-dihydroindolo[3,2-*b*]indole (2a).[1] The general procedure (GP-1) was followed using **1a** (19.6 mg, 0.050 mmol), (SPhos)AuNTf$_2$ (0.5 mg, 0.6 μmol, 1.1 mol%) and $Rh_2(esp)_2$ (1.1 mg, 1.5 μmol, 2.9 mol%) for 24 h. Purification by preparative TLC (hexane:AcOEt = 4:1) yielded **2a** (14.8 mg, 0.041 mmol, 81%) as a white solid. Mp 186–188 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.60 (s, 3H), 6.84 (d, J = 7.0 Hz, 2H), 7.20 (t, J = 7.7 Hz, 1H), 7.26–7.38 (m, 5H), 7.57 (d, J = 8.5 Hz, 2H), 8.20 (s, 1H), 8.34 (d, J = 8.5 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.2, 112.2, 116.1, 116.8, 117.8, 120.0, 120.1, 120.7, 123.0, 123.1, 123.9, 124.7, 126.5, 129.2, 129.3, 133.8, 140.1, 140.4, 144.4; HRMS (ESI) calcd for $C_{21}H_{17}N_2O_2S$ $[M + H]^+$ 361.1005, found 361.1004; IR (ν/cm^{-1}): 3396, 1166.



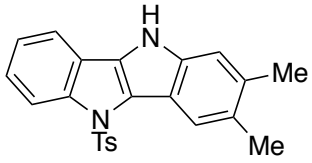
2-(2-Azidophenyl)-1-tosylindole (3a). White solid, mp 35–37 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 6.56 (s, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.19–7.24 (m, 2H), 7.28 (d, J = 7.0 Hz, 1H), 7.32–7.41 (m, 4H), 7.47–7.53 (m, 2H), 8.29 (d, J = 8.0Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.8, 113.6, 115.9, 118.4, 121.2, 124.1, 124.2, 124.4, 125.2, 127.1, 129.6, 130.0, 130.7, 133.1, 135.6, 136.7, 137.6, 140.3, 145.0; HRMS (ESI) calcd for $C_{21}H_{16}N_4NaO_2S$ [M + Na]$^+$ 411.0886, found 411.0885; IR (ν/cm^{-1}): 2117, 2089, 1367, 1172.



5,10-Ditosyl-5,10-dihydroindolo[3,2-*b*]indole.[2] A Schlenk tube containing a magnetic stirring bar was charged with **2a** (31.4 mg, 0.087 mmol) and NaH (60% suspension in mineral oil, 5.3 mg, 0.13 mmol) under nitrogen atmosphere. At 0 °C, THF (0.45 mL) was added to the tube, and the mixture was stirred for 10 min. Then, a solution of *p*-toluenesulfonyl chloride (33.2 mg, 0.174 mmol) in THF (0.45 mL) was added, and the mixture was allowed to stand at room temperature. After 18 h, the reaction mixture was quenched with ice water, diluted with water, and extracted with AcOEt. The combined organic layer was washed with brine, water, then saturated NH_4Cl aqueous solution, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by preparative TLC (hexane–AcOEt = 5:1) to give the title compound (28.7 mg, 0.056 mmol, 64%) as a white solid. Mp 277–279 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 6H), 7.01 (d, J = 8.5 Hz, 4H), 7.40–7.46 (m, 4H), 7.48–7.51 (m, 4H), 8.33–8.37 (m, 2H), 8.50–8.53 (m, 2H). The spectral data matched those reported in the literature.

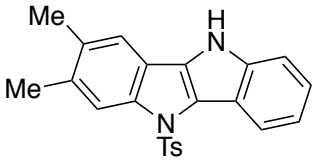


3-Methyl-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (2b). The general procedure (GP-1) was followed using **1b** (40.2 mg, 0.100 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 2.0 mol%) and Rh$_2$(esp)$_2$ (2.3 mg, 3.0 μmol, 3.0 mol%) at 100 °C for 12 h. Purification by preparative TLC (hexane:AcOEt = 4:1) yielded **2b** (25.8 mg, 0.069 mmol, 69%) as a brown solid. Mp 186–189 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.57 (s, 3H), 6.98 (d, J = 8.0 Hz, 2H), 7.13–7.16 (m, 1H), 7.24–7.29 (m, 1H), 7.30–7.37 (m, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.5 Hz, 2H), 8.10 (s, 1H), 8.30–8.34 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 21.8, 111.7, 116.3, 117.3, 117.5, 120.0, 120.2, 123.1, 123.9, 124.6, 124.8, 126.8, 129.38, 129.42, 130.3, 134.0, 138.6, 140.5, 144.3; HRMS (ESI) calcd for $C_{22}H_{19}N_2O_2S$ $[M + H]^+$ 375.1162, found 375.1164; IR (ν/cm^{-1}): 3364, 1169.

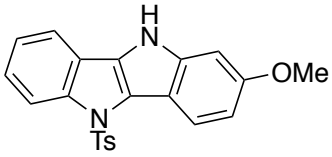


2,3-Dimethyl-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (2c). The general procedure (GP-1) was followed using **1c** (41.8 mg, 0.100 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 2.0 mol%) and Rh$_2$(esp)$_2$ (2.3 mg, 3.0 μmol, 3.0 mol%) at 100 °C for 12 h. Purification by preparative TLC (hexane:AcOEt = 4:1) yielded **2c** (28.2 mg, 0.073 mmol, 72%) as a brown solid. Mp 212–214 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 2.17 (s, 3H), 2.39 (s, 3H), 2.43 (s, 3H), 7.02 (d, J = 8.5 Hz, 2H), 7.18–7.29 (m, 3H), 7.51 (d, J = 7.0 Hz, 1H), 7.55–7.59 (m, 2H), 8.22 (s, 1H), 8.27 (d, J = 8.5 Hz, 1H), 10.5 (s, 1H); ^{13}C NMR (126 MHz, THF-d_8) δ 20.6, 20.7, 21.3, 113.3, 116.2, 117.0, 118.2, 120.8, 121.8, 123.6, 124.5, 124.6, 127.6, 129.2, 130.0, 130.1, 132.4,

135.5, 140.9, 141.5, 145.1; HRMS (ESI) calcd for $C_{23}H_{21}N_2O_2S$ $[M + H]^+$ 389.1318, found 389.1321; IR (ν/cm^{-1}): 3386, 1354, 1171.

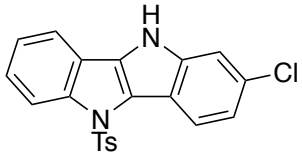


2,3-Dimethyl-10-tosyl-5,10-dihydroindolo[3,2-*b*]indole (2d). The general procedure (GP-1) was followed using **1d** (41.8 mg, 0.100 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 2.0 mol%) and $Rh_2(esp)_2$ (2.3 mg, 3.0 μmol, 3.0 mol%) for 12 h. Purification by preparative TLC (hexane:AcOEt = 5:1) yielded **2d** (12.8 mg, 0.033 mmol, 33%) as a brown solid. Mp 154–156 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 2.16 (s, 3H), 2.32 (s, 3H), 2.42 (s, 3H), 7.09–7.14 (m, 2H), 7.13–7.20 (m, 2H), 7.31 (s, 1H), 7.36–7.41 (m, 1H), 7.56 (d, J = 8.0 Hz, 2H), 8.11 (s, 1H), 8.39–8.43 (m, 1H), 10.61 (s, 1H); ^{13}C NMR (126 MHz, THF-d_8) δ 20.1, 20.8, 21.3, 112.8, 117.7, 118.0, 119.0, 119.8, 120.5, 120.6, 123.0, 123.2, 127.6, 130.1, 130.7, 132.2, 134.2, 135.5, 140.6, 141.5, 145.0; HRMS (ESI) calcd for $C_{23}H_{21}N_2O_2S$ $[M + H]^+$ 389.1318, found 389.1320; IR (ν/cm^{-1}): 3432, 1454, 1161.

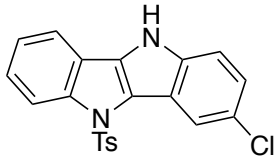


2-Methoxy-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (2e). The general procedure (GP-1) was followed using **1e** (41.7 mg, 0.100 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 2.0 mol%) and $Rh_2(esp)_2$ (2.3 mg, 3.0 μmol, 3.0 mol%) at 100 °C for 12 h. Purification by preparative TLC (hexane:AcOEt = 2:1) yielded **2e** (24.9 mg, 0.064 mmol, 64%) as a yellow solid. Mp 202–204 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 2.16 (s, 3H), 3.84 (s, 3H), 6.87 (dd, J = 8.8, 2.3 Hz, 1H), 6.92 (d, J = 1.5 Hz, 1H), 6.99–7.05 (m, 2H), 7.20–7.29 (m, 2H), 7.48–7.52 (m, 1H), 7.58

(d, J = 8.5 Hz, 2H), 8.26–8.34 (m, 2H), 10.51 (s, 1H); ^{13}C NMR (126 MHz, THF-d_8) δ 21.3, 55.6, 96.3, 110.5, 112.2, 116.9, 117.9, 121.4, 121.8, 123.9, 124.3, 124.5, 127.6, 129.4, 130.2, 135.5, 141.0, 142.8, 145.2, 158.1; HRMS (ESI) calcd for $C_{22}H_{19}N_2O_3S$ $[M + H]^+$ 391.1111, found 391.1114; IR (ν/cm^{-1}): 3361, 1162.

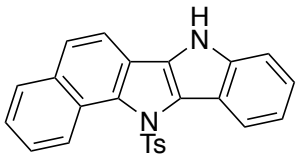


2-Chloro-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (2f). The general procedure (GP-1) was followed using **1f** (42.1 mg, 0.100 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 2.0 mol%) and $Rh_2(esp)_2$ (2.2 mg, 2.9 μmol, 2.9 mol%) at 100 °C for 12 h. Purification by preparative TLC (hexane:AcOEt = 5:1) yielded **2f** (27.2 mg, 0.069 mmol, 69%) as a brown solid. Mp 219–221 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 2.18 (s, 3H), 7.01–7.08 (m, 2H), 7.18–7.23 (m, 1H), 7.24–7.30 (m, 1H), 7.31–7.38 (m, 1H), 7.44–7.48 (m, 1H), 7.55–7.61 (m, 3H), 8.29–8.34 (m, 1H), 8.38–8.44 (m, 1H), 11.00 (s, 1H) ^{13}C NMR (126 MHz, THF-d_8) δ 21.3, 112.9, 116.3, 117.0, 118.7, 121.2, 121.4, 121.7, 123.3, 124.8, 125.6, 127.6, 129.0, 130.3, 131.4, 135.3, 141.7, 141.9, 145.5; HRMS (ESI) calcd for $C_{21}H_{16}ClN_2O_2S$ $[M + H]^+$ 395.0620, found 395.0616; IR (ν/cm^{-1}): 3360, 1356, 1165.

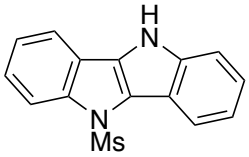


3-Chloro-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (2g). A Schlenk tube containing a magnetic stirring bar was charged with **1g** (33.7 mg, 0.080 mmol) and (IPr)AuNTf$_2$ (1.8 mg, 2.1 μmol, 2.0 mol%) under nitrogen atmosphere. 1,2-Dichloroethane (0.8 mL) was added via a syringe through the septum, and the mixture was stirred at 80 °C for 5 h. The reaction mixture

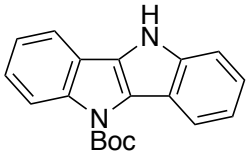
was cooled to room temperature, and passed through a plug of Florisil® eluting with hexane–AcOEt (1:1). The filtrate was concentrated, and the residue was purified by preparative TLC (hexane:AcOEt = 3:1) to give the title compound (10.6 mg, 0.027 mmol, 34%) as a yellow solid. Mp 177–179 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.22 (s, 3H), 7.02 (d, J = 8.5 Hz, 2H), 7.25–7.33 (m, 2H), 7.34–7.41 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.5 Hz, 2H), 8.28 (br s, 1H), 8.32 (d, J = 8.5 Hz, 1H), 8.52 (d, J = 2.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5, 112.9, 116.3, 117.8, 117.9, 119.7, 119.8, 122.5, 123.5, 124.1, 125.3, 126.6, 126.7, 129.5, 130.3, 133.9, 138.4, 140.6, 144.6; HRMS (ESI) calcd for $C_{21}H_{15}ClN_2NaO_2S$ $[M + Na]^+$ 417.0435, found 417.0438; IR (ν/cm^{-1}): 3356, 1169.



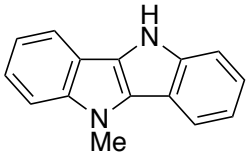
12-Tosyl-7,12-dihydrobenzo[*g*]indolo[3,2-*b*]indole (2h). The general procedure (GP-1) was followed using **1h** (35.1 mg, 0.080 mmol), (SPhos)AuNTf$_2$ (1.4 mg, 1.6 μmol, 2.0 mol%) and $Rh_2(esp)_2$ (1.8 mg, 2.4 μmol, 3.0 mol%) at 100 °C for 12 h. Purification by preparative TLC (hexane:AcOEt = 6:1) yielded **2h** (7.3 mg, 0.018 mmol, 22%) as a black solid. Mp 151–154 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 2.07 (s, 3H), 6.71 (d, J = 8.5 Hz, 2H), 6.78–6.82 (m, 2H), 7.17–7.23 (m, 2H), 7.37–7.41 (m, 1H), 7.44–7.49 (m, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.58–7.63 (m, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 8.33–8.39 (m, 1H), 9.11 (d, J = 8.0 Hz, 1H), 10.55 (s, 1H); ^{13}C NMR (126 MHz, THF-d_8) δ 21.2, 112.9, 117.1, 120.2, 120.98, 121.03, 122.5, 123.2, 125.6, 126.5, 126.8, 126.9, 127.8, 128.2, 129.1, 129.2, 132.5, 133.4, 134.0, 139.4, 141.6, 144.8; HRMS (ESI) calcd for $C_{25}H_{19}N_2O_2S$ $[M + H]^+$ 411.1162, found 411.1161; IR (ν/cm^{-1}): 3407, 1170.



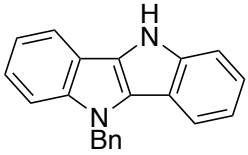
5-Mesyl-5,10-dihydroindolo[3,2-*b*]indole (2i). The general procedure (GP-1) was followed using **1i** (37.7 mg, 0.121 mmol), (SPhos)AuNTf$_2$ (2.1 mg, 2.4 μmol, 2.0 mol%) and Rh$_2$(esp)$_2$ (2.8 mg, 3.7 μmol, 3.1 mol%) at 100 °C for 12 h. Purification by preparative TLC (hexane:AcOEt = 4:1) yielded **2i** (21.2 mg, 0.075 mmol, 62%) as a brown solid. Mp 201–203 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 2.89 (s, 3H), 7.08–7.14 (m, 1H), 7.17–7.23 (m, 1H), 7.32–7.37 (m, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.71–7.76 (m, 1H), 8.14–8.20 (m, 1H), 8.21–8.26 (m, 1H), 10.84 (s, 1H); ^{13}C NMR (126 MHz, THF-d_8) δ 37.8, 112.9, 116.5, 117.4, 118.6, 120.5, 120.9, 121.2, 123.5, 124.1, 124.6, 125.2, 130.0, 141.8, 141.9; HRMS (ESI) calcd for $C_{15}H_{12}N_2NaO_2S$ $[M + Na]^+$ 307.0512, found 307.0509; IR (ν/cm^{-1}): 3402, 1357, 1163.



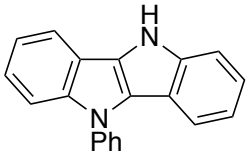
5-Boc-5,10-dihydroindolo[3,2-*b*]indole (2j). [3] The general procedure (GP-1) was followed using **1j** (34.3 mg, 0.103 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 2.0 mol%) and Rh$_2$(esp)$_2$ (2.4 mg, 3.2 μmol, 3.1 mol%) at 100 °C for 12 h. Purification by preparative TLC (hexane:AcOEt = 6:1) yielded **2j** (19.6 mg, 0.064 mmol, 62%) as a brown solid. Mp 162–165 °C (lit. >200 °C); ^{1}H NMR (500 MHz, THF-d_8) δ 1.79 (s, 9H), 7.03–7.10 (m, 1H), 7.12–7.18 (m, 1H), 7.22–7.31 (m, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.67–7.71 (m, 1H), 8.22–8.33 (m, 1H), 8.44 (d, J = 8.0 Hz, 1H), 10.6, (s, 1H); ^{13}C NMR (126 MHz, THF-d_8) δ 28.4, 84.0, 112.3, 117.4, 117.6, 117.9, 119.4, 119.9, 122.1, 122.8, 123.0, 124.3, 128.2, 141.5, 151.3; HRMS (ESI) calcd for $C_{19}H_{18}N_2NaO_2$ $[M + Na]^+$ 329.1260, found 329.1260; IR (ν/cm^{-1}): 3420, 3397, 1723, 1449, 1299, 1151, 1141, 1131.



5-Methyl-5,10-dihydroindolo[3,2-*b*]indole (2k). The general procedure (GP-1) was followed using **1k** (49.8 mg, 0.201 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 1.0 mol%) and Rh$_2$(esp)$_2$ (4.6 mg, 6.1 μmol, 3.0 mol%) at 100 °C for 16 h. Purification by preparative TLC (hexane:AcOEt = 6:1) yielded **2k** (28.0 mg, 0.127 mmol, 63%) as a grayish solid. Mp 155–158 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 4.09 (s, 3H), 7.01–7.07 (m, 2H), 7.13 (t, J = 7.5 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.39–7.44 (m, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.86–7.91 (m, 1H), 10.30 (s, 1H); ^{13}C NMR (126 MHz, THF-d_8) δ 31.6, 110.1, 112.8, 116.0, 116.3, 117.9, 118.3, 118.6, 118.9, 122.1, 122.2, 125.6, 128.4, 142.0, 142.4; HRMS (ESI) calcd for $C_{15}H_{13}N_2$ [M + H]$^+$ 221.1073, found 221.1076; IR (ν/cm^{-1}): 3223, 1472.

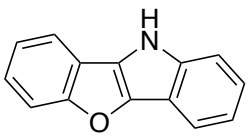


5-Benzyl-5,10-dihydroindolo[3,2-*b*]indole (2l). The general procedure (GP-1) was followed using **1l** (32.4 mg, 0.100 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 1.0 mol%) and Rh$_2$(esp)$_2$ (2.3 mg, 3.0 μmol, 3.0 mol%) at 100 °C for 18 h. Purification by preparative TLC (hexane:AcOEt = 12:1) yielded **2l** (21.0 mg, 0.071 mmol, 71%) as a pale yellow solid. Mp 188–190 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 5.74 (s, 2H), 6.93–6.98 (m, 1H), 7.03–7.23 (m, 8H), 7.40–7.47 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 10.36 (s, 1H); ^{13}C NMR (126 MHz, THF-d_8) δ 49.2, 110.7, 112.7, 116.15, 116.21, 118.1, 118.3, 118.9, 122.2, 122.3, 126.0, 127.4, 127.9, 129.3, 139.8, 141.99, 142.04; HRMS (ESI) calcd for $C_{21}H_{16}N_2Na$ [M + Na]$^+$ 319.1206, found 319.1205; IR (ν/cm^{-1}): 3391, 1464.

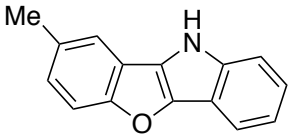


5-Phenyl-5,10-dihydroindolo[3,2-*b*]indole (2m).[4] The general procedure (GP-1) was followed using **1m** (31.3 mg, 0.101 mmol), (SPhos)AuNTf$_2$ (1.8 mg, 2.0 μmol, 1.0 mol%) and Rh$_2$(esp)$_2$ (2.3 mg, 3.0 μmol, 3.0 mol%) at 100 °C for 12 h. Purification by preparative TLC (hexane:AcOEt = 10:1) yielded **2m** (19.6 mg, 0.069 mmol, 69%) as a yellow solid. Mp 162–164 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 6.94–6.99 (m, 1H), 7.12–7.22 (m, 3H), 7.37–7.43 (m, 1H), 7.44–7.51 (m, 2H), 7.59–7.64 (m, 3H), 7.75 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 7.0 Hz, 1H), 10.49 (s, 1H); ^{13}C NMR (126 MHz, THF-d_8) δ 111.4, 112.9, 116.0, 117.2, 118.5, 118.7, 119.0, 120.3, 122.5, 123.1, 126.1, 126.9, 127.3, 130.4, 140.4, 141.6, 142.1; HRMS (ESI) calcd for $C_{20}H_{15}N_2$ $[M + H]^+$ 283.1230, found 283.1228; IR (ν/cm^{-1}): 3405, 1455.

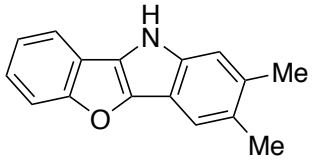
General Procedure for the Base-Promoted Rhodium(II)-Catalysed Cascade Cyclisation of 2-[(2-Azidophenyl)ethynyl]phenols 4 (GP-2). A Schlenk tube containing a magnetic stirring bar was charged with 2-[(2-azidophenyl)ethynyl]phenol **4** (0.100 mmol), Rh$_2$(esp)$_2$ (3.8 mg, 50 μmol, 5.0 mol%) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) under nitrogen atmosphere. Toluene (1.0 mL) was added via a syringe through the septum, and the mixture was stirred at 80 °C for the indicated period of time. After completion, the reaction mixture was filtered through a plug of Florisil® eluting with hexane–AcOEt (2:1~3:1). The filtrate was concentrated, and the residue was purified by preparative TLC (hexane–AcOEt or toluene–hexane) to give 10*H*-benzofuro[3,2-*b*]indole **5**.



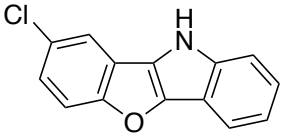
10*H*-Benzofuro[3,2-*b*]indole (5a).[5] The general procedure (GP-2) was followed using **4a** (23.5 mg, 0.100 mmol), $Rh_2(esp)_2$ (3.8 mg, 5.0 μmol, 5.0 mol%) and K_2CO_3 (27.4 mg, 0.198 mmol, 2.0 equiv) for 12 h. Purification by preparative TLC (hexane:AcOEt = 6:1) yielded **5a** (16.3 mg, 0.079 mmol, 79%) as a white solid. Mp 194–197 °C (lit. 196–198 °C, 196.5–197.5 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19–7.33 (m, 4H), 7.41–7.45 (m, 1H), 7.59–7.65 (m, 2H), 7.82 (d, J = 8.0 Hz, 1H), 8.00 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 112.5, 112.7, 114.2, 117.1, 117.8, 118.7, 120.3, 122.6, 122.9, 123.8, 125.1, 139.6, 143.6, 159.1; HRMS (ESI) calcd for $C_{14}H_{10}NO$ $[M + H]^+$ 208.0757, found 208.0761; IR (ν/cm^{-1}): 3410, 1396.



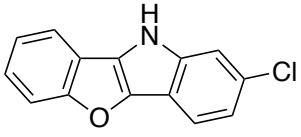
8-Methyl-10*H*-benzofuro[3,2-*b*]indole (5b). The general procedure (GP-2) was followed using **4b** (24.8 mg, 0.100 mmol), $Rh_2(esp)_2$ (3.9 mg, 5.1 μmol, 5.2 mol%) and K_2CO_3 (27.5 mg, 0.199 mmol, 2.0 equiv) for 18 h. Purification by preparative TLC (toluene:hexane = 2:1) yielded **5b** (11.7 mg, 0.053 mmol, 53%) as a brown solid. Mp 176–178 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 2.46 (s, 3H), 7.14–7.20 (m, 2H), 7.21–7.26 (m, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.55–7.59 (m, 2H), 7.77 (d, J = 8.0 Hz, 1H), 10.51 (s, 1H); ^{13}C NMR (126 MHz, acetone-d_6) δ 21.5, 112.9, 113.8, 114.6, 117.3, 119.1, 119.9, 120.6, 123.3, 125.8, 126.4, 133.0, 140.8, 144.1, 158.6; HRMS (ESI) calcd for $C_{15}H_{12}NO$ $[M + H]^+$ 222.0913, found 222.0915; IR (ν/cm^{-1}): 3403, 1459, 1188, 1129, 1102.



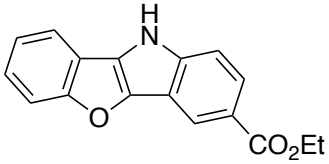
2,3-Dimethyl-10*H*-benzofuro[3,2-*b*]indole (5c). The general procedure (GP-2) was followed using **4c** (26.4 mg, 0.100 mmol), $Rh_2(esp)_2$ (3.8 mg, 5.0 μmol, 5.0 mol%), and K_2CO_3 (27.9 mg, 0.202 mmol, 2.0 equiv) for 12 h. Purification by preparative TLC (toluene:hexane = 1:1) yielded **5c** (17.1 mg, 0.073 mmol, 72%) as a brown solid. Mp 206–209 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 2.37 (s, 6H), 7.27–7.33 (m, 2H), 7.35 (s, 1H), 7.54 (s, 1H), 7.59–7.64 (m, 1H), 7.72–7.76 (m, 1H), 10.26 (s, 1H); ^{13}C NMR (126 MHz, acetone-d_6) δ 20.2, 20.7, 113.1, 113.2, 114.2, 117.5, 118.8, 120.2, 123.5, 124.2, 125.8, 129.2, 132.5, 140.1, 143.8, 159.9; HRMS (ESI) calcd for $C_{16}H_{14}NO$ $[M + H]^+$ 236.1070, found 236.1073; IR (ν/cm^{-1}): 3437, 1462, 1441, 1188, 1136.



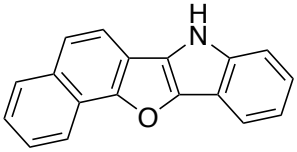
8-Chloro-10*H*-benzofuro[3,2-*b*]indole (5d). The general procedure (GP-2) was followed using **4d** (27.0 mg, 0.100 mmol), $Rh_2(esp)_2$ (3.9 mg, 5.1 μmol, 5.1 mol%) and K_2CO_3 (27.5 mg, 0.199 mmol, 2.0 equiv) for 18 h. Purification by preparative TLC (hexane:AcOEt = 8:1) yielded **5d** (20.6 mg, 0.085 mmol, 85%) as a pale yellow solid. Mp 183–185 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 7.16–7.21 (m, 1H), 7.24–7.34 (m, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.76–7.80 (m, 2H), 10.54 (s, 1H); ^{13}C NMR (126 MHz, acetone-d_6) δ 114.0, 114.2, 114.6, 117.6, 118.7, 120.9, 121.1, 124.1, 124.4, 125.4, 128.6, 141.1, 145.3, 158.4; HRMS (ESI) calcd for $C_{14}H_9ClNO$ $[M + H]^+$ 242.0367, found 242.0369; IR (ν/cm^{-1}): 3426, 1448, 1374, 1309.



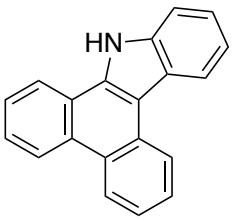
2-Chloro-10*H*-benzofuro[3,2-*b*]indole (5e). The general procedure (GP-2) was followed using **4e** (27.1 mg, 0.100 mmol), $Rh_2(esp)_2$ (3.8 mg, 5.0 μmol, 5.0 mol%) and K_2CO_3 (27.9 mg, 0.202 mmol, 2.0 equiv) for 12 h. Purification by preparative TLC (hexane:AcOEt = 10:1) yielded **5e** (10.8 mg, 0.045 mmol, 44%) as a grayish solid. Mp 193–196 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, J = 8.7, 5.8 Hz, 1H), 7.30–7.37 (m, 2H), 7.48 (d, J = 2.0 Hz, 1H), 7.60–7.64 (m, 1H), 7.66–7.69 (m, 1H), 7.73 (d, J = 8.5 Hz, 1H), 8.11 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 112.5, 112.79, 112.84, 117.8, 117.9, 118.5, 121.1, 122.9, 124.2, 125.7, 128.6, 139.7, 143.1, 159.2; HRMS (ESI) calcd for $C_{14}H_9ClNO$ $[M + H]^+$ 242.0367, found 242.0364; IR (ν/cm^{-1}): 3428, 1444, 1396.



3-(Ethoxycarbonyl)-10*H*-benzofuro[3,2-*b*]indole (5f). The general procedure (GP-2) was followed using **4f** (30.7 mg, 0.100 mmol), $Rh_2(esp)_2$ (3.8 mg, 5.0 μmol, 5.0 mol%) and K_2CO_3 (27.8 mg, 0.201 mmol, 2.0 equiv) for 12 h. Purification by preparative TLC (hexane:AcOEt = 6:1) yielded **5f** (17.4 mg, 0.062 mmol, 62%) as a brown solid. Mp 192–194 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 1.41 (t, J = 6.8 Hz, 3H), 4.39 (q, J = 7.0 Hz, 2H), 7.33–7.43 (m, 2H), 7.65–7.72 (m, 2H), 7.84 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 8.52 (s, 1H), 10.97 (s, 1H); ^{13}C NMR (126 MHz, acetone-d_6) δ 14.7, 61.2, 113.48, 113.51, 114.0, 119.4, 119.5, 119.7, 123.2, 123.9, 124.3, 125.4, 127.9, 142.8, 143.9, 160.3, 167.4; HRMS (ESI) calcd for $C_{17}H_{14}NO_3$ $[M + H]^+$ 280.0968, found 280.0967; IR (ν/cm^{-1}): 3298, 1674.



7*H*-Naphtho[2′,1′:4,5]furo[3,2-*b*]indole (5g). The general procedure (GP-2) was followed using **4g** (28.5 mg, 0.100 mmol), $Rh_2(esp)_2$ (3.9 mg, 5.1 μmol, 5.1 mol%) and K_2CO_3 (27.8 mg, 0.201 mmol, 2.0 equiv) for 12 h. Purification by preparative TLC (toluene:hexane = 2:1) yielded **5g** (8.1 mg, 0.031 mmol, 32%) as a greenish solid. Mp 171–174 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 7.24–7.33 (m, 2H), 7.56–7.61 (m, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.71–7.75 (m, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.90–7.94 (m, 1H), 7.99 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.50 (d, J = 8.5 Hz, 1H), 10.67 (s, 1H); ^{13}C NMR (126 MHz, acetone-d_6) δ 113.76, 113.81, 114.7, 115.0, 117.1, 118.3, 120.6, 120.7, 123.2, 124.2, 125.9, 127.6, 127.7, 129.5, 132.1, 140.9, 143.5, 154.7; HRMS (ESI) calcd for $C_{18}H_{12}NO$ $[M + H]^+$ 258.0913, found 258.0914; IR (ν/cm^{-1}): 3417, 1447, 1240, 1190, 1057.

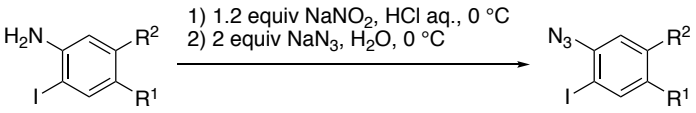


Dibenzo[*a*,*c*]carbazole (7).[6] A Schlenk tube containing a magnetic stirring bar was charged with 2-[(2-azidophenyl)ethynyl]biphenyl (**6**, 29.5 mg, 0.100 mmol) and (IPr)AuNTf$_2$ (4.3 mg, 5.0 μmol, 5.0 mol%) under nitrogen atmosphere. 1,2-Dichloroethane (1.0 mL) was added via a syringe through the septum, and the mixture was stirred at 80 °C for 3 h. After completion, the reaction mixture was filtered through a plug of Florisil® eluting with hexane–AcOEt (3:1). The filtrate was concentrated, and the residue was purified by preparative TLC (hexane:AcOEt = 8:1) to give the title compound (24.6 mg, 0.092 mmol, 92%) as a white solid. Mp 189–190 °C (lit. 185–188 °C, 187–189 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 7.40 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.59–7.66 (m, 1H), 7.71–7.80 (m, 3H), 7.83 (t, J = 7.5 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.88–8.97 (m, 3H), 11.53 (s, 1H); ^{13}C NMR (126 MHz, acetone-d_6) δ 112.6, 113.0, 121.1, 122.4, 122.7, 123.9, 124.47, 124.54,

124.6, 124.7, 124.8, 125.0, 125.3, 127.2, 127.8, 128.3, 130.8, 131.1, 135.3, 139.8; HRMS (ESI) calcd for $C_{20}H_{14}N$ $[M + H]^+$ 268.1121, found 268.1118; IR (ν/cm^{-1}): 3412, 1459.

