Electronic supplementary information (ESI)

Heterogenization of Amine-Functionalized Ionic Liquid Using Graphene Oxide as Support Material: A Highly Efficient Catalyst for the Synthesis of 3-Substituted Indoles via Yonemitsu-Type Reaction

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NMR data for representative products

2-((5-bromo-1H-indol-3-yl)(phenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table2, entry 1). Light pink solid, IR (ν_{max} /cm^{-1}, KBr): 3300, 2954, 2881, 1627, 1548, 1456, 1384, 1253, 1151, 1103, 1028, 885, 673. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.97 (br s, 1H), 10.48 (br s, 1H), 7.31-7.29 (m, 2H), 7.20-7.07 (m, 6H), 6.95 (s, 1H), 5.74 (s, 1H), 2.26 (m, 4H), 0.99 (s, 1H) ppm. ^{13}C NMR (DMSO- d_6): δ 144.66, 135.13, 129.73, 128.58, 127.98, 126.34, 125.57, 123.41, 121.26, 116.70, 116.42, 113.86, 111.13, 35.33, 32.14, 28.44 ppm. HRMS (ES) Calcd: 423.0834. Found: 424.0906 $[M + H]^+$ and 426.0889 $[MH + 2]^+$.

2-((5-Bromo-1H-indol-3-yl)(2-chlorophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table2, entry 2). White solid, IR (ν_{max} /cm^{-1}, KBr): 3282, 2954, 2376, 2320, 1705, 1635, 1564, 1463, 1381, 1249, 1151, 1089, 1029, 885, 800, 675. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.98 (br s, 1H), 10.33 (br s, 1H), 7.31-7.28 (m, 2H), 7.10-7.03 (m, 5H), 6.88 (s, 1H), 5.82 (s, 1H), 2.36-2.10 (m, 4H), 0.97 (s, 6H) ppm. ^{13}C NMR (DMSO-d_6) : 171.39 141.73, 135.56, 133.23, 132.40, 129.18, 127.60, 126.57, 126.24, 123.62, 121.00, 119.20, 115.44, 114.84, 114.06, 111.25, 43.82, 34.21, 31.98, 28.58, 28.33 ppm. HRMS (ES) Calcd: 457.0444. Found: 458.0521 $[M + H]^+$ and 460.051 $[MH + 2]^+$.

2-((5-bromo-1H-indol-3-yl)(4-chlorophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table2, entry 3). Light pink solid, IR (ν_{max} /cm^{-1}, KBr): 3330, 3150, 2958, 1589, 1489, 1458, 1375, 1242, 1062, 887, 796, 678. ^{1}H NMR (400 MHz, DMSO-d_6) : δ 11.02 (s, 1H), 10.60 (s, 1H), 7.32 (m,

2H), 7.23 (m, 2H), 7.13-7.11 (m, 3H), 6.97 (s, 1H), 5.72 (s, 1H), 2.23 (m, 2H), 2.14 (s, 2H), 0.99 (s, 6H) ppm. ^{13}C NMR (DMSO- d_6) : 142.66, 139.27, 135.17, 131.76, 130.36, 129.24, 127.89, 126.62, 122.53, 121.68, 120.64, 116.44, 114.50, 112.50, 111.29, 50.78, 43.26, 32.13, 31.77, 28.41 ppm. HRMS (ES) Calcd: 457.0444. Found: 458.0503 $[M + H]^+$ and 460.0486 $[MH + 2]^+$.

2-((5-Bromo-1H-indol-3-yl)(2-fluorophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table 2, entry 4). Off white solid, IR (ν_{max} /cm^{-1}, KBr): 3350, 3150, 2965, 2360, 1700, 1640, 1563, 1470, 1375, 1270, 1224, 1154, 1087, 1030, 670. ^{1}H NMR (400 MHz, DMSO-d_6) : δ 10.95 (br s, 1H), 10.50 (br s, 1H), 7.38 (d, J=8.4 Hz, 1H), 7.15-7.05 (m, 5H), 6.85 (d, J=8.4 Hz, 1H), 5.68 (s, 1H), 2.28-2.26 (m, 4H), 0.99 (s, 6H) ppm. ^{13}C NMR (DMSO-d_6) : δ 160.82, 142.72, 134.23, 133.54, 132.49, 128.21, 125.56, 123.84, 121.45, 119.20, 118.75, 115.43, 114.50, 111.48, 34.25, 31.19, 29.54 ppm. HRMS (ES) Calcd: 441.0740. Found: 442.0820 $[M + H]^+$ and 444.0805 $[MH + 2]^+$.

2-((2-Chlorophenyl)(1H-indol-3-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table2, entry 5). White solid, IR (ν_{max} /cm^{-1}, KBr): 3334, 3161, 2958, 2922, 1635, 1564, 1463, 1377, 1246, 1151, 1074, 885, 794. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.73 (s, 1H), 10.22 (s, 1H), 7.29 (t, 2H), 7.10-6.96 (m, 5H), 6.84-6.79 (m, 2H), 5.87 (s, 1H), 2.37-2.10 (m, 4H), 0.98 (s, 6H) ppm. ^{13}C NMR (DMSO- d_6) : 142.22, 136.91, 133.18, 132.76, 129.00, 127.30, 125.99, 124.83, 121.19, 118.98, 118.62, 115.43, 115.11, 111.90, 34.36, 32.00, 31.24 ppm. HRMS (ES) Calcd: 379.1339. Found: 380.1408 $[M + H]^+$ and 382.1386 $[MH + 2]^+$.

