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Supporting Information

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Tao Wang,[a] Shuai Shi,[a] Daniel Pflästerer,[a] Eva Rettenmeier,[a] Matthias Rudolph,[a] Frank Rominger,[a] and A. Stephen K. Hashmi*[a, b]

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Synthesis of Polycyclic Indole Skeletons by a Gold(I)-Catalyzed Cascade Reaction

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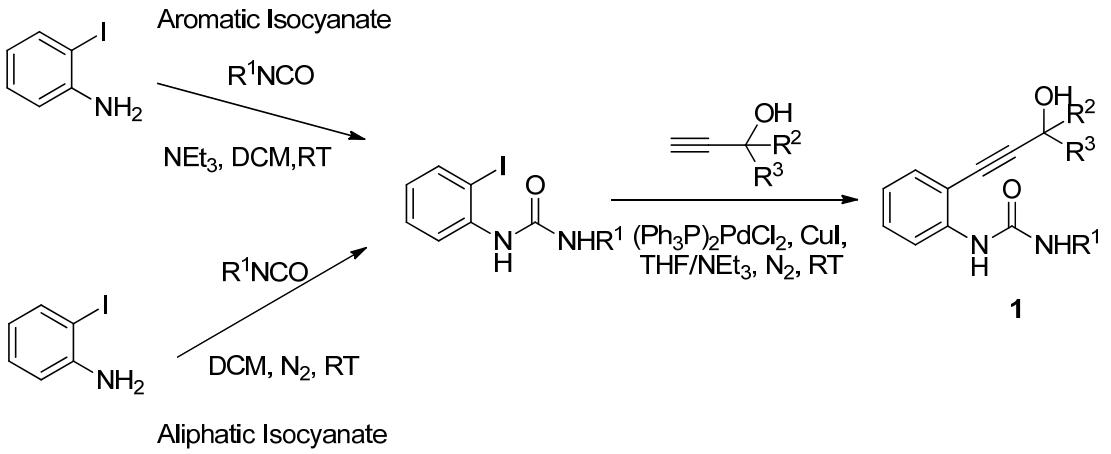
General Information: Chemicals (Aldrich, Fluka, Lancaster, and Merck) were used without further purification. Dichloromethane and toluene were dried from dried machine. NMR spectra were recorded on Bruker, ARX300 and AMX250 spectrometers. Chemical shifts were referenced to residual solvent protons. Signal multiplicity as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). MS spectra were recorded on a Finnigan MAT 90 a Varian 711 or a micrOTOF-Q spektometer. IR spectra were recorded on a Bruker Vector 22. Flash chromatography was performed with Macherey-Nagel silica gel SiO_2 (40-63 μm), Thin-layer chromatography (TLC) was performed on precoated polyester sheets (POLYGRAM SIL /GUV254), and components were visualized by observation under UV light or by treating the plates with phosphomolybdic acid hydrate followed by heating.

General procedure for synthesis of substrates 1.



Synthesis of (2-iodophenyl)urea:

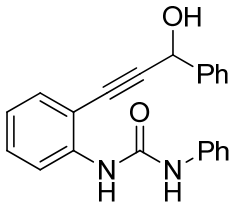
For aromatic isocyanates: To a solution of 2-iodo-benzenamin (2 mmol) and isocyanate (2.2 mmol) in dichloromethane (10 mL) was added 455 mg (4.5 mmol) of triethylamine. The resulting solution was stirred at room temperature for 12 hours. The precipitate was filtered and washed with dichloromethane (2mL*3). The solid obtained was air-dried and was used directly for next step without further purification.

For aliphatic isocyanates: 2-iodoaniline (2.28 mmol) and isocyanate (2.74 mmol) were dissolved in 1 mL of anhydrous dichloromethane under nitrogen. The solution was stirred at room temperature under nitrogen for 24 hours. The precipitate was filtered and washed with dichloromethane (2mL*3). The solid obtained was air-dried and was used directly for next step without further purification.

Synthesis of substrate 1:

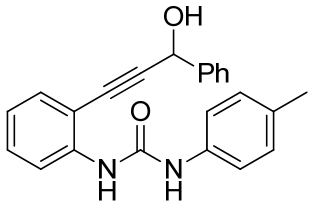
(2-iodophenyl)urea (1 mmol), propargylic alcohol (1.1 mmol) were dissolved in a mixture solvent of THF (10 mL) and NEt_3 (5 mL) under nitrogen. $Pd(PPh_3)_4$ (14 mg, 0.02 mmol) and CuI (7.6 mg, 0.04 mmol) were added and the reaction mixture was stirred at room temperature for 2 hours. The solvent was removed and the crude product was purified via column chromatography on silica gel (hexane / ethyl acetate 6:1 to 3:1) to yield substrate**1** in good to excellent yields.

1-(2-(3-hydroxy-3-phenylprop-1-yn-1-yl)phenyl)-3-phenylurea (1a).



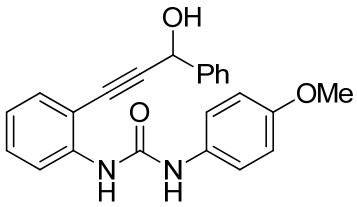
Yield: 88%, white solid, m.p. 167-168 ^{o}C; ^{1}H NMR [300 MHz, $(CD_3)CO$]: δ = 8.71 (sbr, 1 H), 8.26 (d, 1 H, *J* = 8.3 Hz), 8.00 (sbr, 1 H), 7.64 (d, 2 H, *J* = 7.1 Hz), 7.54 (d, 2 H, *J* = 7.7 Hz), 7.41-7.25 (m, 7 H), 7.02-6.97 (m, 2 H), 5.75 (d, 1 H, *J* = 5.7 Hz), 5.25 (d, 1 H, *J* = 5.7 Hz); ^{13}C NMR [75 MHz, $(CD_3)CO$]: δ = 153.5, 143.0, 142.0, 141.0, 133.2, 130.6, 130.0, 129.6, 129.1, 128.0, 123.7, 123.2, 120.7, 120.1, 112.7, 98.1, 82.1, 65.4 ppm; IR (ATR): $\tilde{\nu}$ = 3275, 3059, 3036, 1950, 1742, 1645, 1598, 1578, 1547, 1497, 1478, 1446, 1295, 1247, 1216, 1185, 1159, 1112, 1078, 1024, 1001, 966, 919, 899, 822, 752, 742, 714, 693, 660, 633 cm^{-1}; HRMS (ESI): calculated for $C_{22}H_{18}N_2O_2Na$ $[M+Na]^+$: 365.1260, found 365.1263.

1-(2-(3-hydroxy-3-phenylprop-1-yn-1-yl)phenyl)-3-(p-tolyl)urea (1b).



Yield: 85%, yellow solid, m.p. 171-172 ^{o}C; ^{1}H NMR [500 MHz, $(CD_3)CO$]: δ = 8.55 (sbr, 1 H), 8.27 (d, 1 H, *J* = 8.3 Hz), 7.93 (sbr, 1 H), 7.63 (d, 2 H, *J* = 7.4 Hz), 7.41-7.37 (m, 5 H), 7.35-7.30 (m, 2 H), 7.09 (d, 2 H, *J* = 8.3 Hz), 6.98 (td, 1 H, J_1 = 7.6 Hz, J_2 = 1.0 Hz), 5.74 (d, 1 H, *J* = 5.9 Hz), 5.24 (d, 1 H, *J* = 5.9 Hz), 2.26 (s, 3 H); ^{13}C NMR [125 MHz, $(CD_3)CO$]: δ = 153.2, 142.6, 141.7, 138.0, 132.9, 132.7, 130.3, 130.2, 129.3, 128.8, 127.6, 122.7, 120.2, 120.0, 112.2, 97.7, 81.8, 65.0, 20.8 ppm; IR (ATR): $\tilde{\nu}$ = 3651, 3297, 3031, 1644, 1603, 1577, 1547, 1511, 1492, 1476, 1448, 1406, 1293, 1249, 1216, 1189, 1110, 1079, 1023, 966, 905, 818, 790, 748, 708, 695, 638, 613 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{20}N_2O_2Na$ $[M+Na]^+$: 379.1417, found 379.1420.

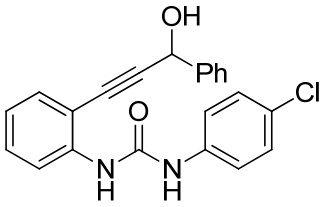
1-(2-(3-hydroxy-3-phenylprop-1-yn-1-yl)phenyl)-3-(4-methoxyphenyl)urea (1c).