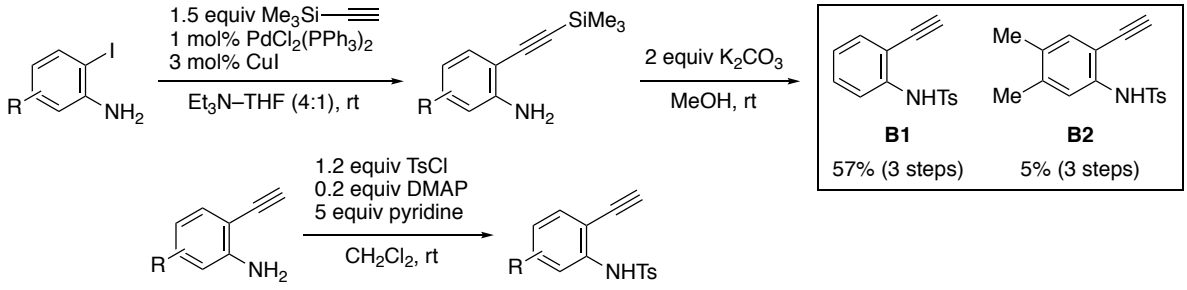
Preparation of 1, 4, and 6

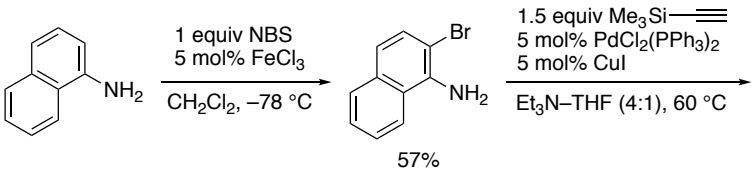
(1) Preparation of 1-azido-2-iodobenzenes A[7]

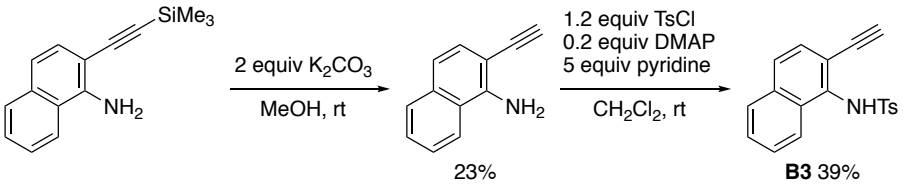


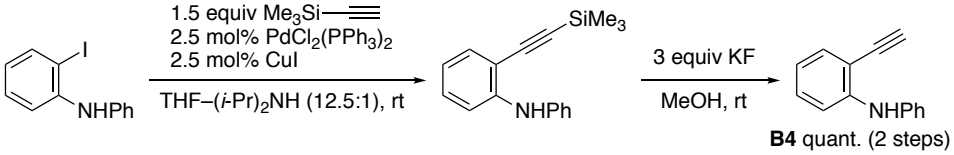
A1	A2	A3	A4	A5	A6	A7
quant.	67%	(crude)	18%	85%	67%	97%

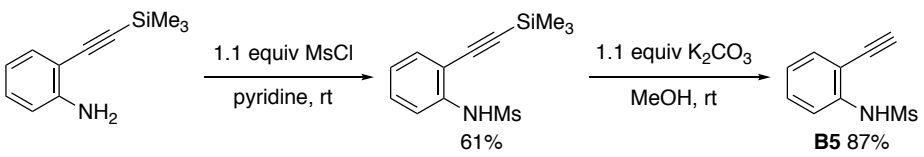
(2) Preparation of 2-alkynylanilines B[8]

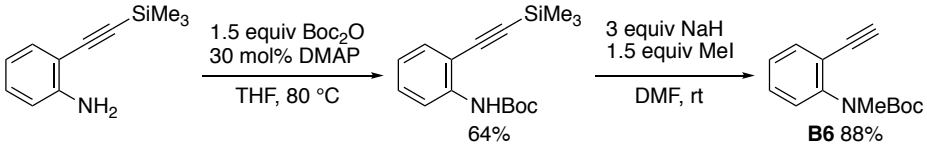




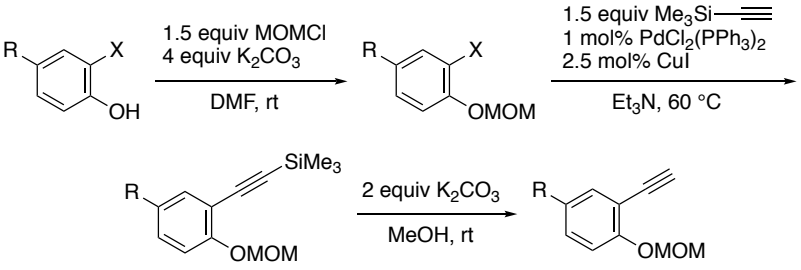


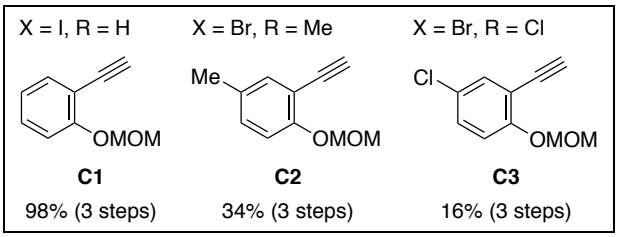




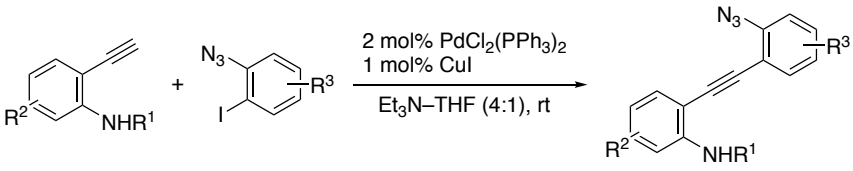


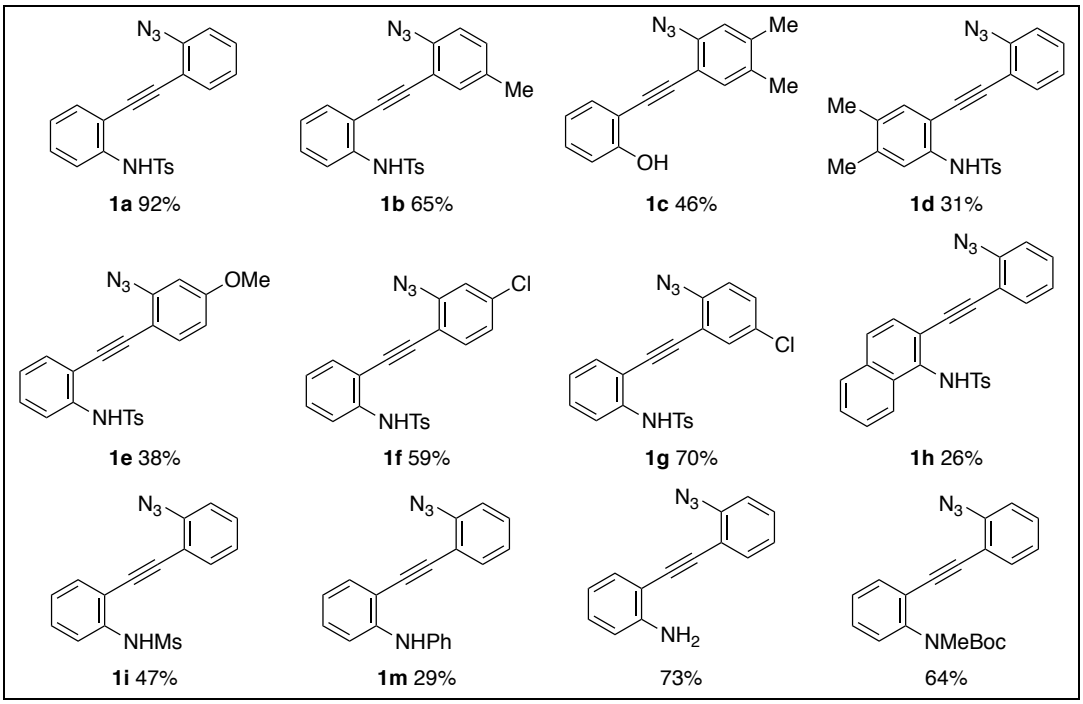
(3) Preparation of *O*-MOM 2-alkynylphenols C[9]

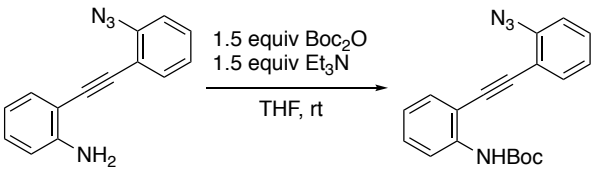




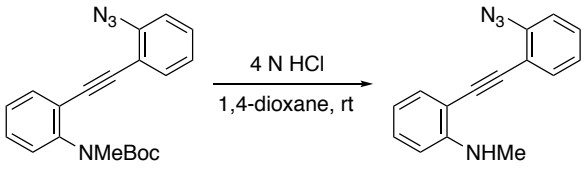
(4) Preparation of 2-[(2-azidophenyl)ethynyl]anilines 1, -phenols 4, and -biphenyl 6[10]



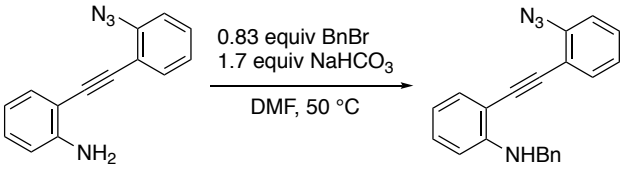




1j 42%



1k 82%



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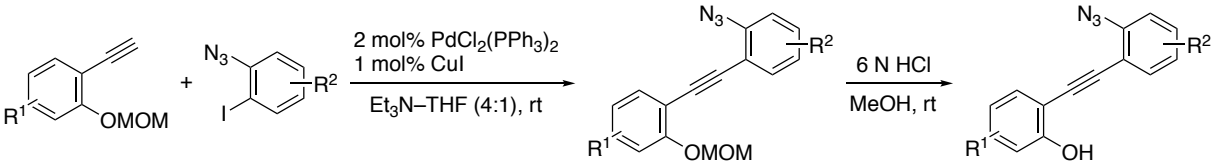
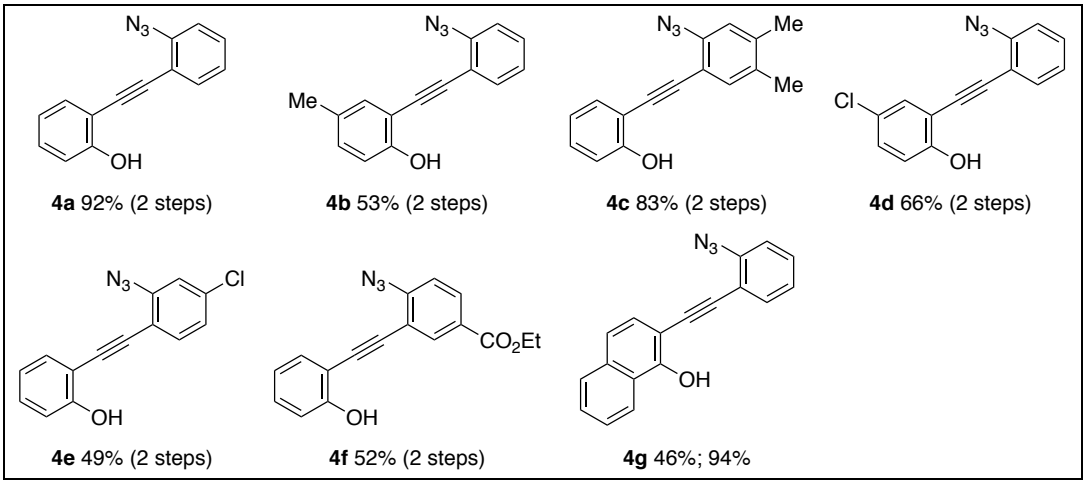
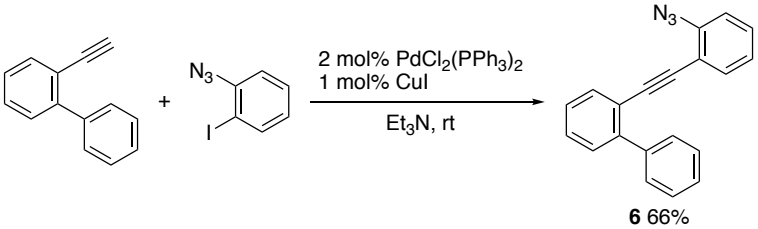




4a 92% (2 steps) **4b** 53% (2 steps) **4c** 83% (2 steps) **4d** 66% (2 steps)