2-((2-Chlorophenyl)(5-methoxy-1H-indol-3-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table2, entry 6). White solid, IR (ν_{max} /cm^{-1}, KBr): 3335, 3240, 2957, 2920, 1630, 1560,1470, 1380, 1240, 1156, 1065, 886, 795. ^{1}H NMR (400 MHz, DMSO-d_6) : δ 10.82 (br s, 1H), 10.37 (br s, 1H), 7.43 (m, 1H), 7.35 (m, 2H), 7.27 (m, 1H), 7.22 (t, 2H), 7.17 (t, 2H), 6.47 (s, 1H), 5.84 (s, 1H), 3.58 (s, 3H), 2.08 (s, 4H), 1.12 (s, 6H) ppm. ^{13}C NMR (DMSO- d_6) : 196.10, 171.08, 153.21, 142.09, 133.23, 132.60, 132.15, 129.06, 127.67, 126.07, 125.55, 115.12, 112.51, 110.92, 101.27, 55.74, 50.79, 43.80, 34.47, 31.97, 28.62, 28.36 ppm. HRMS (ES) Calcd: 409.1445. Found: 410.1448 $[M + H]^+$ and 410.1447 $[MH + 2]^+$.

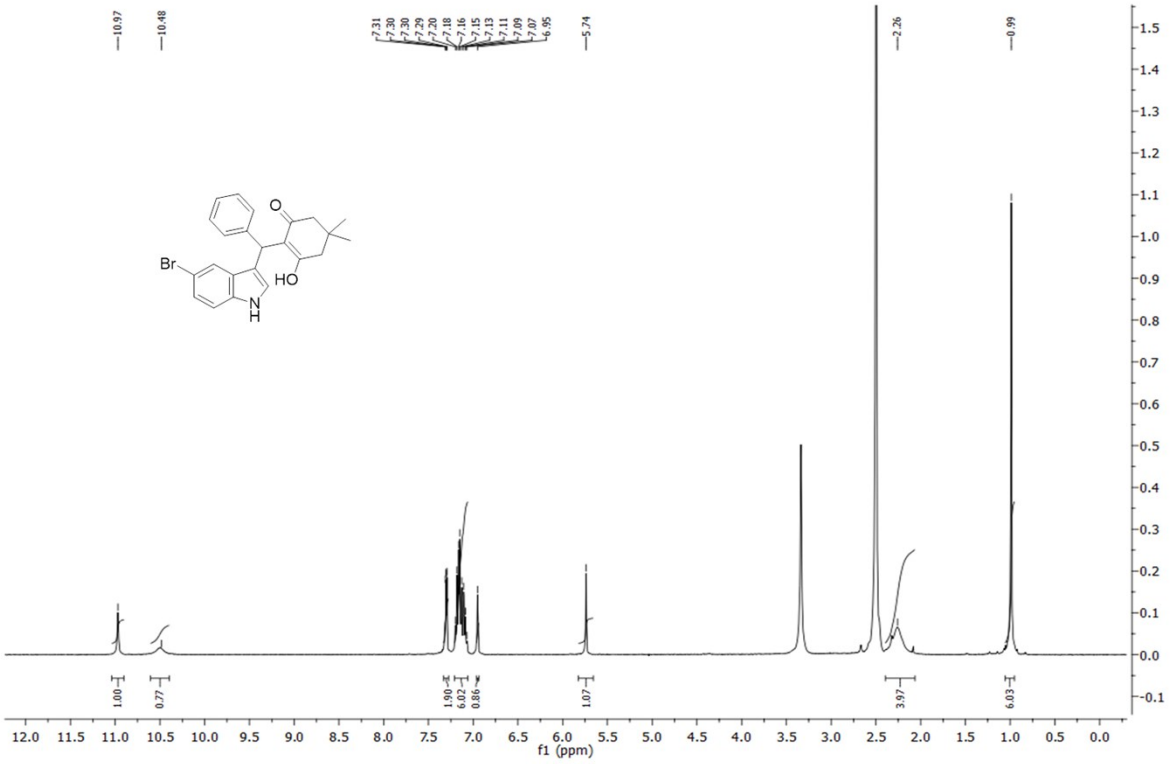
2-((5-bromo-1H-indol-3-yl)(2-nitrophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table2, entry 7). Off white solid, IR (ν_{max} /cm^{-1}, KBr): 3330, 3290, 3020, 2970, 2356, 1700, 1550, 1470, 1398, 1285, 1225, 1150, 1080, 675. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.67 (d, J=8.4 Hz, 1H), 7.42-7.38 (m, 1H), 7.34-7.27 (m, 3H), 7.29-7.21 (m, 1H), 7.13-7.10 (m, 1H), 6.89 (s, 1H), 6.14 (s, 1H), 2.29(s, 2H), 2.04 (s, 2H), 0.92(s, 6H) ppm. ^{13}C NMR (DMSO- d_6): δ 159.23, 148.65, 145.36, 138.54, 133.21, 130.80, 129.81, 123.62, 119.59, 115.32, 112.45, 110.26, 38.16, 32.54, 30.50, 28.54 ppm. HRMS (ES) Calcd: 468.0685. Found: 469.0448 $[M + H]^+$.