Yield: 75%, yellow solid, m.p. 175-176 ^{o}C; ^{1}H NMR [400 MHz, $(CD_3)CO$]: δ = 8.59 (sbr, 1 H), 8.27 (d, 1 H, *J* = 8.4 Hz), 7.93 (sbr, 1 H), 7.64-7.62 (m, 2 H), 7.46-7.29 (m, 7 H), 6.97 (td, 1 H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 6.88-6.84 (m, 2 H), 5.72 (d, 1 H, *J* = 5.5 Hz), 5.28 (d, 1 H, *J* = 5.5 Hz), 3.75 (s, 3 H); ^{13}C NMR [100 MHz, $(CD_3)CO$]: δ = 156.5, 153.4, 142.7, 142.0, 133.6, 132.8, 130.2, 129.3, 128.7, 127.7, 122.6, 121.9, 120.1, 114.9, 112.1, 97.9, 81.7, 65.0, 55.7 ppm; IR (ATR): $\tilde{\nu}$ =

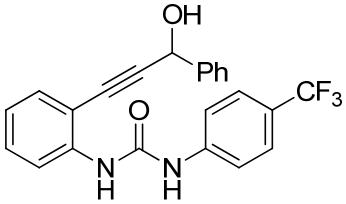
3299, 3063, 2938, 2838, 1643, 1605, 1578, 1547, 1508, 1475, 1450, 1411, 1301, 1244, 1180, 1168, 1108, 1079, 1023, 960, 911, 828, 793, 756, 695, 636, 610 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{20}N_2O_3Na$ $[M+Na]^+$: 395.1366, found 395.1370.

1-(4-chlorophenyl)-3-(2-(3-hydroxy-3-phenylprop-1-yn-1-yl)phenyl)urea (1d).



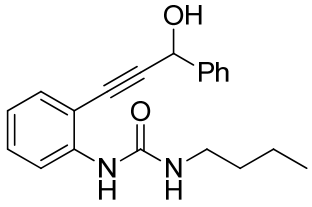
Yield: 80%, white solid, m.p. 188-189 ^oC; ^1H NMR [500 MHz, $(CD_3)CO$]: δ = 8.79 (sbr, 1 H), 8.23 (d, 1 H, *J* = 8.4 Hz). 7.98 (sbr, 1 H), 7.63 (d, 2 H, *J* = 7.3 Hz), 7.55 (d, 2 H, *J* = 8.8 Hz), 7.43-7.28 (m, 7 H), 7.02 (t, 1 H, *J* = 7.6 Hz), 5.74 (d, 1 H, *J* = 5.9 Hz), 5.20 (d, 1 H, *J* = 5.9 Hz); ^{13}C NMR [125 MHz, $(CD_3)CO$]: δ = 152.9, 142.7, 141.5, 139.7, 133.0, 130.3, 129.6, 129.3, 128.8, 127.7, 123.1, 121.0, 120.4, 112.5, 97.9, 81.7, 65.1 ppm; IR (ATR): $\tilde{\nu}$ = 3325, 3059, 2926, 2850, 1946, 1810, 1683, 1631, 1598, 1577, 1549, 1497, 1446, 1395, 1303, 1250, 1216, 1175, 1114, 1085, 1048, 1029, 1002, 986, 947, 917, 894, 824, 776, 748, 723, 692, 642, 607 cm^{-1}; HRMS (ESI): calculated for $C_{22}H_{17}ClN_2O_2Na$ $[M+Na]^+$: 399.0871, found 399.0872.

1-(2-(3-hydroxy-3-phenylprop-1-yn-1-yl)phenyl)-3-(4-(trifluoromethyl)phenyl)urea (1e).



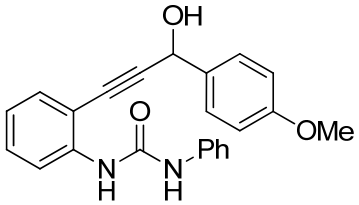
Yield: 70%, white solid, m.p. 189-190 ^oC; ^1H NMR [300 MHz, $(CD_3)CO$]: δ = 9.12 (sbr, 1 H), 8.24 (d, 1 H, *J* = 8.3 Hz), 8.10 (sbr, 1 H), 7.75 (d, 2 H, *J* = 8.5 Hz), 7.65-7.60 (m, 4 H), 7.44-7.28 (m, 5 H), 7.03 (t, 1 H, *J* = 7.5 Hz), 5.77 (d, 1 H, *J* = 5.0 Hz), 5.30 (d, 1 H, *J* = 5.0 Hz). ^{13}C NMR [75 MHz, $(CD_3)CO$]: δ = 253.3, 144.8, 143.0, 141.7, 133.3, 130.7, 129.7, 129.2, 128.0, 127.3 (q, J_{F-C} = 3.9 Hz), 123.7, 121.0, 119.5, 113.2, 98.2, 82.1, 65.5 ppm; ^{19}F NMR [282 MHz, $(CD_3)CO$]: -62.2 ppm; IR (ATR): $\tilde{\nu}$ = 3292, 3062, 1914, 1649, 1602, 1577, 1542, 1492, 1477, 1449, 1410, 1328, 1300, 1251, 1224, 1183, 1155, 1108, 1070, 1047, 1025, 1017, 968, 905, 867, 845, 798, 747, 711, 694, 639 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{16}F_3N_2O_2$ $[M-H]^-$: 409.1169, found 409.1182.

1-butyl-3-(2-(3-hydroxy-3-phenylprop-1-yn-1-yl)phenyl)urea (1f).



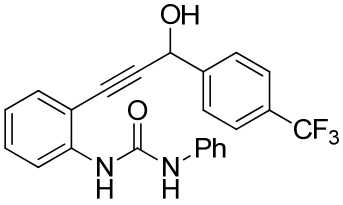
Yield: 83%, yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.96 (d, 1 H, *J* = 8.3 Hz), 7.55 (d, 2 H, *J* = 7.5 Hz), 7.38-7.19 (m, 6 H), 6.91 (t, 1 H, *J* = 7.6 Hz), 5.68 (s, 1 H), 5.34 (s, 1 H), 4.74 (s, 1 H), 3.05-2.99 (m, 2 H), 1.33-1.16 (m, 4 H), 0.82 (t, 3 H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 156.3, 141.4, 141.1, 132.2, 130.3, 129.2, 128.9, 127.2, 122.7, 120.0, 112.2, 96.5, 82.7, 65.3, 40.6, 32.6, 20.6, 14.1 ppm; IR (ATR): $\tilde{\nu}$ = 3330, 2958, 2931, 2871, 2220, 1652, 1606, 1549, 1493, 1447, 1379, 1302, 1249, 1219, 1159, 1097, 1043, 1016, 964, 917, 821, 755, 698, 641, 614 cm^{-1}; HRMS (ESI): calculated for $C_{20}H_{22}N_2O_2Na$ $[M+Na]^+$: 345.1574, found 345.1579.

1-(2-(3-hydroxy-3-(4-methoxyphenyl)prop-1-yn-1-yl)phenyl)-3-phenylurea (1g).



Yield: 83%, yellow solid, m.p. 134-135 ^{o}C; ^{1}H NMR [300 MHz, $(CD_3)CO$]: δ = 8.69 (sbr, 1 H), 8.26 (d, 1 H, *J* = 8.4 Hz), 7.96 (sbr, 1 H), 7.56-7.51 (m, 4 H), 7.41-7.25 (m, 4 H), 7.02-6.91 (m, 4 H), 5.69 (d, 1 H, *J* = 5.7 Hz), 5.13 (d, 1 H, *J* = 5.7 Hz), 3.78 (s, 3 H); ^{13}C NMR [125 MHz, $(CD_3)CO$]: δ = 160.9, 153.5, 142.1, 141.1, 135.2, 133.2, 130.6, 130.1, 129.4, 123.7, 123.2, 120.7, 120.1, 115.0, 112.9, 98.4, 82.0, 65.1, 56.0 ppm; IR (ATR): $\tilde{\nu}$ = 3566, 3295, 3063, 2958, 2932, 2830, 2223, 1946, 1868, 1771, 1649, 1601, 1579, 1544, 1509, 1478, 1464, 1446, 1379, 1301, 1245, 1174, 1109, 1079, 1030, 1015, 986, 965, 898, 871, 826, 803, 752, 716, 692, 681, 646, 608 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{19}N_2O_3$ $[M-H]^-$: 371.1401, found 371.1411.

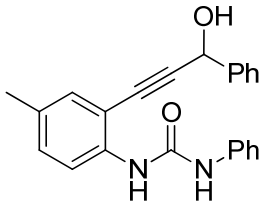
1-(2-(3-hydroxy-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)phenyl)-3-phenylurea (1h).



Yield: 73%, white solid, m.p. 200-201 ^{o}C; ^{1}H NMR [300 MHz, $(CD_3)CO$]: δ = 8.64 (sbr, 1 H), 8.24 (d, 1 H, *J* = 8.4 Hz), 7.97 (sbr, 1 H), 7.87 (d, 2 H, *J* = 8.2 Hz), 7.73 (d, 2 H, *J* = 8.2 Hz), 7.52 (d, 2 H, *J* = 8.2 Hz),7.42-7.25 (m, 4 H), 7.00 (t, 2 H, *J* = 7.5 Hz), 5.88 (d, 1 H, *J* = 5.9 Hz), 5.52 (d,

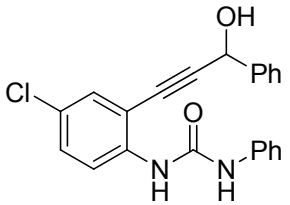
1 H, *J* = 5.9 Hz). ^{13}C NMR [75 MHz, $(CD_3)CO$]: δ = 153.5, 147.5, 142.1, 141.0, 133.4, 130.8, 130.1, 128.6, 126.6 (q, JF-C= 3.9 Hz), 123.7, 123.3, 120.9, 120.1, 112.6, 97.2, 82.7, 64.8 ppm; ^{19}F NMR [282 MHz, $(CD_3)CO$]: -62.9 ppm; IR (ATR): $\tilde{\nu}$= 3302, 1641, 1619, 1598, 1579, 1551, 1496, 1479, 1447, 1414, 1391, 1325, 1304, 1248, 1223, 1164, 1111, 1068, 1051, 1016, 975, 914, 897, 849, 826, 796, 751, 718, 692, 646, 633 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{16}F_3N_2O_2$ $[M-H]^-$: 409.1169, found 409.1182.