4e 49% (2 steps) **4f** 52% (2 steps) **4g** 46%; 94%



6 66%

1 J. Cai, B. Wu, G. Rong, C. Zhang, L. Qiu and X. Xu, *Org. Lett.*, 2018, **20**, 2733–2736.

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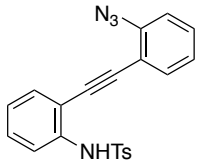
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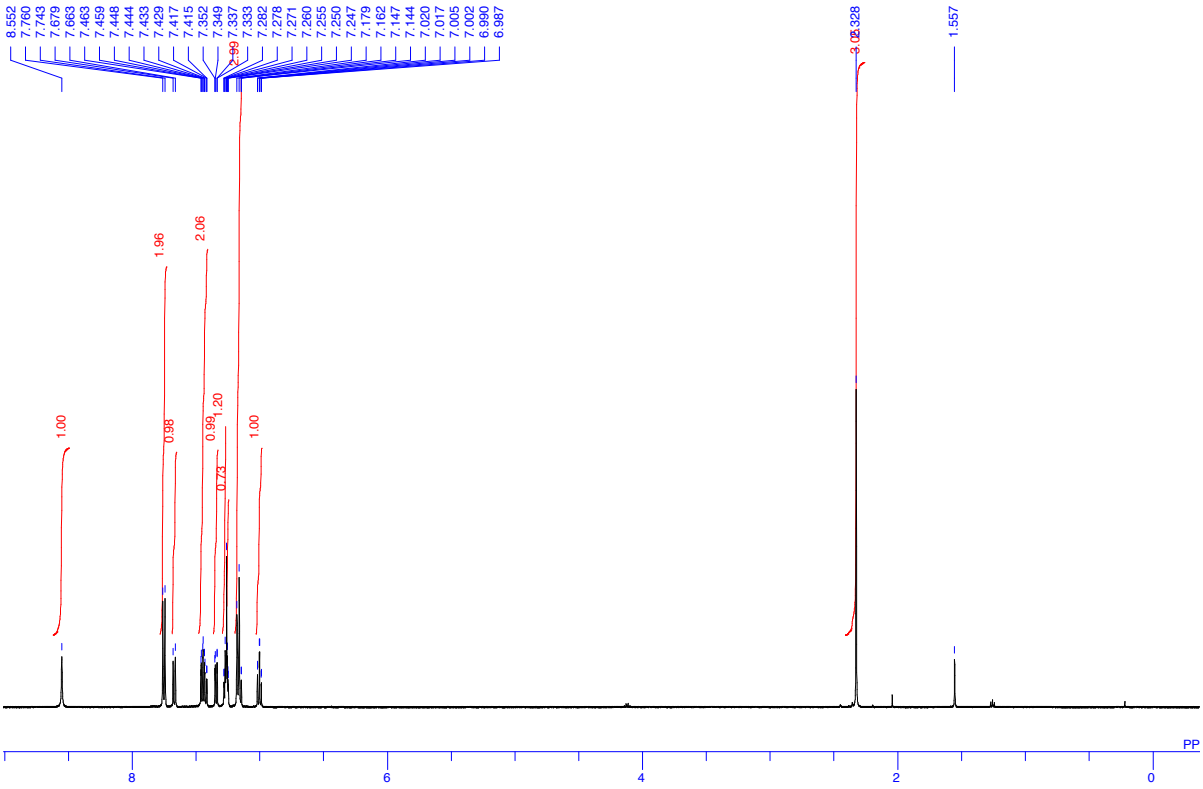
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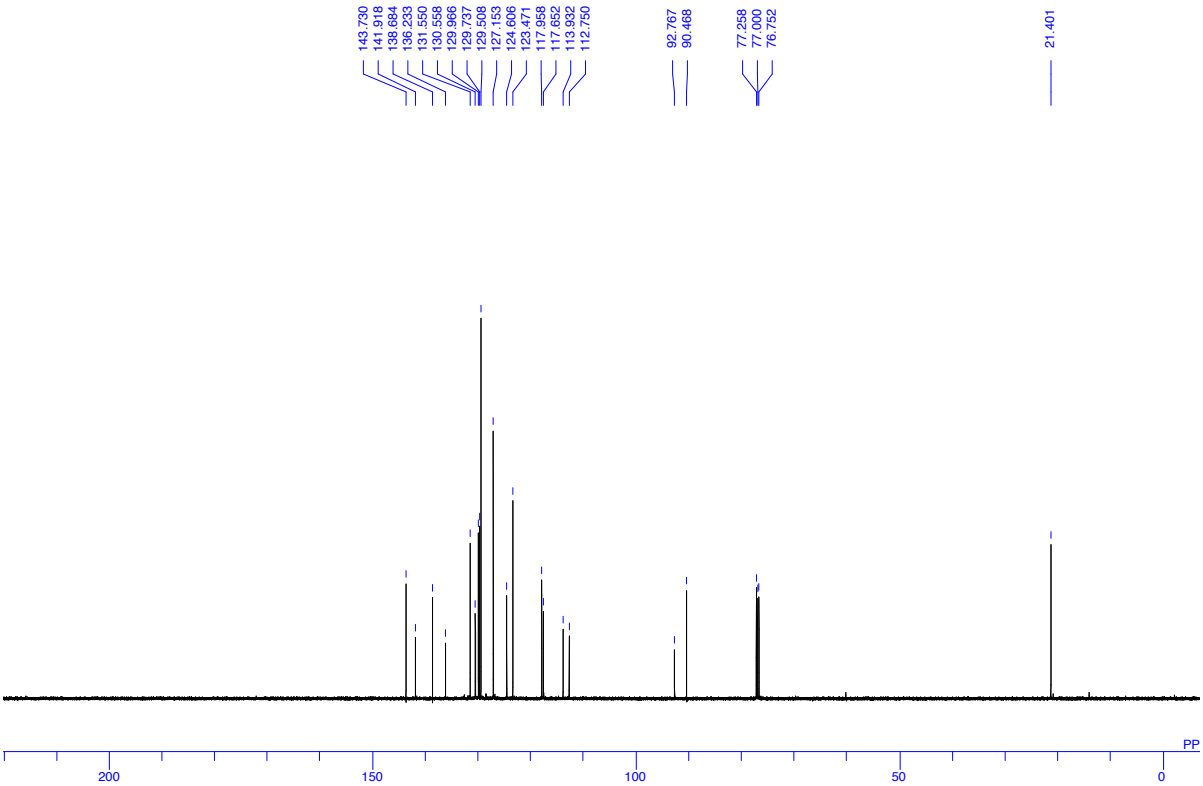
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50
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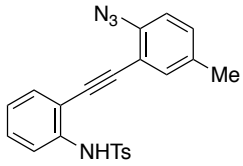
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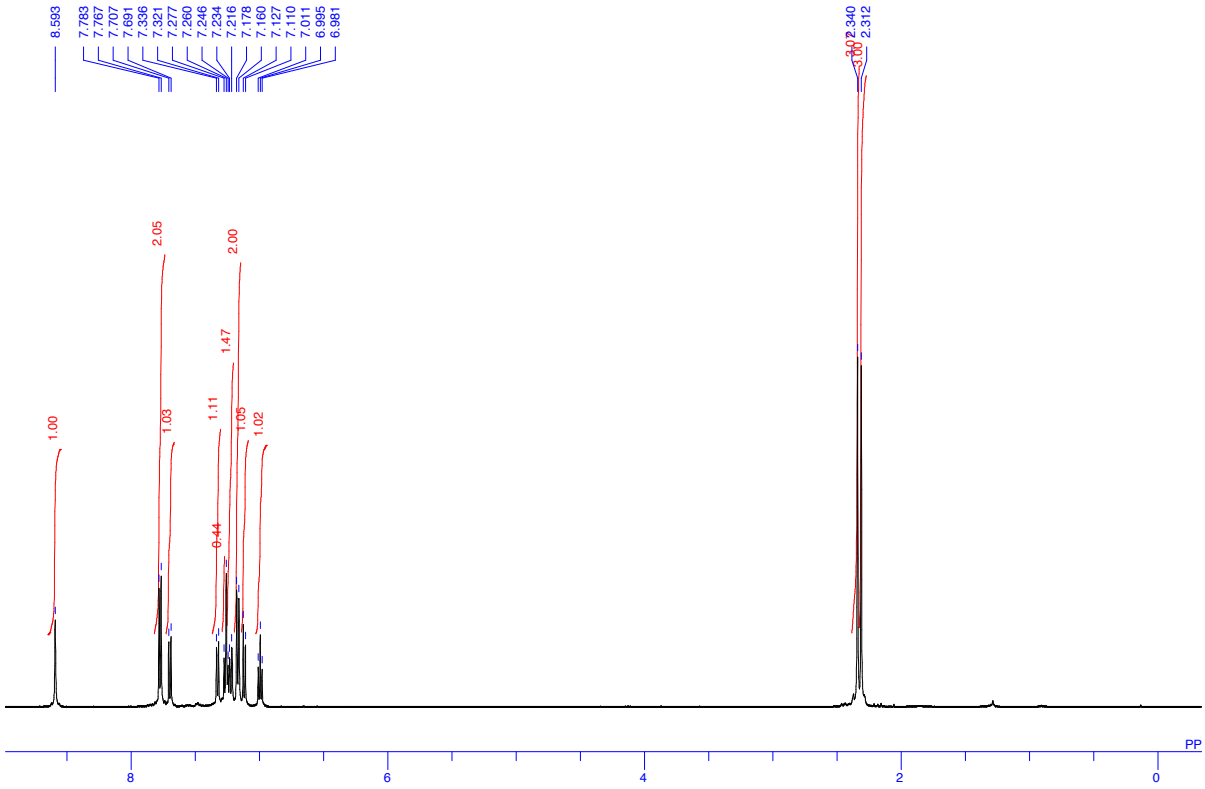
Me
NHTs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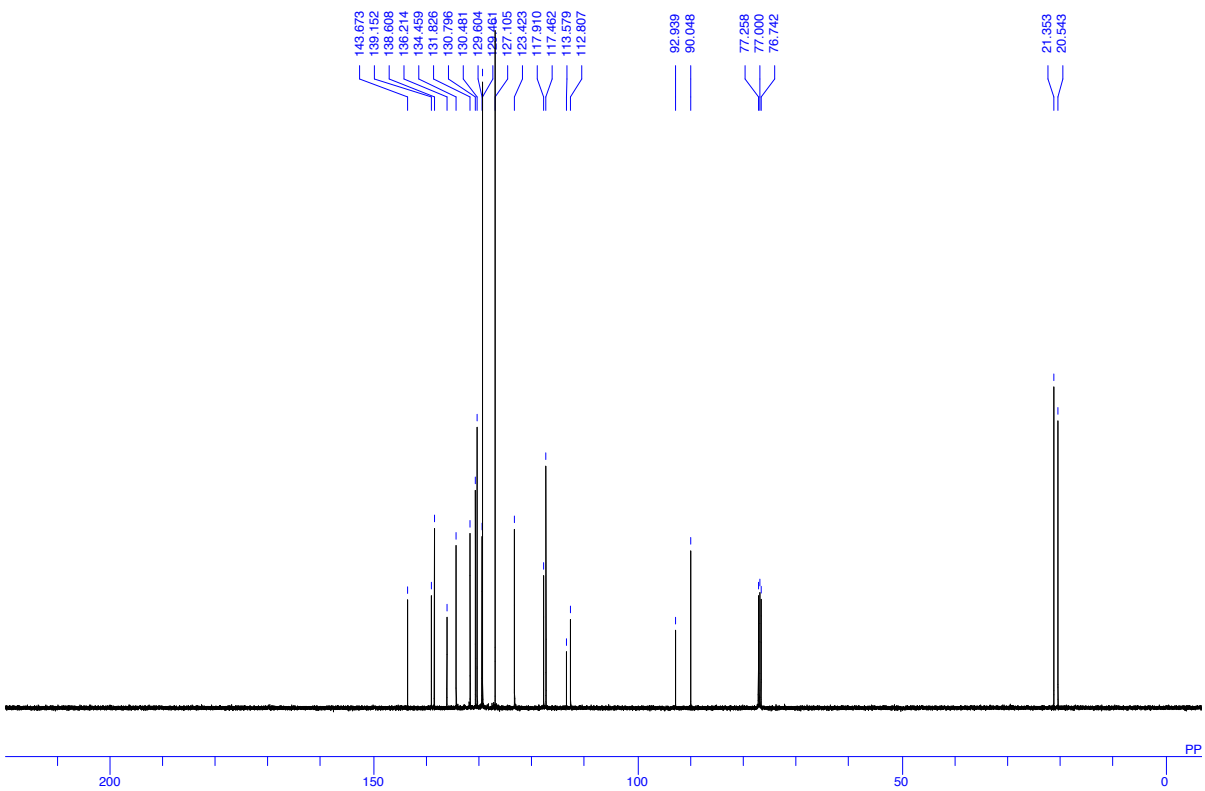
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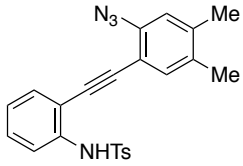
1c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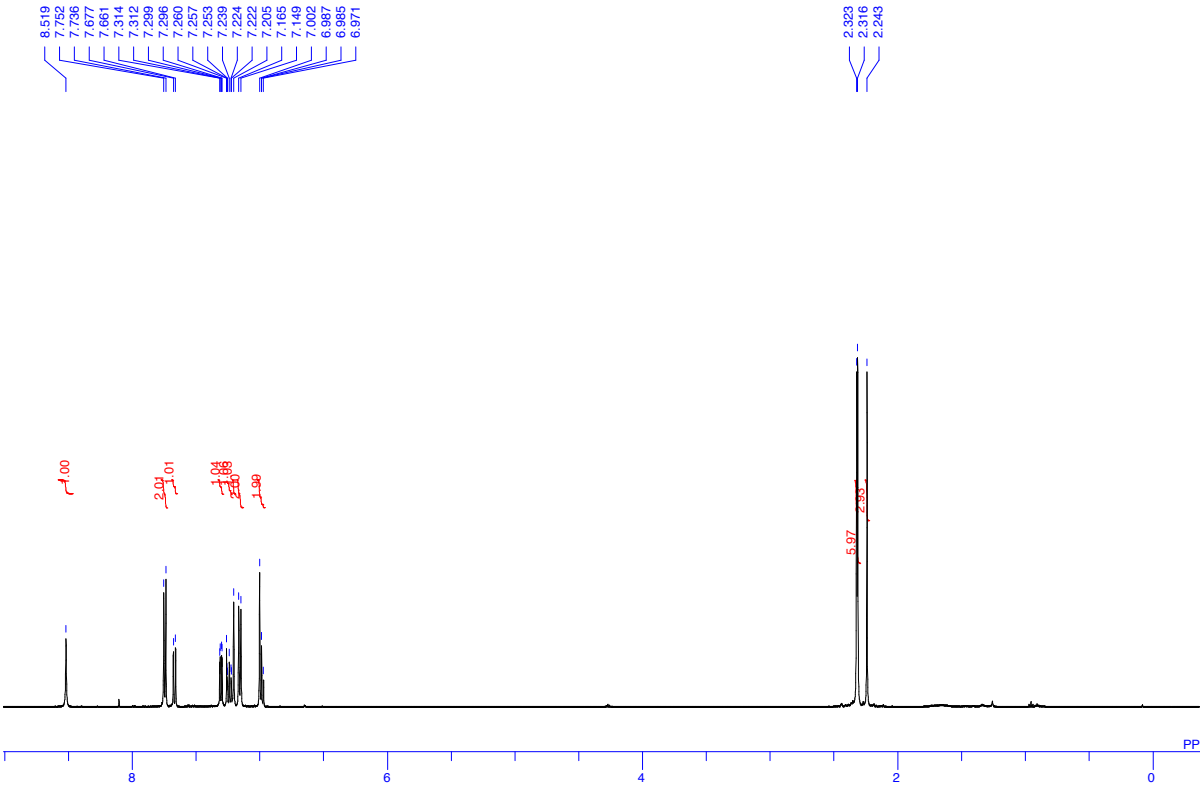
Me
Me
NHTs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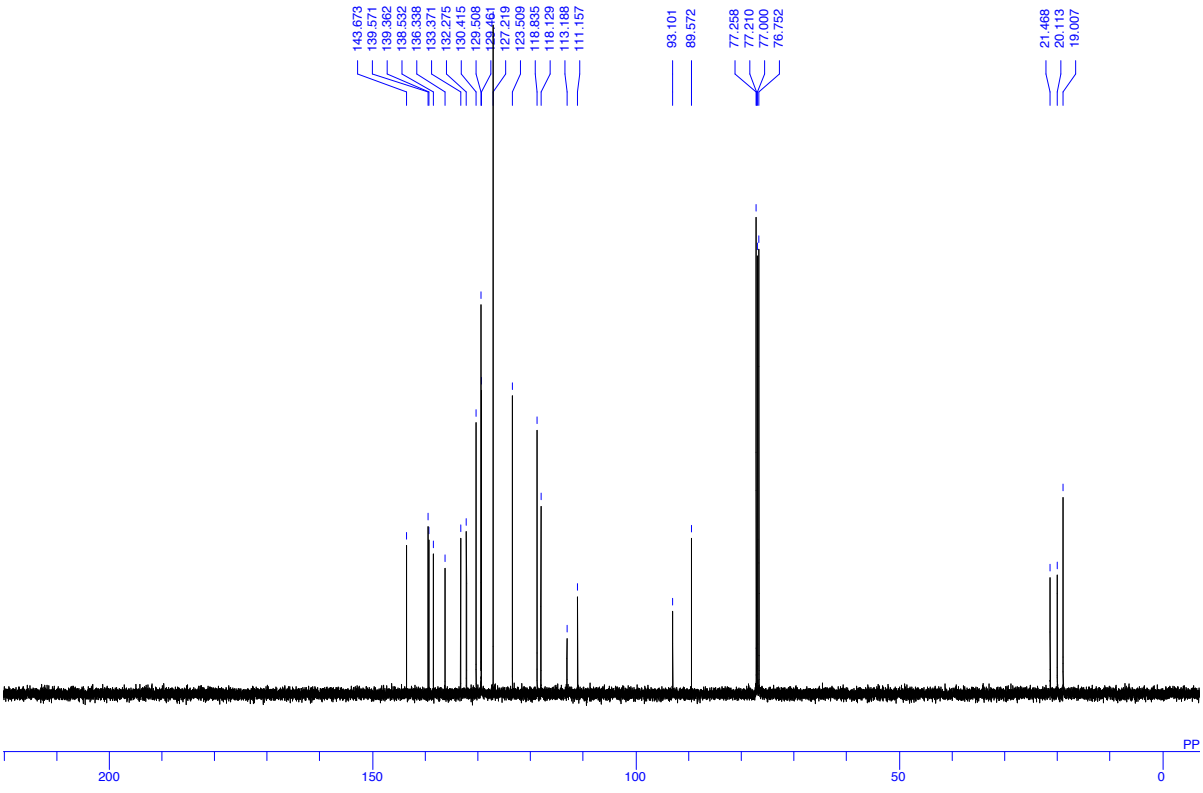
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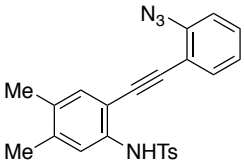
1d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Me
Me
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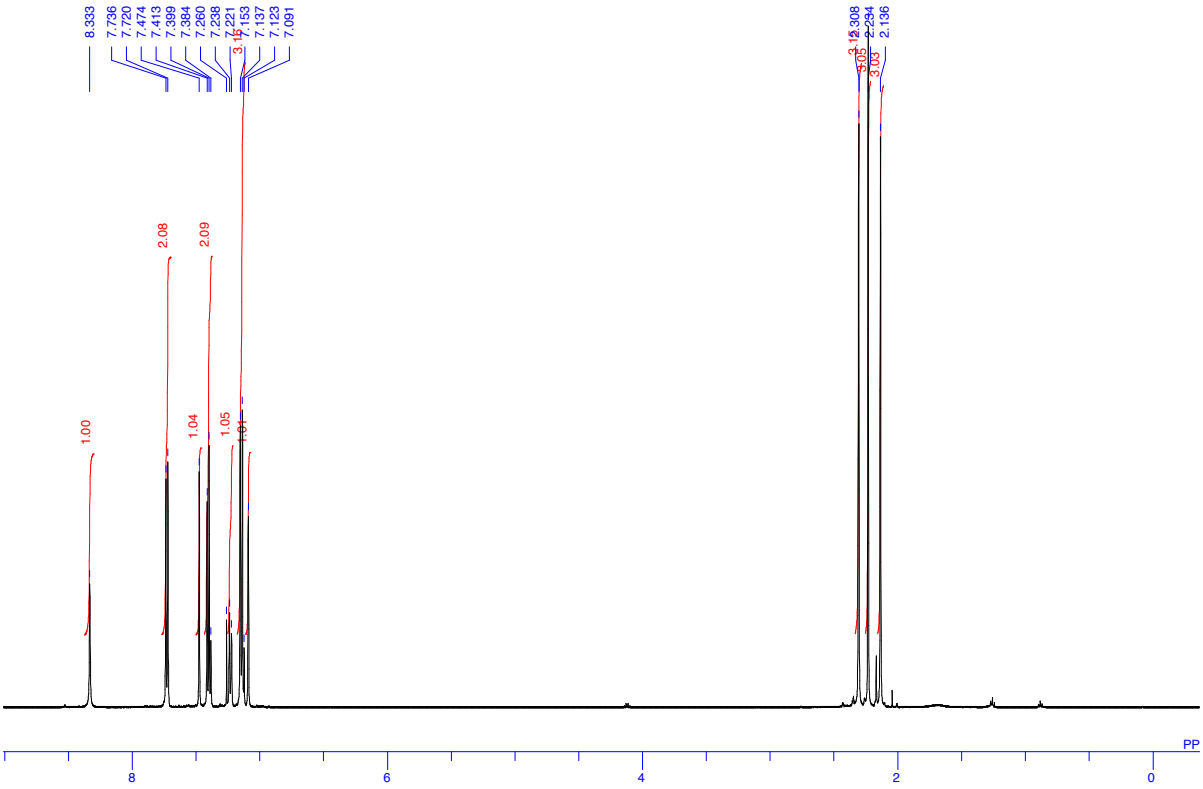
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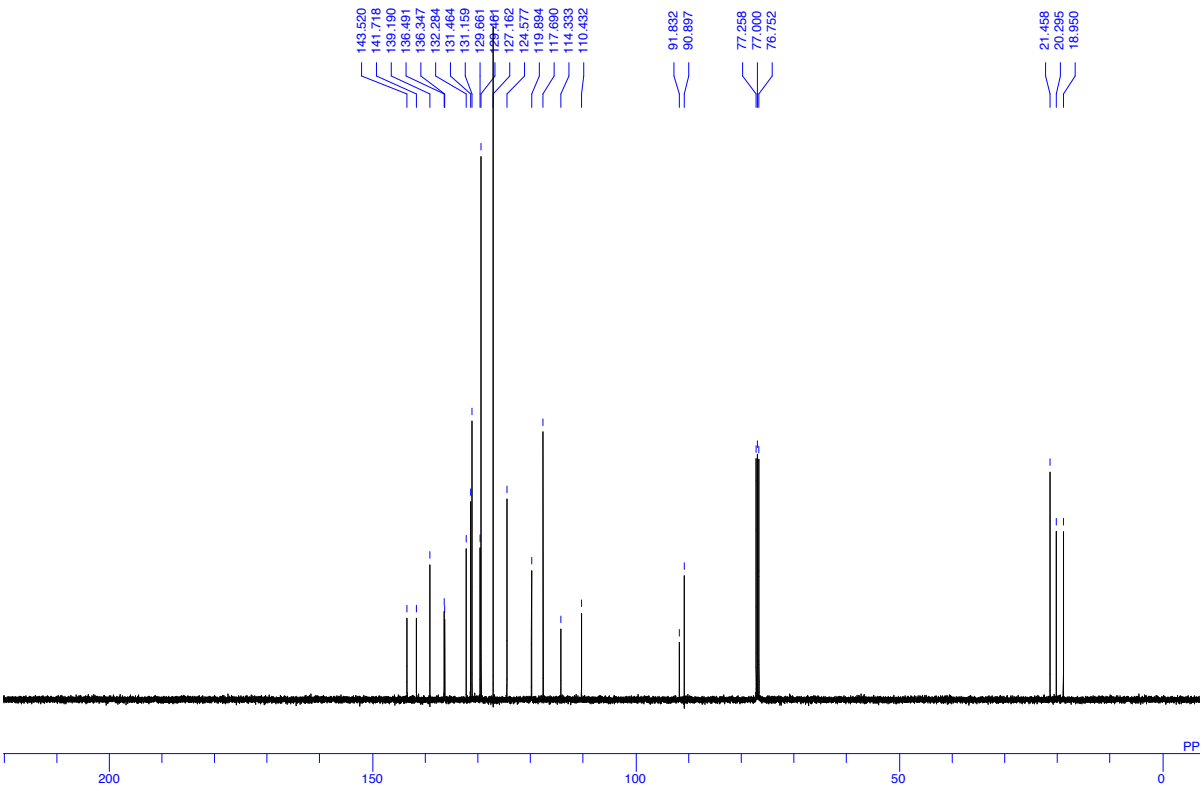
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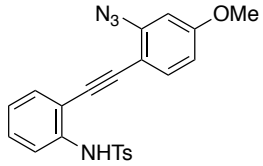
1e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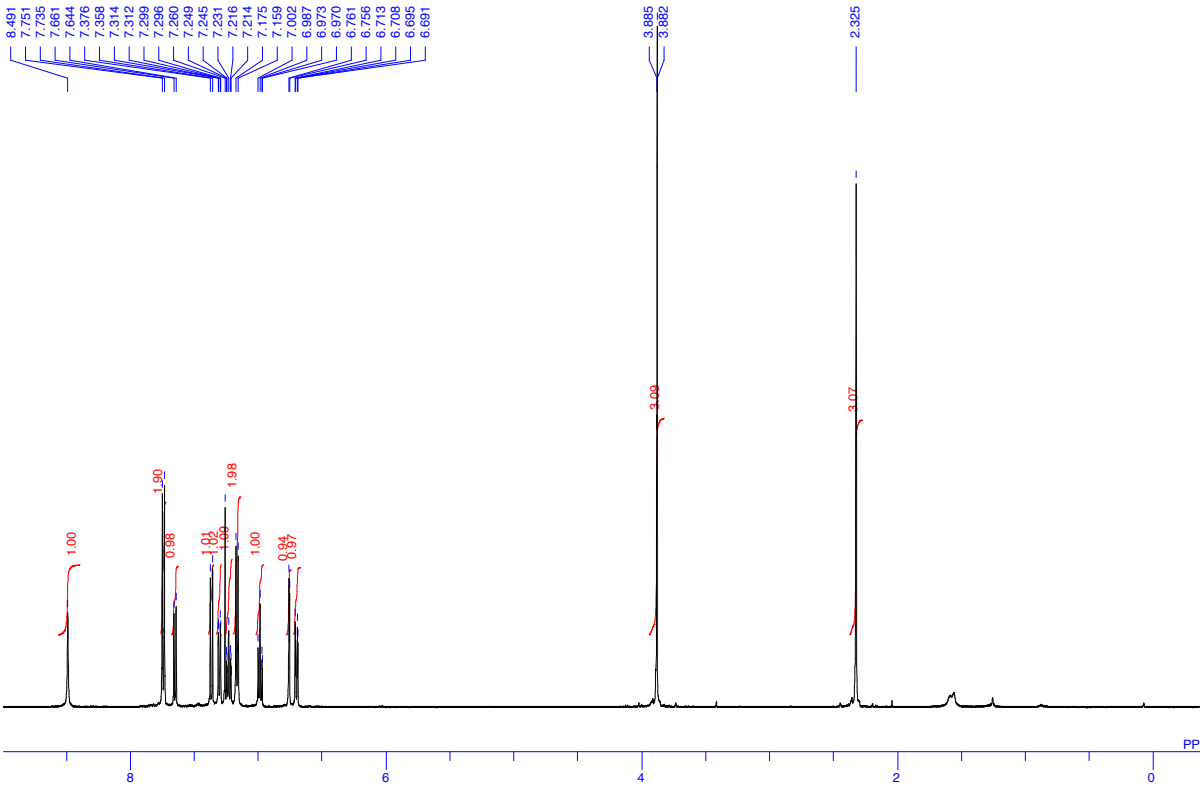
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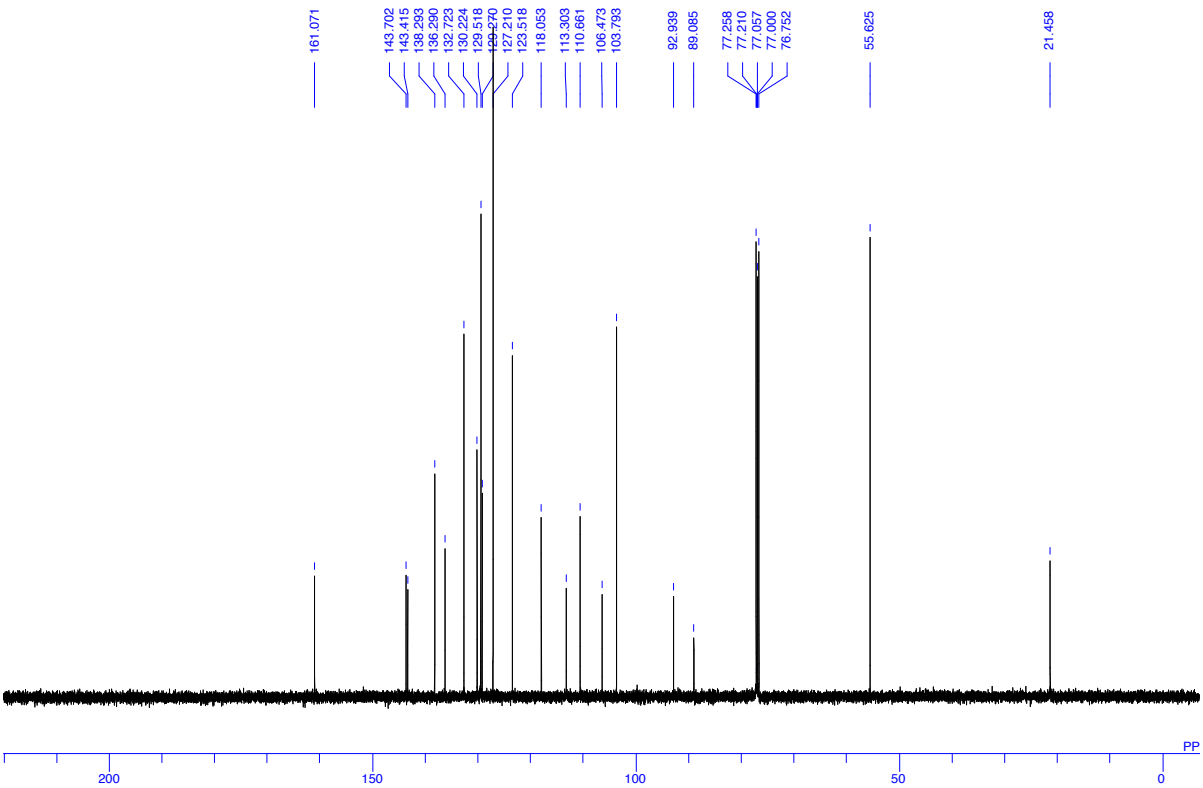
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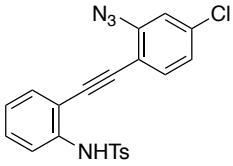
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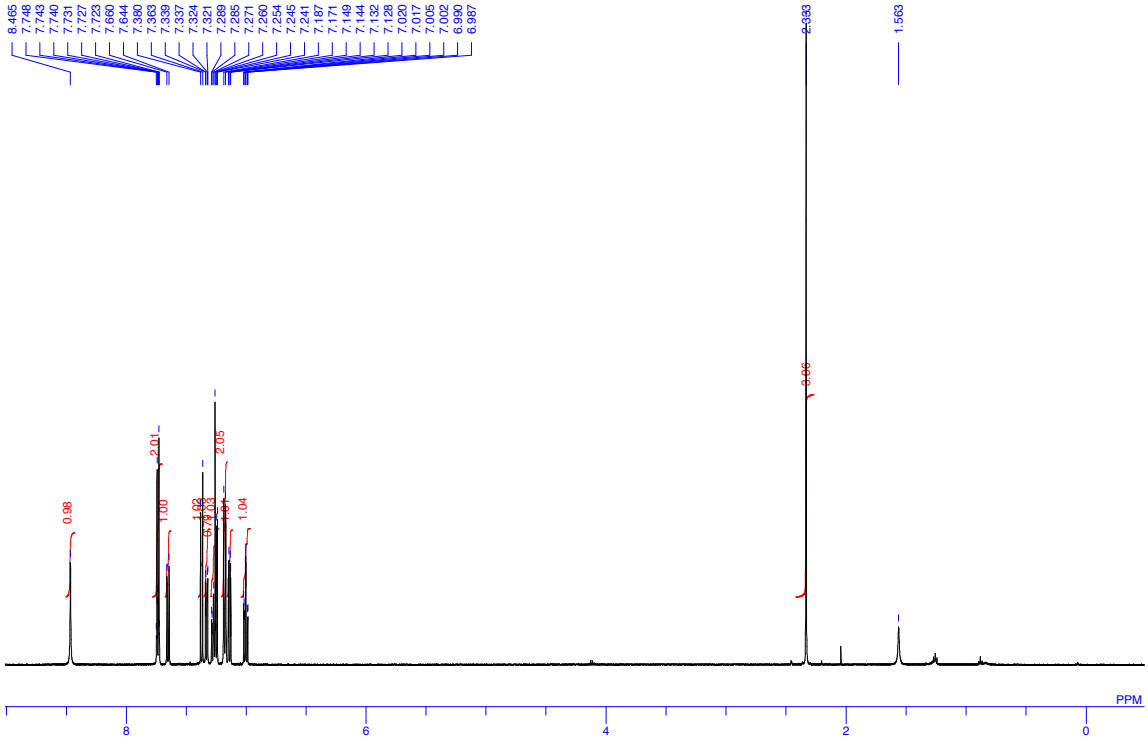
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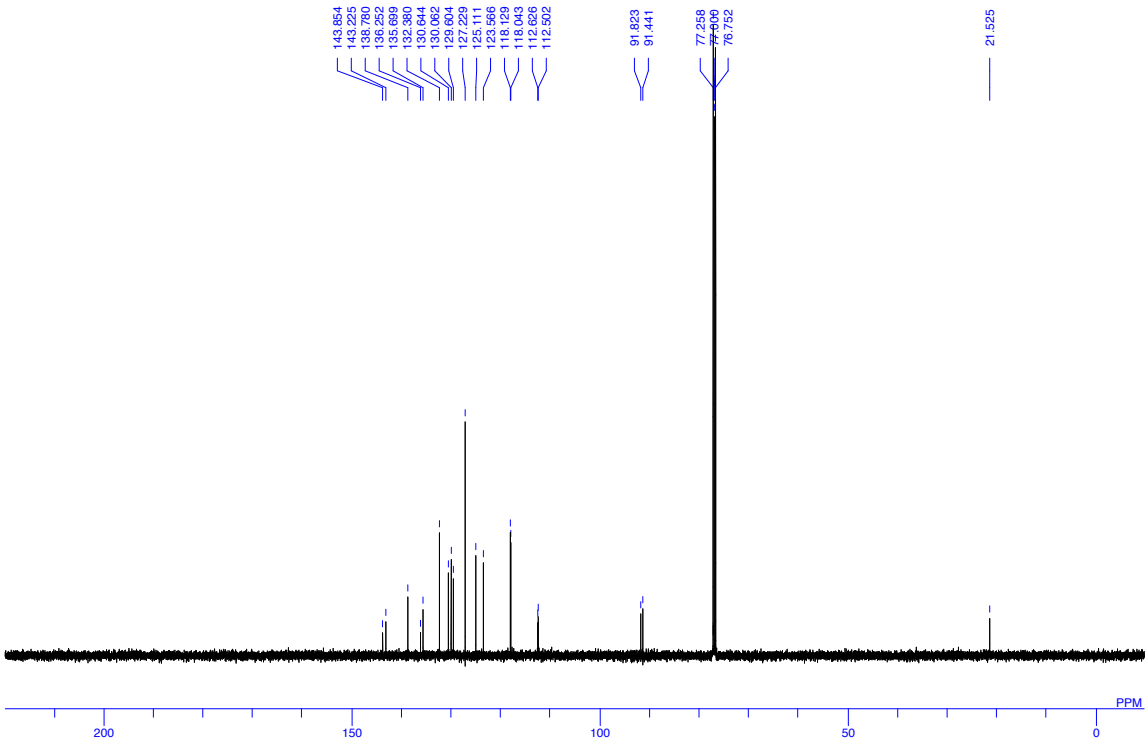
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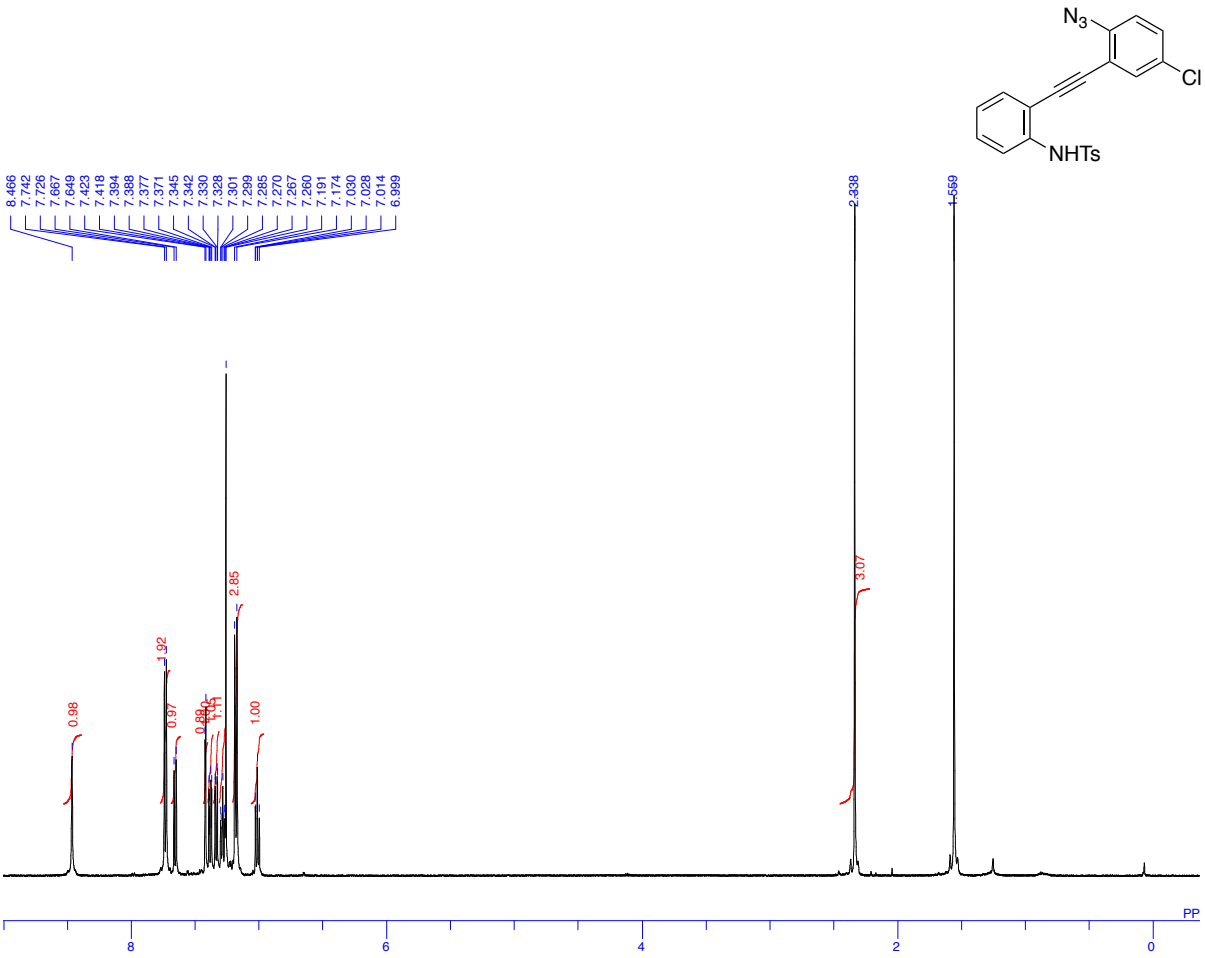
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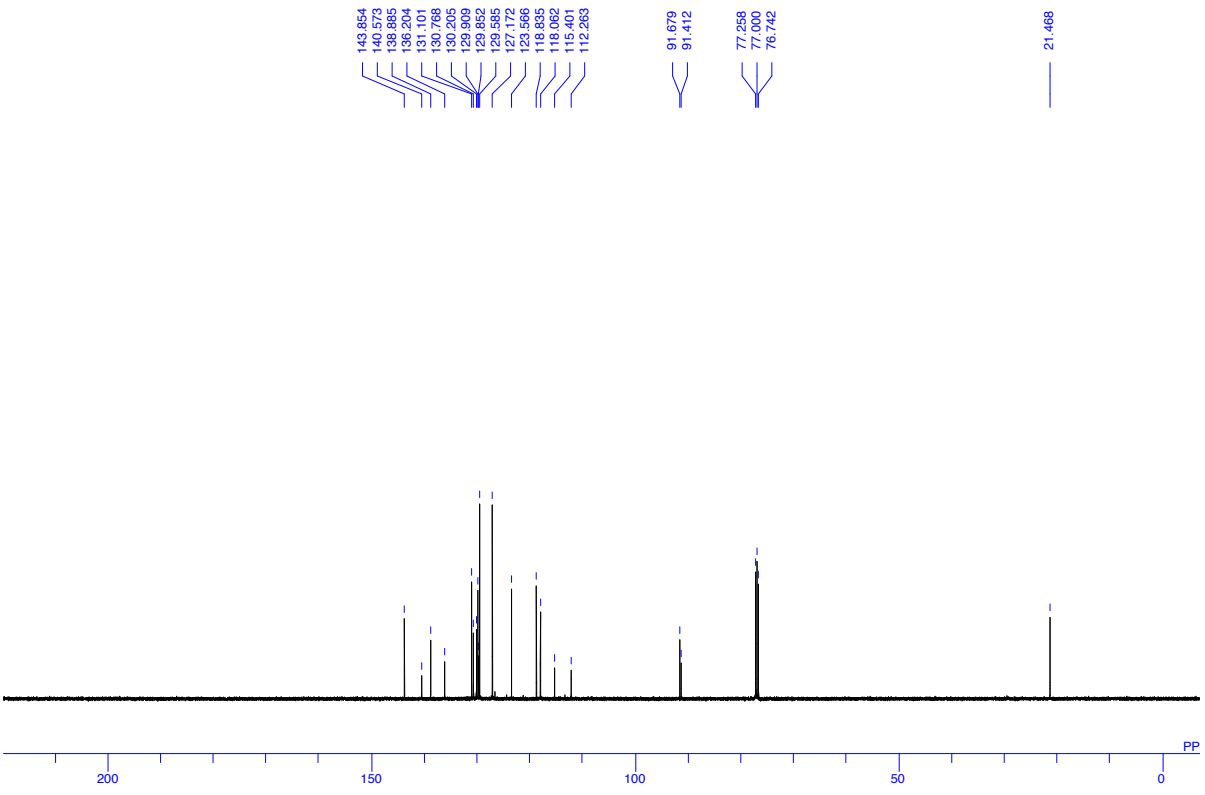
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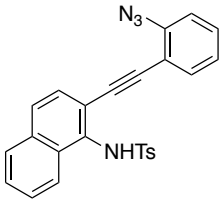
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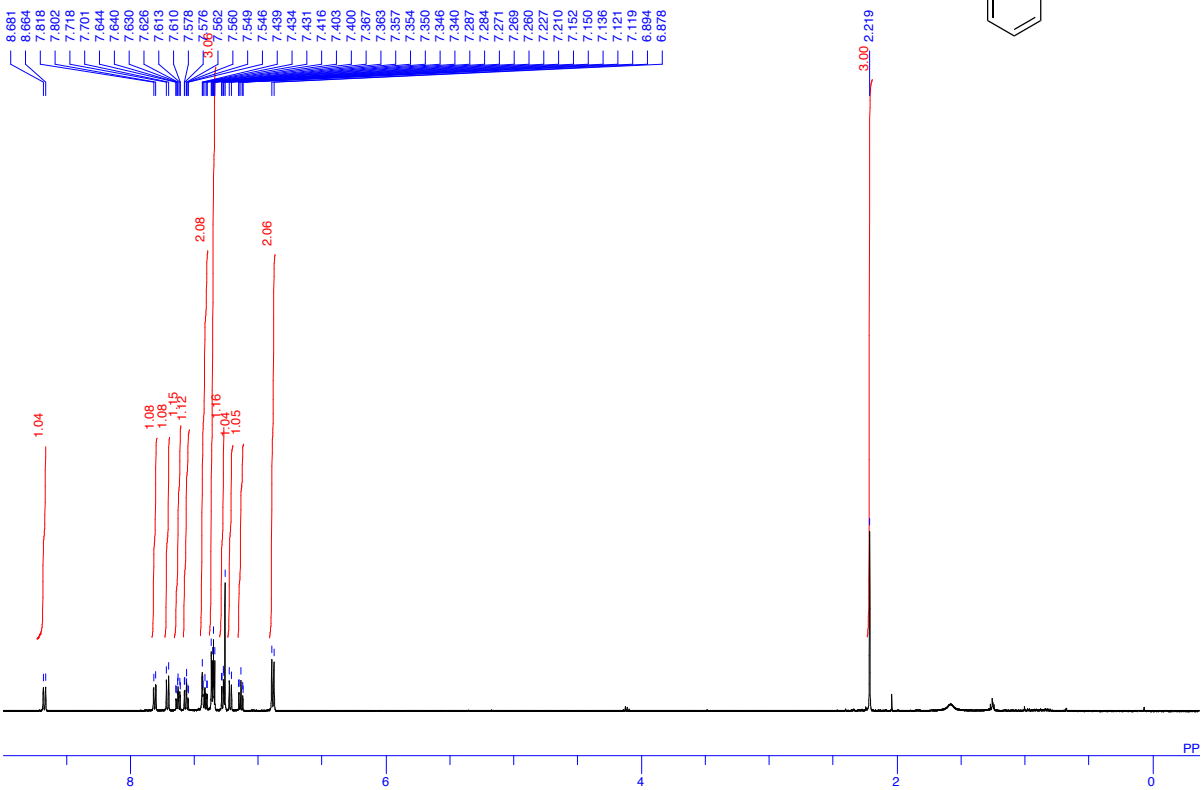
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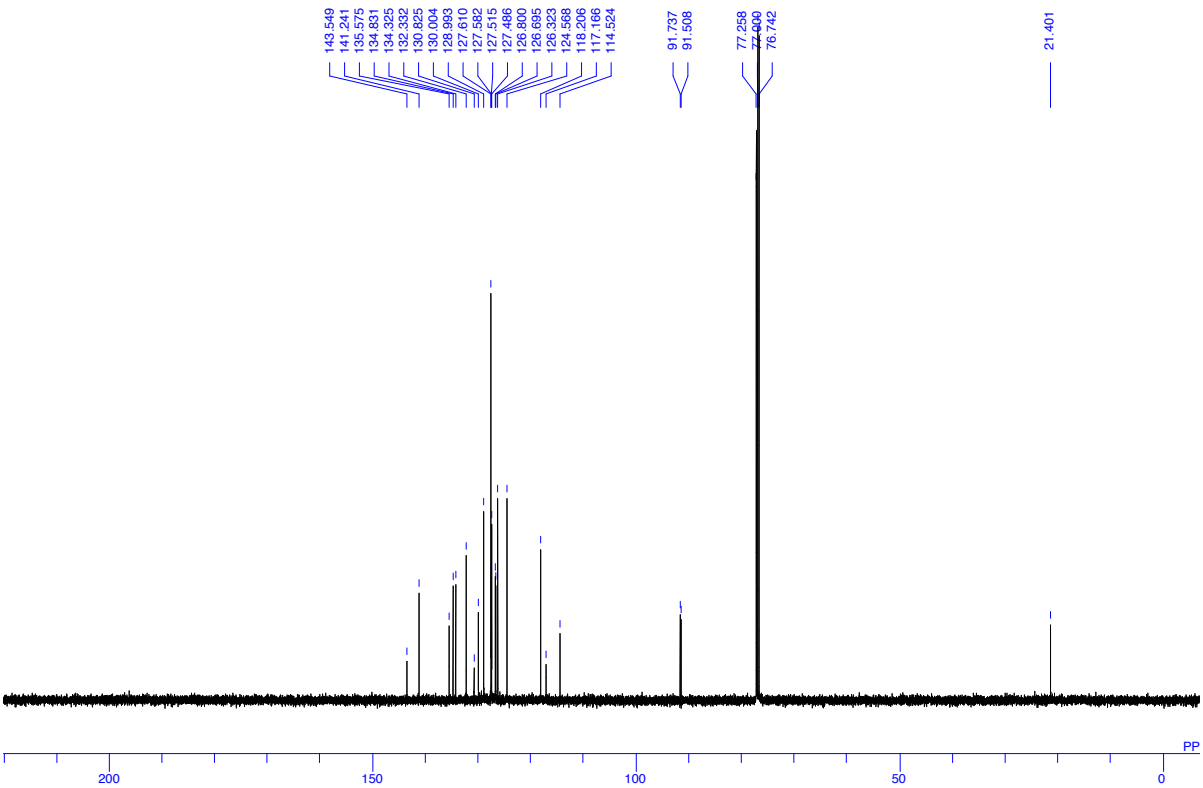
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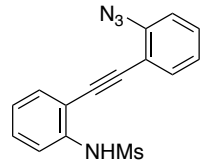
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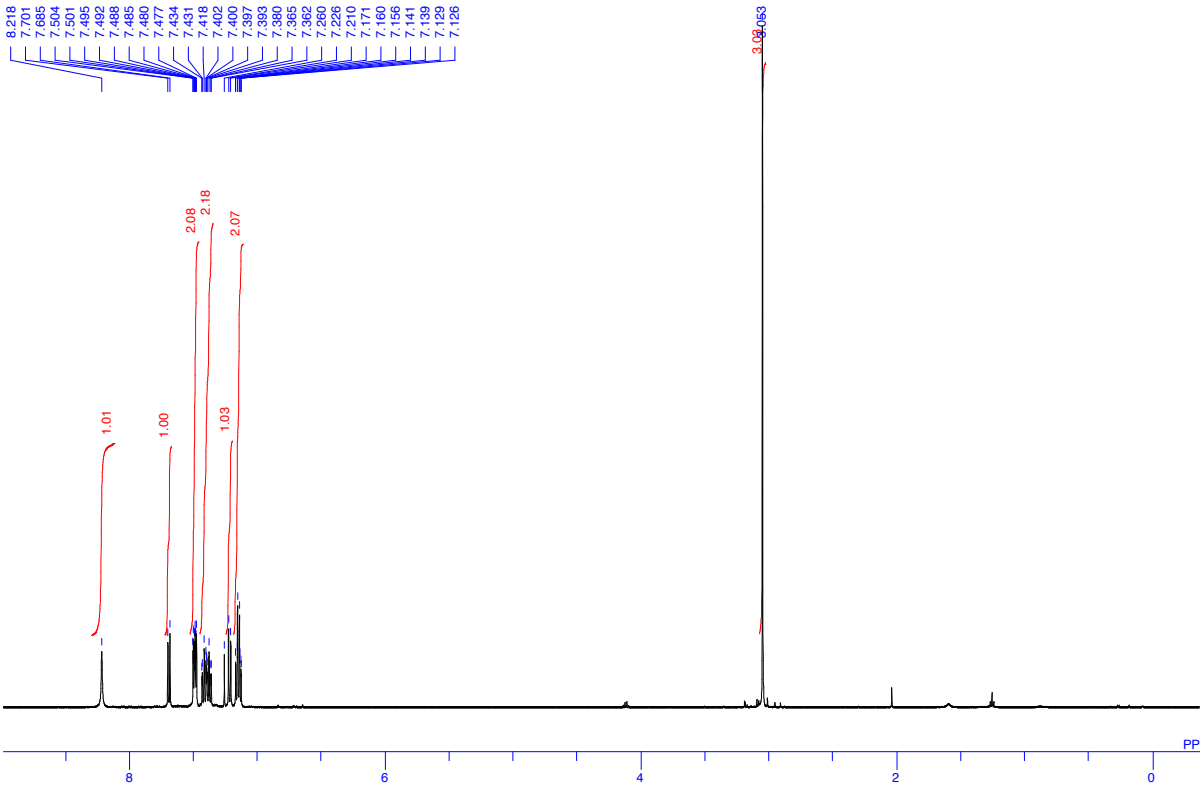
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7.402
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7.260
7.226
7.210
7.171
7.160
7.156
7.141
7.139
7.129
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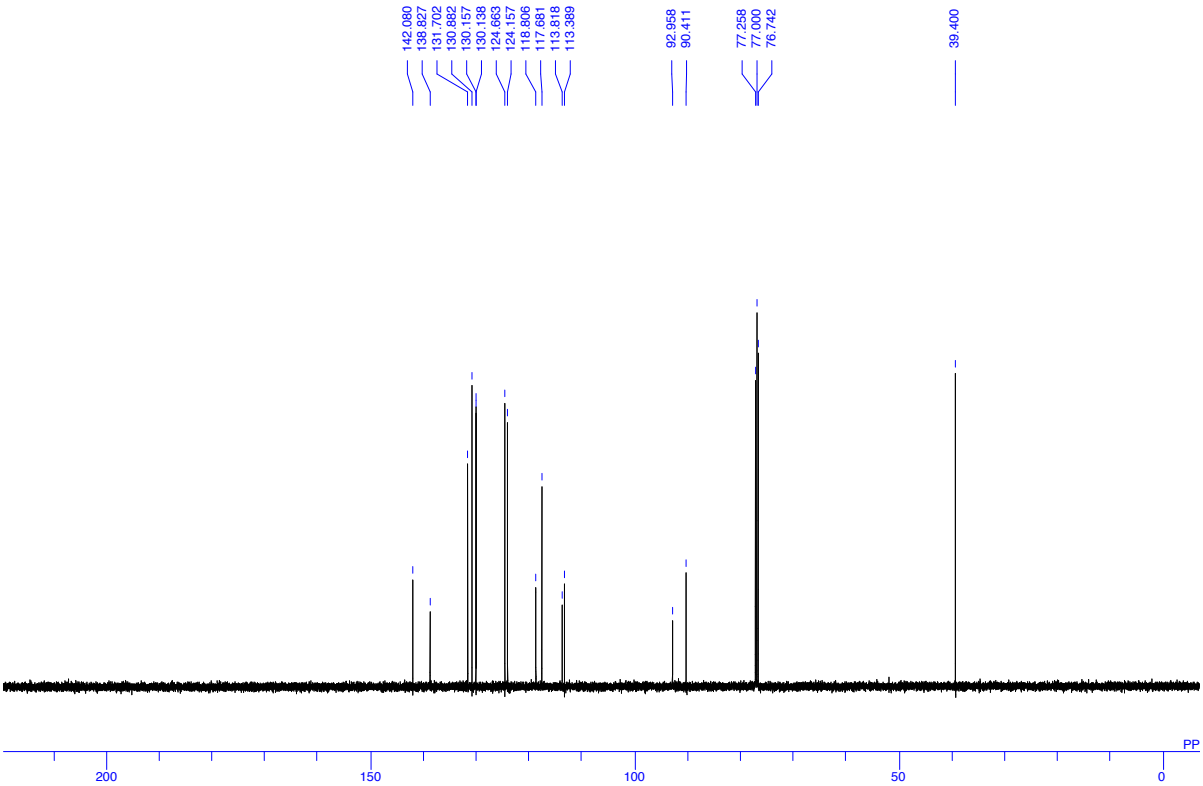
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100
50
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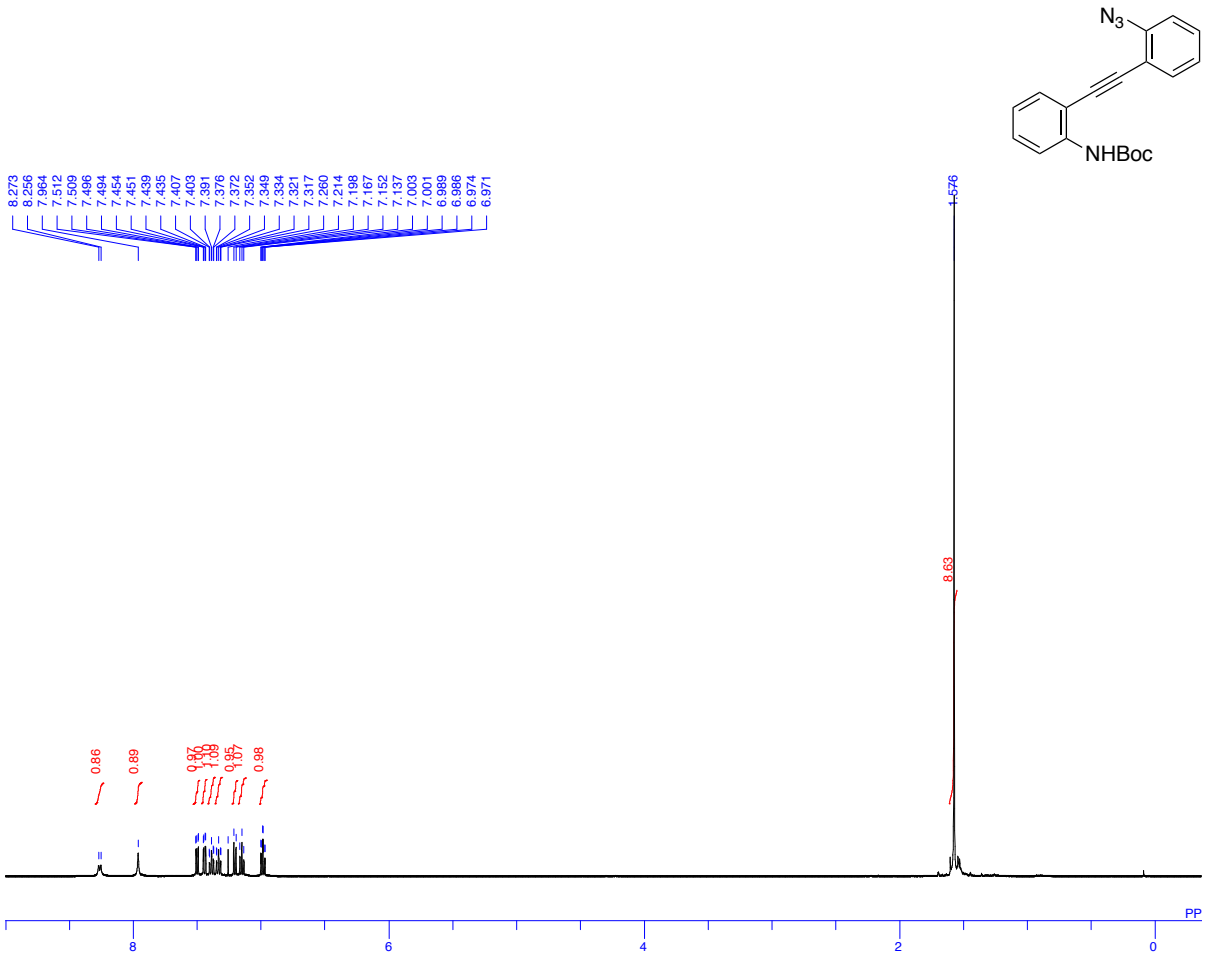
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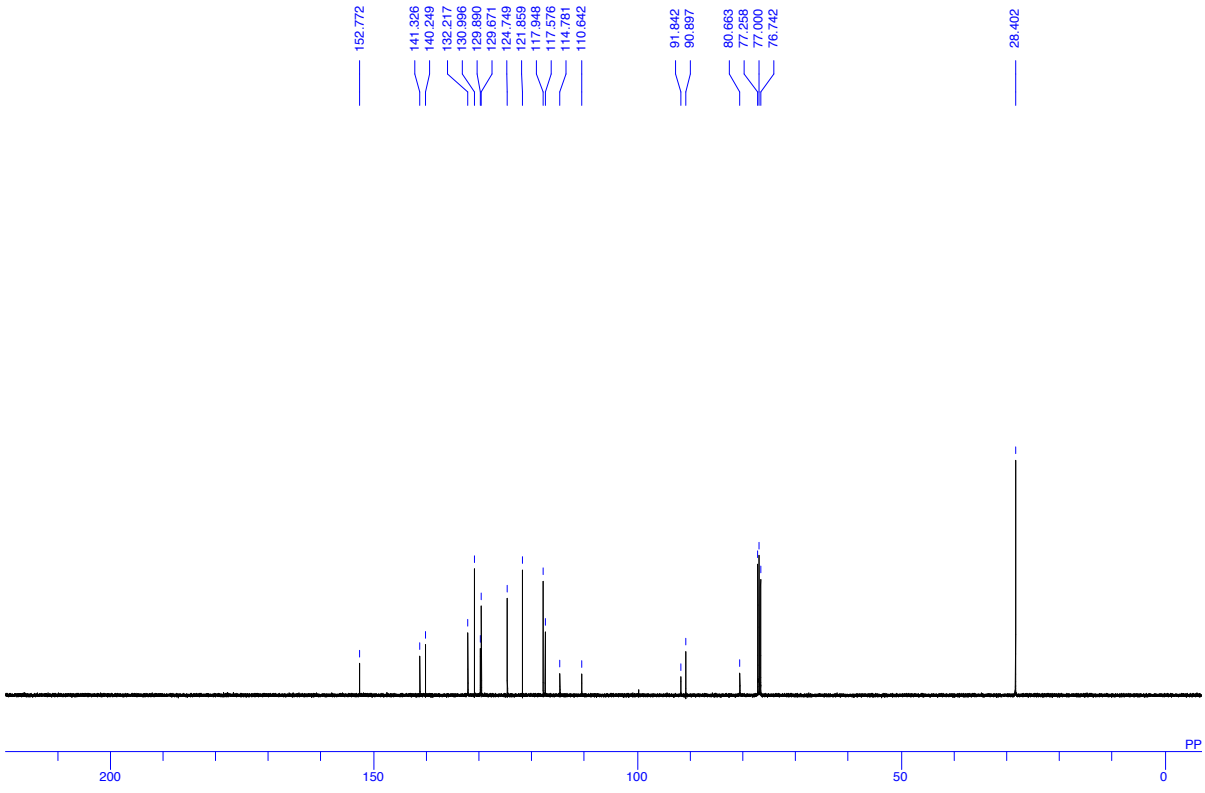
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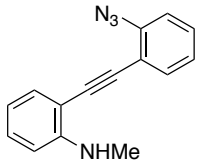
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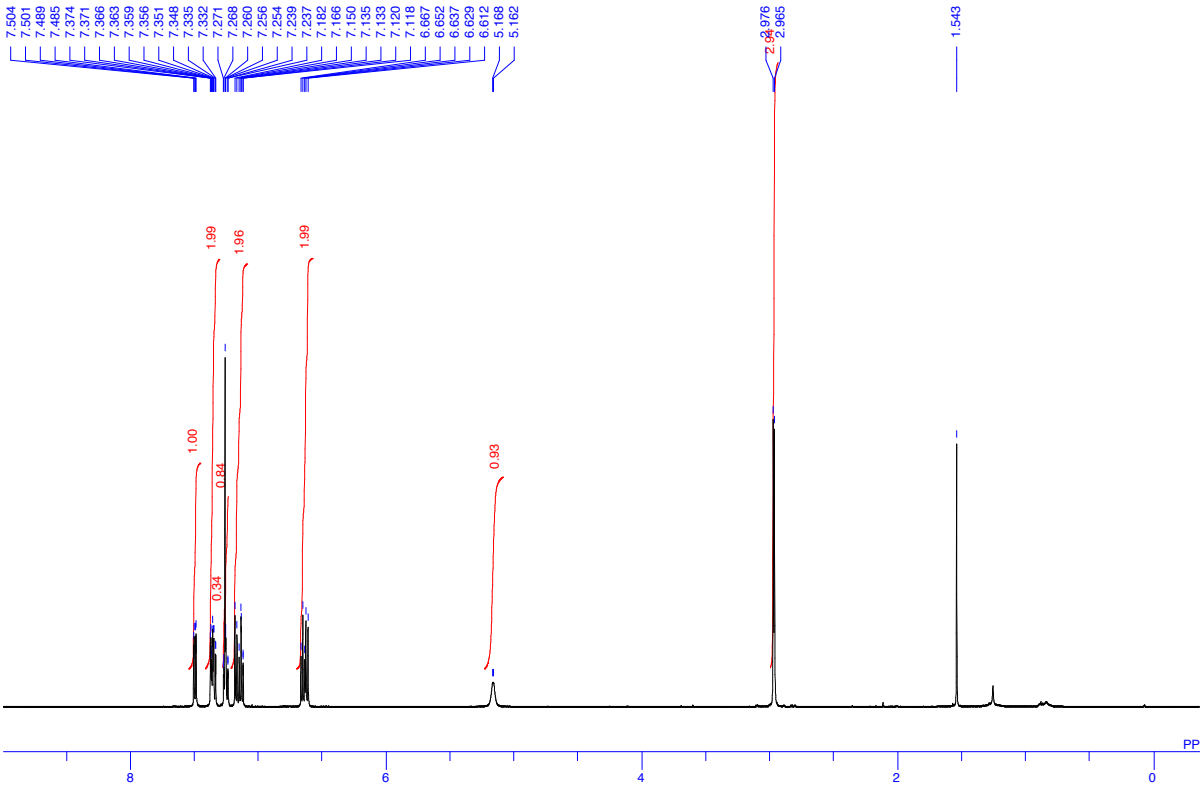
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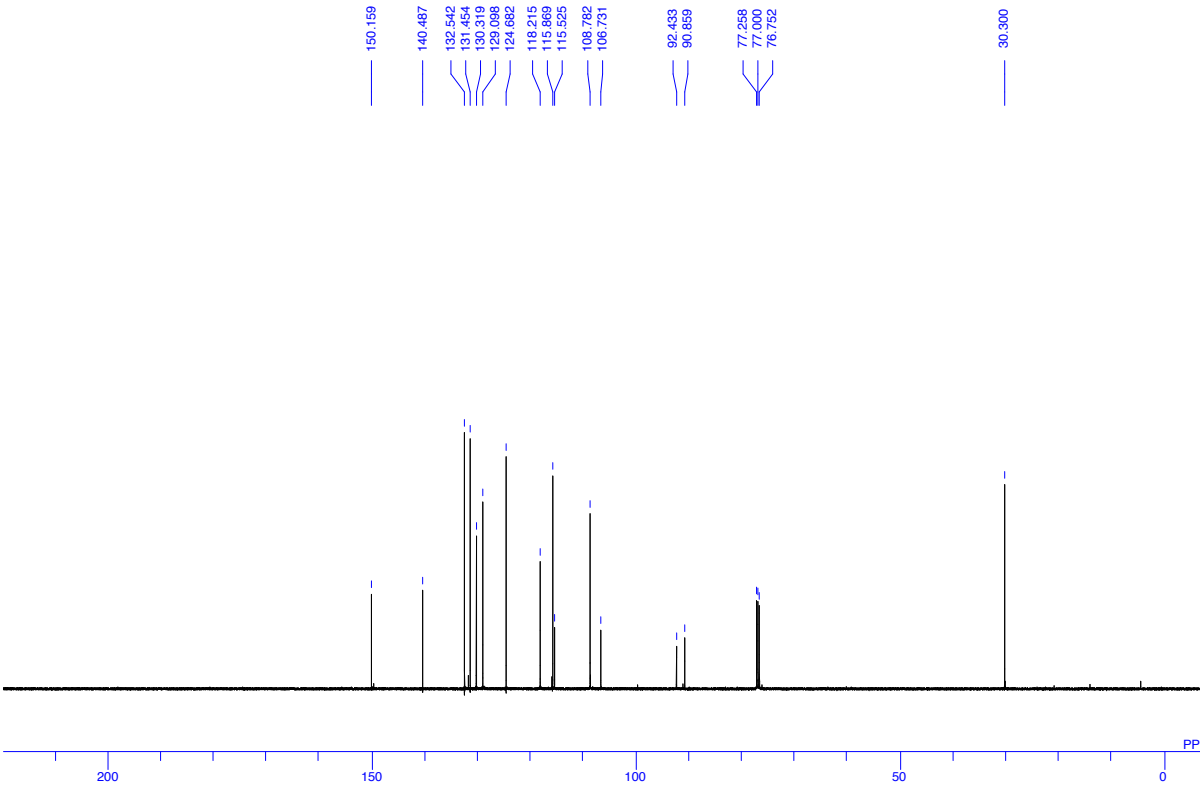
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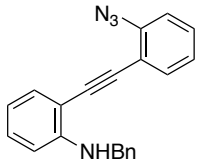
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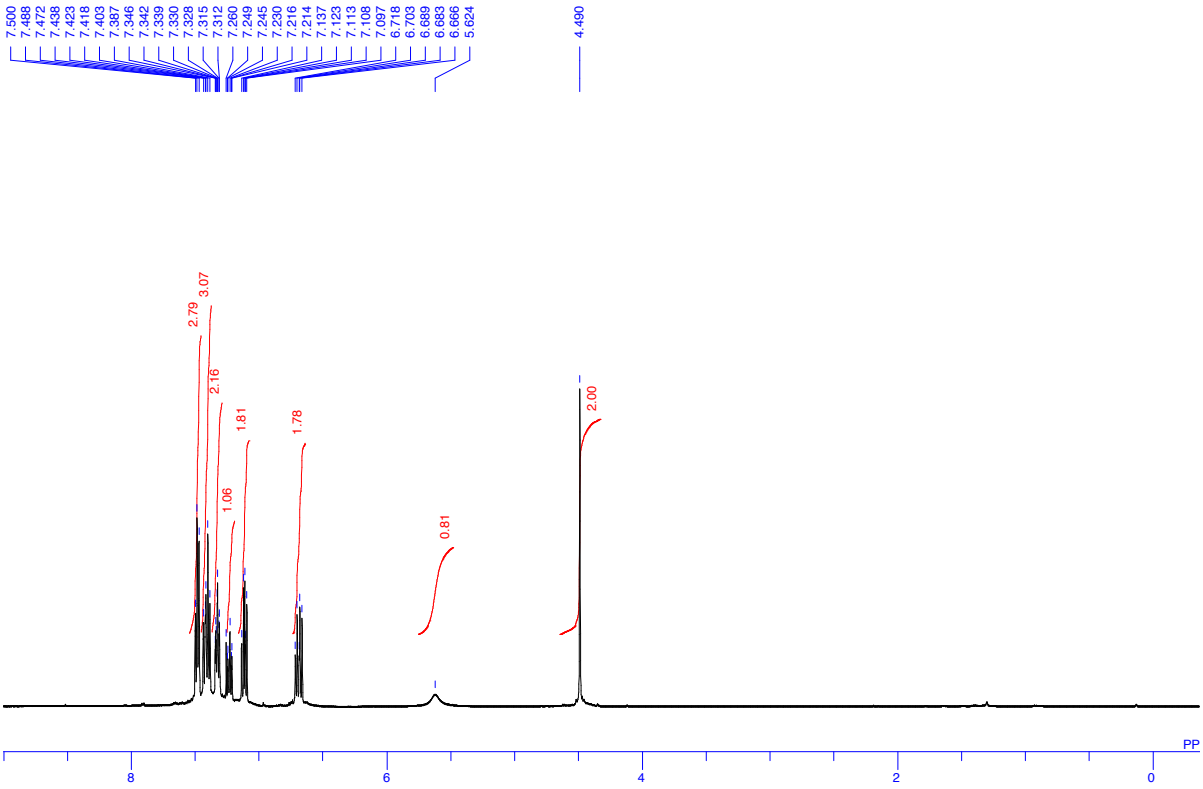
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6.666
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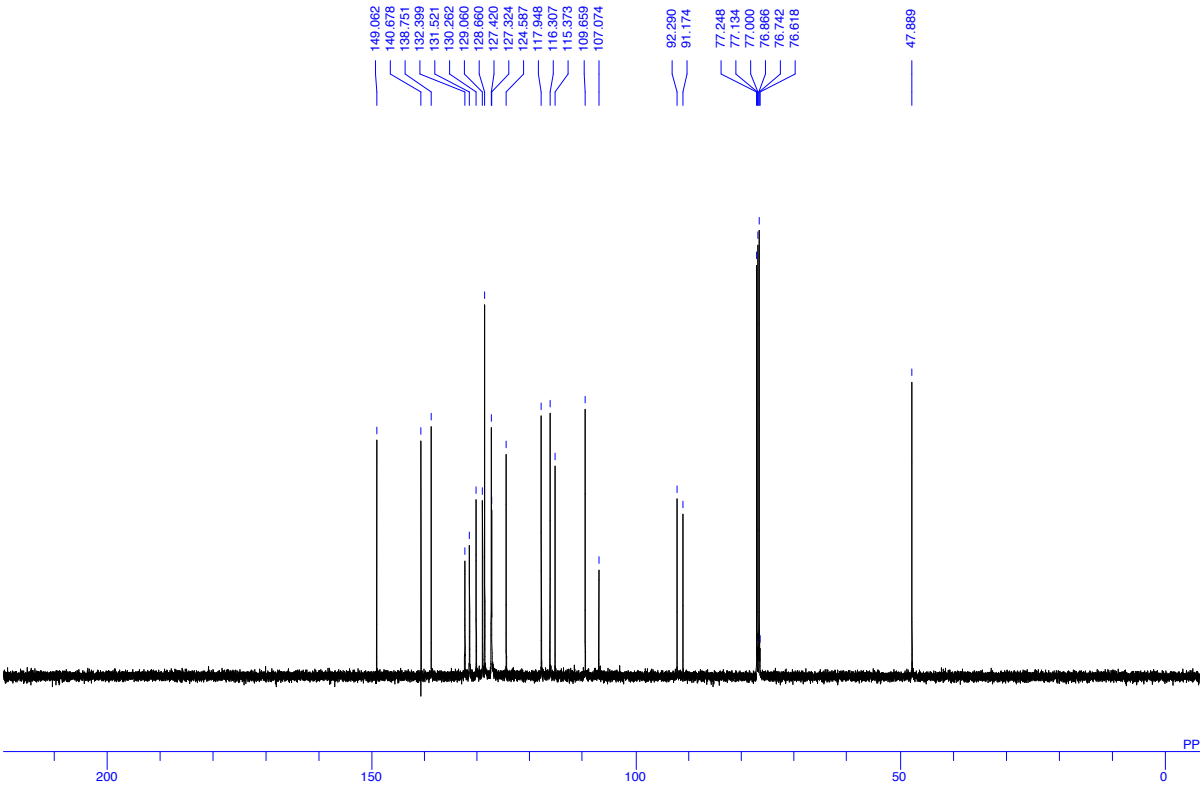
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116.307
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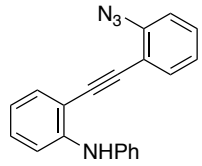
1m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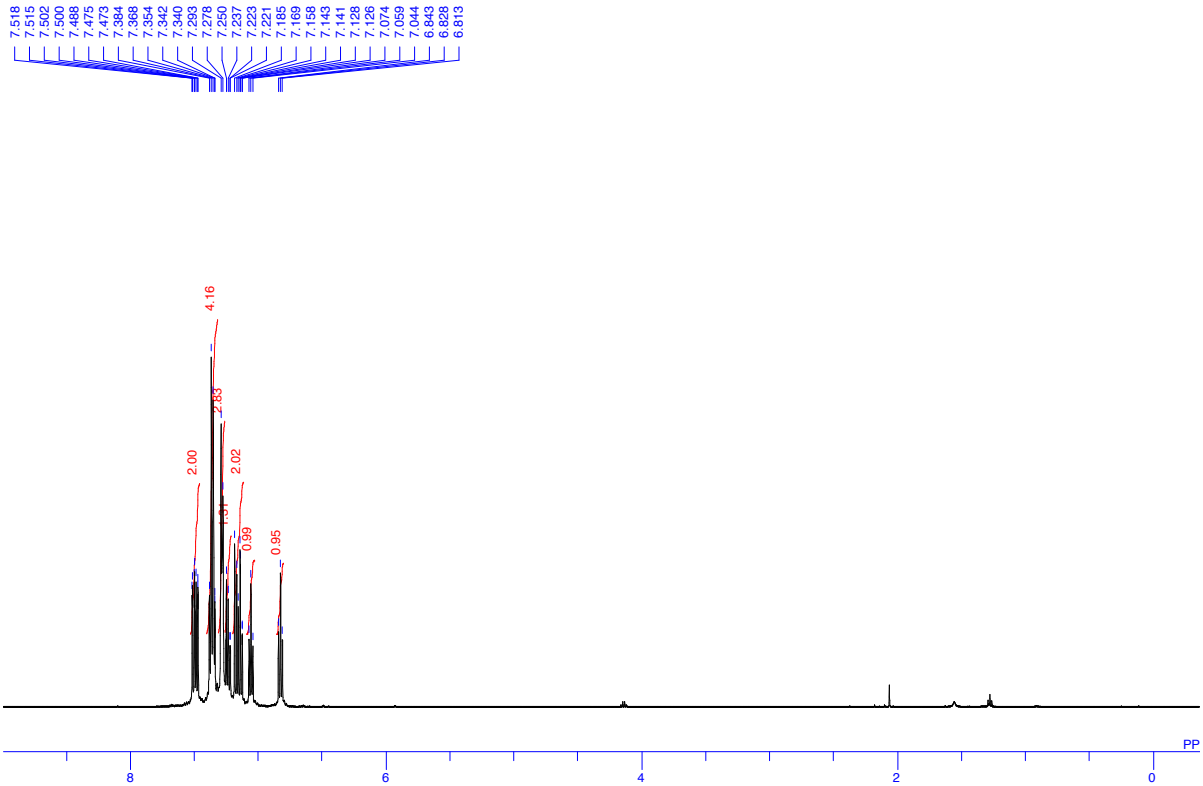
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7.250
7.237
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7.221
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7.126
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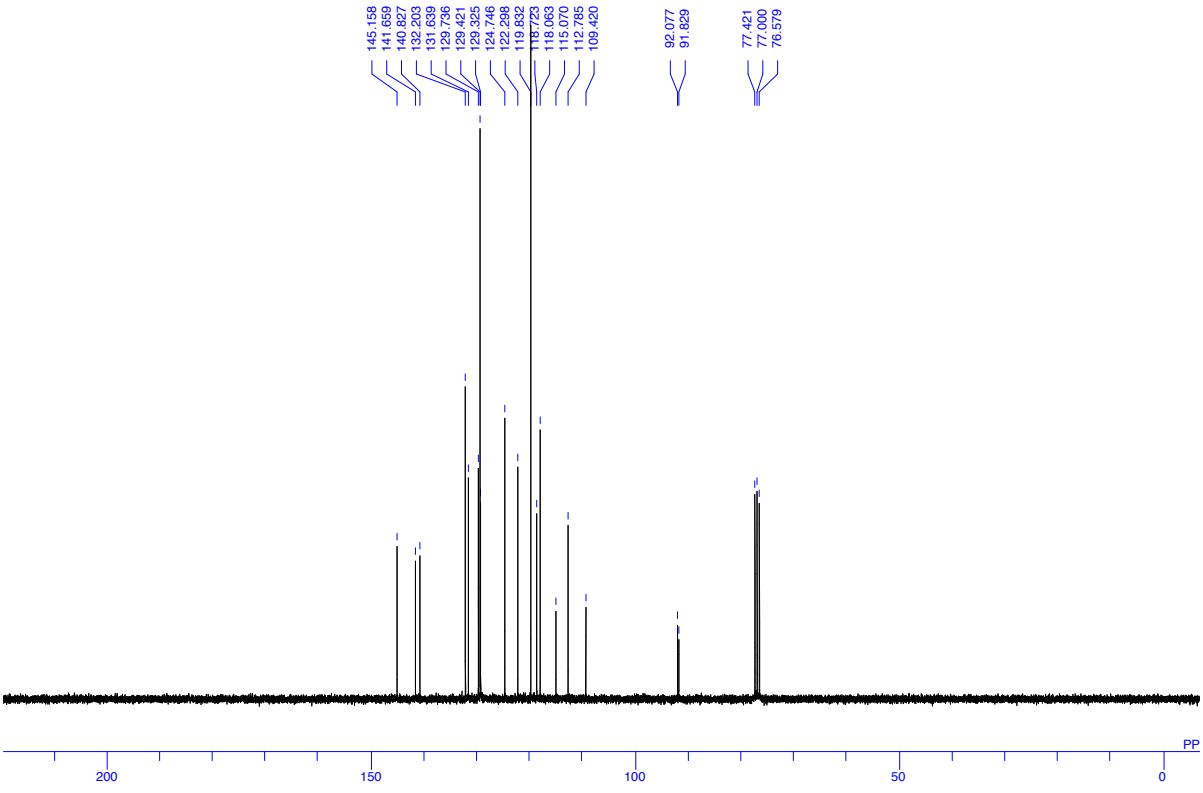
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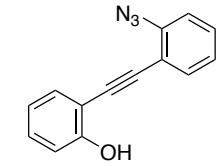
4a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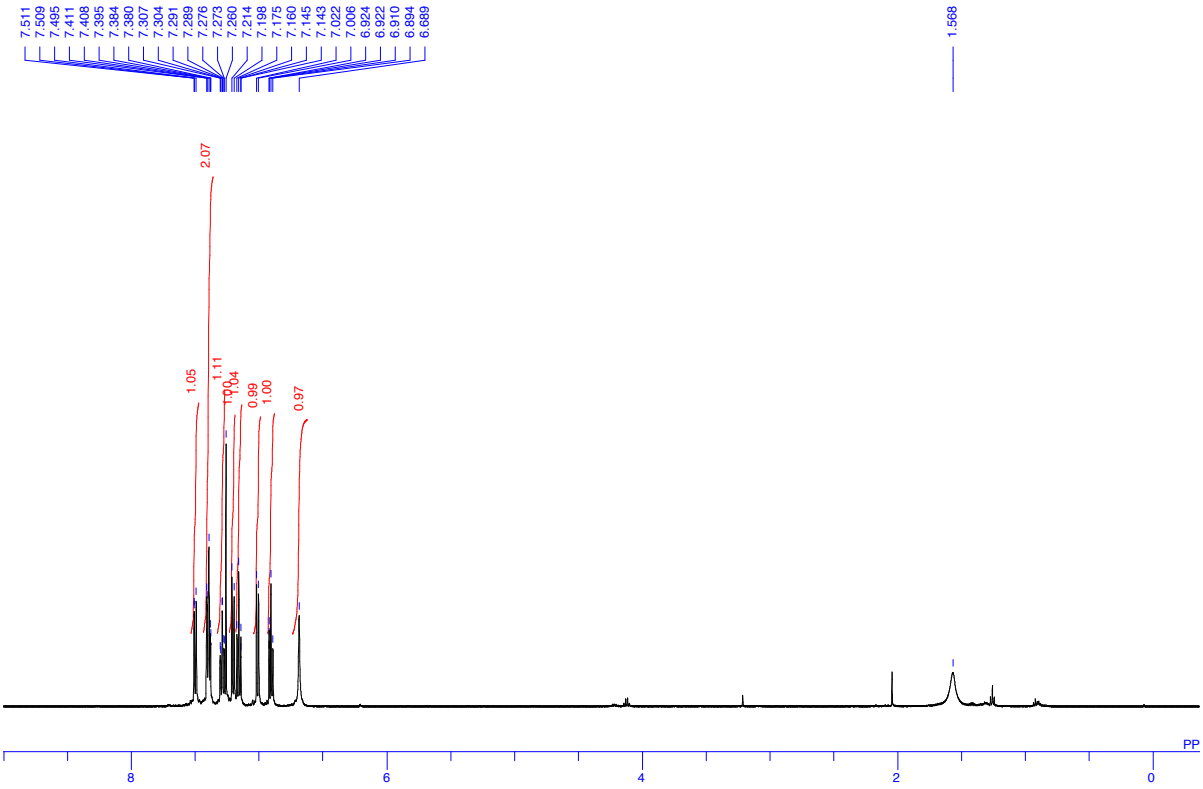
OH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6.910
6.894
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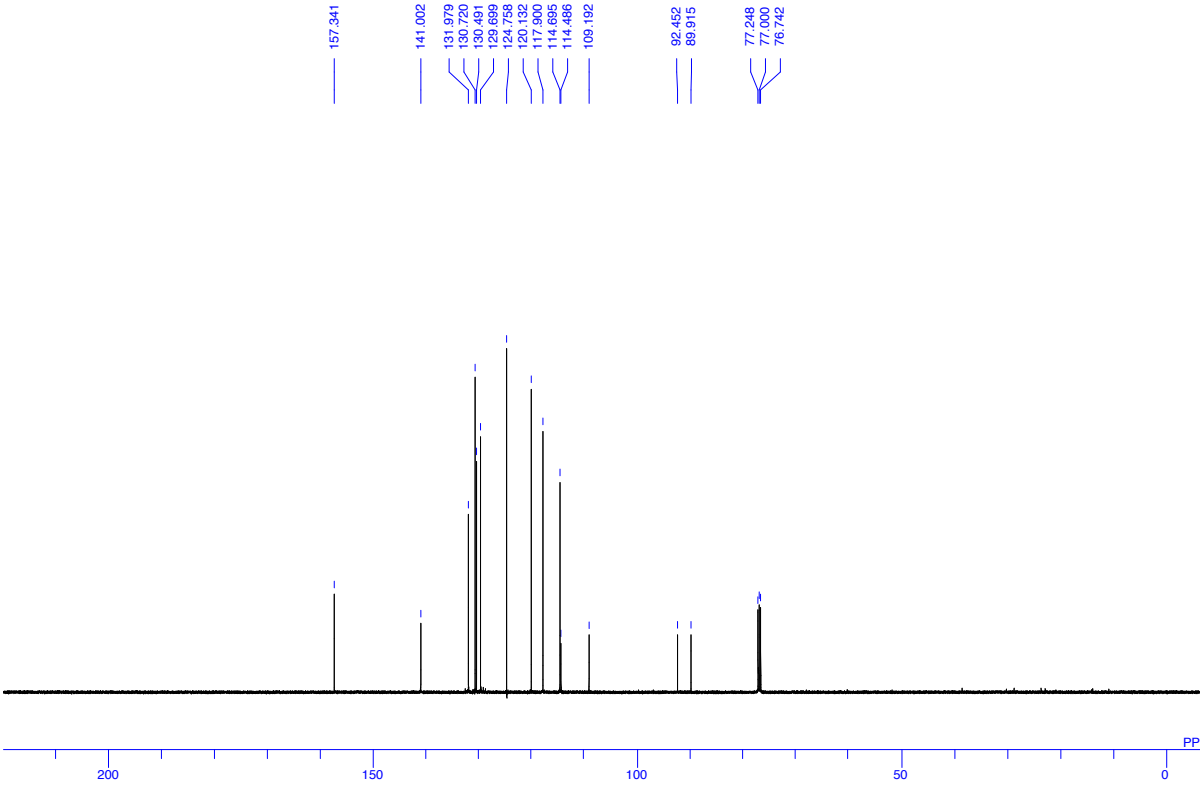
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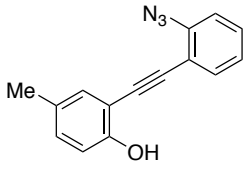
4b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Me
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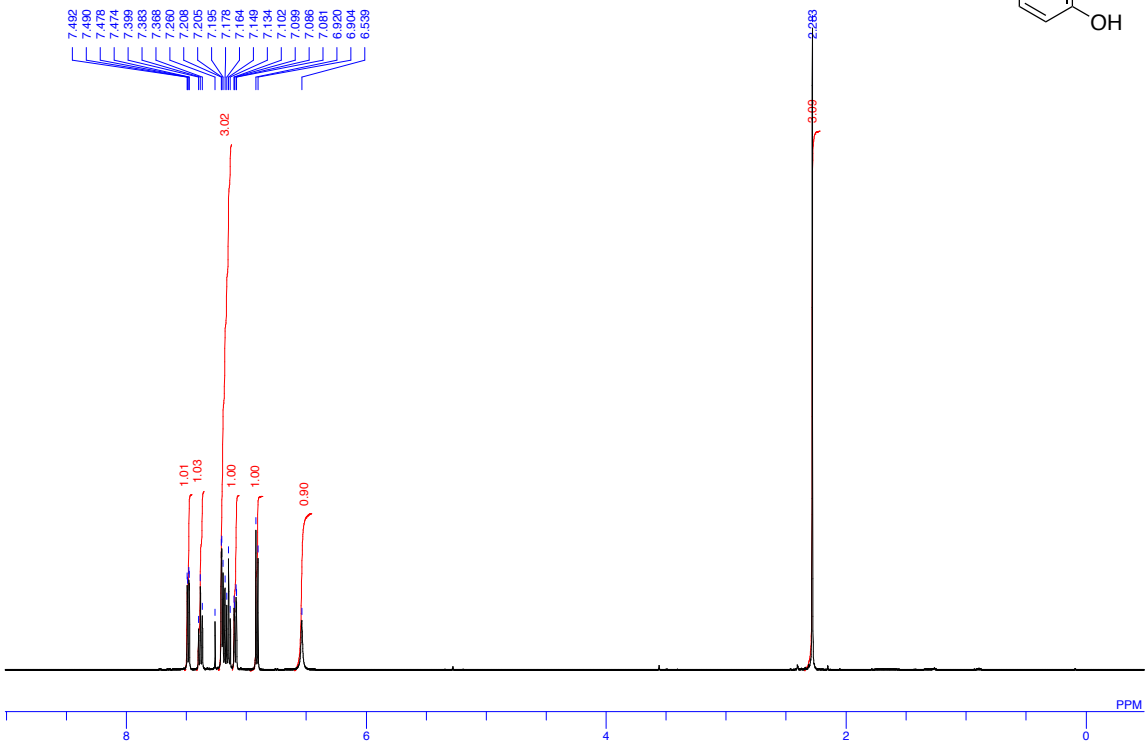
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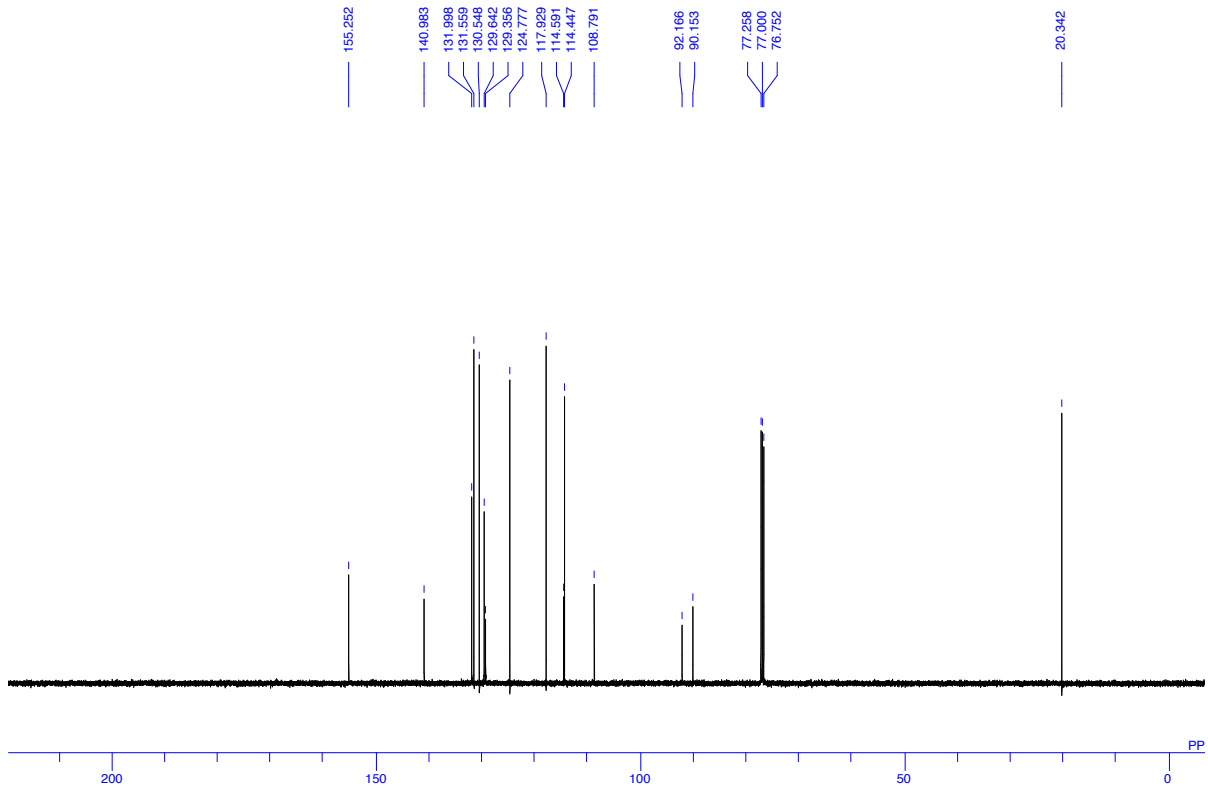
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90.153
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77.000
76.752
20.342
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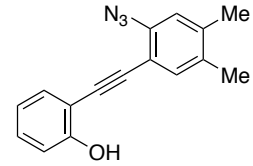
100
50
0