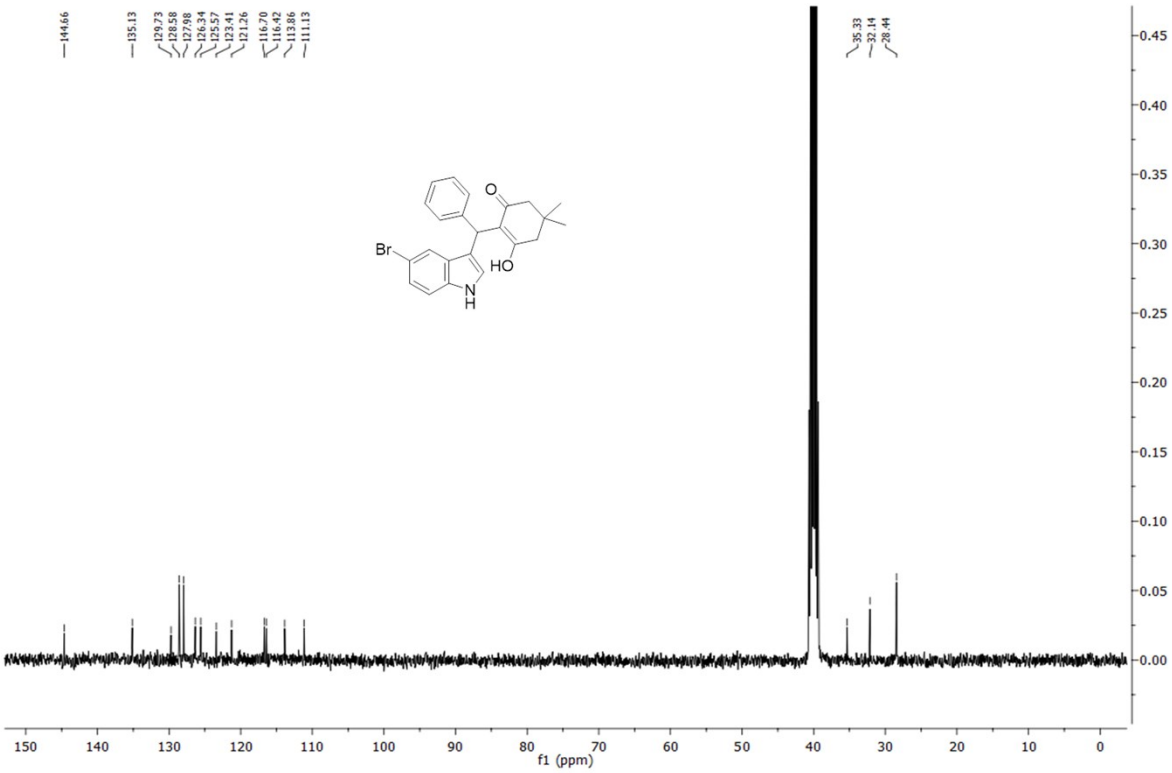
2-((5-bromo-1H-indol-3-yl)(4-nitrophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table2, entry 8). Off white solid, IR (ν_{max} /cm^{-1}, KBr): 3345, 3260, 3110, 2975, 2350, 1720, 1558, 1479, 1290, 1250, 1145, 1075, 670. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.07 (s, 1H), 10.74 (s, 1H), 8.04 (d, J=8.8 Hz, 2H), 7.72 (d, J=8.8 Hz, 2H), 7.32-7.28 (m, 3H), 5.81 (s, 1H), 2.37 (s, 2H), 2.13 (s,2H), 0.96 (s, 6H) ppm. ^{13}C NMR (DMSO- d_6) : δ 162.45, 149.54, 145.36, 137.30, 132.25, 131.72, 130.52, 128.23, 127.54, 123.82, 121.29, 120.50, 119.86, 114.13, 112.62, 110.30, 39.56, 33.14, 31.38, 29.99 ppm. HRMS (ES) Calcd: 468.0685. Found: 469.0683 $[M + H]^+$.