1-(2-(3-hydroxy-3-phenylprop-1-yn-1-yl)-4-methylphenyl)-3-phenylurea (1i).



Yield: 76%, white solid, m.p. 178-179 ^{o}C; ^{1}H NMR [300 MHz, $(CD_3)CO$]: δ = 8.64 (sbr, 1 H), 8.12 (d, 1 H, *J* = 8.5 Hz), 7.89 (sbr, 1 H), 7.63 (d, 2 H, *J* = 7.6 Hz), 7.52 (d, 2 H, *J* = 8.3 Hz), 7.41-7.15 (m, 7 H), 6.99 (t, 1 H, *J* = 7.4 Hz), 5.73 (d, 1 H, *J* = 5.9 Hz), 5.23 (d, 1 H, *J* = 5.9 Hz), 2.26 (s, 3 H); ^{13}C NMR [125 MHz, $(CD_3)CO$]: δ = 153.2, 142.7, 140.9, 139.3, 133.0, 132.3, 131.0, 129.7, 129.3, 128.8, 127.7, 123.2, 120.5, 119.6, 112.4, 97.3, 82.0, 65.1, 20.5 ppm; IR (ATR): $\tilde{\nu}$= 3289, 3026, 1637, 1586, 1554, 1497, 1443, 1294, 1254, 1220, 1186, 1131, 1078, 1042, 1028, 1005, 897, 809, 778, 738, 714, 692, 640, 614 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{19}N_2O_2$ $[M-H]^-$: 355.1452, found 355.1462.

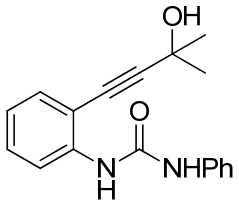
1-(4-chloro-2-(3-hydroxy-3-phenylprop-1-yn-1-yl)phenyl)-3-phenylurea (1j).



Yield: 77%, white solid, m.p. 203-204 ^{o}C; ^{1}H NMR [500 MHz, $(CD_3)CO$]: δ = 8.70 (sbr, 1 H), 8.28 (d, 1 H, *J* = 9.0 Hz), 8.03 (sbr, 1 H), 7.63 (d, 2 H, *J* = 7.5 Hz), 7.52 (d, 2 H, *J* = 7.8 Hz), 7.42-7.27 (m, 7 H); 7.02 (t, 1 H, *J* = 7.4 Hz), 5.74 (d, 1 H, *J* = 5.4 Hz), 5.27 (d, 1 H, *J* = 5.4 Hz); ^{13}C NMR [125 MHz, $(CD_3)CO$]: δ = 152.9, 142.4, 140.6, 140.5, 132.1, 130.2, 129.8, 129.4, 128.9, 127.7, 127.0, 123.5, 121.7, 119.7, 114.0, 99.0, 80.4, 65.0 ppm; IR (ATR): $\tilde{\nu}$= 3291, 3060, 3028, 1942, 1894, 1636, 1598, 1576, 1544, 1493, 1476, 1445, 1400, 1291, 1247, 1207, 1184, 1158, 1124, 1088, 1037, 1024, 980, 913, 897, 879, 836, 803, 773, 752, 730, 707, 691, 638 cm^{-1}; HRMS (ESI):

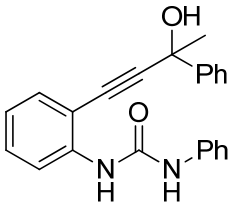
calculated for $C_{22}H_{17}ClN_2O_2Na$ $[M+Na]^+$: 399.0871, found 399.0874.

1-(2-(3-hydroxy-3-methylbut-1-yn-1-yl)phenyl)-3-phenylurea (1k).



Yield: 95%, white solid, m.p. 126-127 ^oC; ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.97 (d, 1 H, J = 8.2 Hz), 7.69 (sbr, 1 H), 7.52 (sbr, 1 H), 7.37-7.34 (m, 2 H), 7.30-7.19 (m, 4 H), 7.04 (t, 1 H, J = 7.3 Hz), 6.94 (td, 1 H, J_1 = 7.6 Hz, J_2 = 1.0 Hz), 3.86 (sbr, 1 H), 1.55 (s, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 153.9, 140.0, 138.8, 132.3, 129.8, 129.6, 124.4, 123.5, 121.4, 121.0, 113.4, 100.9, 78.5, 66.5, 31.7 ppm; IR (ATR): $\tilde{\nu}$= 3323, 2985, 2934, 1664, 1601, 1582, 1525, 1499, 1444, 1363, 1302, 1254, 1220, 1157, 1112, 1045, 963, 907, 823, 749, 692, 634 cm^{-1}; HRMS (ESI): calculated for $C_{18}H_{18}N_2O_2Na$ $[M+Na]^+$: 317.1261, found 317.1265.

1-(2-(3-hydroxy-3-phenylbut-1-yn-1-yl)phenyl)-3-phenylurea (1l).

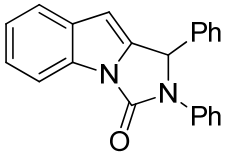


Yield: 70%, yellow solid, m.p. 175-176 ^oC; ^1H NMR (500 MHz, CD_3OD): δ = 8.01 (d, 1 H, J = 8.3 Hz), 7.73-7.71 (m, 2 H), 7.46-7.42 (m, 3 H), 7.37-7.25 (m, 6 H), 7.06-7.01 (m, 2 H), 1.86 (s, 3 H); ^{13}C NMR (125 MHz, CD_3OD): δ = 155.1, 147.2, 141.3, 140.5, 133.3, 130.5, 130.1, 129.5, 128.8, 126.3, 124.2, 124.0, 121.7, 120.6, 114.2, 100.4, 81.2, 71.3, 34.0 ppm; IR (KBr): $\tilde{\nu}$= 3325, 1655, 1599, 1580, 1525, 1498, 1445, 1366, 1302, 1253, 1221, 1159, 1141, 1088, 1048, 1028, 940, 893, 749, 693, 606 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{20}N_2O_2Na$ $[M+Na]^+$: 379.1417, found 379.1420.

General Procedure for Gold(I)-catalyzed Cascade Reactions.

Urea**1** (0.4 mmol) was added to a suspension of IPrAuCl (0.02 mmol, 12.4 mg) and $AgNTf_2$ (0.02 mmol, 7.8 mg) in a mixed solvent (2.2 ml, Toluene/CH_3CN = 10:1), the resulting suspension was stirred at 110 ^oC for 12 h. After that the solution was removed by evaporation and the residue was purified by column chromatography on silica gel (petrol ether/EtOAc = 10:1) to afford the desired product.

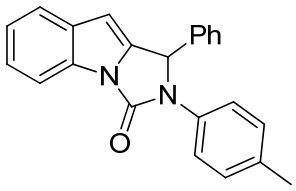
1,2-diphenyl-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4a).



Yield: 71%, white solid, m.p. 167-168 ^{o}C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.09 (d, 1 H, *J* = 7.9 Hz), 7.60-7.53 (m, 3 H), 7.39-7.24 (m, 9 H), 7.17-7.12 (m, 1 H), 6.28 (s, 1 H), 6.27 (s, 1 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 150.8, 139.1, 137.9, 137.8, 134.0, 131.1, 129.7, 129.5, 129.3, 127.6, 125.6, 124.0, 123.5, 123.0, 121.8, 113.2, 98.4, 61.4 ppm; IR (ATR): $\tilde{\nu}$= 3060, 2924, 2850, 1725, 1599, 1501, 1491, 1479, 1450, 1405, 1371, 1334, 1306, 1289, 1252, 1231, 1172, 1158, 1144, 1126, 1108, 1075, 1057, 1028, 981, 937, 911, 893, 856, 845, 832, 791, 781, 767, 747, 707, 692, 658, 641, 616 cm^{-1}; HRMS (ESI): calculated for $C_{22}H_{16}N_2ONa$ $[M+Na]^+$: 347.1155, found 347.1159.

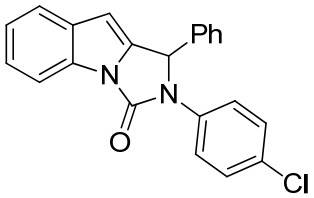
4a (2% ee), Enantiomeric excess was determined by HPLC with a Chiralpak IB column (85:15 hexane: 2-propanol, 1 mL/min, 280 nm); minor enantiomer tr = 7.6 min, major enantiomer tr = 8.0 min; (2% ee).

1-phenyl-2-(*p*-tolyl)-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4b).