4c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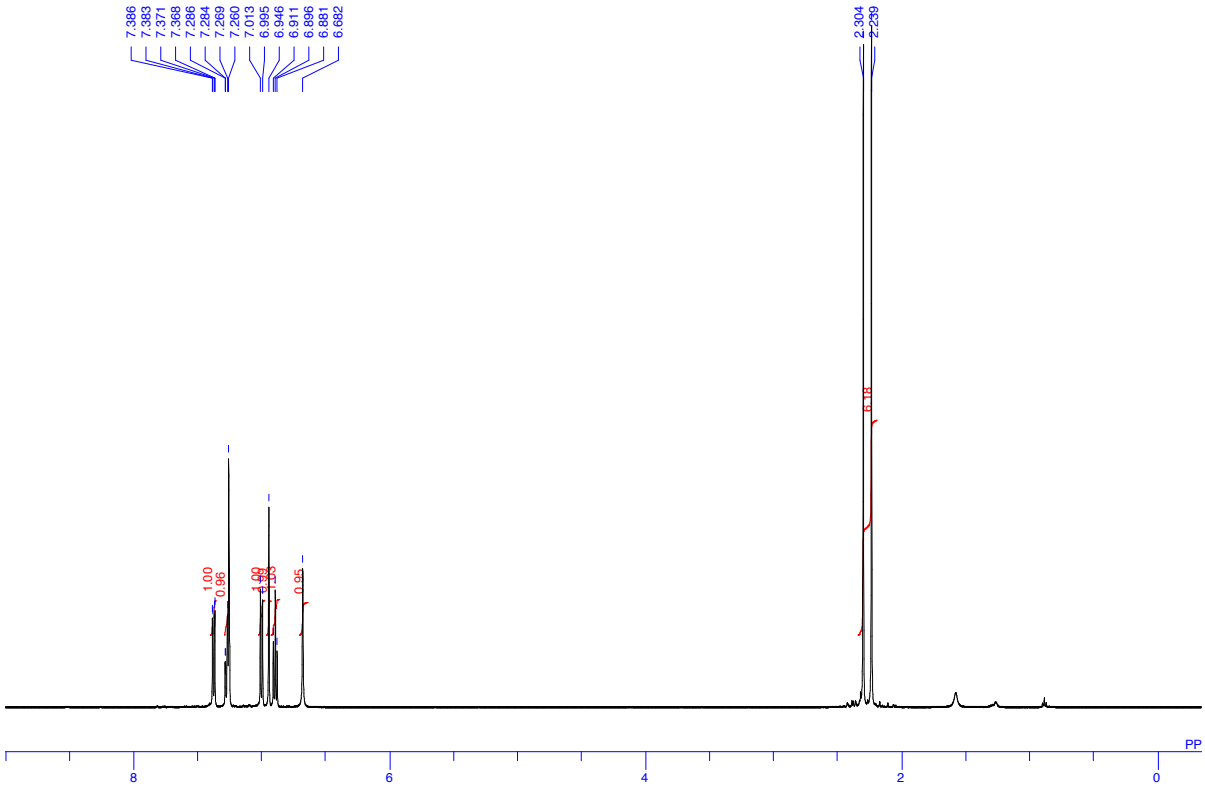
Me
Me
OH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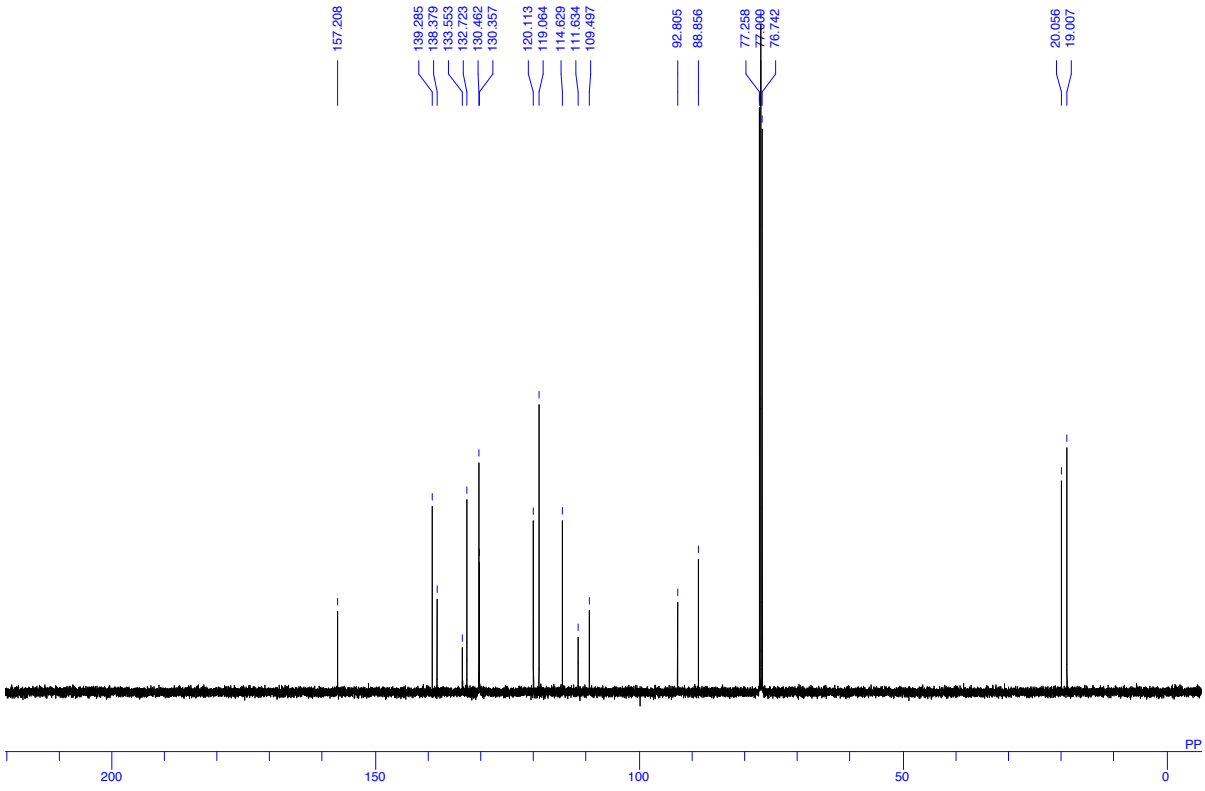
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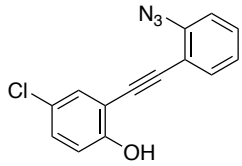
4d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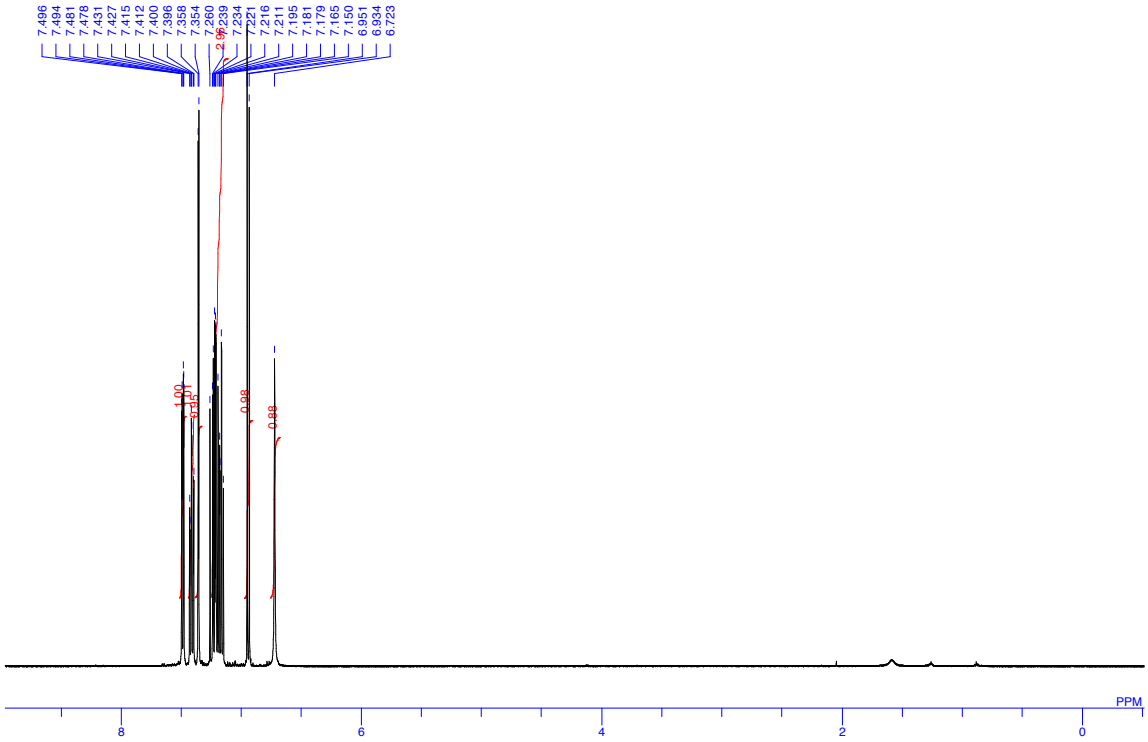
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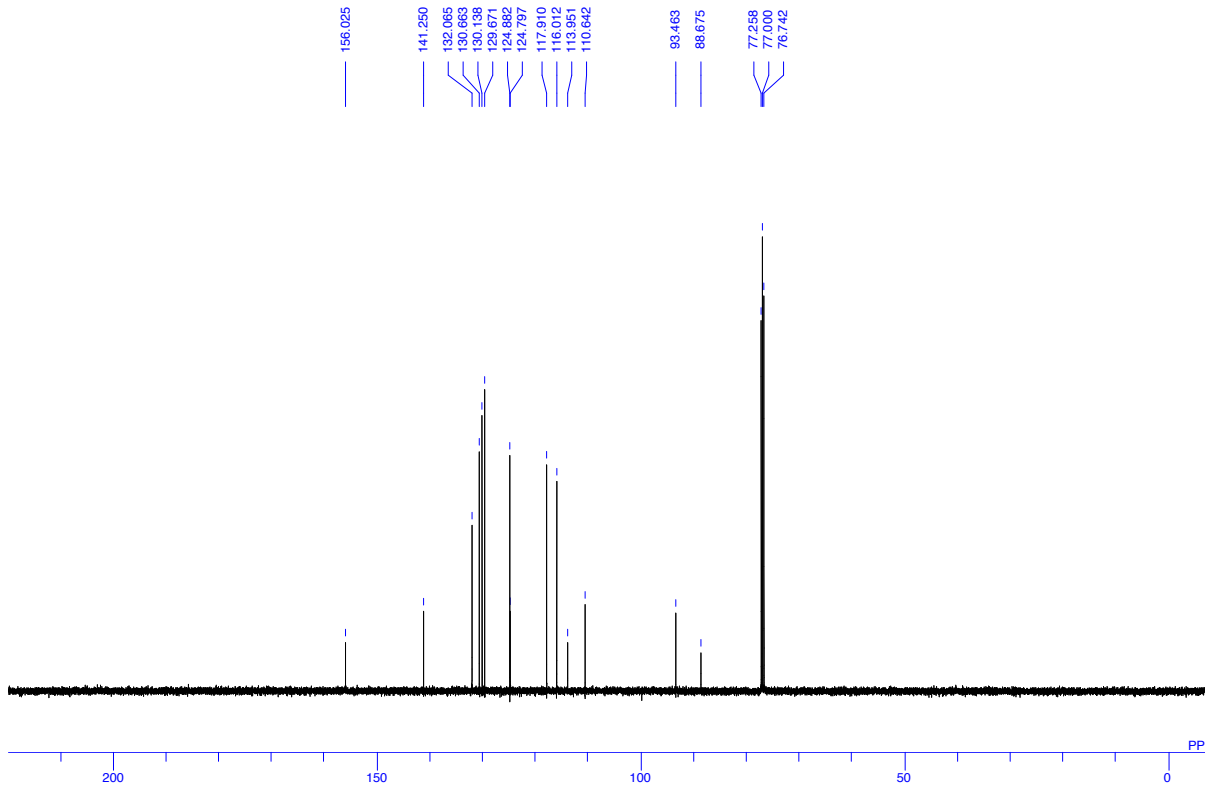
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0