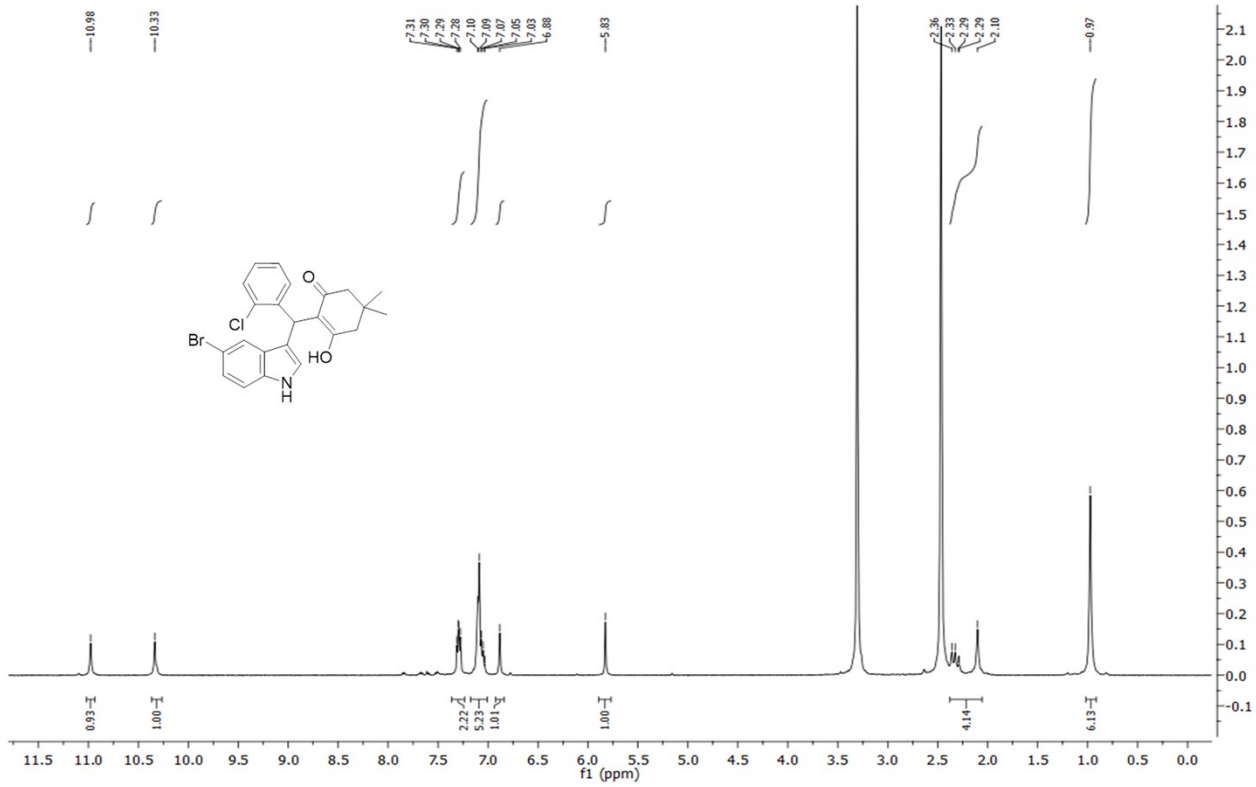
2-((5-Bromo-1H-indol-3-yl)(pyridine-2-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table2, entry 9). White solid, IR (ν_{max} /cm^{-1}, KBr): 3338, 3238, 2929, 1579, 1466, 1426, 1375, 1243, 1115, 1015, 886, 780. ^{1}H NMR (400 MHz, DMSO-d_6) : δ 10.97 (s, 1H), 8.55-8.54 (m, 1H), 7.94-7.89 (m, 1H), 7.62 (d, J=8.0 Hz, 1H), 7.42-7.38 (m, 2H), 7.24 (d, J=8.8 Hz, 1H), 7.11-7.08 (m, 1H), 6.83 (s, 1H), 5.98 (s, 1H), 2.30-2.17 (m, 4H), 0.90 (s, 6H) ppm. ^{13}C NMR (DMSO- d_6) : 162.74, 147.41, 140.07, 136.86, 126.82, 124.36, 123.13, 121.56, 119.11, 118.80, 115.71, 114.68, 111.91, 38.33, 31.63, 28.37 ppm. HRMS (ES) Calcd: 424.0786. Found: 425.0790 $[M + H]^+$.

2-((1H-indol-3-yl)(pyridin-2-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone (Table2, entry 10). White solid, IR (ν_{max} /cm^{-1}, KBr): 3395, 2957, 2882, 1721, 1630, 1544, 1510, 1420, 1374, 1280, 1250, 1178, 1084, 1049, 874, 805, 750. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.74 (s, 1H), 8.52 (d, J=8.4 Hz, 1H), 7.90 (t, 1H), 7.62 (d, J=8.4 Hz, 1H), 7.37 (t, 1H), 7.26 (d, J=8.4 Hz 2H), 6.98 (t, 1H), 6.83 (t, 1H), 6.79 (s, 1H), 6.02 (s, 1H), 2.27-2.18 (m, 4H), 0.91 (s, 6H) ppm. ^{13}C NMR (DMSO- d_6) :

δ 162.74, 147.41, 140.07, 136.86, 124.36, 123.13, 121.56, 119.11, 118.80, 115.71, 114.68, 111.91, 33.33, 31.63, 28.37 ppm. HRMS (ES) Calcd: 346.1681. Found: 346.1686.