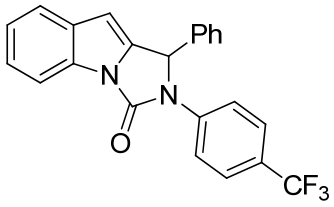
Yield: 53%, yellow solid, m.p. 183-184 ^{o}C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.09 (d, 1 H, *J* = 8.1 Hz), 7.58 (d, 1 H, *J* = 7.8 Hz), 7.41-7.24 (m, 9 H), 7.15 (d, 2 H, *J* = 8.3 Hz), 6.27 (s, 1 H), 6.21 (s, 1 H), 2.30 (s, 3 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 150.9, 139.3, 137.9, 135.7, 135.0, 133.9, 131.1, 130.1, 129.7, 129.3, 127.7, 123.9, 123.4, 122.9, 121.7, 113.1, 98.4, 61.6, 21.1 ppm; IR (ATR): $\tilde{\nu}$= 3030, 2919, 1721, 1613, 1591, 1516, 1493, 1479, 1452, 1406, 1368, 1335, 1316, 1288, 1248, 1231, 1172, 1157, 1142, 1127, 1106, 1077, 1058, 1032, 1015, 982, 965, 927, 911, 850, 832, 796, 783, 763, 738, 711, 694, 674, 653, 638, 615 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{18}N_2ONa$ $[M+Na]^+$: 361.1311, found 361.1316.

2-(4-chlorophenyl)-1-phenyl-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4d).



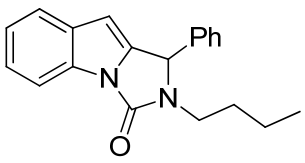
Yield: 70%, white solid, m.p. 164-165 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.08 (d, 1 H, *J* = 8.0 Hz), 7.59-7.50 (m, 3 H), 7.38-7.25 (m, 9 H), 6.28 (s, 1 H), 6.21 (s, 1 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 150.6, 138.8, 137.5, 136.6, 134.0, 131.1, 130.6, 129.8, 129.6, 129.5, 127.5, 124.1, 123.6, 123.5, 121.8, 113.2, 98.7, 61.4 ppm; IR (ATR): $\tilde{\nu}$ = 3566, 3067, 3027, 2925, 1944, 1868, 1724, 1599, 1541, 1495, 1478, 1449, 1417, 1401, 1368, 1335, 1285, 1257, 1228, 1201, 1177, 1156, 1143, 1127, 1115, 1096, 1078, 1058, 1029, 1012, 982, 934, 909, 847, 818, 792, 781, 770, 738, 720, 707, 693, 669, 648, 628, 616 cm^{-1}; HRMS (ESI): calculated for $C_{22}H_{16}ClN_2O$ $[M+H]^+$: 359.0946, found 359.0948.

1-phenyl-2-(4-(trifluoromethyl)phenyl)-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4e).



Yield: 75%, white solid, m.p. 165-166 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.09 (d, 1 H, *J* = 8.0 Hz), 7.78 (d, 2 H, *J* = 8.5 Hz), 7.61-7.56 (m, 3 H), 7.39-7.25 (m, 7 H), 6.29 (s, 2 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 150.5, 141.3, 138.5, 137.3, 134.0, 131.1, 129.9, 129.5, 127.1, 127.0 (q, J_{F-C} = 261 Hz), 126.7 (q, J_{F-C} = 3.9 Hz), 124.2, 123.8, 121.9, 120.9, 113.2, 98.8, 61.0 ppm; ^{19}F NMR (282 MHz, CD_2Cl_2): δ = -62.5 ppm; IR (ATR): $\tilde{\nu}$ = 2927, 1738, 1615, 1522, 1480, 1452, 1426, 1405, 1366, 1320, 1302, 1257, 1167, 1113, 1071, 1056, 1013, 982, 839, 795, 779, 744, 707, 694, 662, 649, 633 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{15}F_3N_2ONa$ $[M+Na]^+$: 415.1029, found 415.1031.

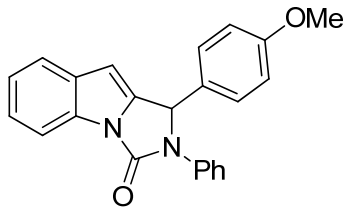
2-butyl-1-phenyl-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4f).



Yield: 41%, yellow solid, m.p. 74-75 °C; ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.00 (d, 1 H, *J* = 8.1 Hz), 7.55 (d, 1 H, *J* = 7.8 Hz), 7.41-7.38 (m, 3 H), 7.32-7.27 (m, 3 H), 7.23-7.19 (m, 1 H), 6.21 (s,

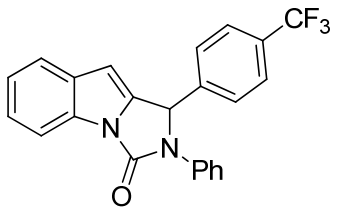
1 H), 5.61 (s, 1 H); 3.72-3.65 (m, 1 H), 2.95-2.89 (m, 1 H), 1.55-1.48 (m, 2 H), 1.37-1.27 (m, 2 H), 0.90 (t, 3 H, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 152.3, 140.5, 137.6, 133.7, 131.0, 129.7, 129.5, 128.3, 123.6, 122.8, 121.6, 112.8, 97.9, 60.2, 41.4, 30.4, 20.4, 14.0 ppm; IR (ATR): $\tilde{\nu}$ = 3431, 3086, 3061, 3032, 2959, 2929, 2872, 2316, 1955, 1868, 1810, 1734, 1613, 1584, 1520, 1493, 1478, 1453, 1412, 1391, 1351, 1312, 1267, 1216, 1184, 1156, 1114, 1101, 1085, 1071, 1027, 1002, 970, 933, 912, 859, 831, 794, 779, 746, 707, 695, 670, 655, 638, 617 cm^{-1}; HRMS (ESI): calculated for $C_{20}H_{20}N_2ONa$ $[M+Na]^+$: 327.1468, found 327.1469.

1-(4-methoxyphenyl)-2-phenyl-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4g).



Yield: 40%, yellow solid, m.p. 155-156 °C; ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.07 (d, 1 H, *J* = 8.1 Hz), 7.58 (d, 1 H, *J* = 7.9 Hz), 7.52-7.50 (m, 2 H), 7.36-7.33 (m, 3 H), 7.28-7.22 (m, 3 H), 7.15 (t, 1 H, *J* = 7.4 Hz), 6.85-6.82 (m, 2 H), 6.27 (s, 1 H), 6.21 (s, 1 H), 3.74 (s, 3 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 160.5, 150.7, 139.5, 137.7, 134.0, 131.1, 129.49, 129.48, 129.0, 125.6, 123.9, 123.4, 123.0, 121.7, 115.0, 113.1, 98.3, 61.1, 55.8 ppm; IR (ATR): $\tilde{\nu}$ = 3061, 2931, 2836, 1732, 1611, 1599, 1586, 1511, 1478, 1451, 1422, 1403, 1365, 1329, 1304, 1248, 1171, 1144, 1107, 1030, 981, 934, 897, 840, 800, 782, 741, 697, 652, 636, 623 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{18}N_2O_2Na$ $[M+Na]^+$: 377.1261, found 377.1266.

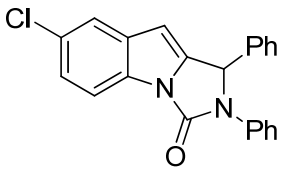
2-phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4h).



Yield: 36%, white solid, m.p. 145-146 °C; ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.07 (d, 1 H, *J* = 8.0 Hz), 7.61-7.57 (m, 3 H), 7.53-7.49 (m, 4 H), 7.37-7.33 (m, 3 H), 7.29-7.25 (m, 1 H), 7.16 (t, 1 H, *J* = 7.4 Hz), 6.35 (s, 1 H), 6.31 (s, 1 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 150.6, 142.0, 138.0, 137.5, 133.8, 131.1, 129.7, 128.0, 126.7 (q, JF-C = 3.9 Hz), 125.8, 124.2, 123.6, 122.4, 121.9, 113.2, 98.9, 60.8 ppm; ^{19}F NMR (282 MHz, CD_2Cl_2): -63.0 ppm; IR (ATR): $\tilde{\nu}$ = 3062, 2926, 2851,

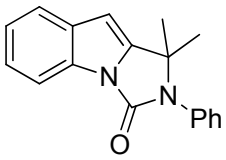
1729, 1619, 1598, 1502, 1479, 1451, 1419, 1403, 1366, 1322, 1254, 1229, 1166, 1124, 1066, 1017, 981, 935, 895, 861, 844, 797, 783, 744, 705, 688, 667, 648, 608 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{15}F_3N_2ONa$ $[M+Na]^+$: 415.1029, found 415.1033.

7-chloro-1,2-diphenyl-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4j).