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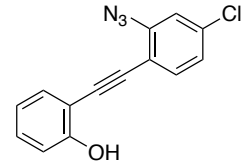
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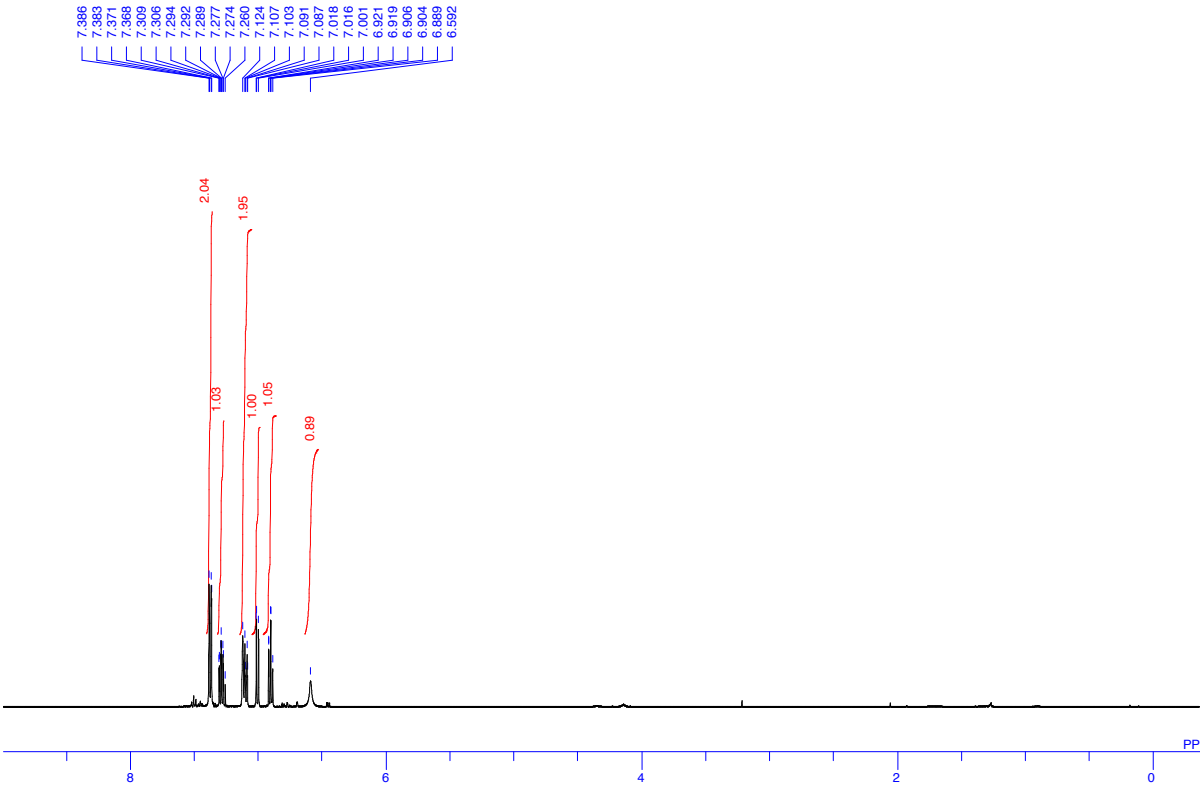
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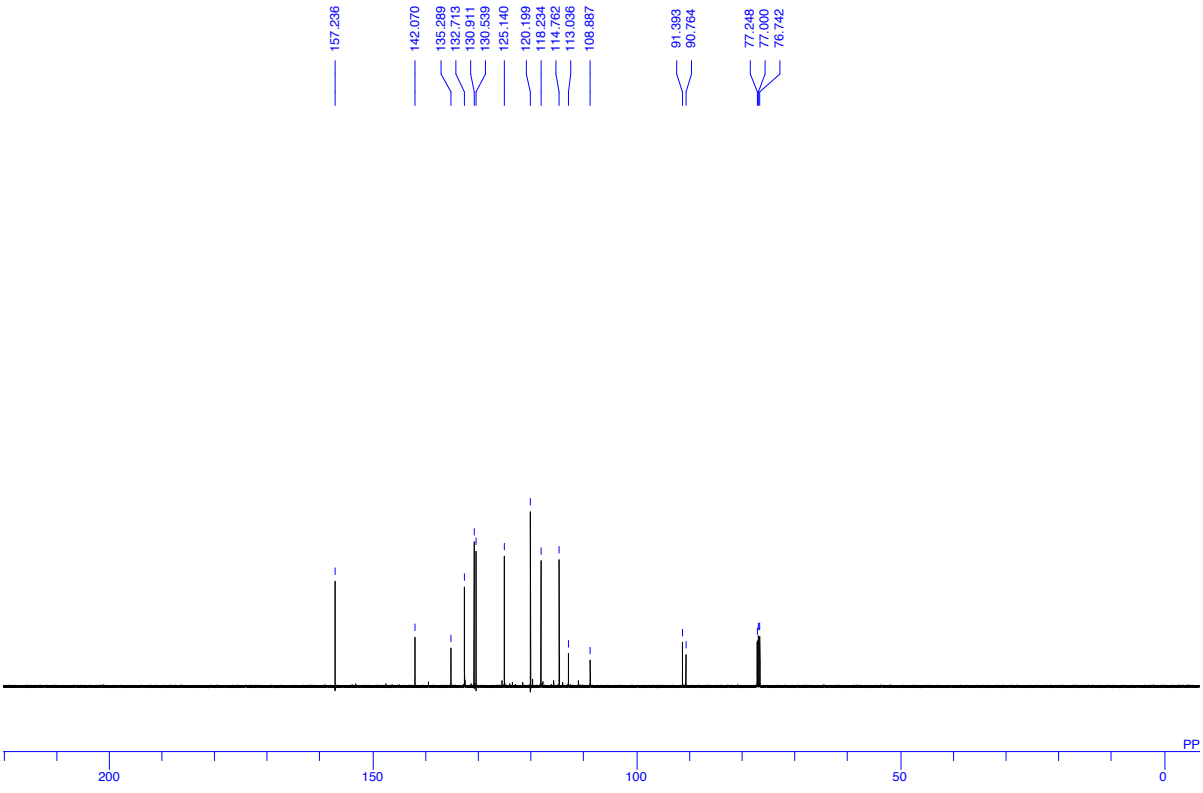
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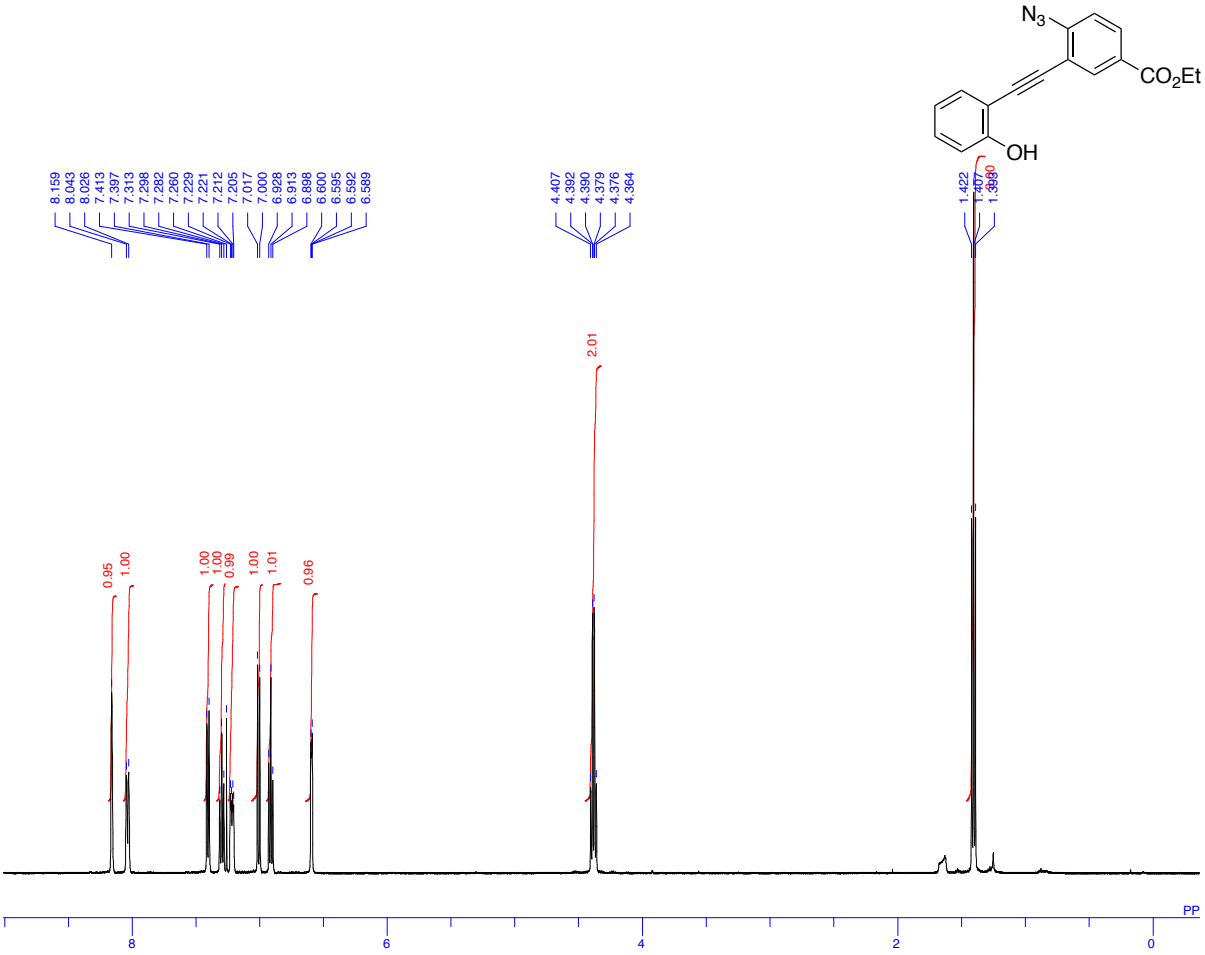
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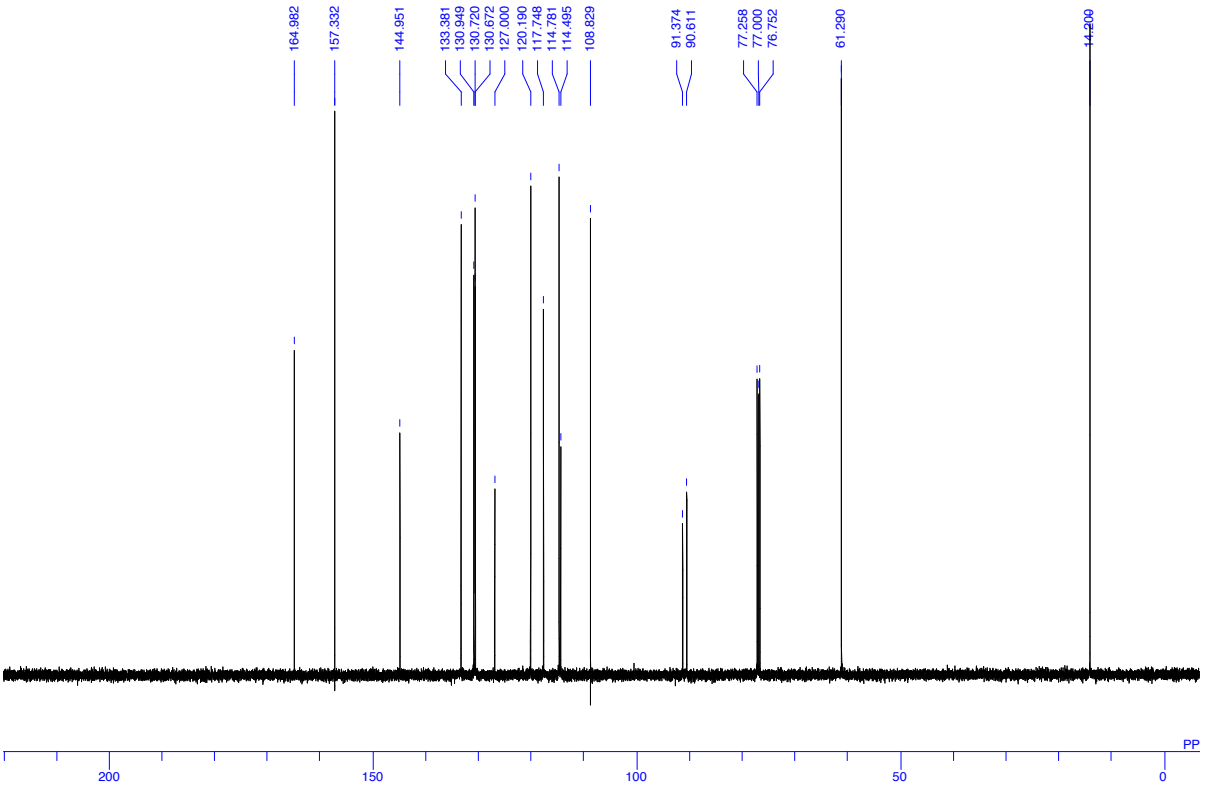
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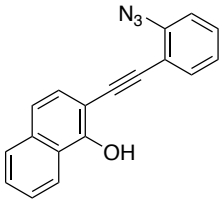
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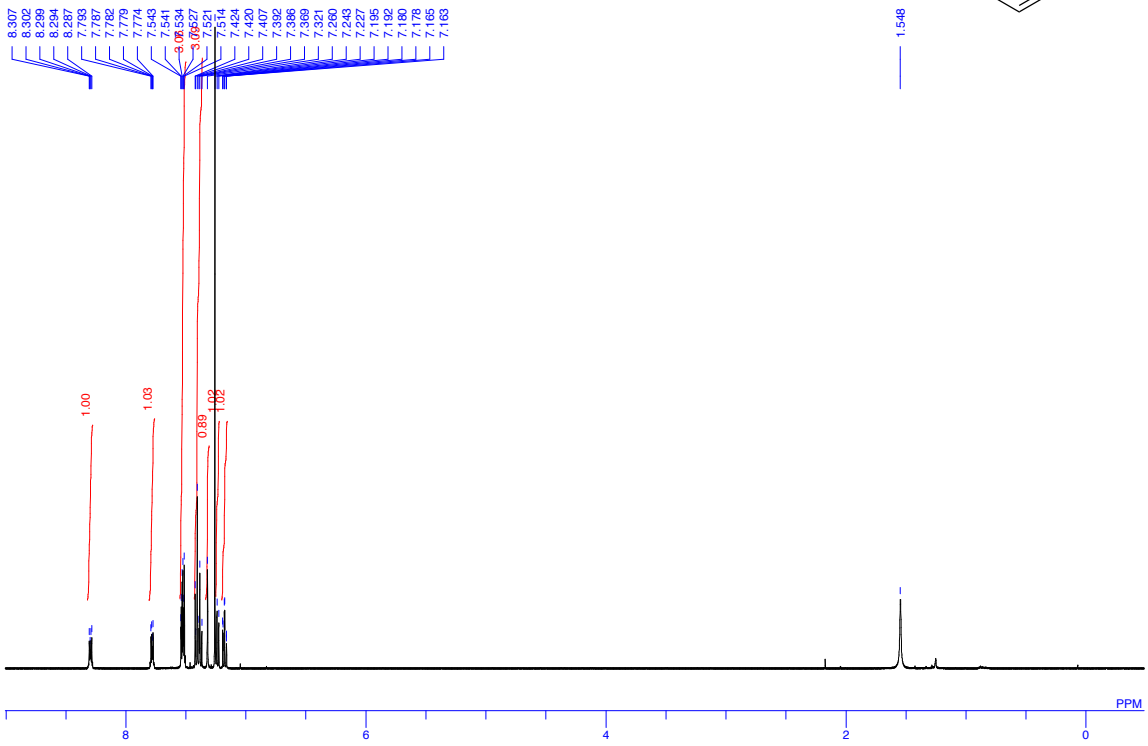
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7.527
7.521
7.514
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7.420
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7.321
7.260
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7.192
7.180
7.178
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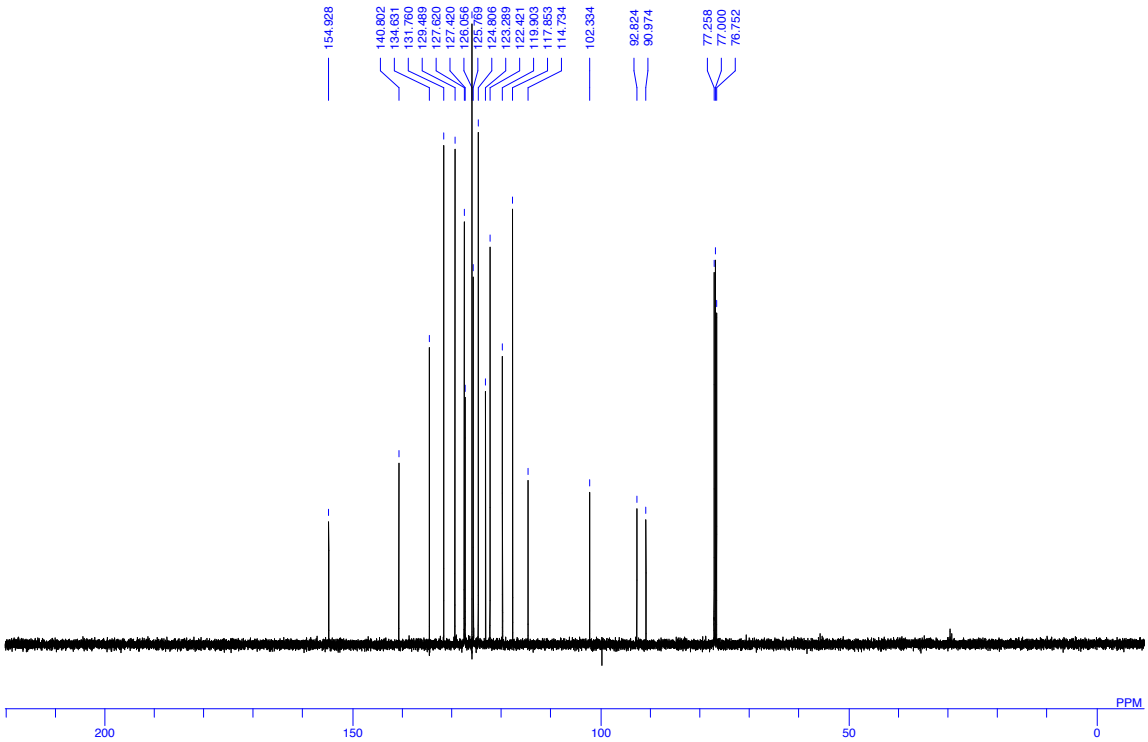
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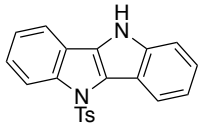
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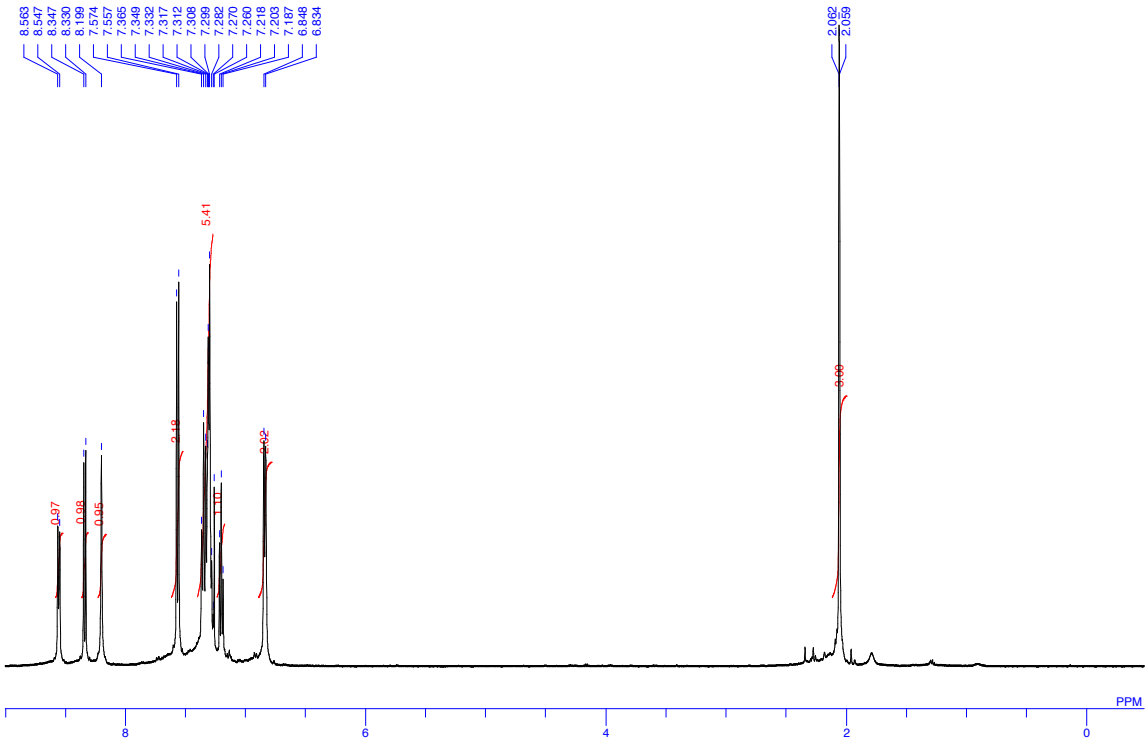
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7.299
7.282
7.270
7.260
7.218
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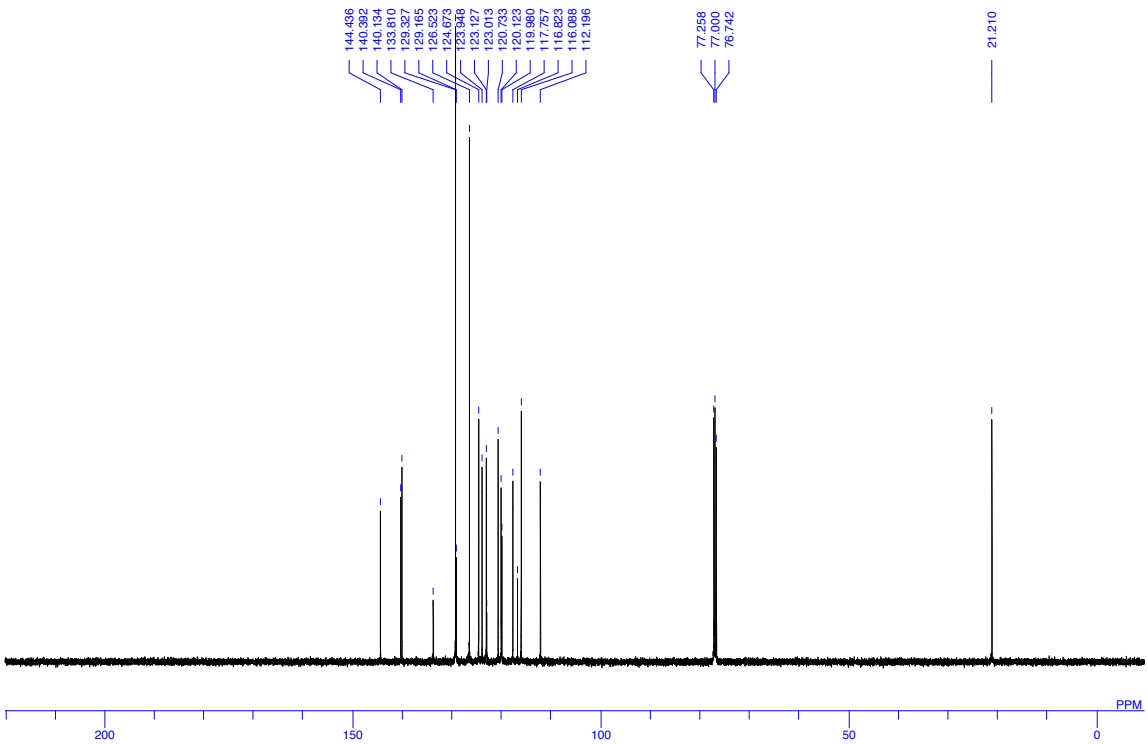
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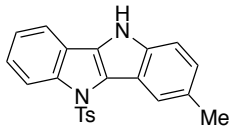
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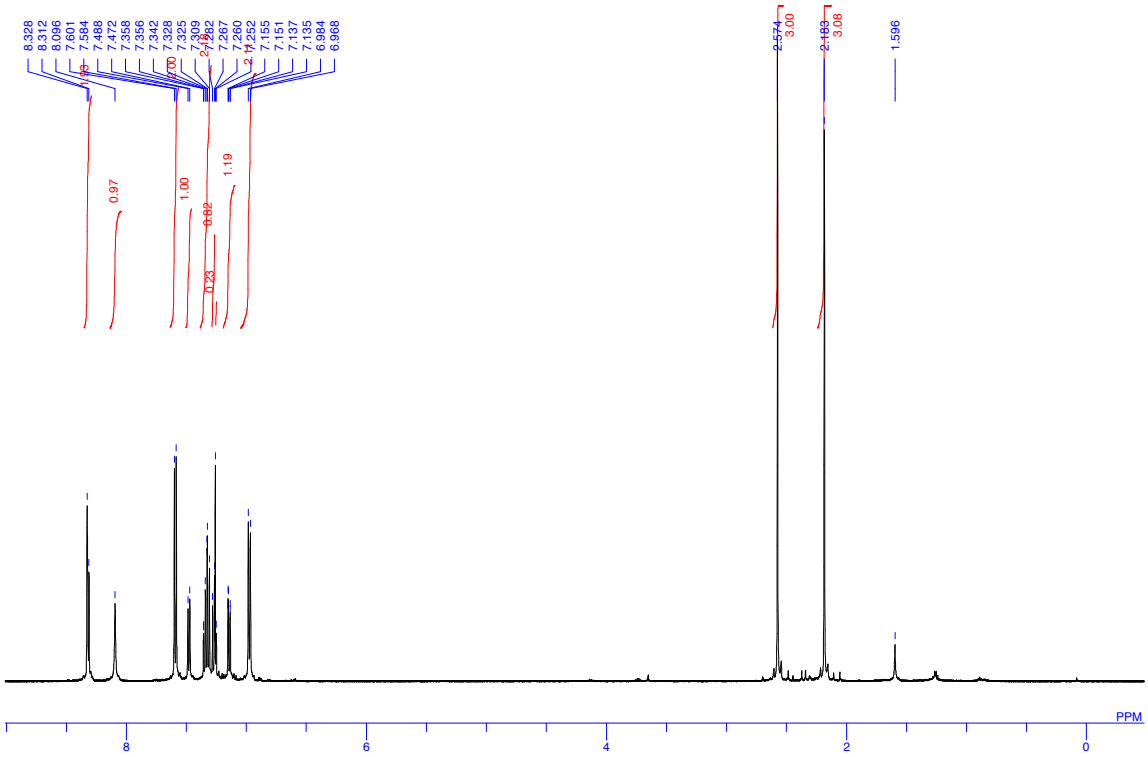
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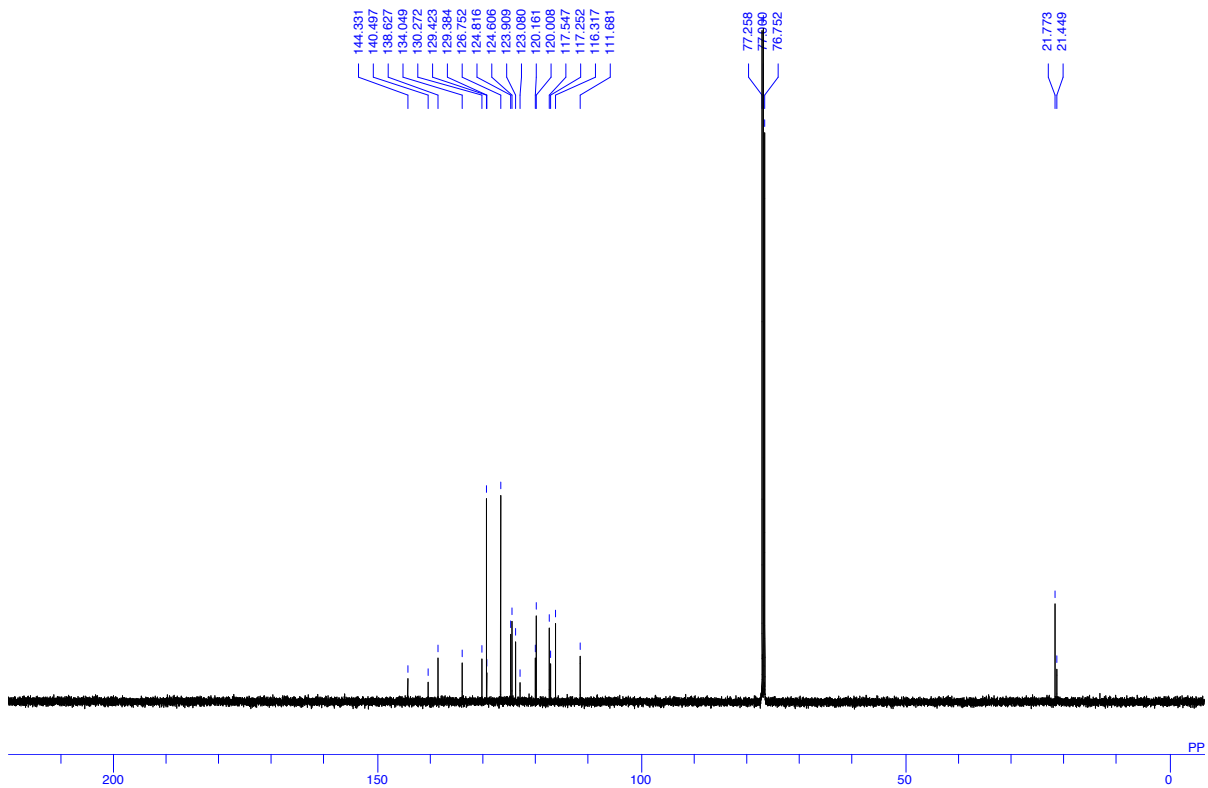
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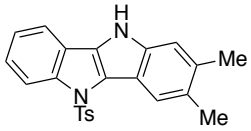
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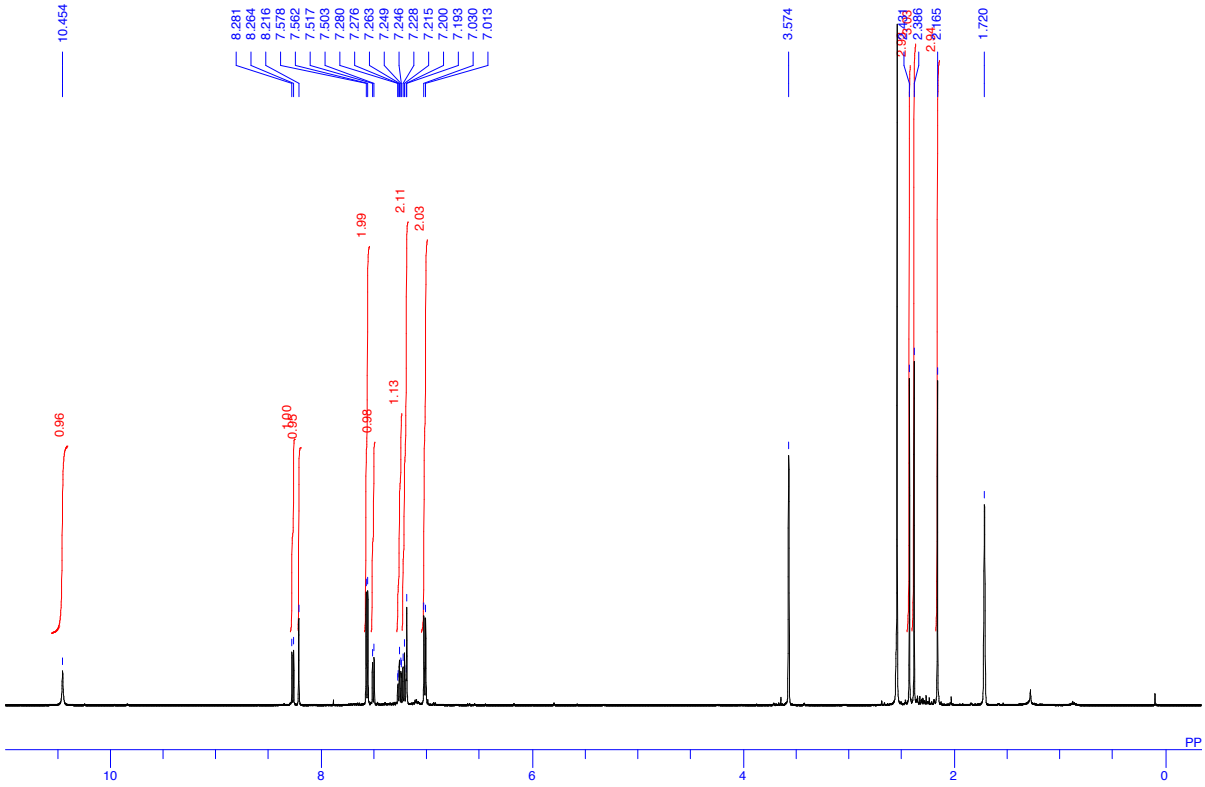
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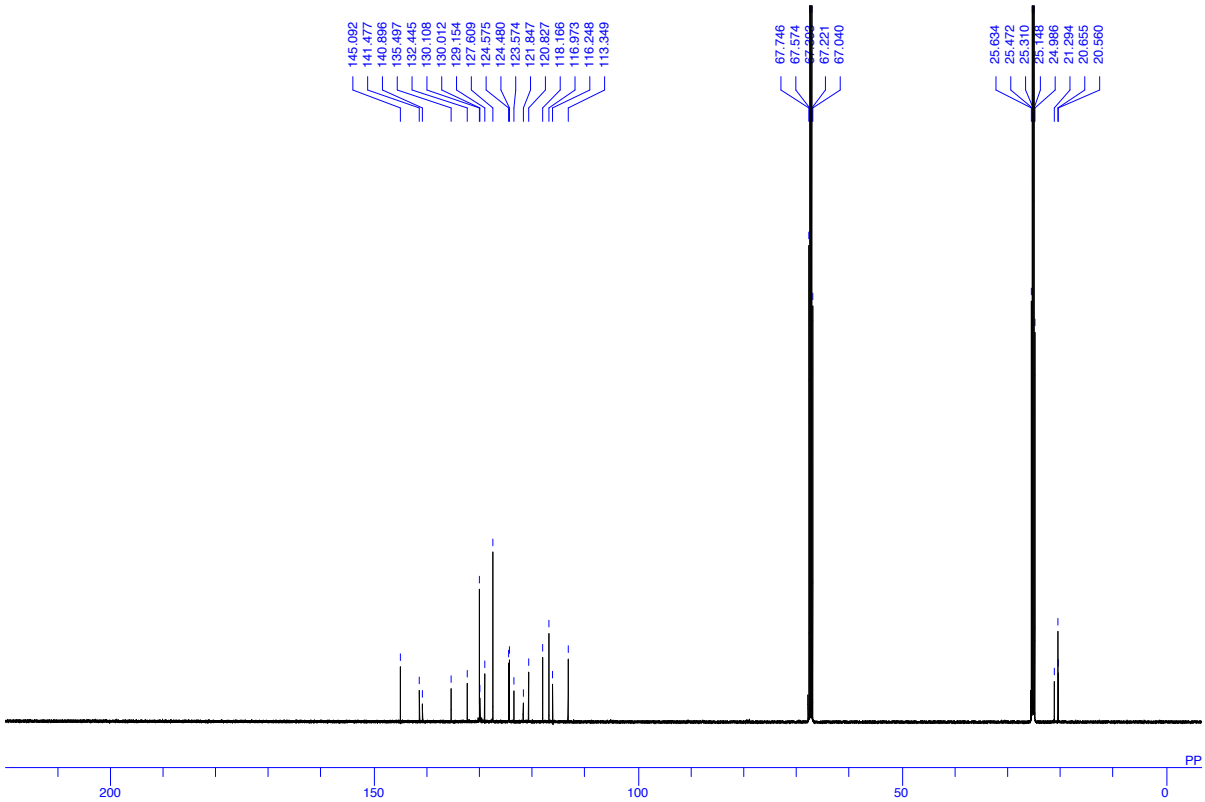
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67.040
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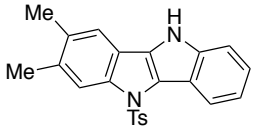
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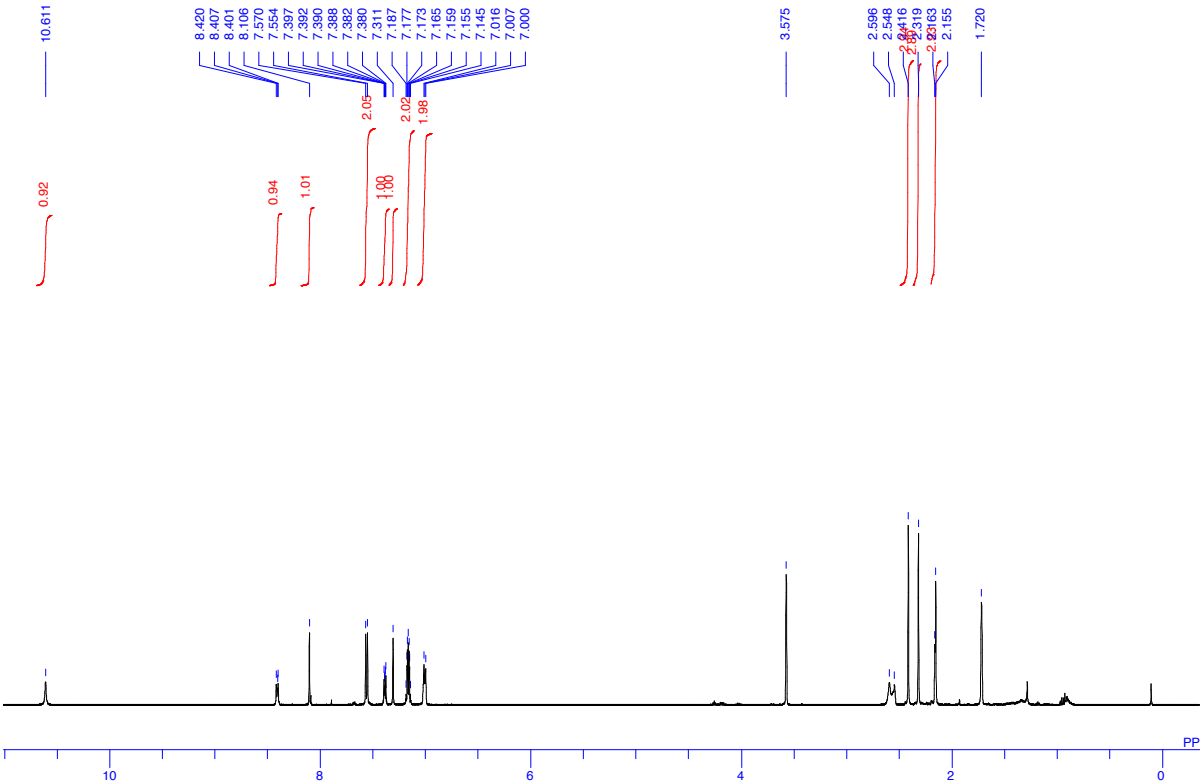
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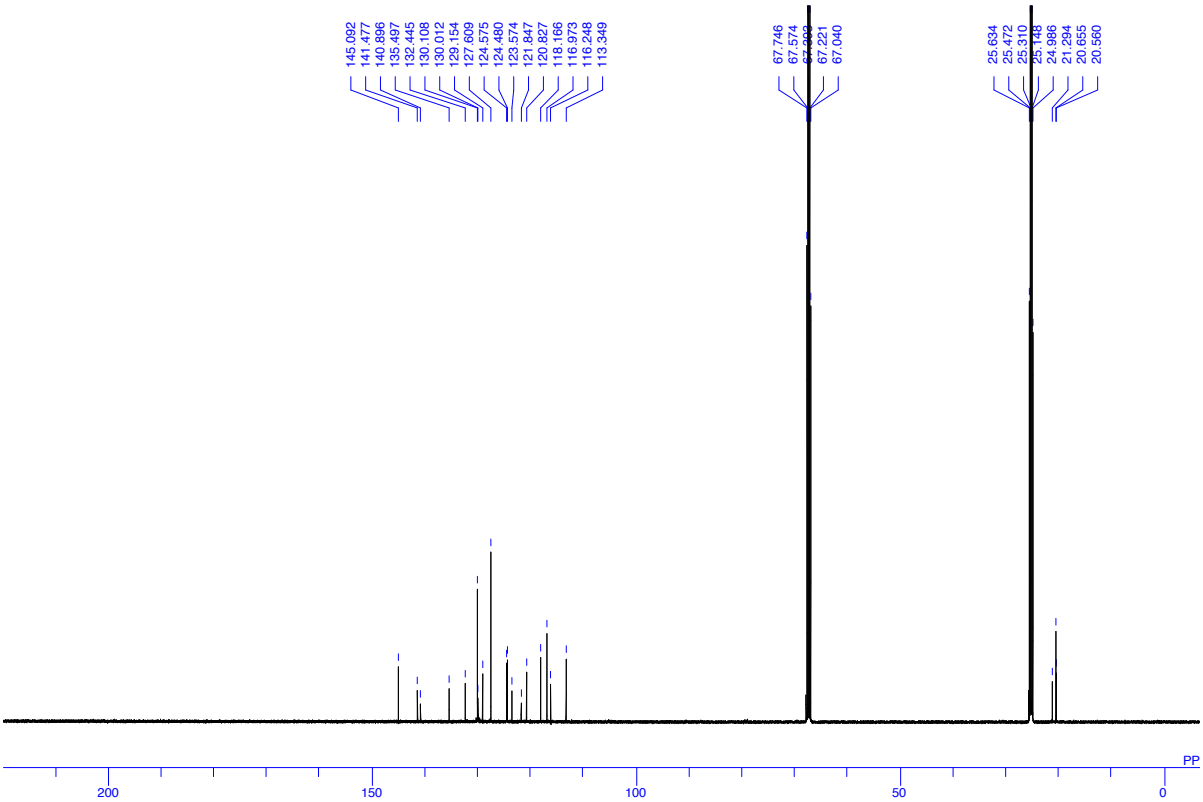
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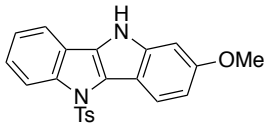