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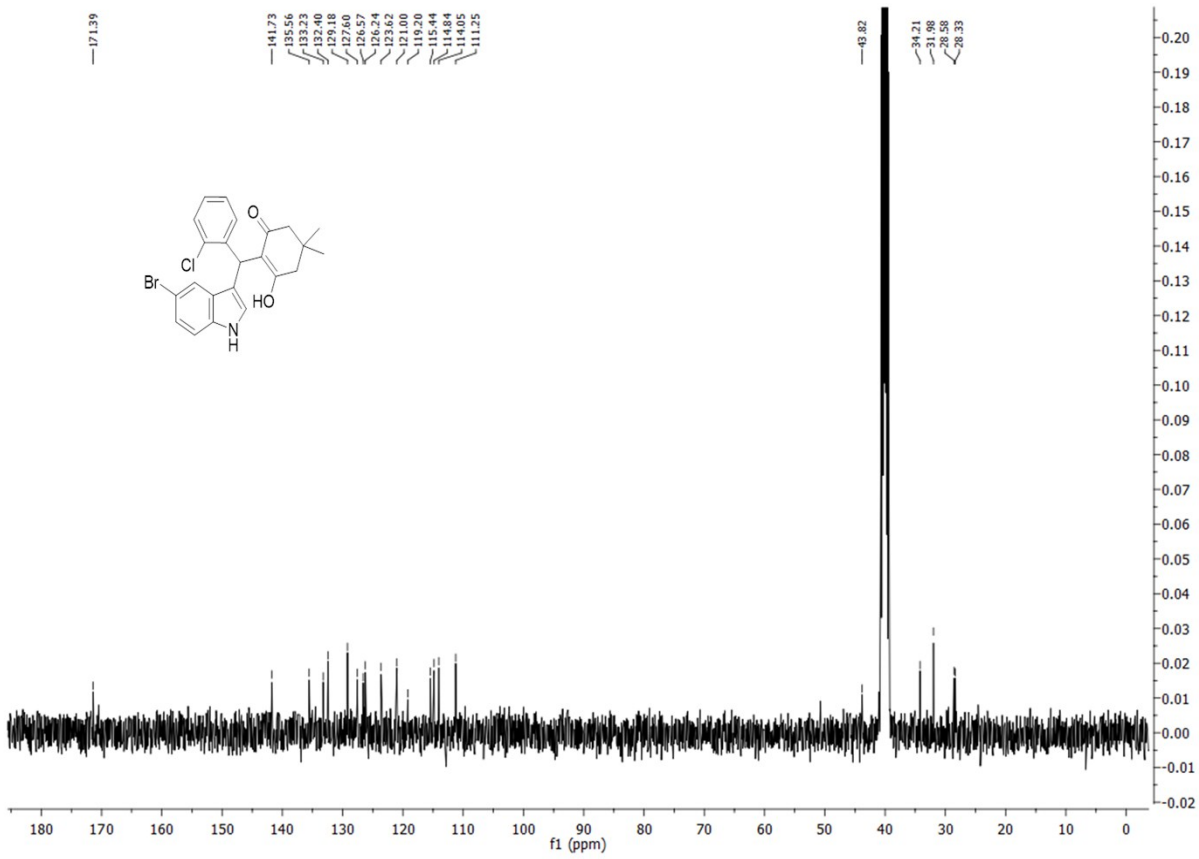
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