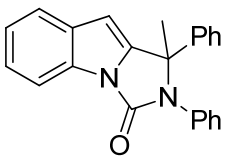
Yield: 45%, yellow solid, m.p. 169-170 °C; ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.01 (d, 1 H, *J* = 8.6 Hz), 7.56-7.51 (m, 3 H), 7.36-7.30 (m, 8 H), 7.15 (t, 1 H, *J* = 7.4 Hz), 6.26 (s, 1 H), 6.25 (s, 1 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 150.4, 140.5, 137.5, 137.3, 135.0, 129.8, 129.6, 129.5, 129.4, 128.9, 127.5, 125.8, 124.2, 122.7, 121.3, 114.1, 98.0, 61.4 ppm; IR (ATR): $\tilde{\nu}$ = 3066, 3035, 2925, 2851, 1953, 1881, 1733, 1598, 1578, 1503, 1455, 1430, 1404, 1363, 1290, 1266, 1252, 1222, 1200, 1185, 1175, 1163, 1124, 1113, 1079, 1061, 1050, 1028, 980, 942, 913, 898, 891, 870, 852, 824, 813, 796, 774, 747, 737, 718, 699, 693, 669, 646, 617 cm^{-1}; HRMS (ESI): calculated for $C_{44}H_{30}Cl_2N_4O_2Na$ $[2M+Na]^+$: 739.1638, found 739.1643.

1,1-dimethyl-2-phenyl-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4k).



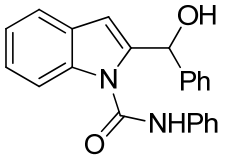
Yield: 77%, white solid, m.p. 192-193 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.98 (d, 1 H, *J* = 7.4 Hz), 7.64 (d, 1 H, *J* = 7.4 Hz), 7.55-7.47 (m, 3 H), 7.38-7.24 (m, 4 H), 6.41 (s, 1 H), 1.61 (s, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 151.3, 146.0, 135.4, 133.9, 131.1, 130.4, 130.0, 129.0, 123.6, 123.1, 121.6, 113.0, 95.8, 61.8, 27.8 ppm; IR (ATR): $\tilde{\nu}$ = 3109, 3058, 2976, 2930, 1730, 1598, 1583, 1494, 1478, 1450, 1427, 1405, 1379, 1338, 1300, 1284, 1225, 1198, 1186, 1172, 1144, 1108, 1089, 1071, 1030, 1006, 971, 931, 907, 844, 837, 807, 749, 702, 680, 654 cm^{-1}; HRMS (ESI): calculated for $C_{18}H_{16}N_2ONa$ $[M+Na]^+$: 299.1155, found 299.1159.

1-methyl-1,2-diphenyl-1*H*-imidazo[1,5-*a*]indol-3(2*H*)-one (4l).



Yield: 62%, yellow solid, m.p. 148-149 ^{o}C; ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.06 (d, 1 H, *J* = 8.1 Hz), 7.60 (d, 1 H, *J* = 7.8 Hz), 7.36-7.25 (m, 10 H), 7.03-7.01 (m, 2 H), 6.25 (s, 1 H), 2.01 (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 151.2, 145.6, 141.7, 135.9, 134.0, 131.0, 129.5, 129.3, 129.0, 128.3, 128.0, 127.1, 123.8, 123.3, 121.8, 113.1, 96.9, 66.3, 24.3 ppm; δ =IR (ATR): $\tilde{\nu}$ = 3113, 3059, 2970, 1732, 1613, 1597, 1585, 1492, 1477, 1450, 1402, 1364, 1339, 1302, 1219, 1203, 1171, 1140, 1103, 1073, 1046, 1026, 1002, 968, 950, 909, 837, 818, 794, 783, 759, 736, 709, 697, 674, 656, 640, 616 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{18}N_2ONa$ $[M+Na]^+$: 361.1311, found 361.1314.

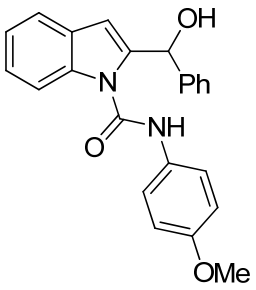
2-(hydroxy(phenyl)methyl)-*N*-phenyl-1*H*-indole-1-carboxamide (2a).



Yield: 50%, yellow solid, m.p. 165-166 ^{o}C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.34 (sbr, 1 H), 8.01 (d, 1 H, *J* = 8.3 Hz), 7.51-7.45 (m, 3 H), 7.37-7.29 (m, 8 H), 7.24-7.12 (m, 2 H), 6.27 (s, 1 H), 6.16 (d, 1 H, *J* = 2.9 Hz), 4.53 (d, 1 H, *J* = 3.7 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 150.7, 140.6, 140.5, 137.9, 137.8, 129.6, 128.8, 128.6, 128.4, 126.7, 125.13, 125.10, 123.0, 121.7, 120.6, 114.7, 110.5, 70.2 ppm; δ =IR (ATR): $\tilde{\nu}$= 3257, 3142, 3026, 2926, 1943, 1679, 1632, 1599, 1567, 1498, 1446, 1414, 1355, 1325, 1300, 1270, 1236, 1214, 1203, 1157, 1118, 1093, 1074, 1006, 950, 878, 856, 818, 796, 780, 752, 742, 717, 690, 671, 618 cm^{-1}; HRMS (ESI): calculated for $C_{22}H_{18}N_2O_2Na$ $[M+Na]^+$: 365.1261, found 365.1261.

2a (>99% ee): Enantiomeric excess was determined by HPLC with a Chiralpak IB column (90:10 hexane: 2-propanol, 1 mL/min, 250 nm); major enantiomer tr = 12.9 min, minor enantiomer tr = 16.2 min, (>99% ee).

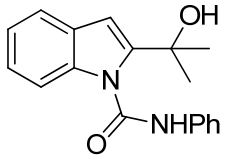
2-(hydroxy(phenyl)methyl)-*N*-(4-methoxyphenyl)-1*H*-indole-1-carboxamide (2c).



Yield: 70%, yellow solid, m.p. 139-140 ^{o}C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.15 (sbr, 1 H),

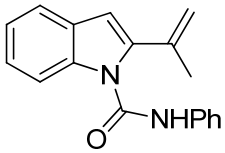
7.98 (d, 1 H, *J* = 8.3 Hz), 7.50 (d, 1 H, *J* = 7.7 Hz), 7.35-7.18 (m, 9 H), 6.85 (d, 2 H, *J* = 8.8 Hz), 6.26 (s, 1 H), 6.13 (d, 1 H, *J* = 3.8 Hz), 4.69 (sbr, 1 H), 3.78 (s, 3 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 157.4, 151.0, 140.7, 140.6, 137.7, 130.7, 128.8, 128.6, 128.3, 126.7, 125.0, 122.9, 122.7, 121.7, 114.7, 114.6, 110.2, 70.1, 56.0 ppm; IR (ATR): $\tilde{\nu}$ = 3272, 3140, 3065, 2928, 2850, 1869, 1680, 1611, 1557, 1512, 1452, 1416, 1319, 1301, 1240, 1178, 1158, 1120, 1088, 1033, 951, 920, 888, 825, 784, 752, 716, 701, 671, 636, 622 cm^{-1}; HRMS (ESI): calculated for $C_{23}H_{19}N_2O_3$ $[M-H]^-$: 371.1401, found 371.1410.

2-(2-hydroxypropan-2-yl)-*N*-phenyl-1*H*-indole-1-carboxamide (2k).

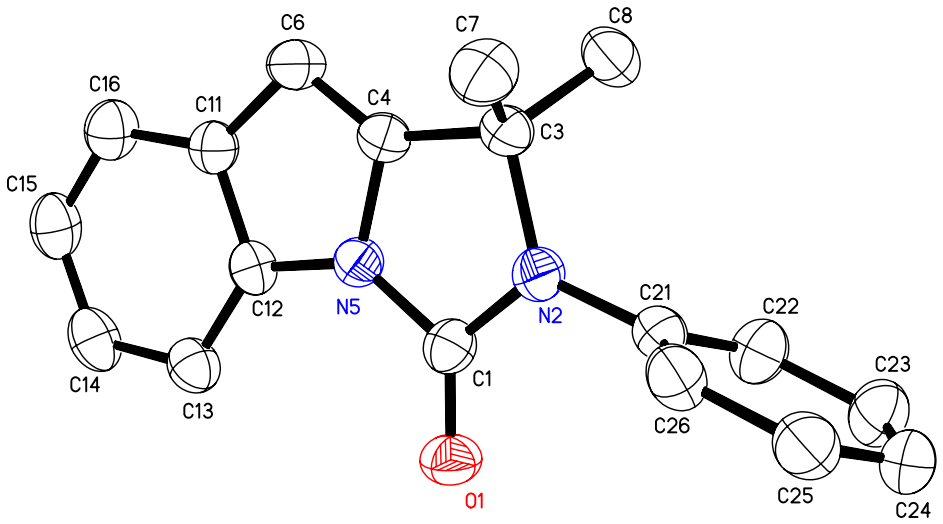


Yield: 50%, yellow solid, m.p. 156-157 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 10.01 (sbr, 1 H), 7.96 (d, 1 H, *J* = 8.3 Hz), 7.63 (d, 2 H, *J* = 8.3 Hz), 7.53 (d, 1 H, *J* = 7.8 Hz), 7.39 (t, 1 H, *J* = 7.8 Hz), 7.30-7.16 (m, 3 H), 6.57 (s, 1 H), 4.27 (s, 1 H), 1.73 (s, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 151.6, 144.2, 138.4, 138.2, 129.7, 128.2, 125.2, 124.8, 122.8, 121.5, 120.5, 114.5, 106.4, 70.0, 29.9 ppm; IR (ATR): $\tilde{\nu}$ = 3281, 2985, 1670, 1636, 1601, 1569, 1501, 1491, 1445, 1391, 1358, 1332, 1295, 1239, 1207, 1189, 1159, 1147, 1132, 1108, 1063, 1018, 958, 918, 886, 847, 811, 755, 733, 691, 680, 638 cm^{-1}; HRMS (ESI): calculated for $C_{18}H_{18}N_2O_2Na$ $[M+Na]^+$: 317.1261, found 317.1263.