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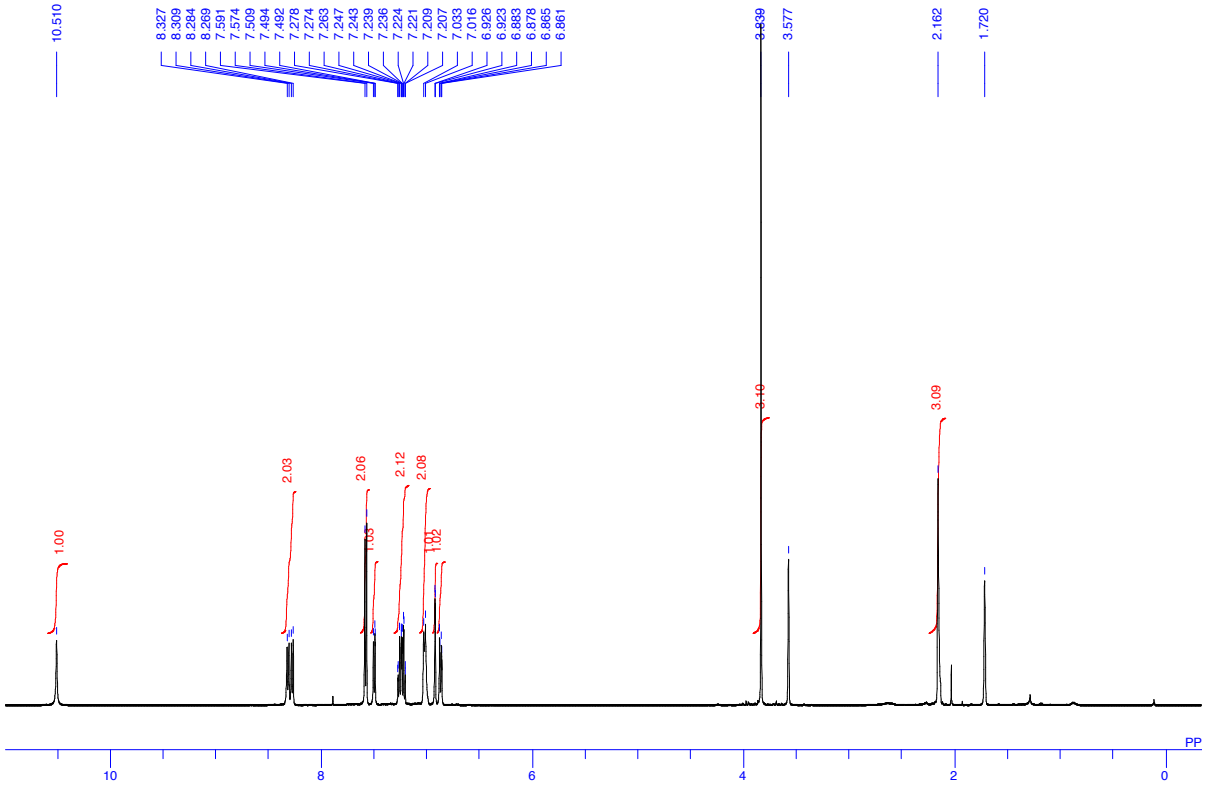
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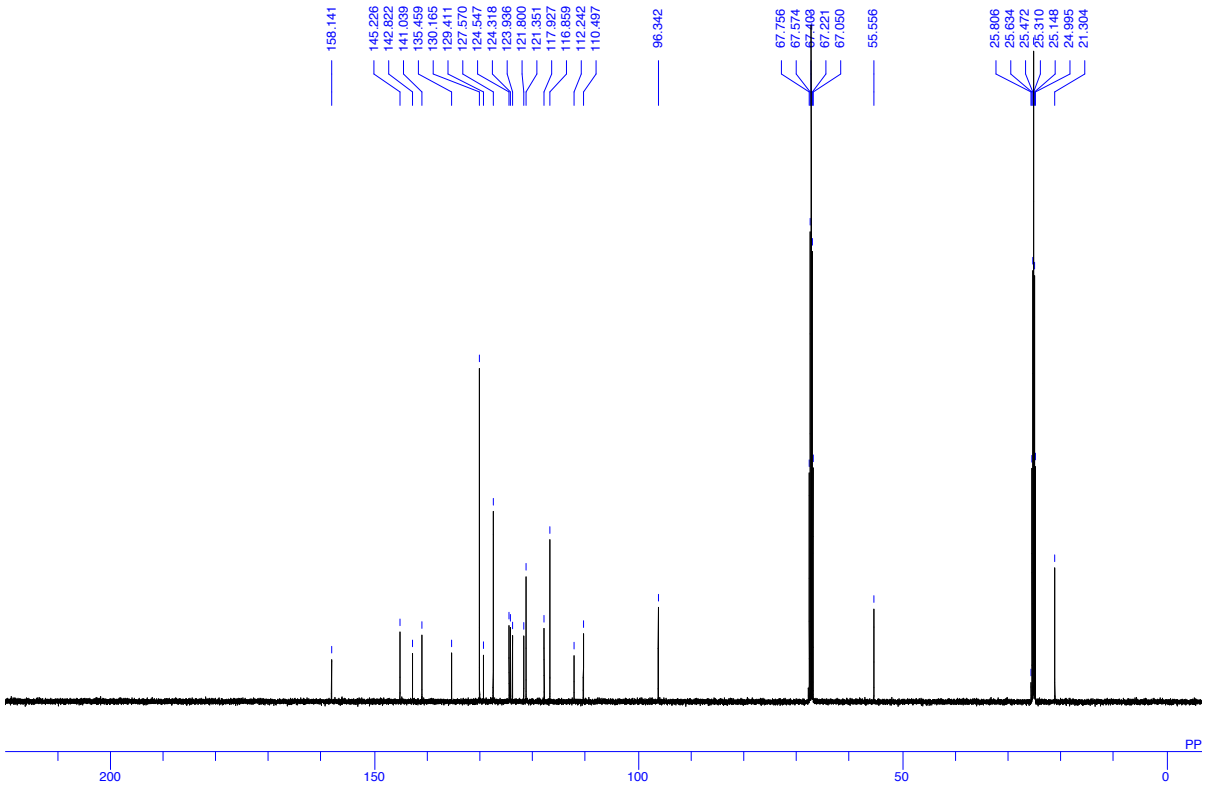
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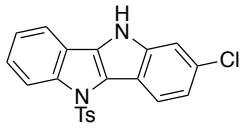
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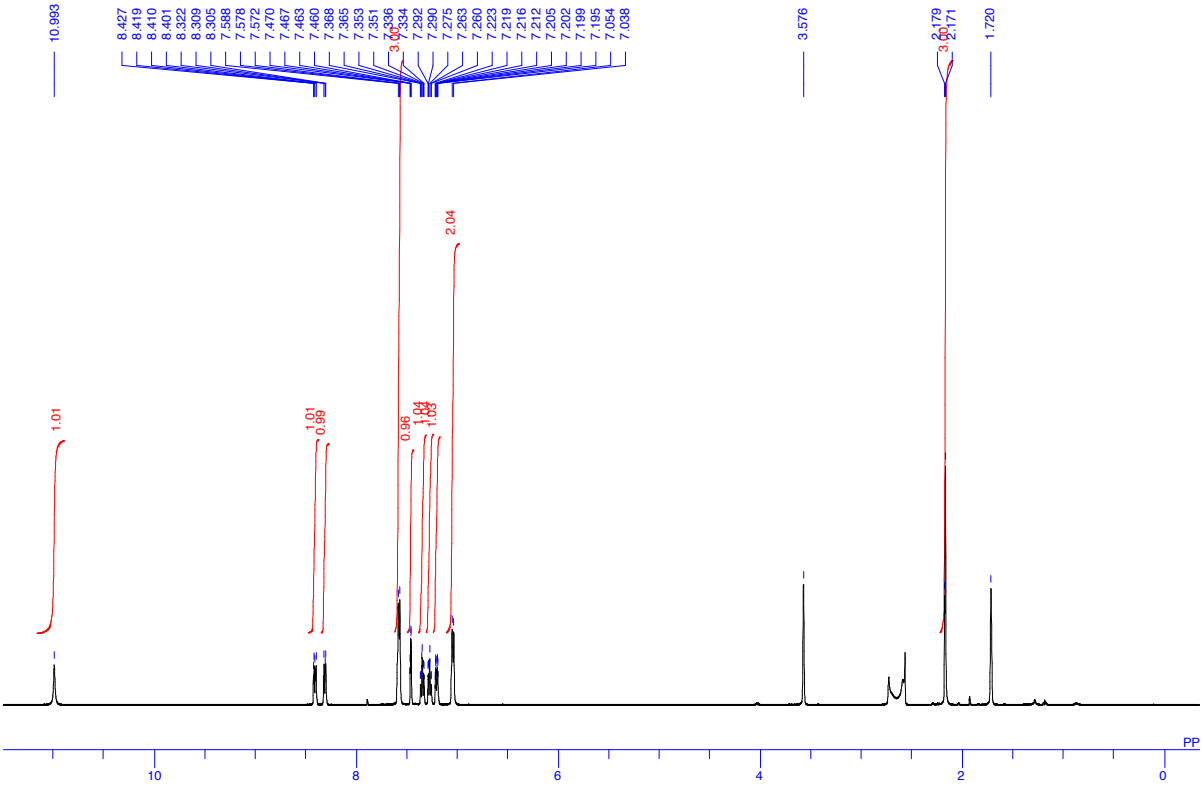
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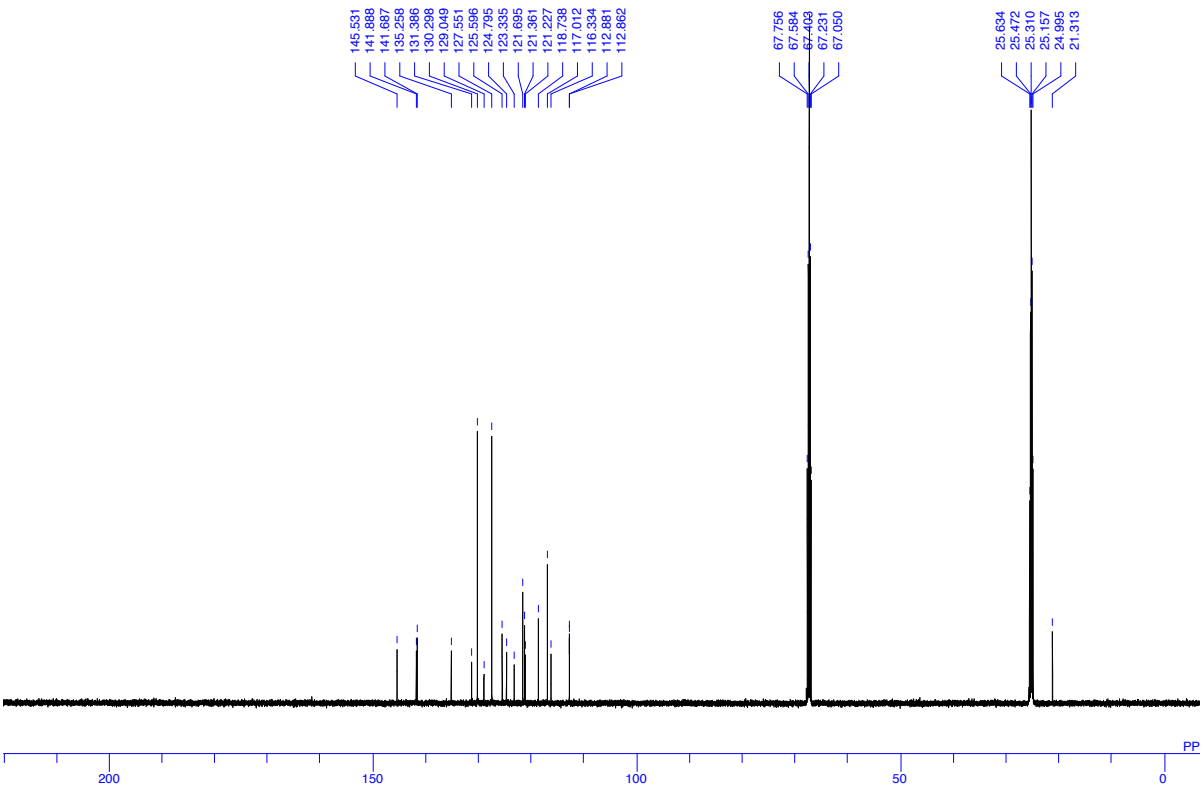
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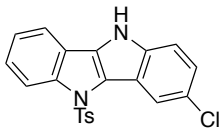
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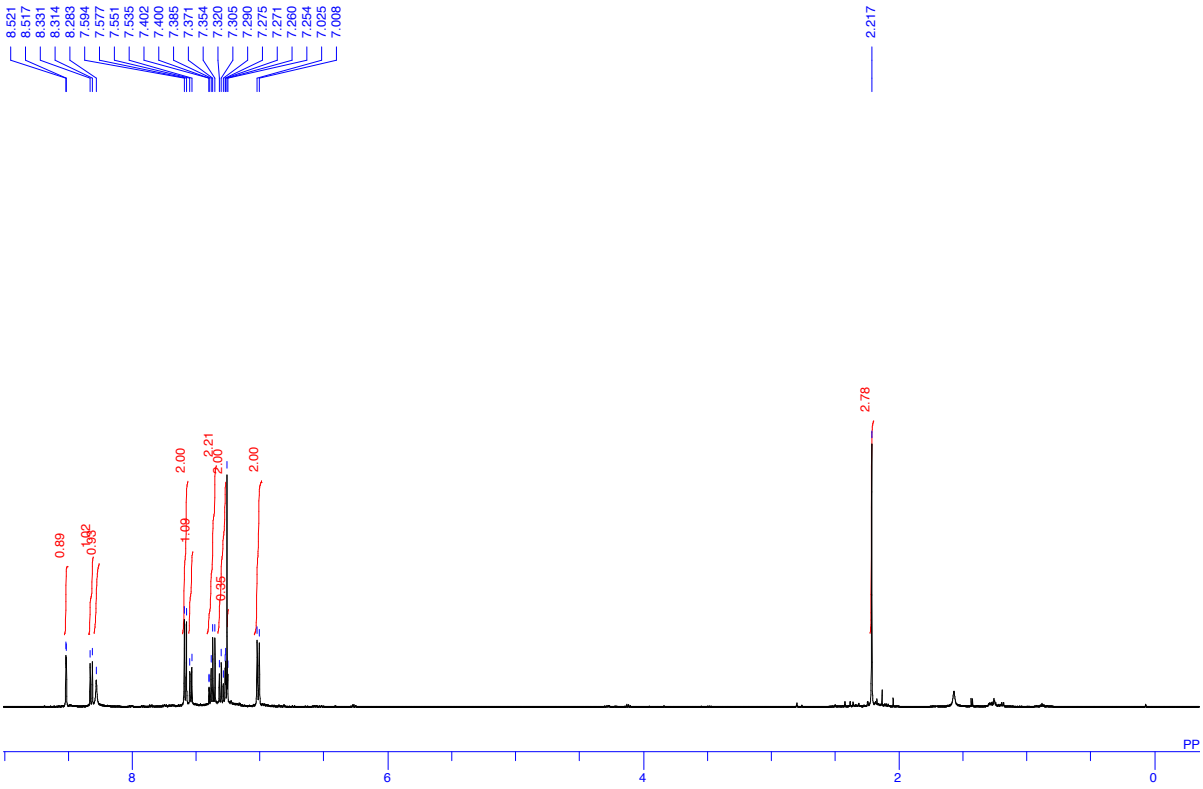
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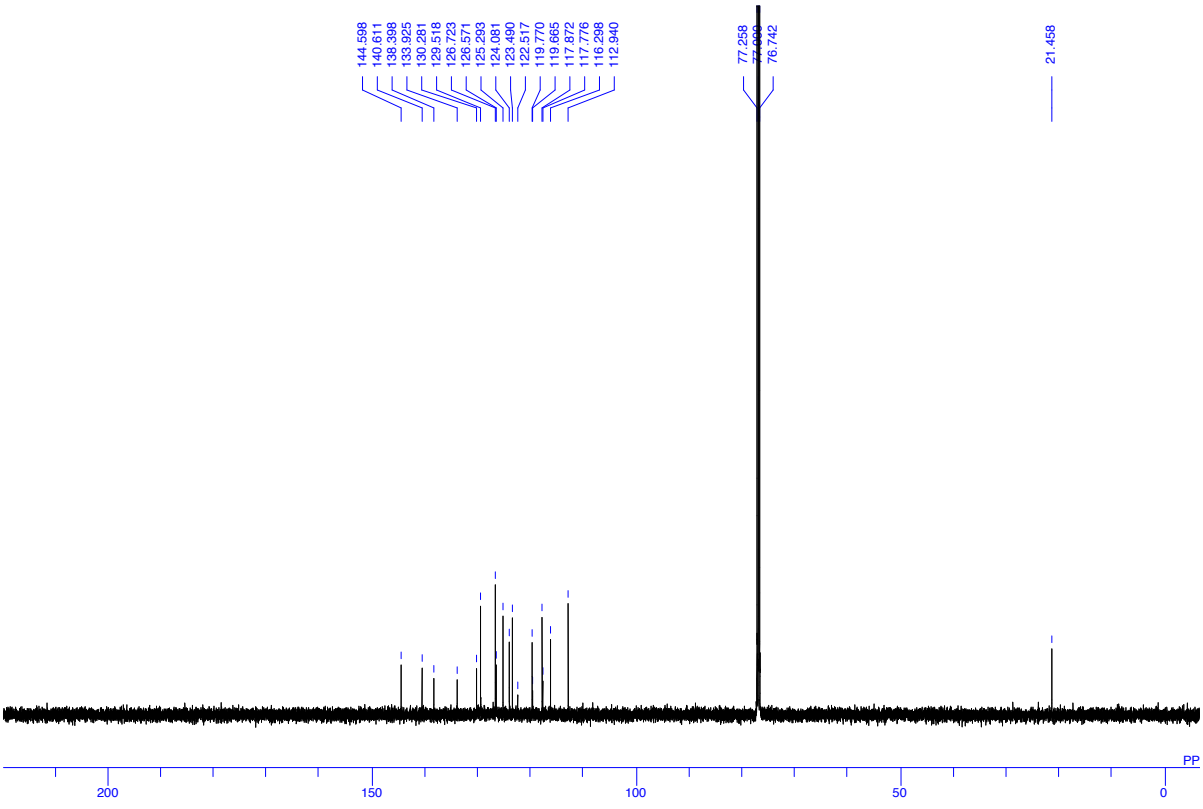
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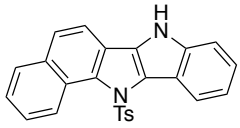
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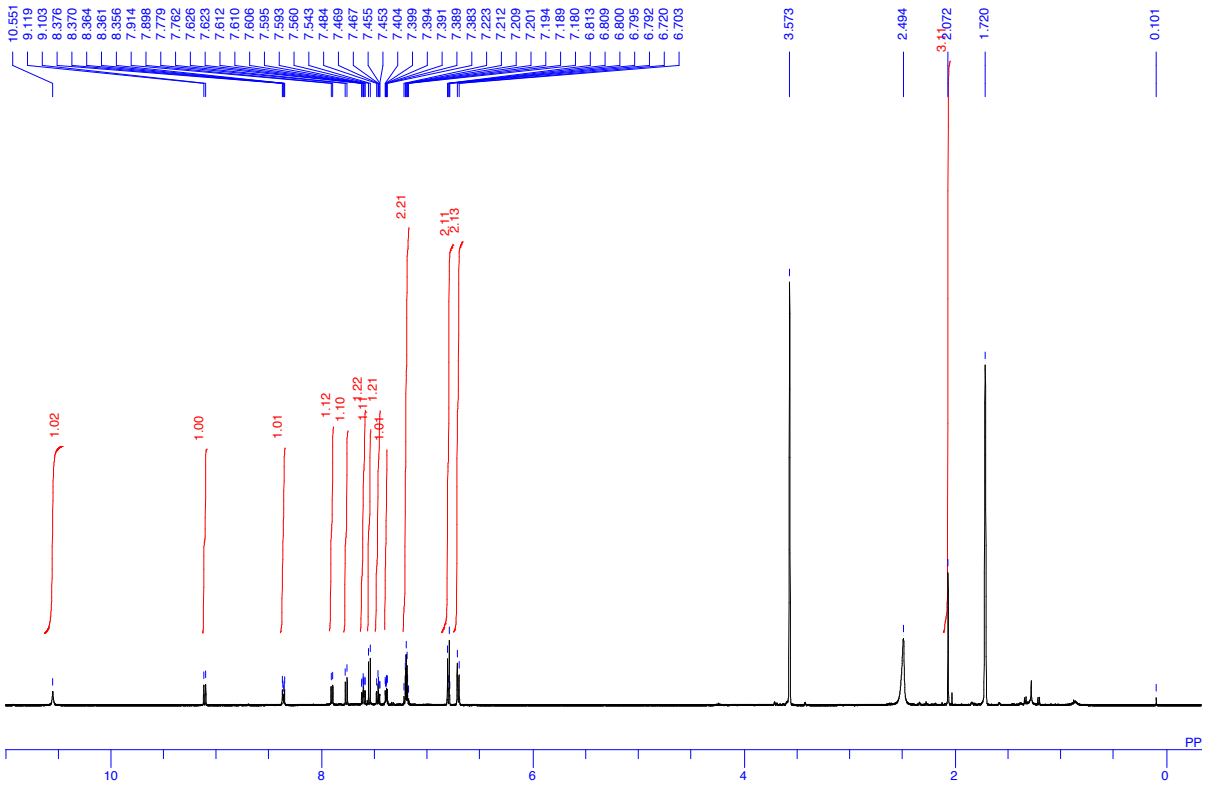
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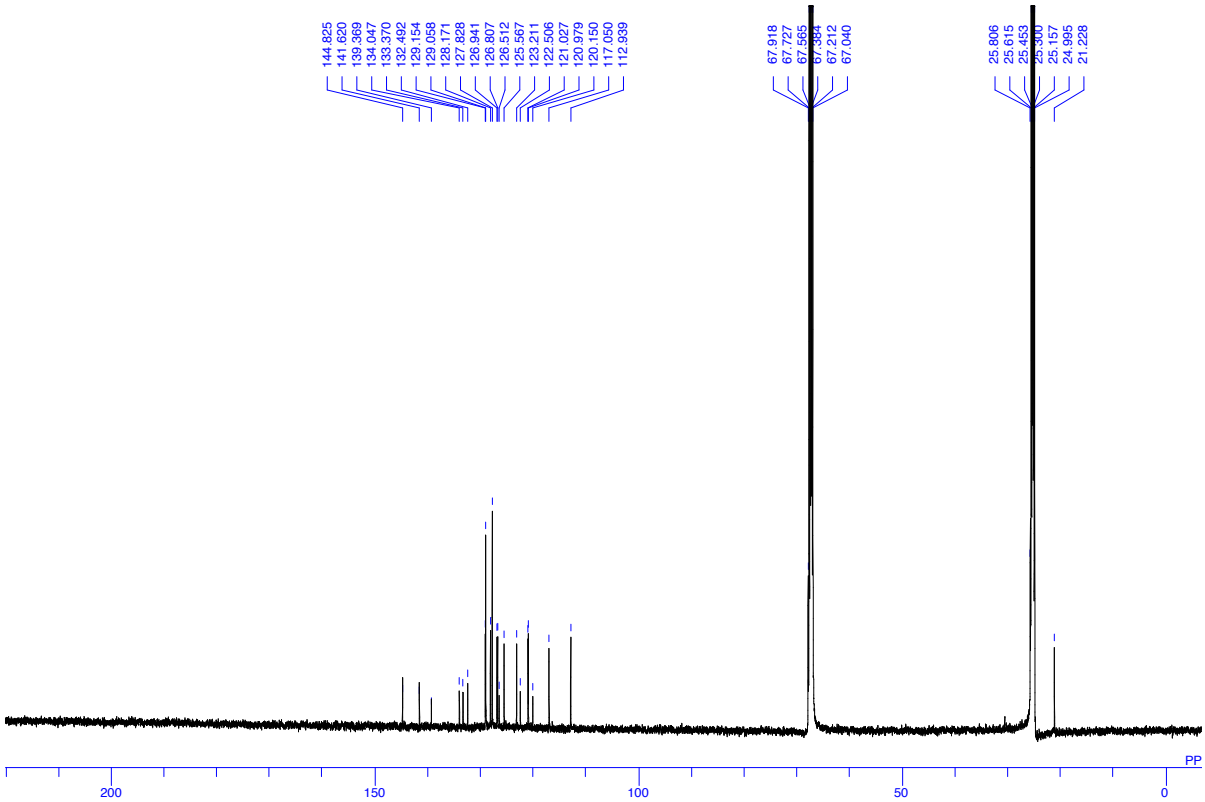
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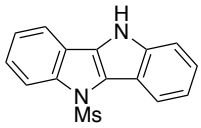
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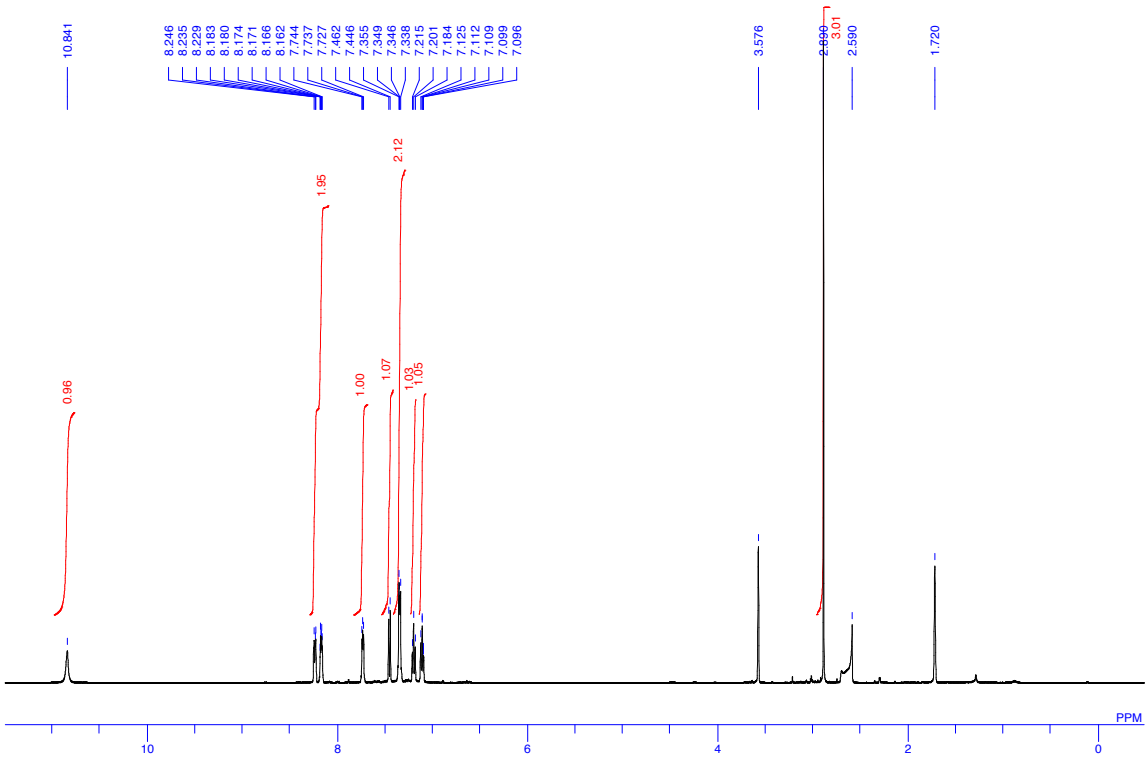
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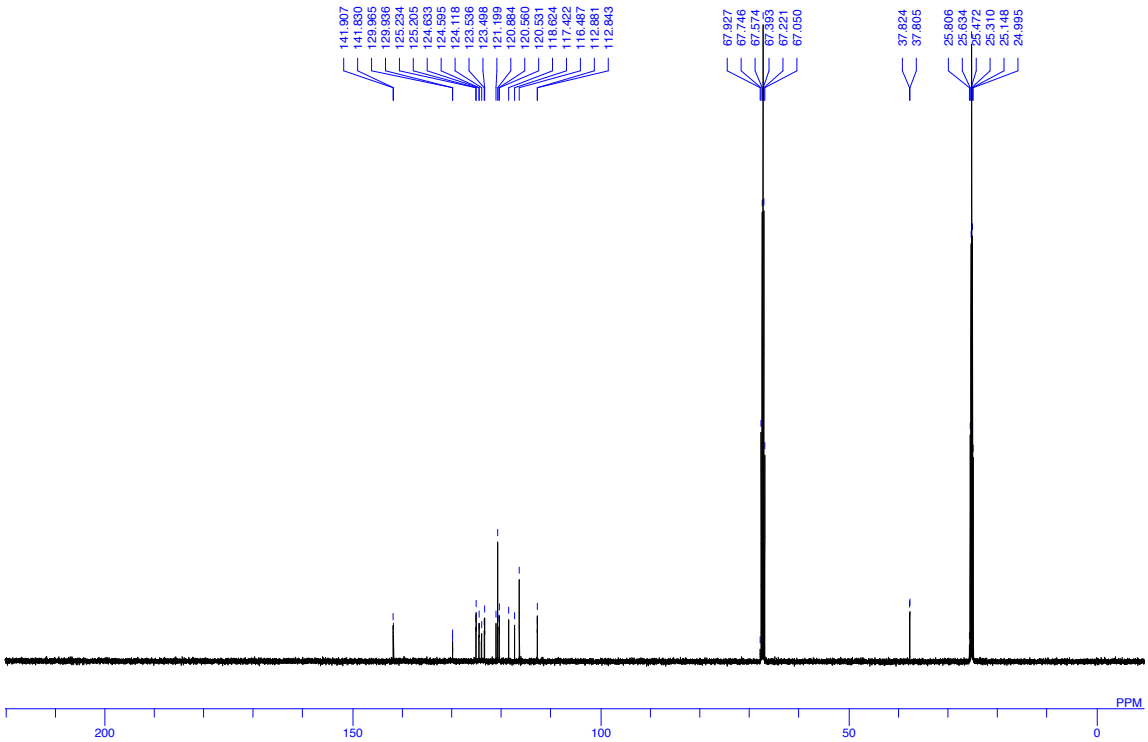
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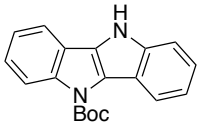
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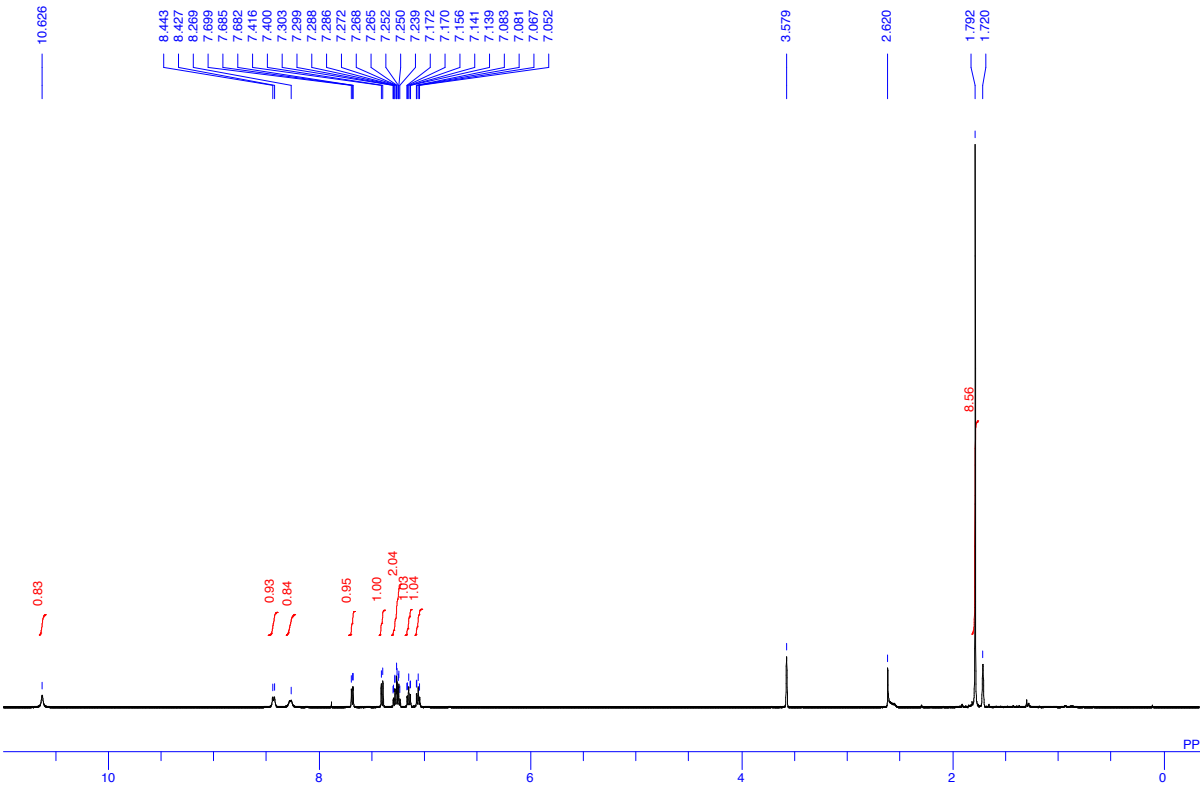
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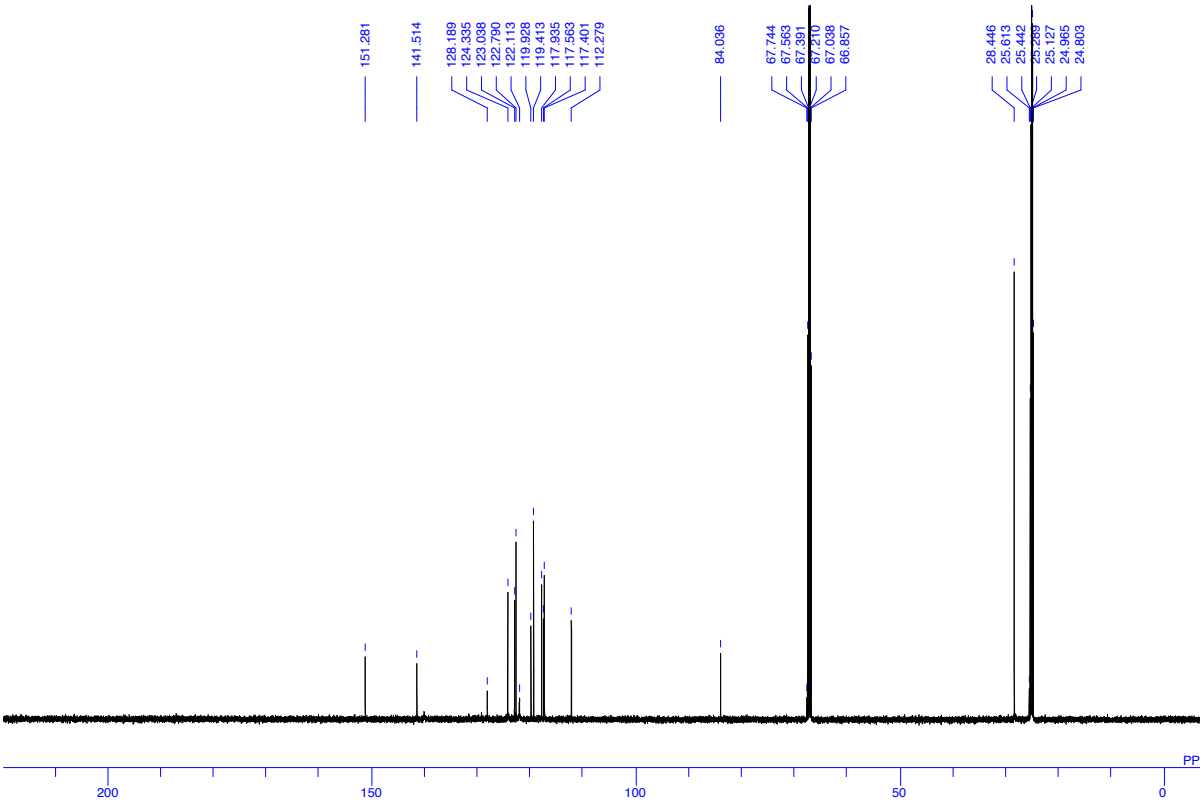
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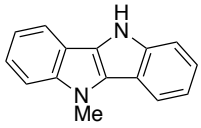
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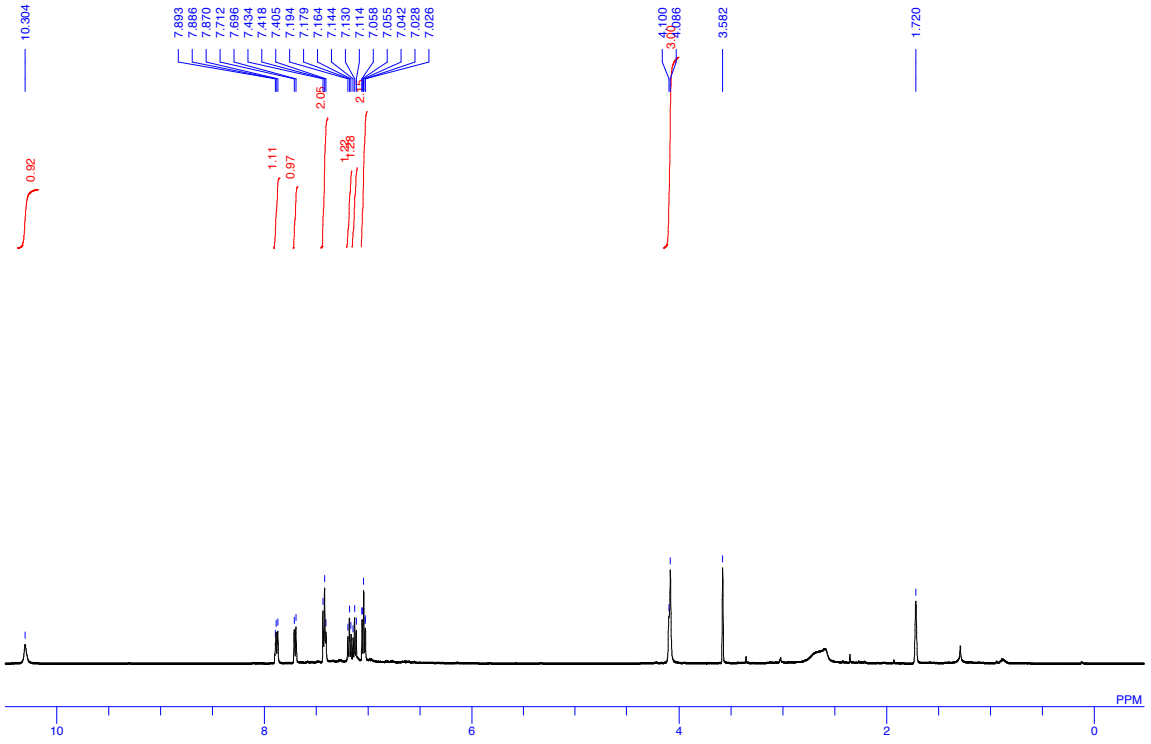
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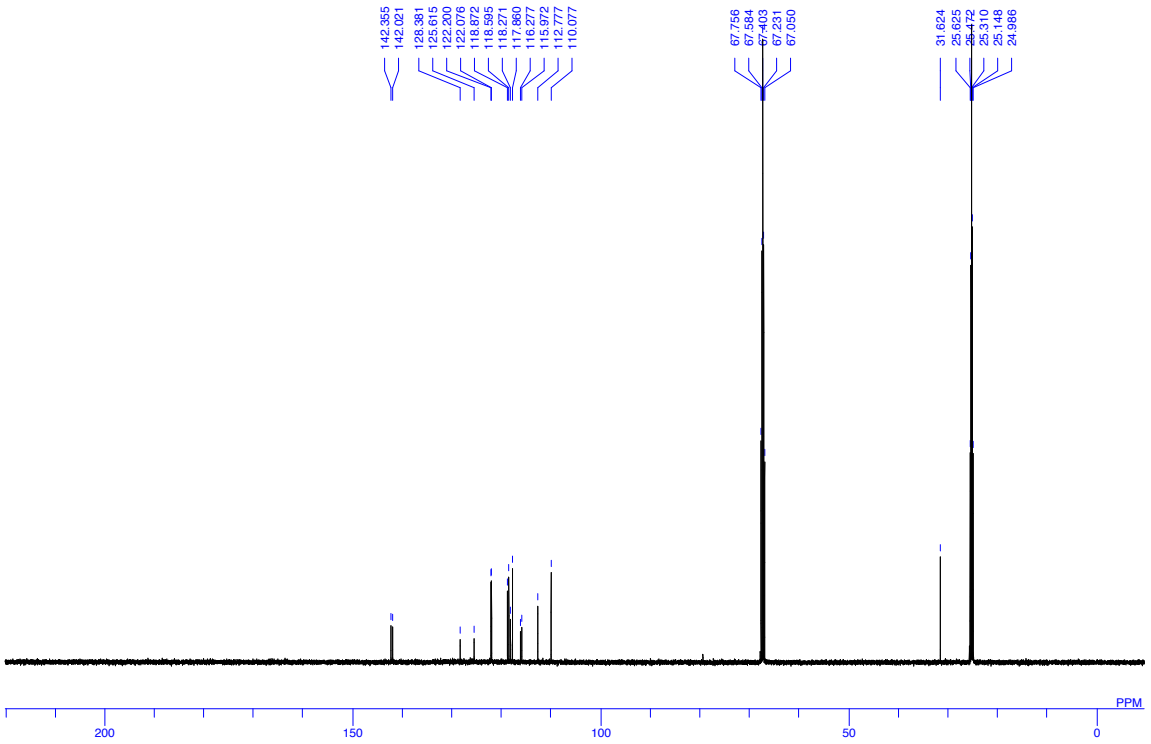
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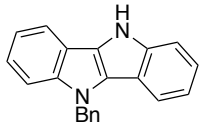
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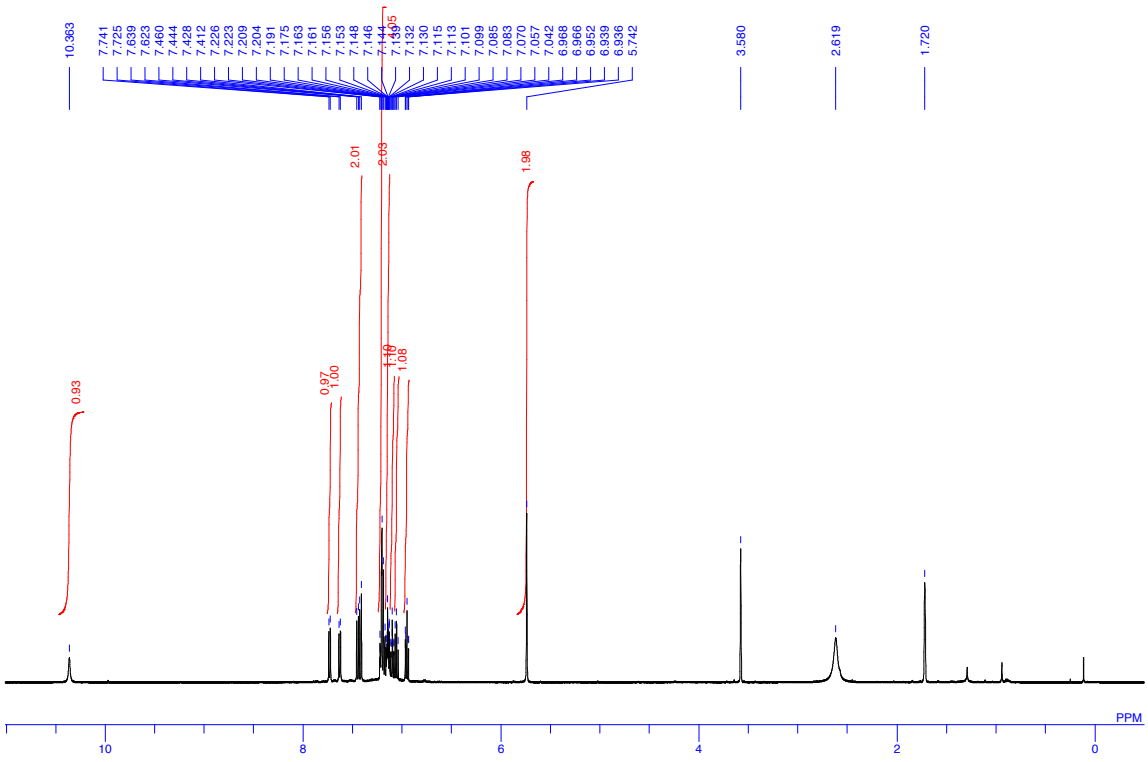
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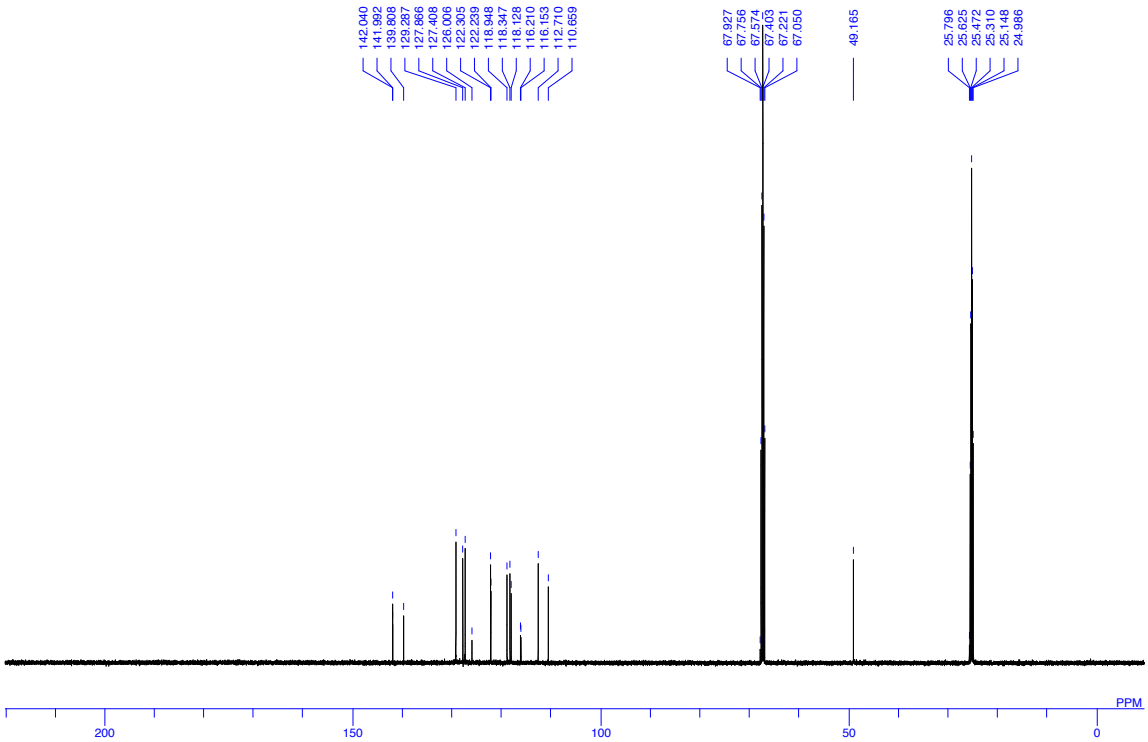
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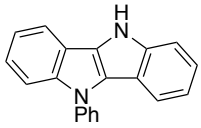
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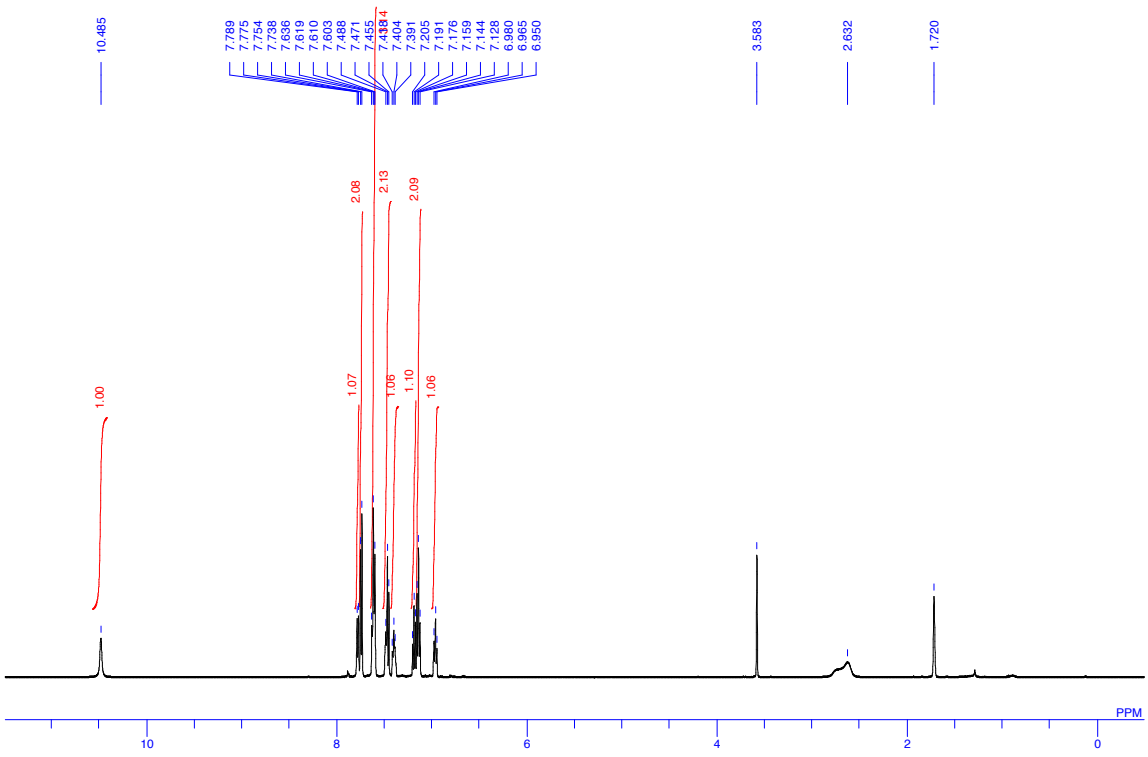