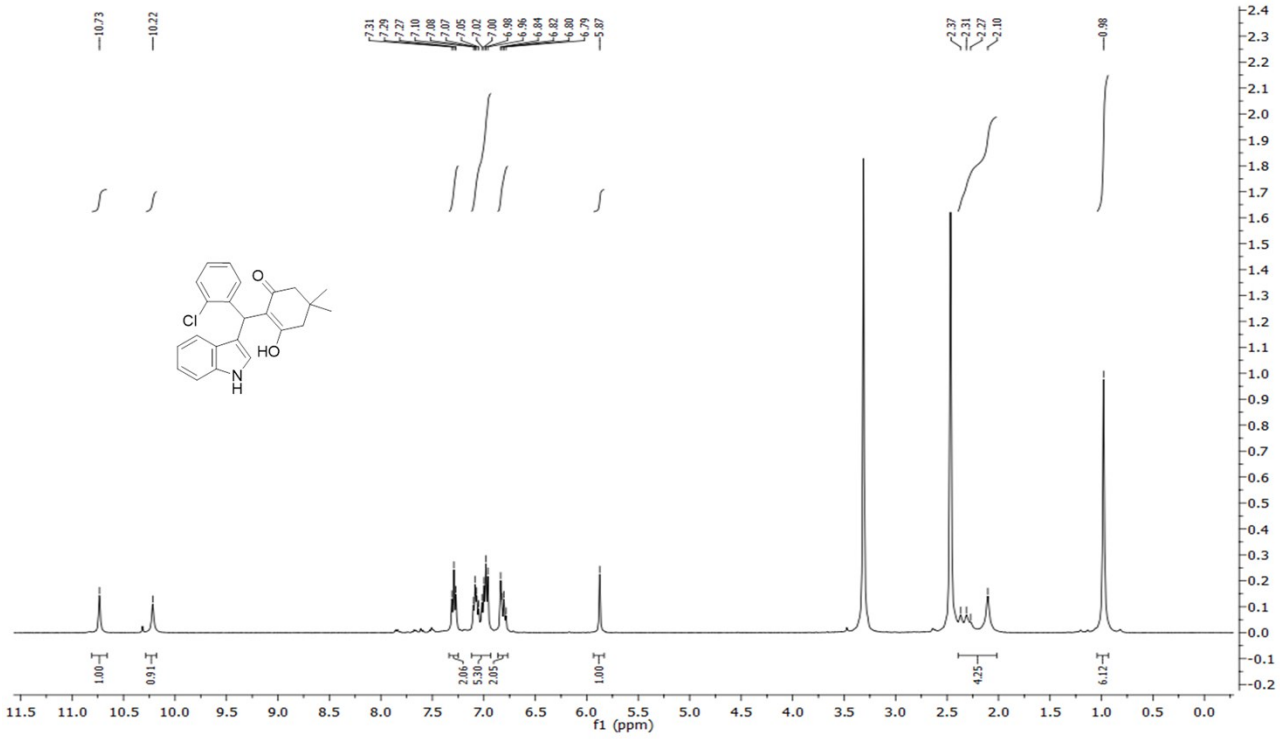
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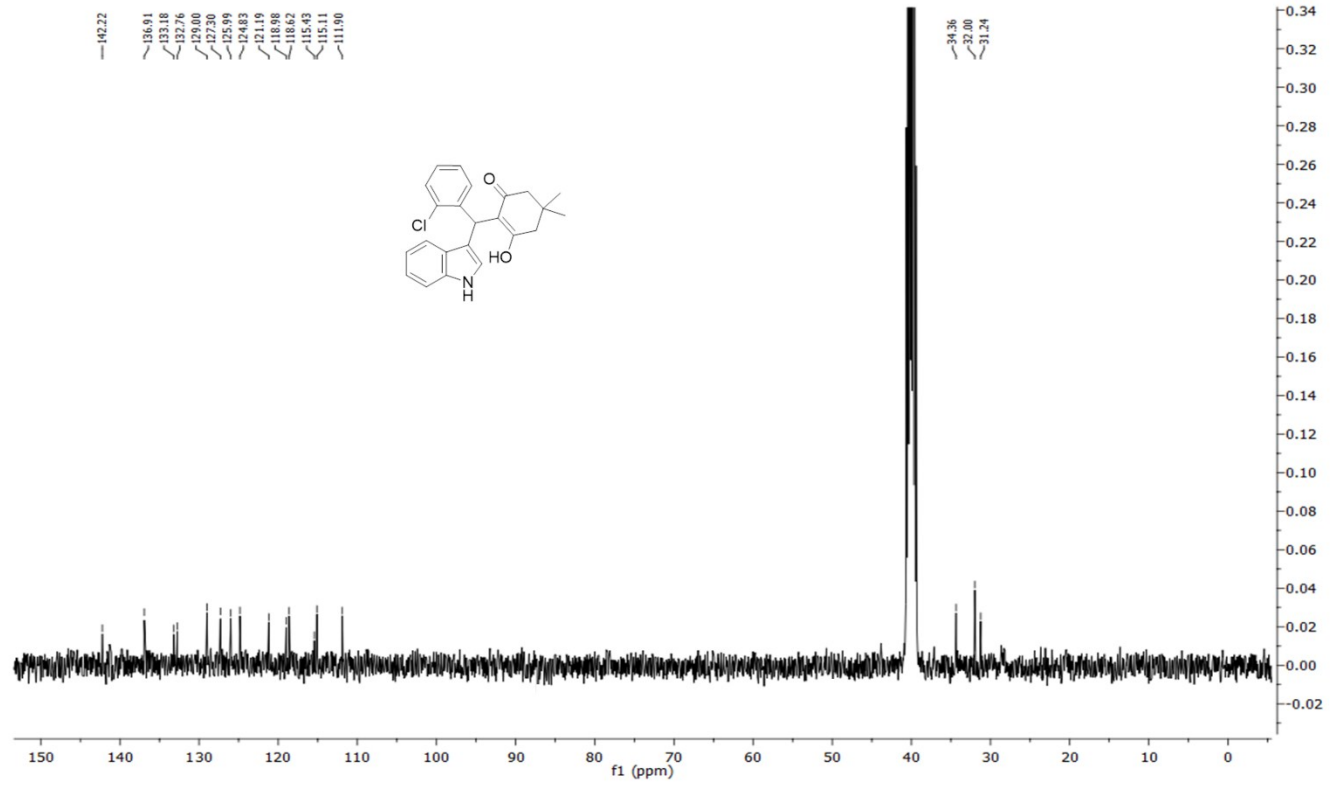