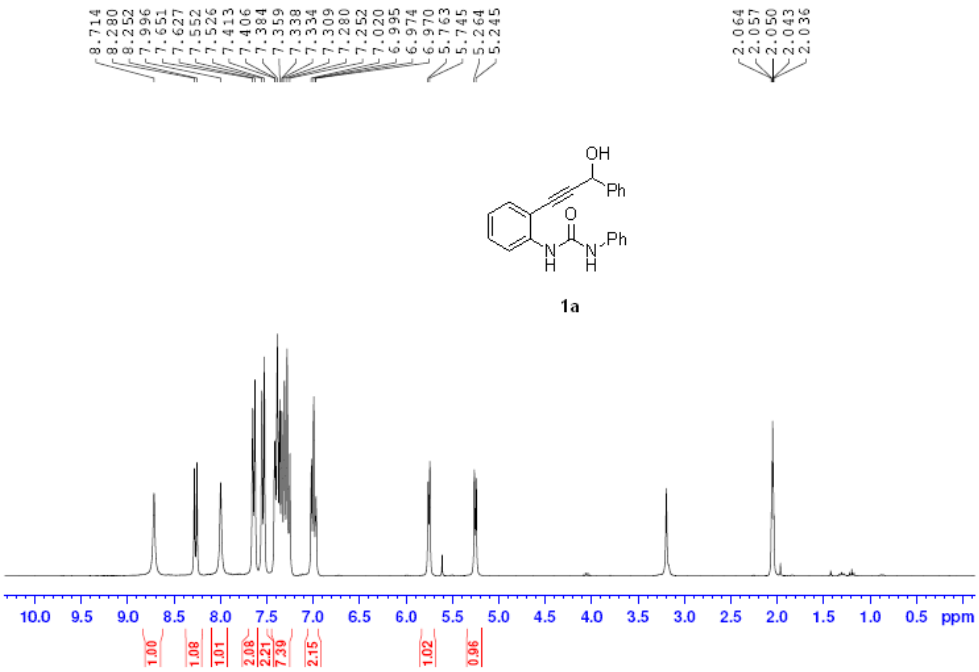
***N*-phenyl-2-(prop-1-en-2-yl)-1*H*-indole-1-carboxamide (3k).**



Yield: 35%, white solid, m.p. 85-86 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.08 (d, 1 H, *J* = 8.2 Hz), 7.62-7.51 (m, 4 H), 7.42-4.16 (m, 5 H), 6.63 (s, 1 H), 5.50 (s, 1 H), 5.43 (s, 1 H), 2.16 (s, 3 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 150.1, 140.1, 138.3, 138.2, 138.0, 129.8, 129.0, 125.3, 124.9, 123.1, 121.2, 120.2, 118.7, 114.4, 108.5, 23.0 ppm; IR (ATR): $\tilde{\nu}$ = 3254, 3050, 2977, 1786, 1682, 1602, 1541, 1499, 1442, 1380, 1365, 1322, 1294, 1272, 1245, 1215, 1200, 1177, 1151, 1113, 1068, 1028, 955, 878, 847, 806, 752, 734, 692, 673, 633 cm^{-1}; HRMS (ESI): calculated for $C_{18}H_{16}N_2ONa$ $[M+Na]^+$: 299.1155, found 299.1156.


C6
C7
C8
C16
C11
C4
C3
C15
C12
N5
N2
C21
C22
C23
C14
C13
C1
C26
O1
C25
C24

4k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8.252
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7.627
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7.526
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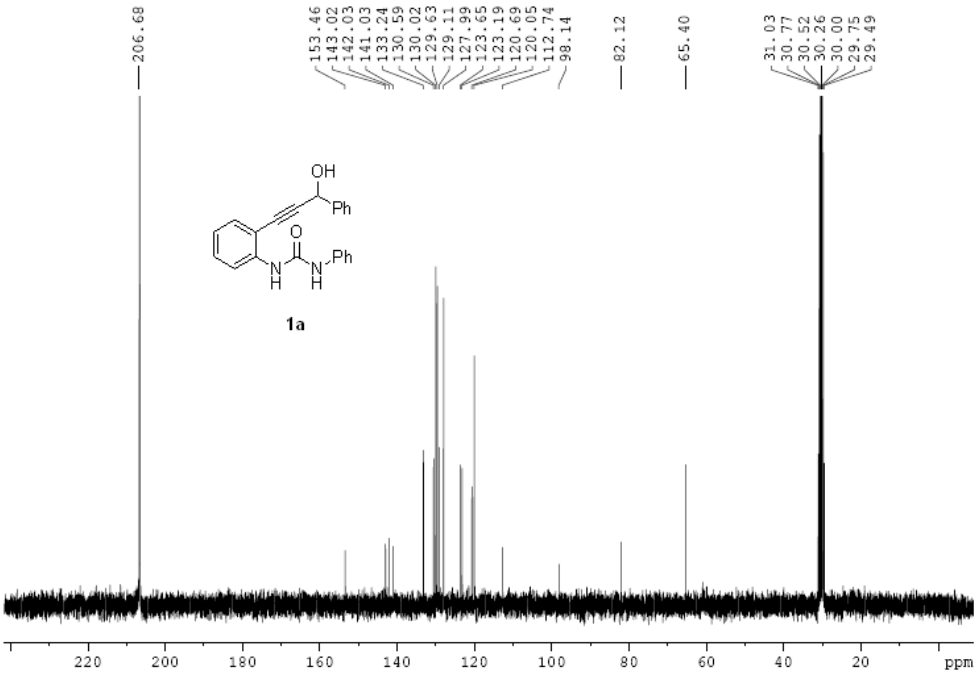
7.406
7.384
7.359
7.338
7.334
7.309
7.280
7.252
7.020
6.995
6.974
6.970
5.763
5.745
5.264
5.245
2.064
2.057
2.050
2.043
2.036
OH
Ph
O
N
H
N
Ph
1a
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.08
1.01
2.08
2.21
7.39
2.15
1.02
0.96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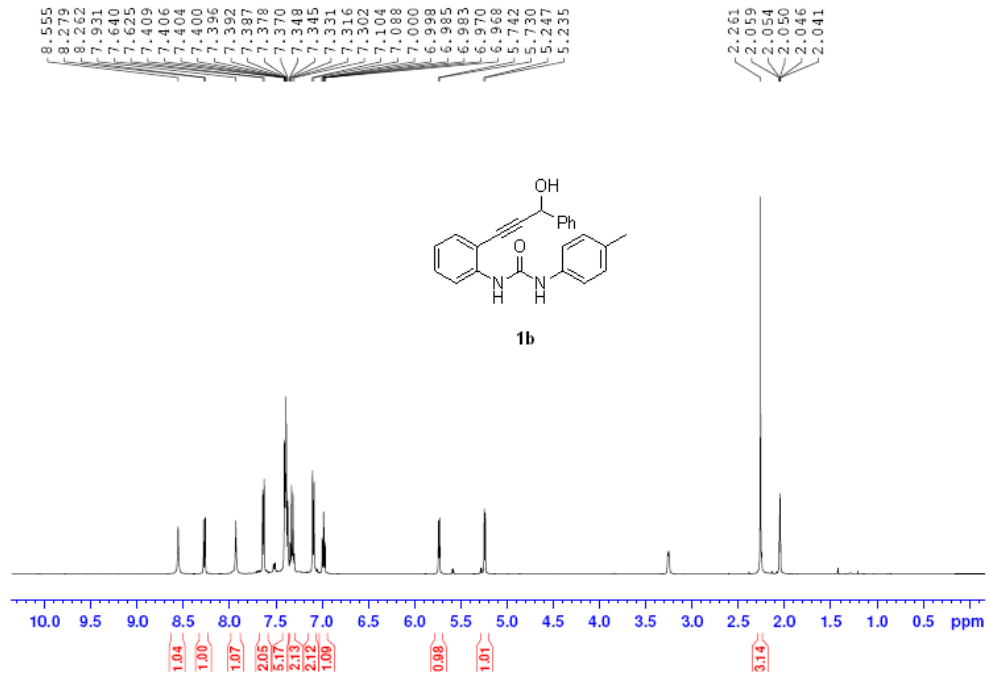
143.02
142.03
141.03
133.24
130.59
130.02
129.63
129.11
127.99
123.65
123.19
120.69
120.05
112.74
98.14
82.12
65.40
31.03
30.77
30.52
30.26
30.00
29.75
29.49
OH
Ph
O
N
H
N
Ph
1a
220 200 180 160 140 120 100 80 60 40 20 ppm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8.279
8.262
7.931
7.640
7.625
7.409
7.406
7.404
7.400
7.396
7.392
7.387
7.378
7.370
7.348
7.345
7.331
7.316
7.302
7.104
7.088
7.000
6.998
6.985
6.983
6.970
6.968
5.742
5.730
5.247
5.235
2.261
2.059
2.054
2.050
2.046
2.041
OH
Ph
O
N
H
N
H
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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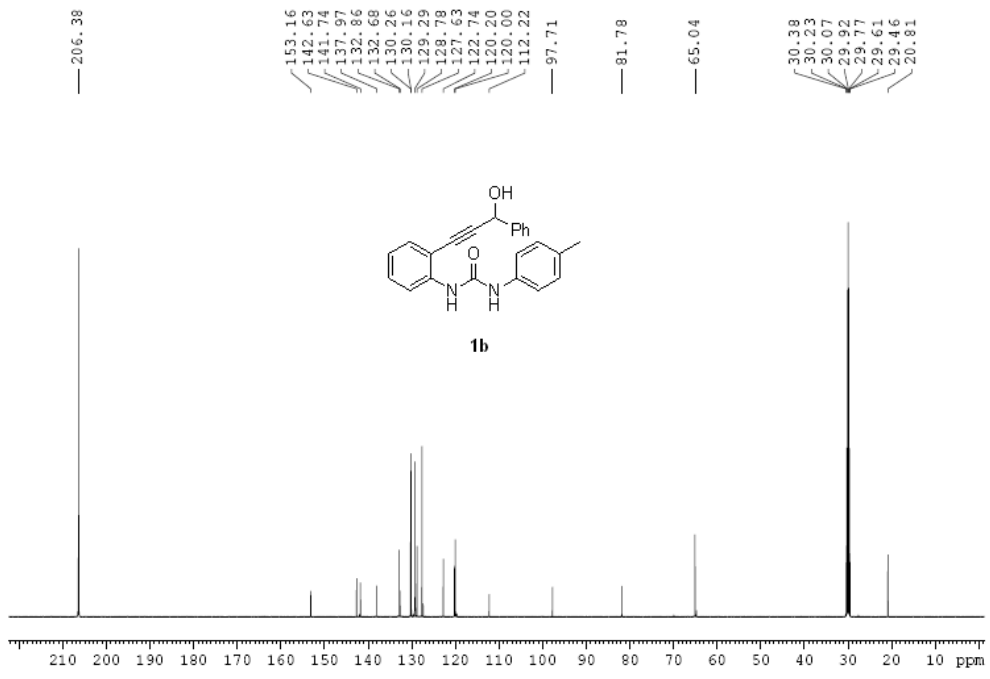
1.00
1.07
2.05
5.17
2.13
2.12
1.09
0.98
1.01
3.14