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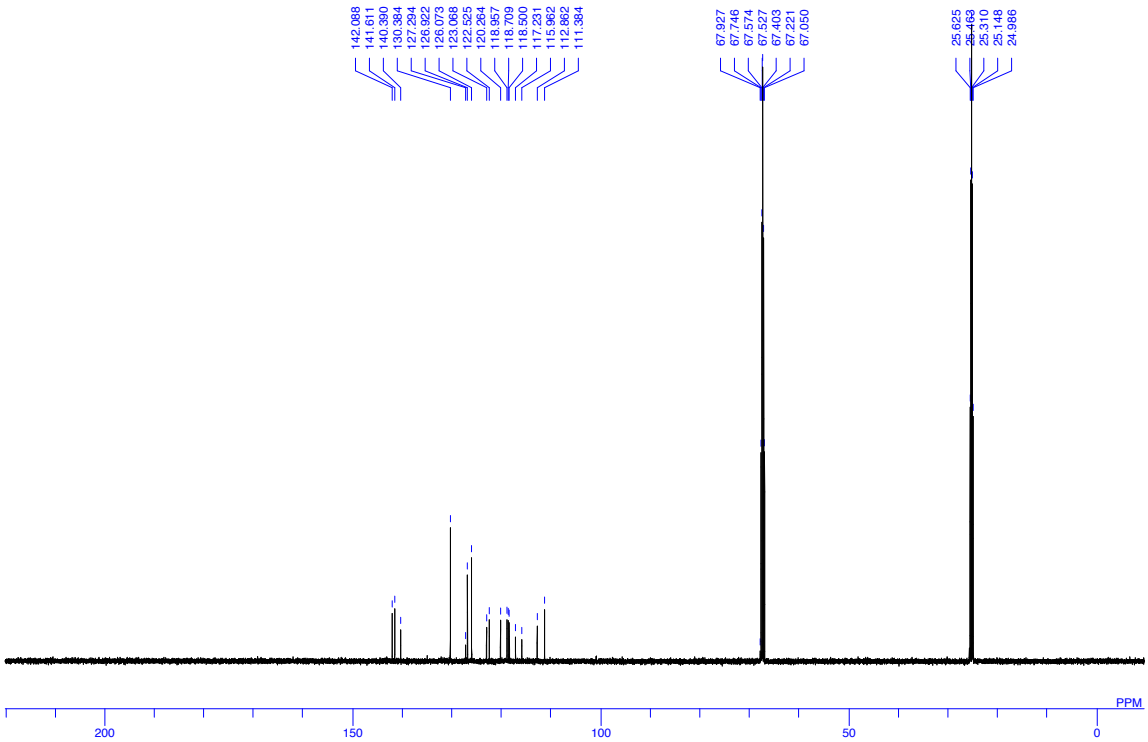
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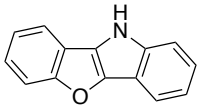
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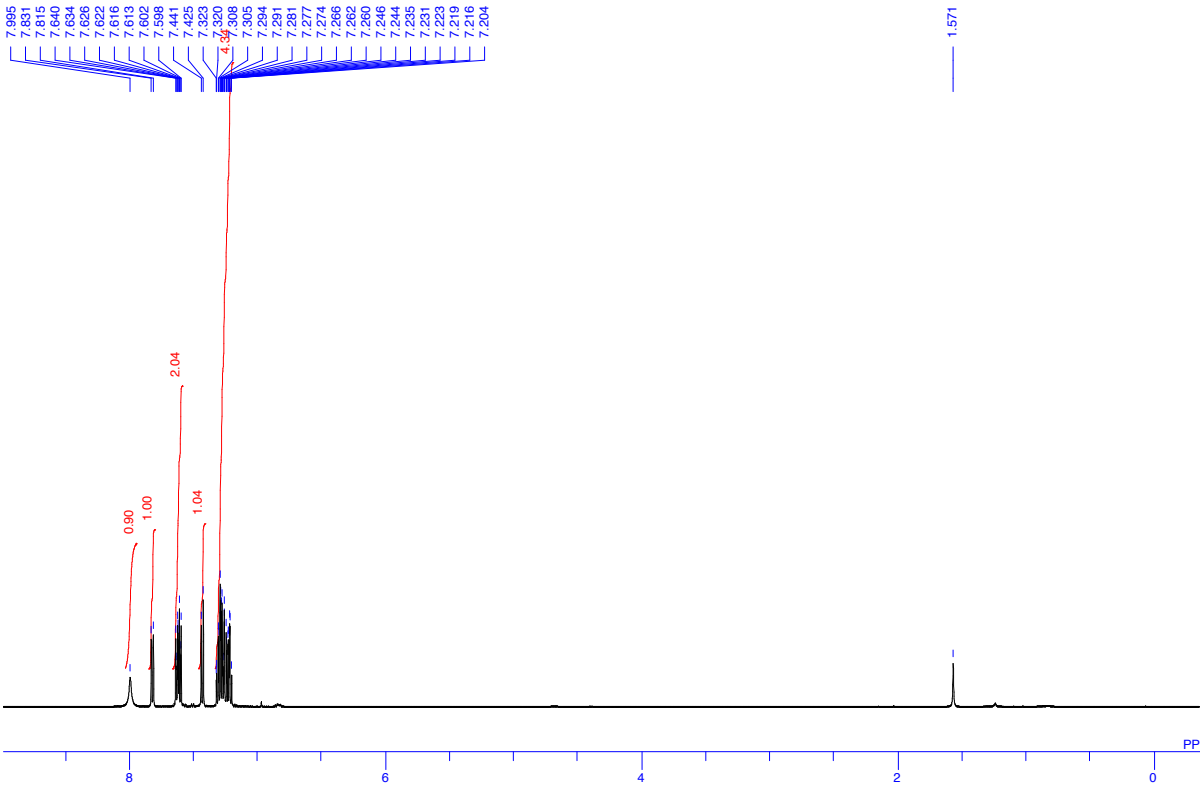
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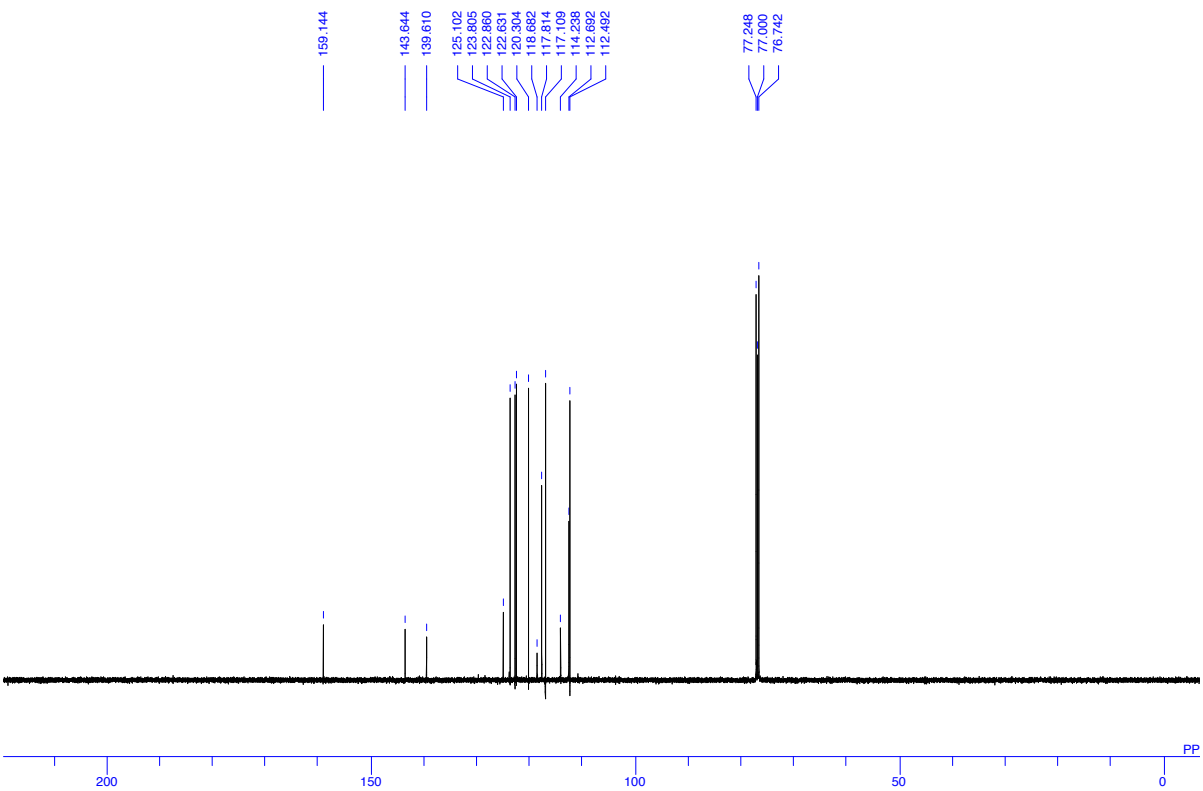
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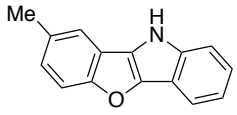
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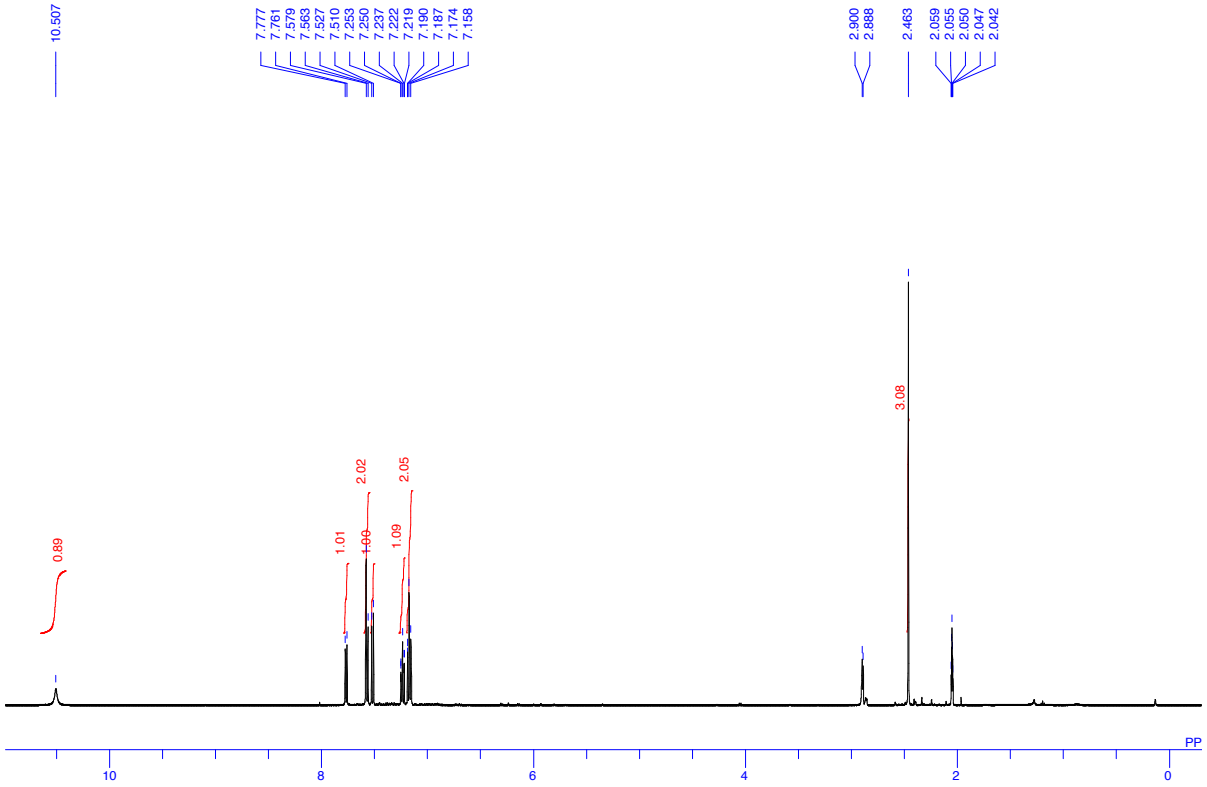
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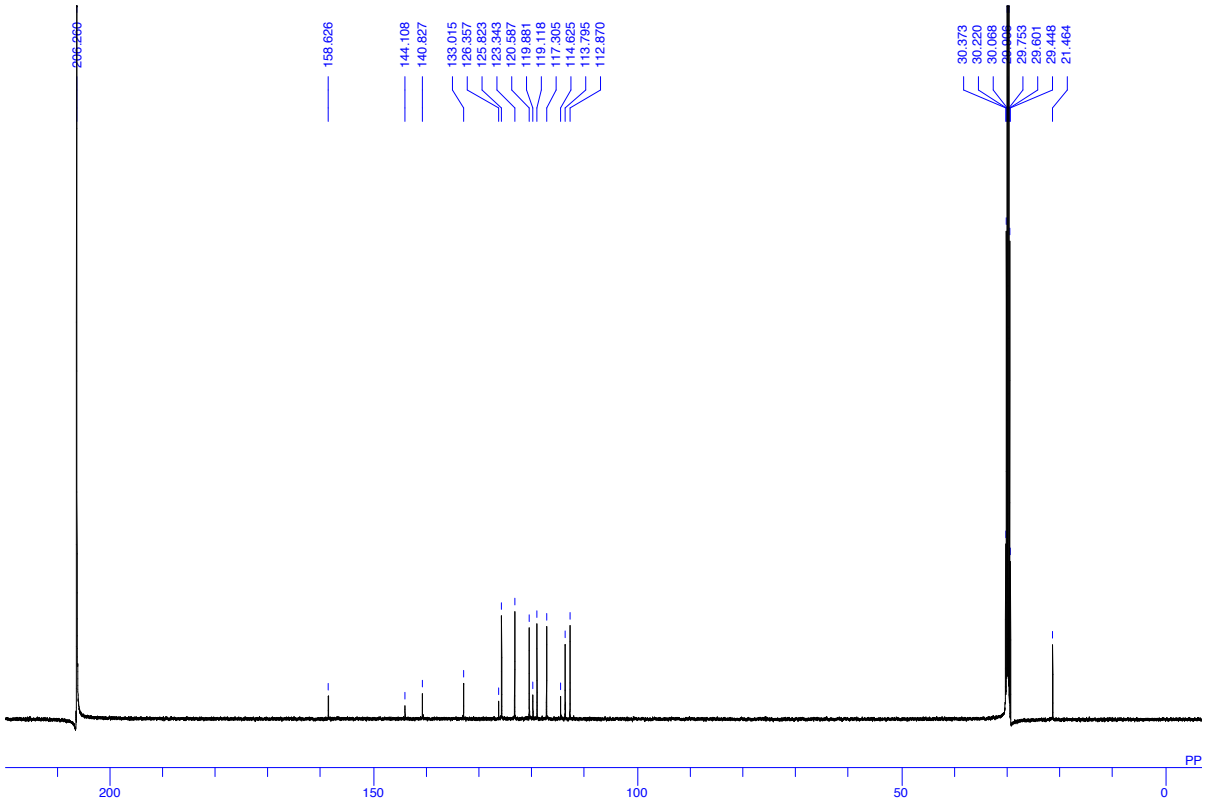
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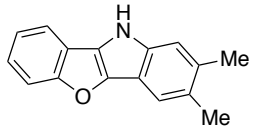
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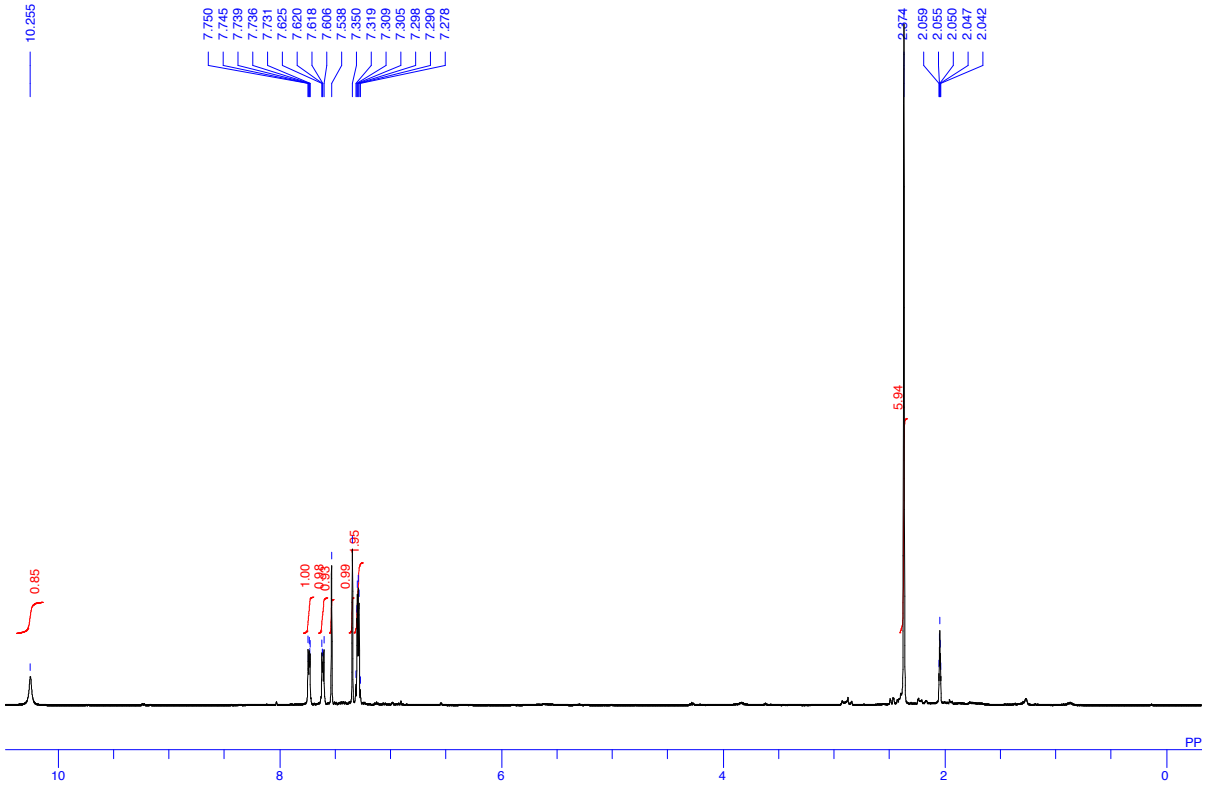
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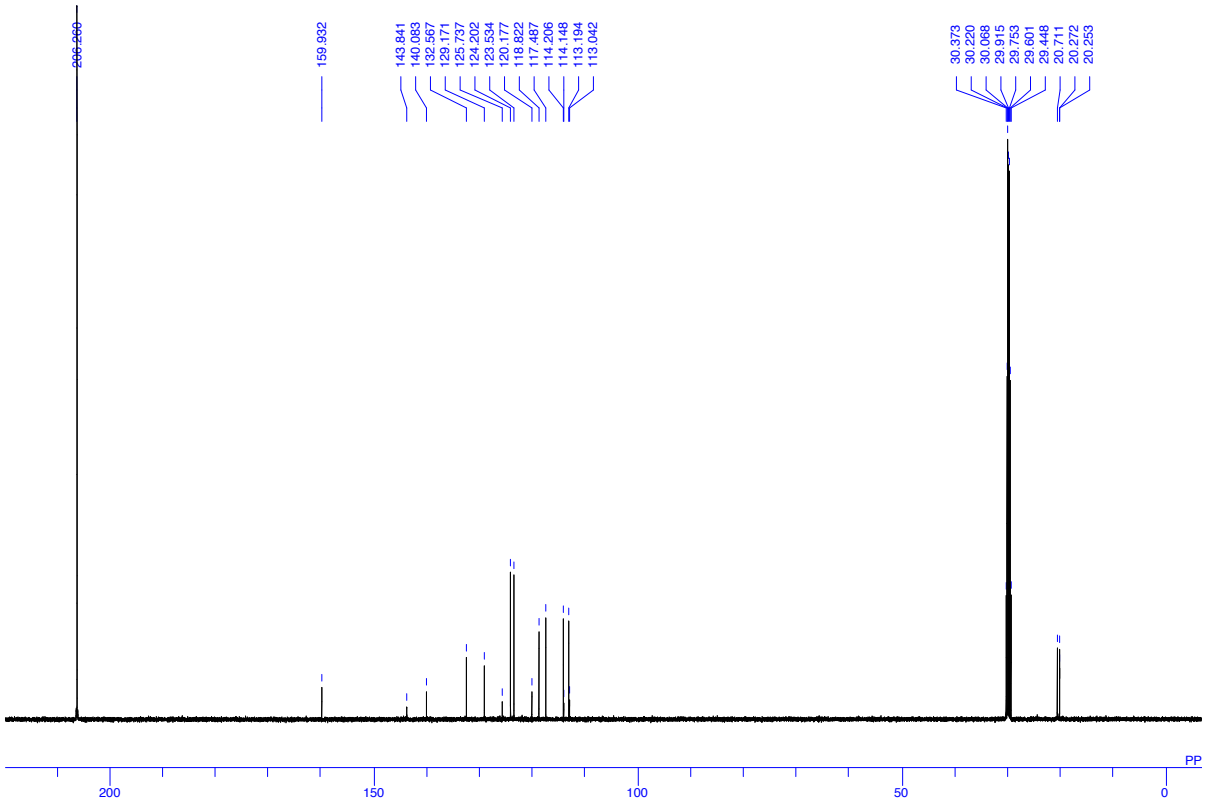
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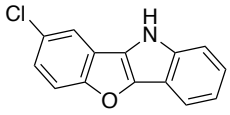
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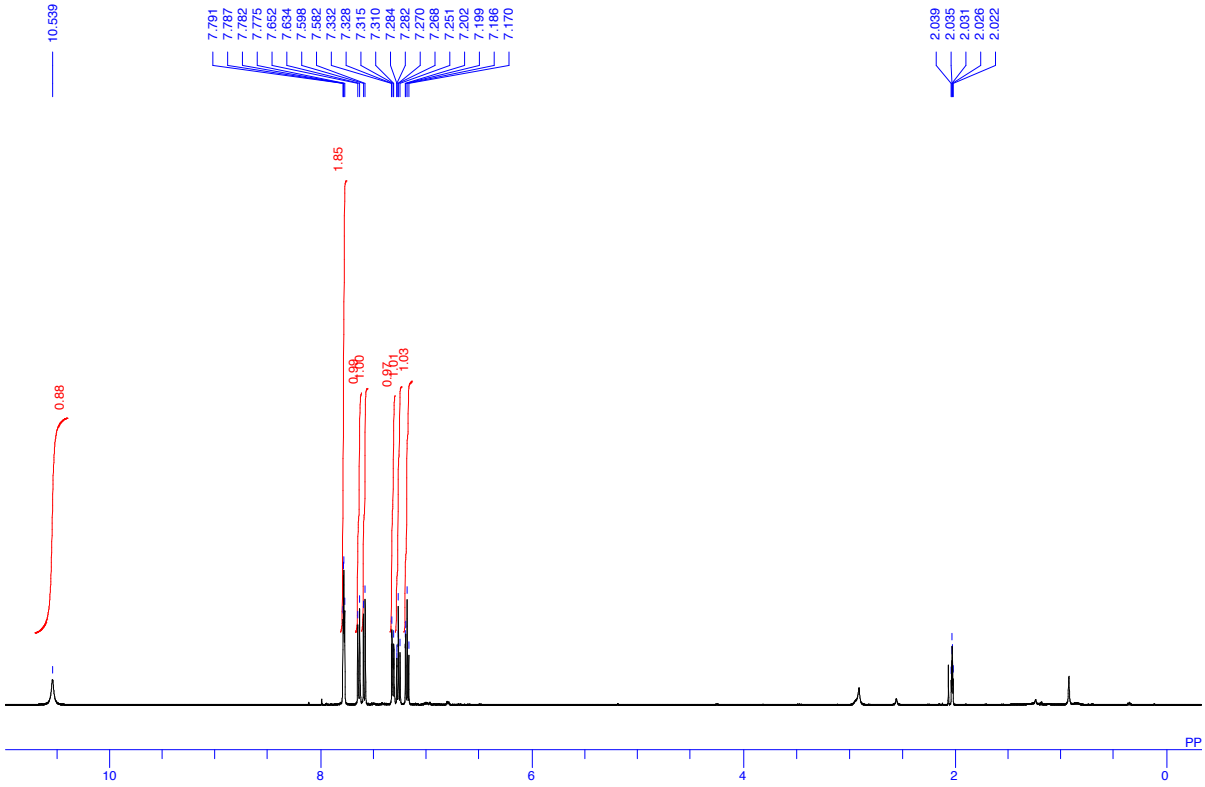
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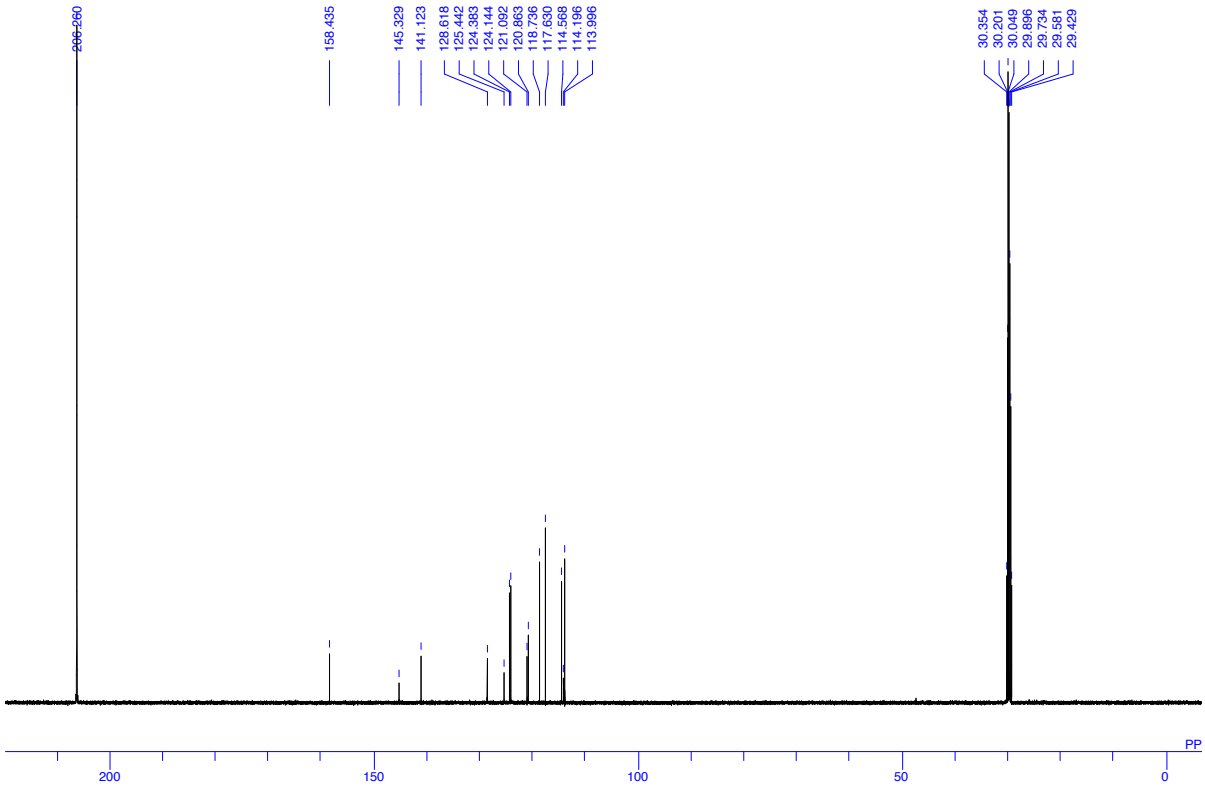
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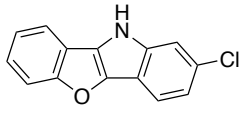
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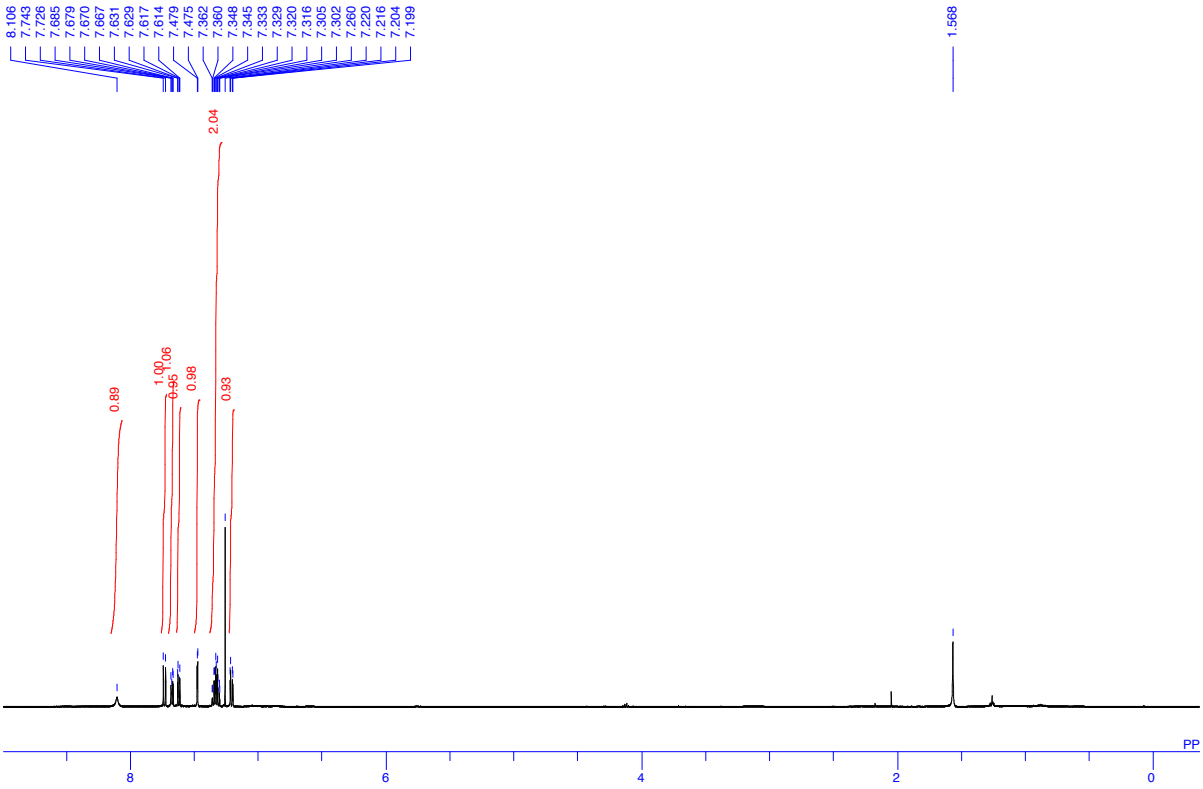
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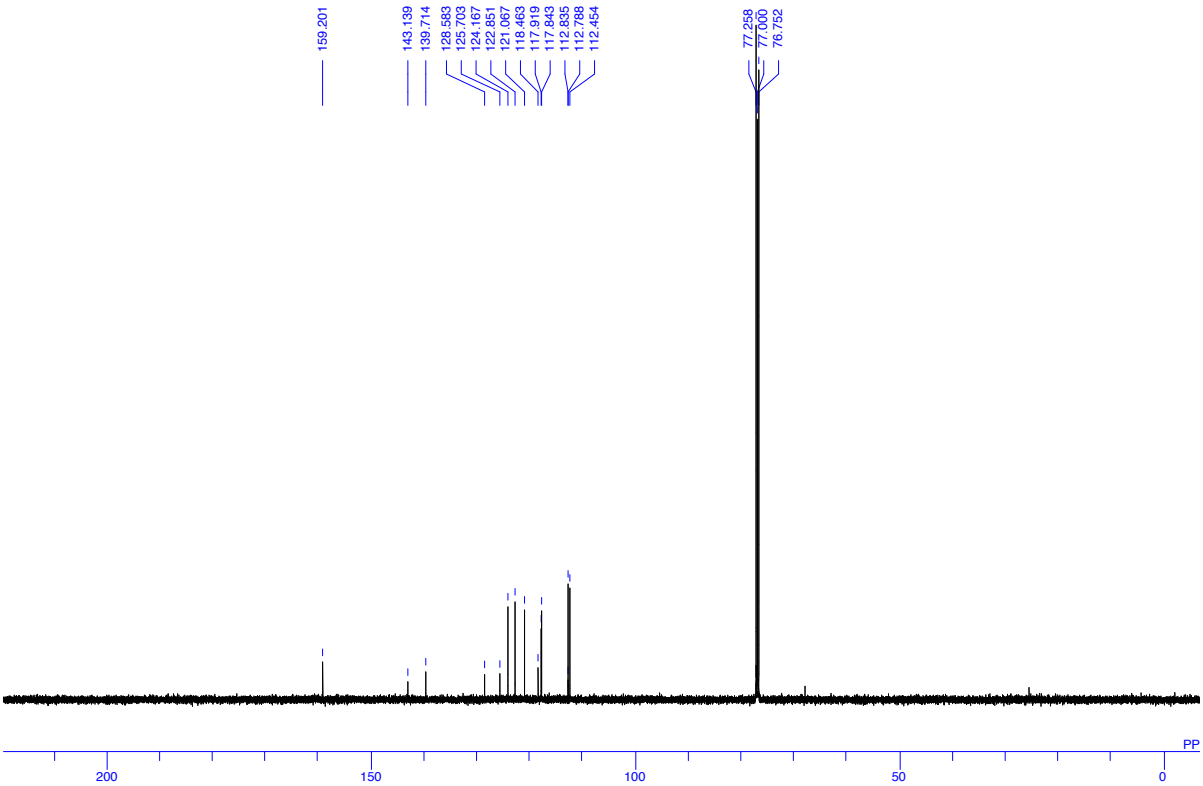
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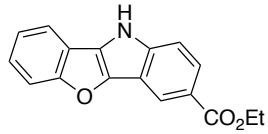
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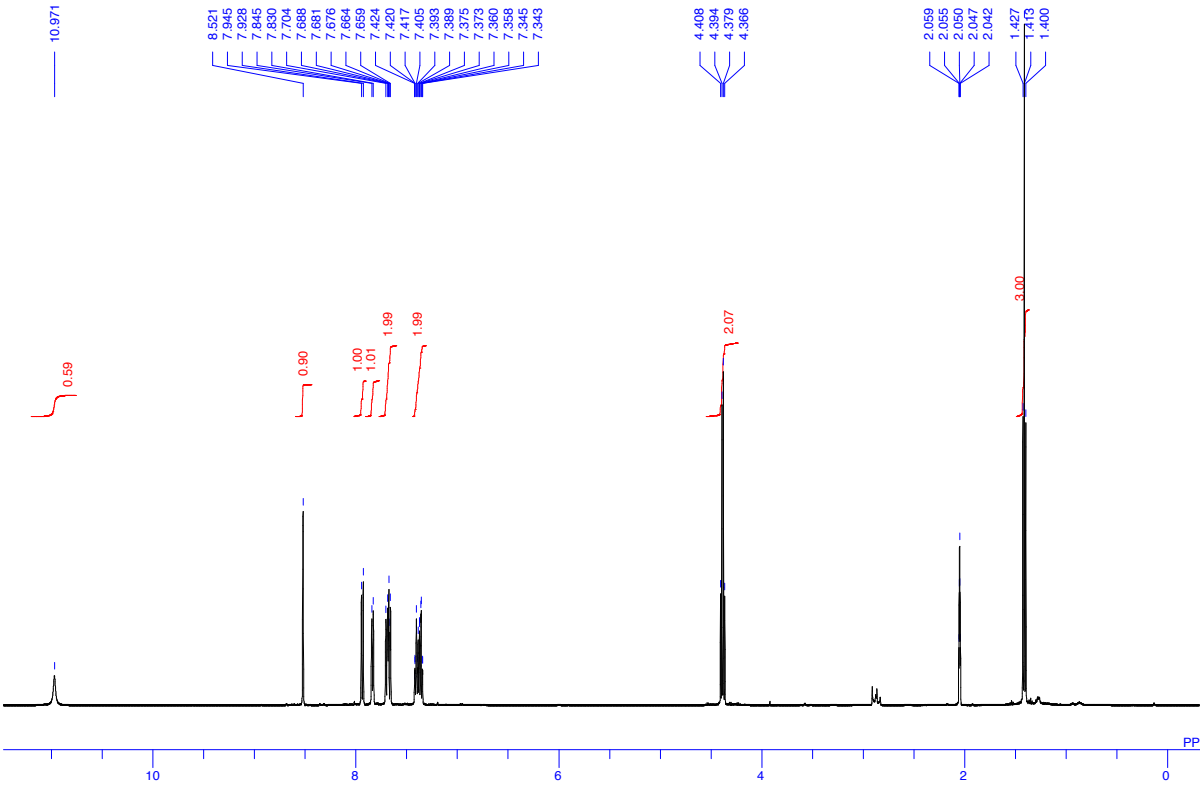
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7.345
7.343
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2.047
2.042
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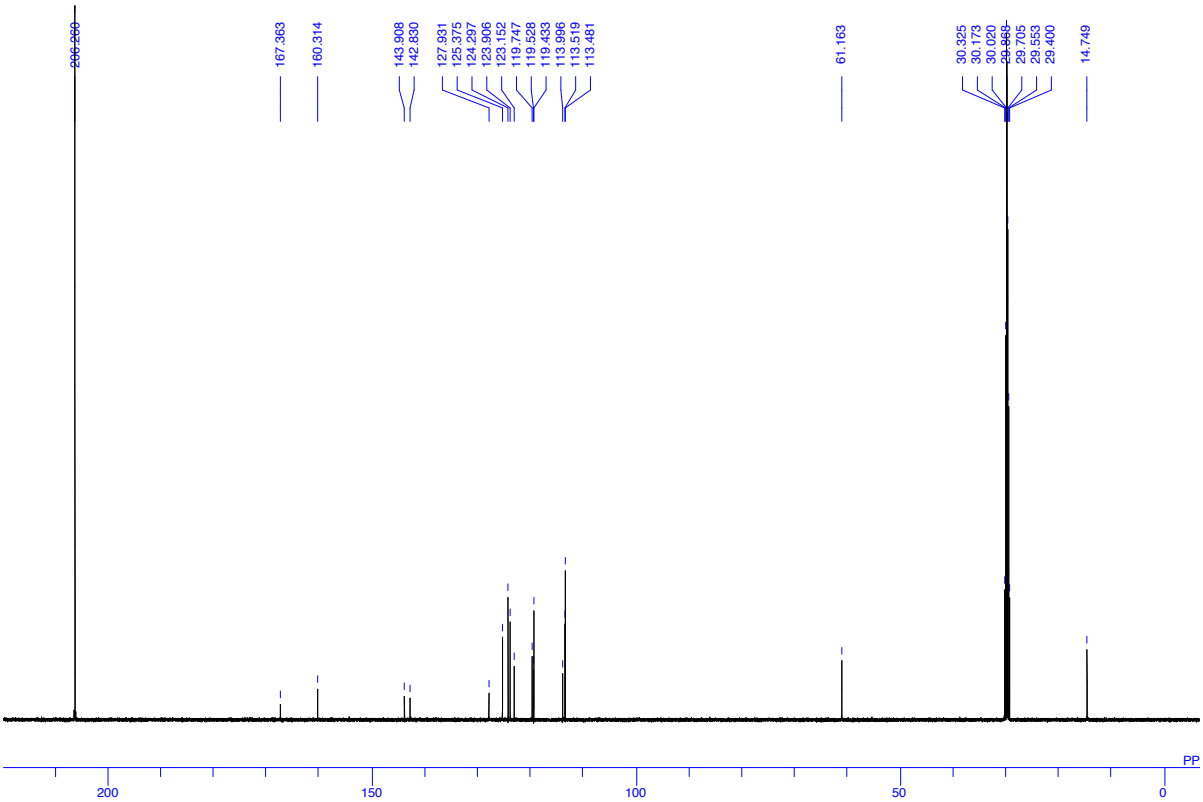
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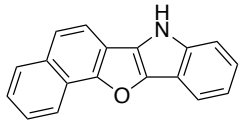
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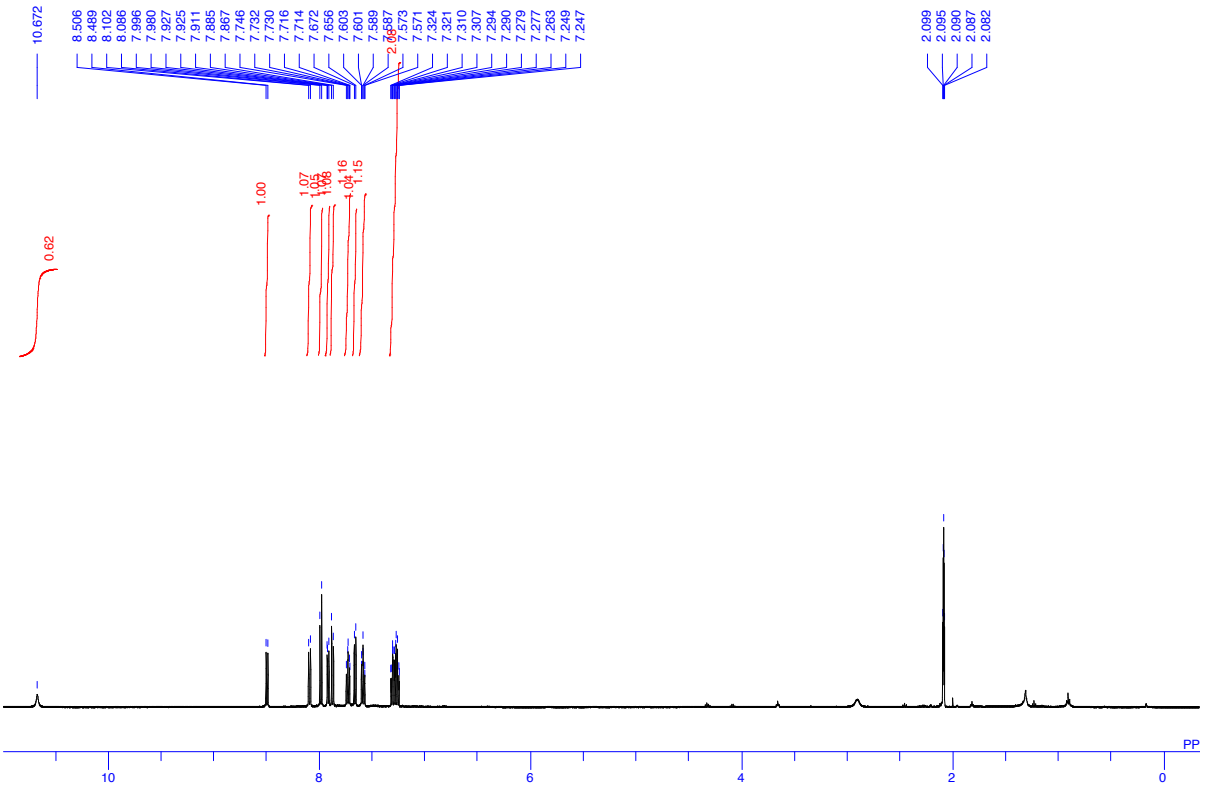
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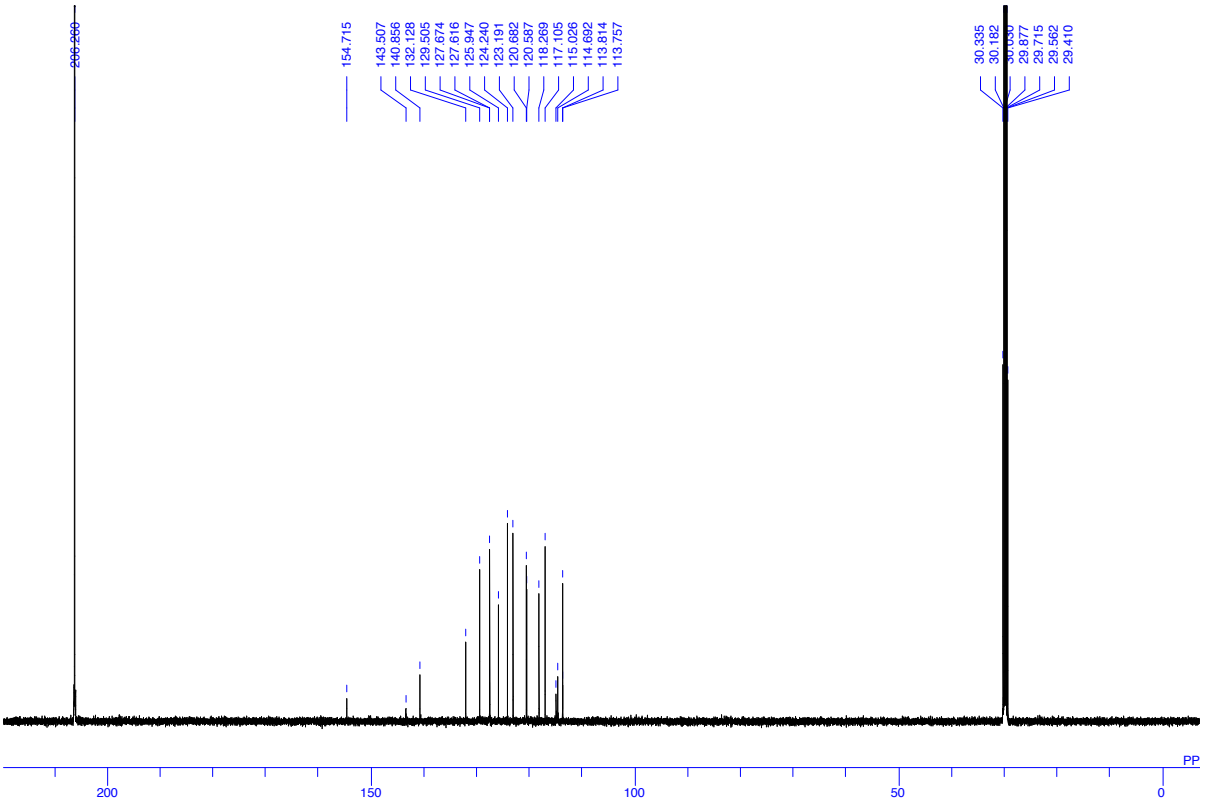
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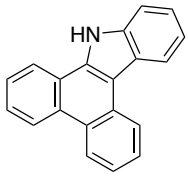
50
0