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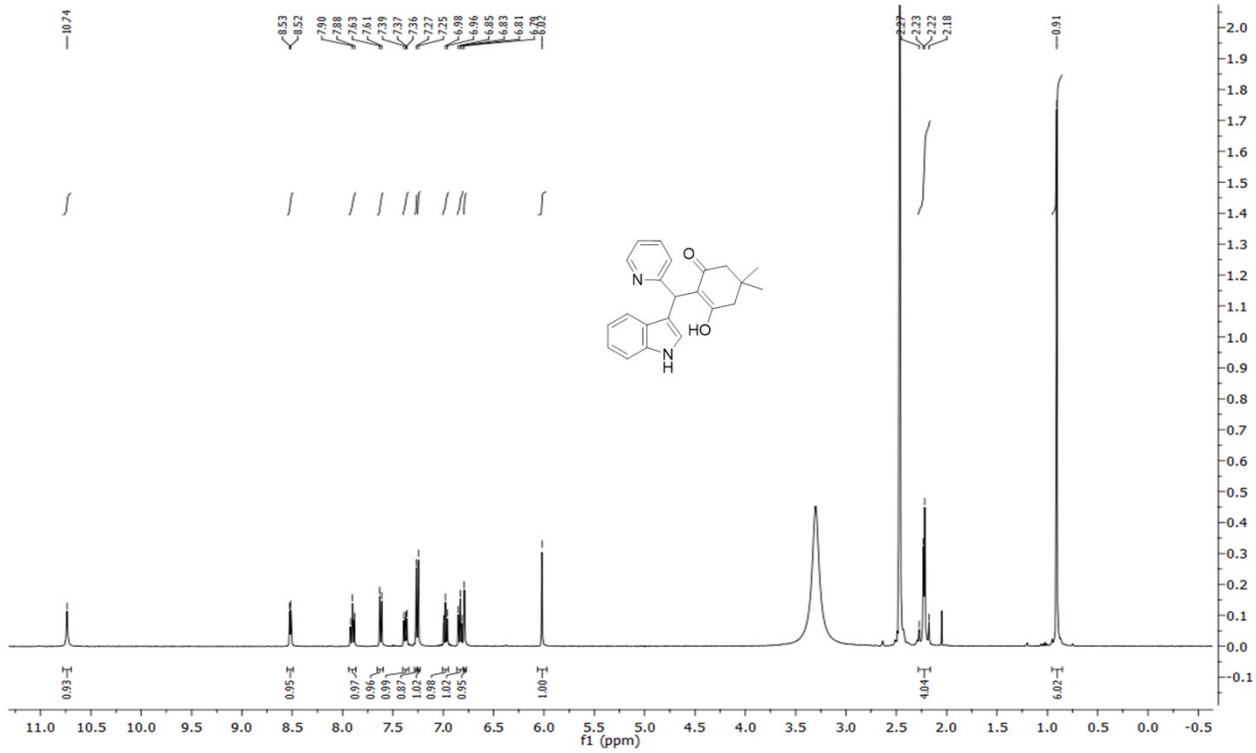
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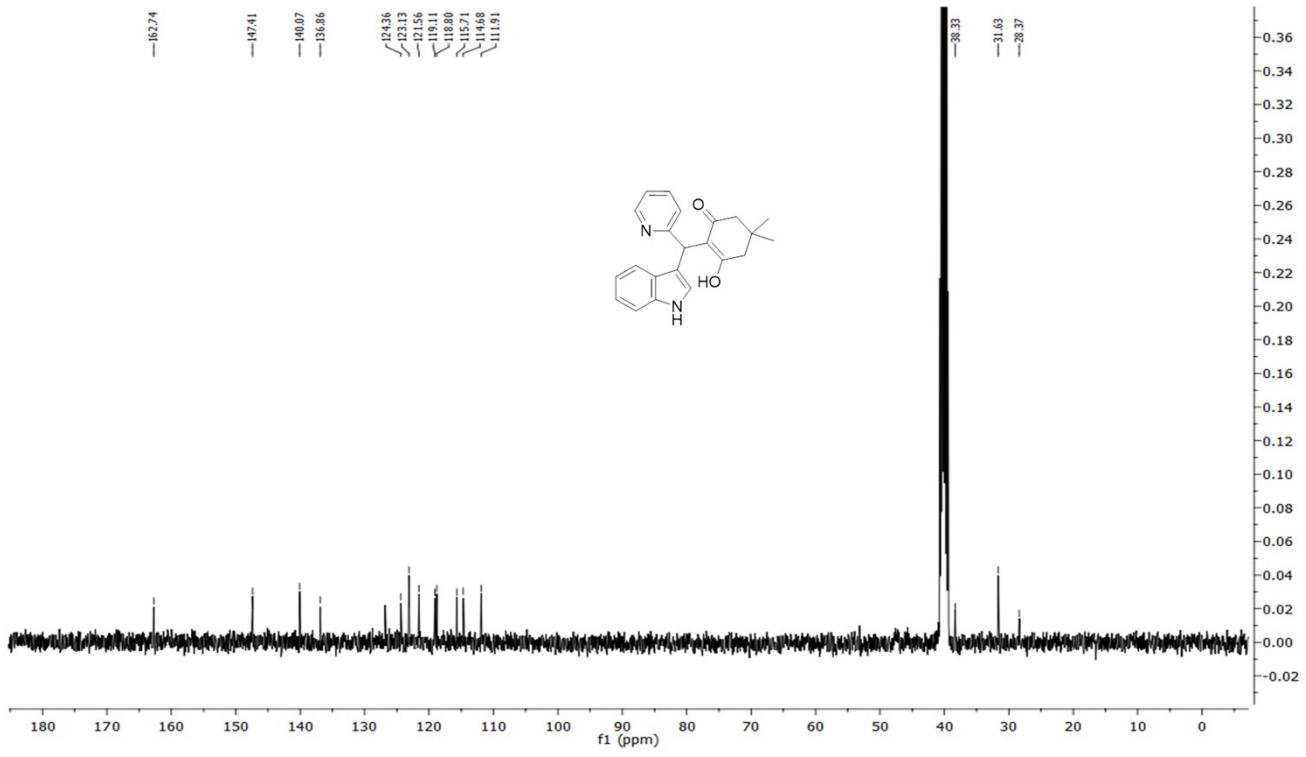