1b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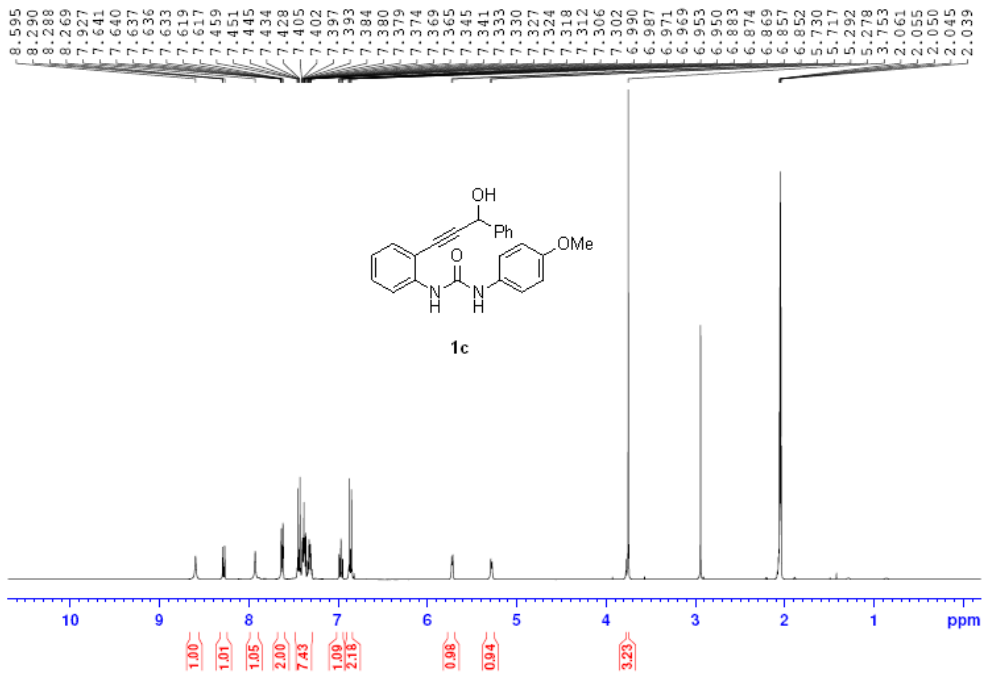
153.16
142.63
141.74
137.97
132.86
132.68
130.26
130.16
129.29
128.78
127.63
122.74
120.20
120.00
112.22
97.71
81.78
65.04
30.38
30.23
30.07
29.92
29.77
29.61
29.46
20.81
OH
Ph
O
N
H
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1b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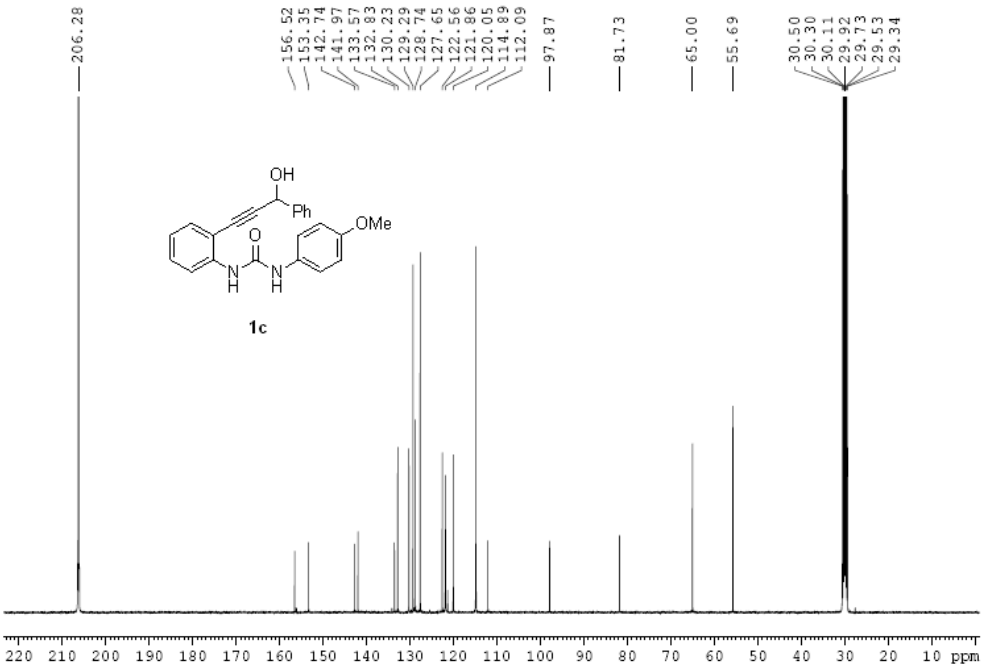
8.290
8.288
8.269
7.927
7.641
7.640
7.637
7.636
7.633
7.619
7.617
7.459
7.451
7.445
7.434
7.428
7.405
7.402
7.397
7.393
7.384
7.380
7.379
7.374
7.369
7.365
7.345
7.341
7.333
7.330
7.327
7.324
7.318
7.312
7.306
7.302
6.990
6.987
6.971
6.969
6.953
6.950
6.883
6.874
6.869
6.857
6.852
5.730
5.717
5.292
5.278
3.753
2.061
2.055
2.050
2.045
2.039
OH
Ph
OMe
O
N
H
N
H
1c
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.05
2.00
7.43
1.09
2.18
0.98
0.94
3.23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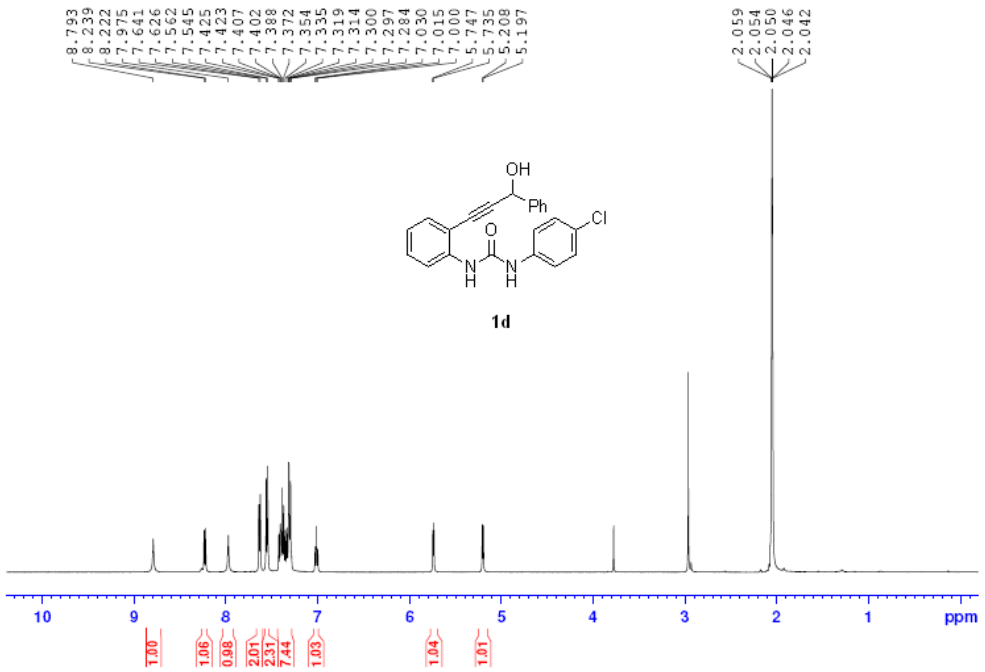
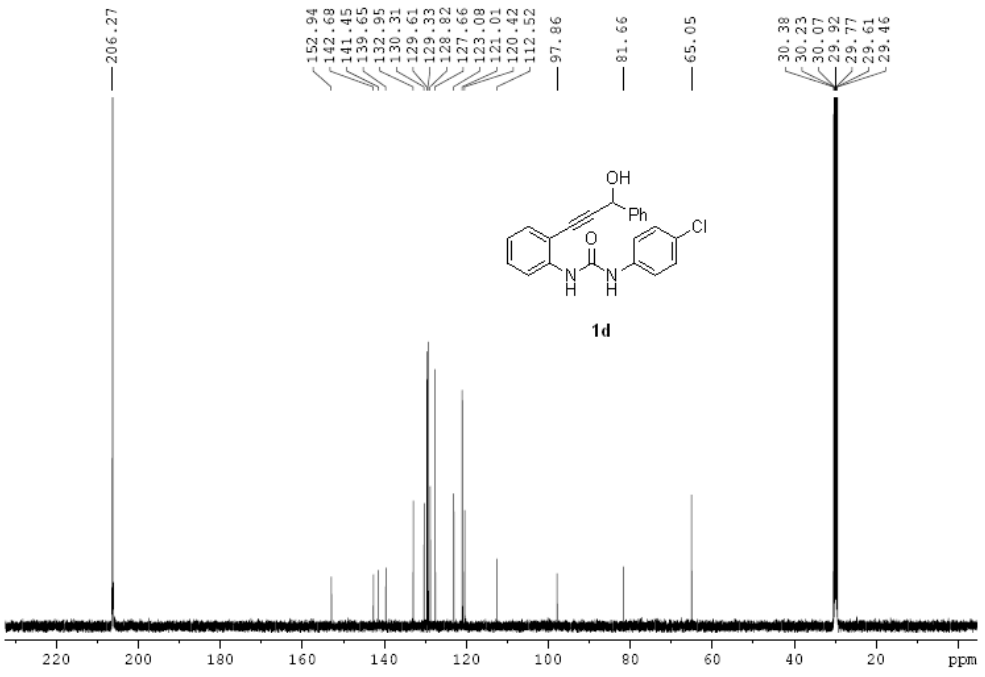
156.52
153.35
142.74