7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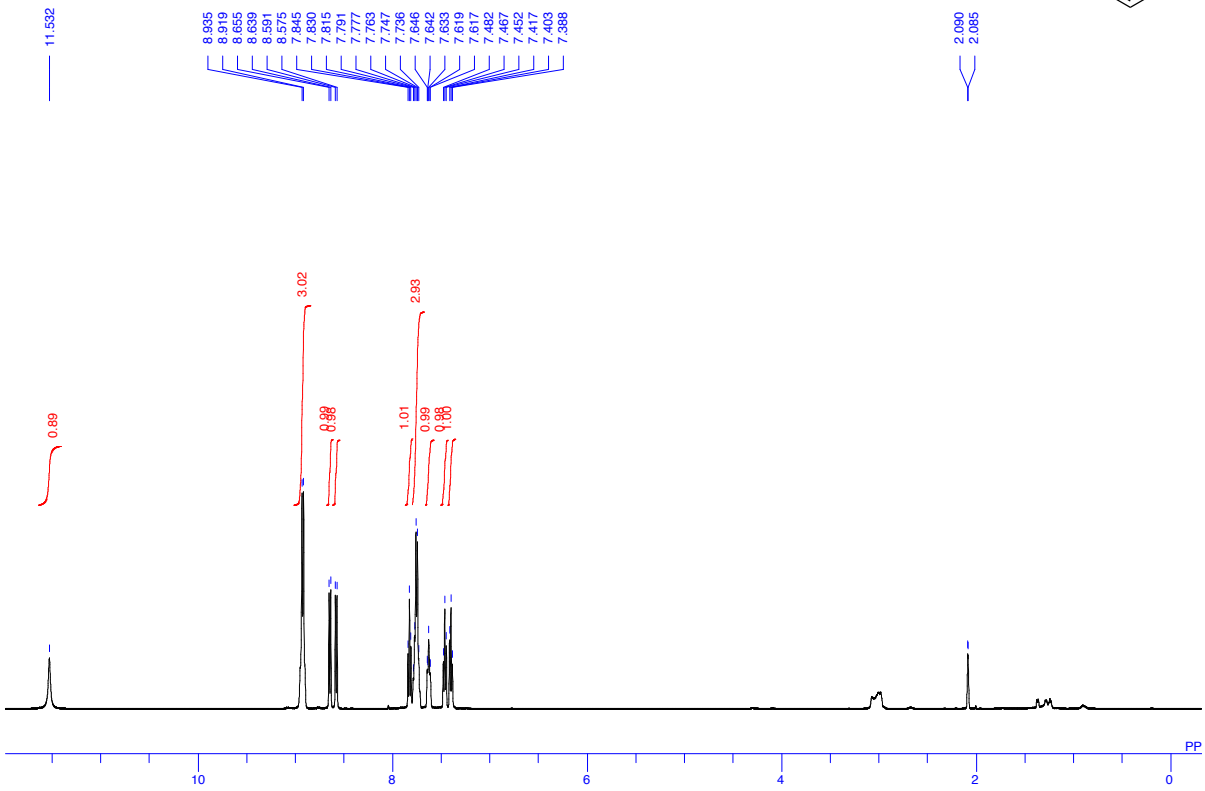
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7.619
7.617
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7.452
7.417
7.403
7.388
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2.085
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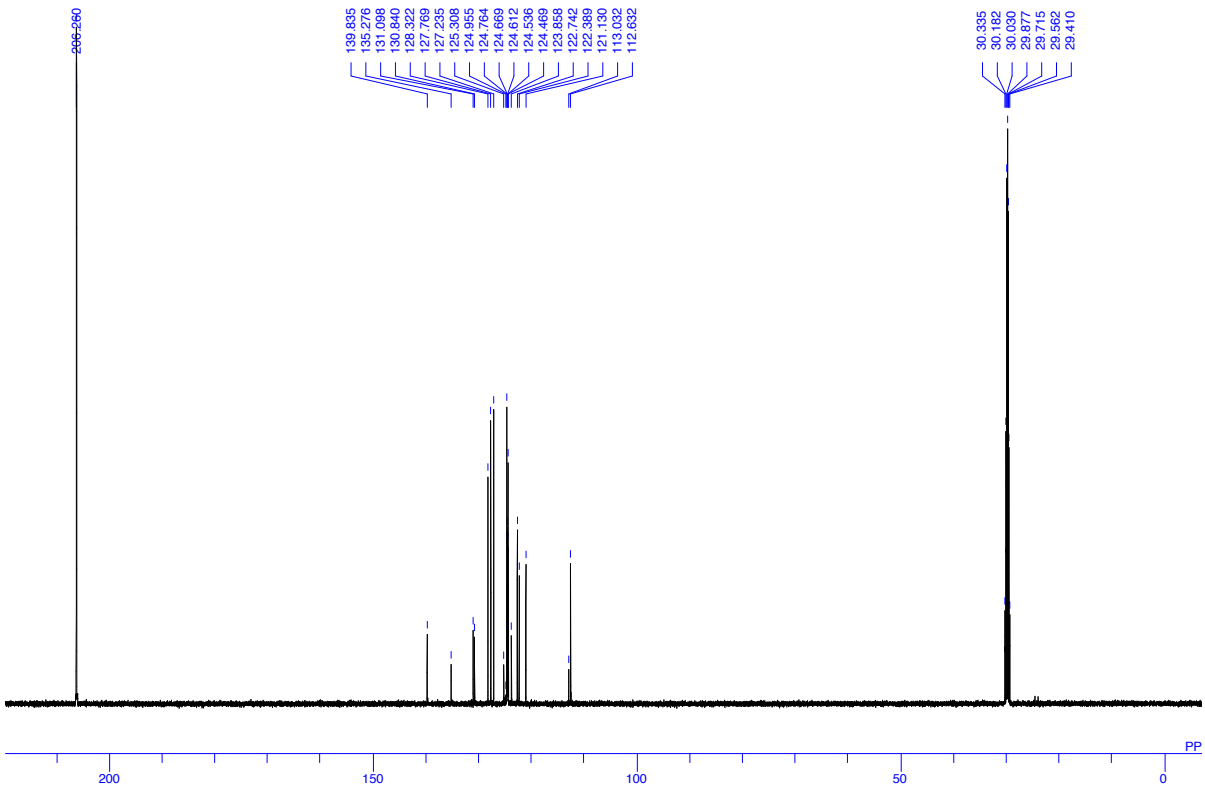
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30.335
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30.030
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29.715
29.562
29.410
PP
200
150
100
50
0