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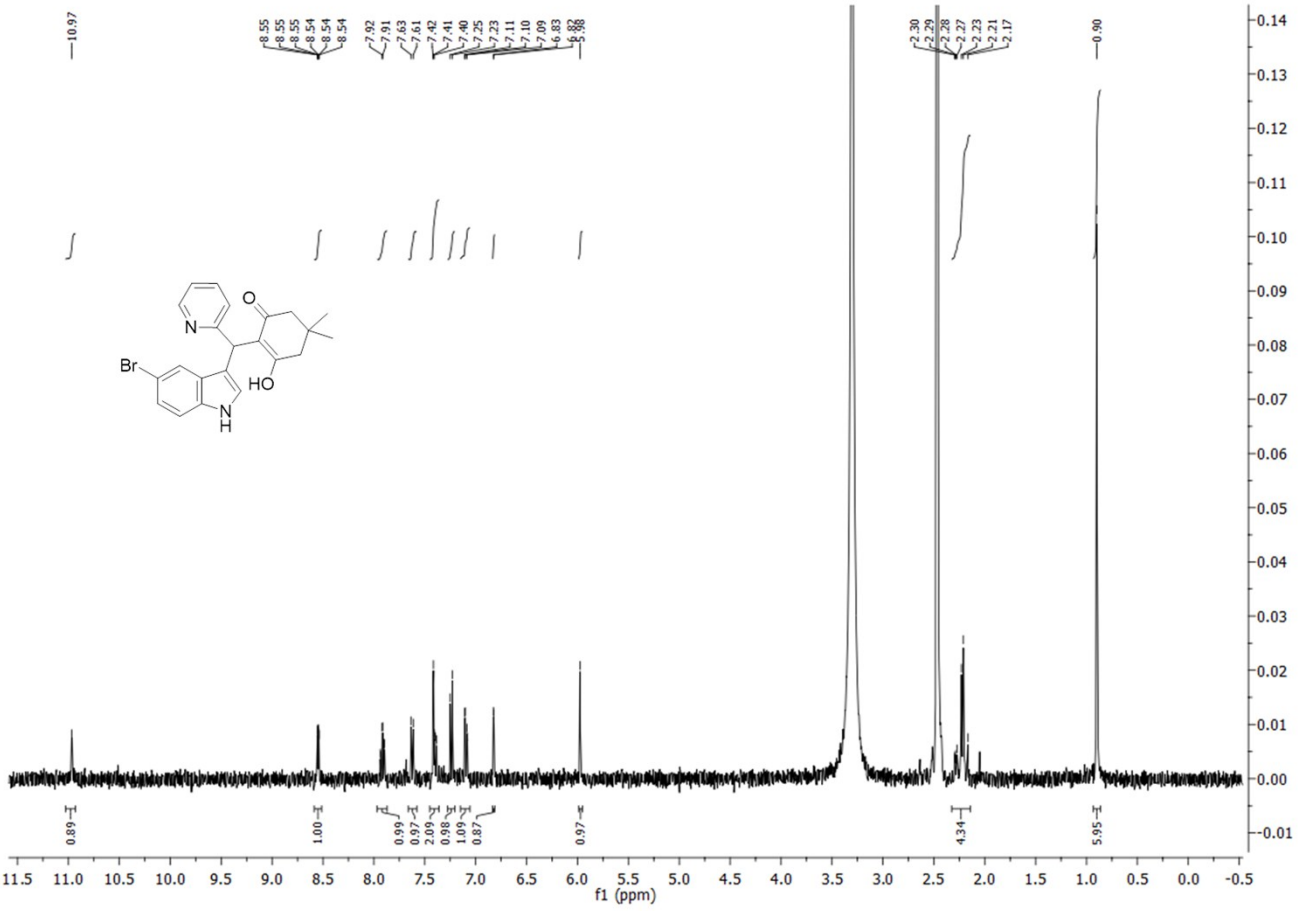
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