141.97
133.57
132.83
130.23
129.29
128.74
127.65
122.56
121.86
120.05
114.89
112.09
97.87
81.73
65.00
55.69
30.50
30.30
30.11
29.92
29.73
29.53
29.34
OH
Ph
OMe
O
N
H
N
H
1c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.793
8.239
8.222
7.975
7.641
7.626
7.562
7.545
7.425
7.423
7.407
7.402
7.388
7.372
7.354
7.335
7.319
7.314
7.300
7.297
7.284
7.030
7.015
7.000
5.747
5.735
5.208
5.197
2.059
2.054
2.050
2.046
2.042
OH
Ph
Cl
O
N
H
N
H
1d
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.06
0.98
2.01
2.31
7.44
1.03
1.04
1.01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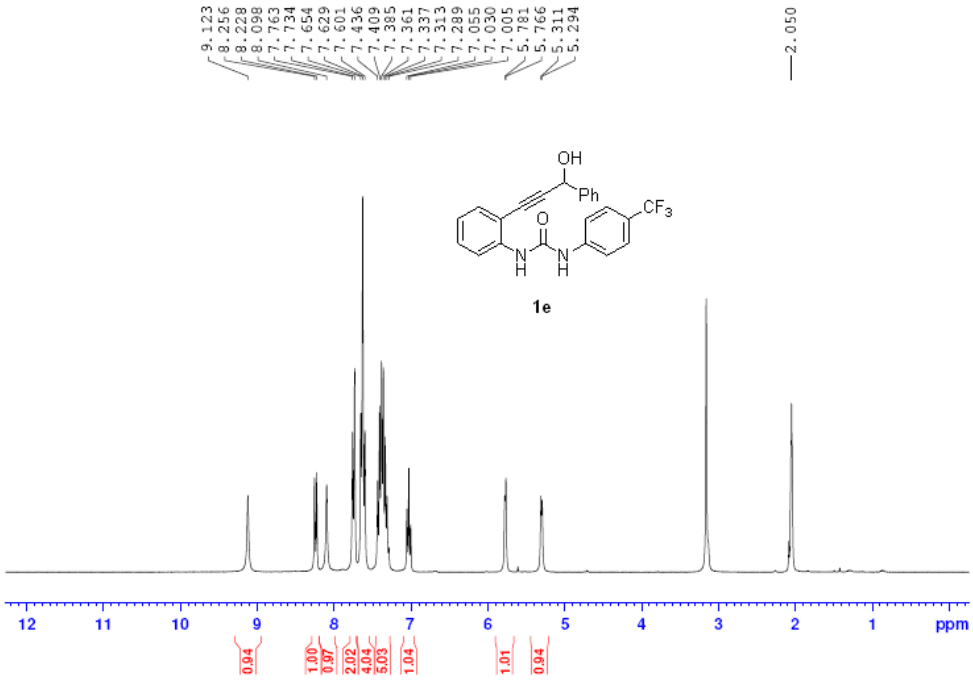
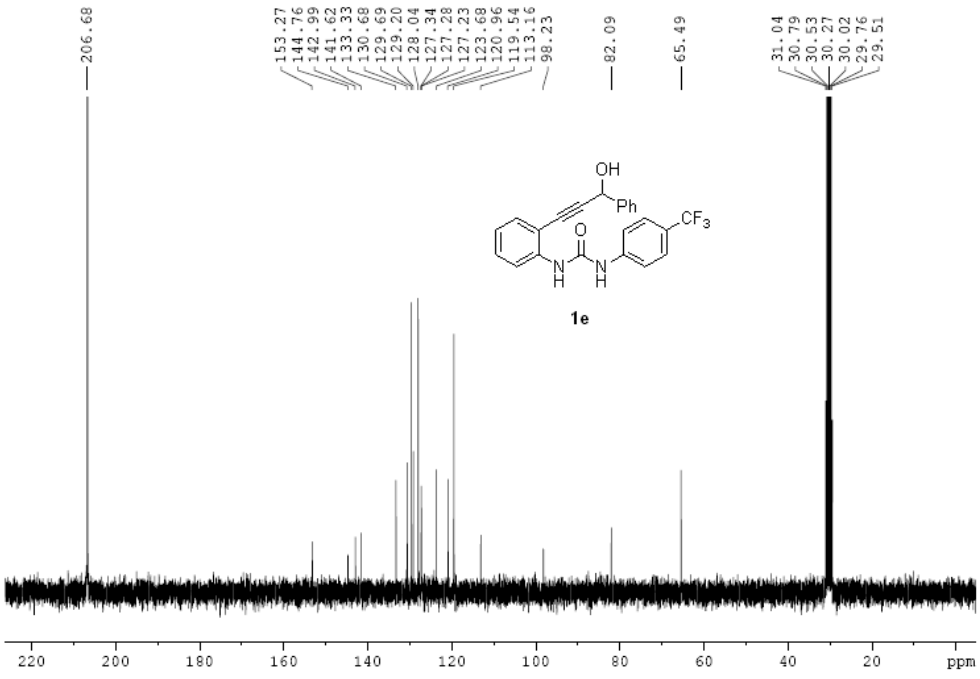
152.94
142.68
141.45
139.65
132.95
130.31
129.61
129.33
128.82
127.66
123.08
121.01
120.42
112.52
97.86
81.66
65.05
30.38
30.23
30.07
29.92
29.77
29.61
29.46
OH
Ph
Cl
O
N
H
N
H
1d
220
200
180
160
140
120
100
80
60
40
20
ppm


9.123
8.256
8.228
8.098
7.763
7.734
7.654
7.629
7.601
7.436
7.409
7.385
7.361
7.337
7.313
7.289
7.055
7.030
7.005
5.781
5.766
5.311
5.294
2.050
OH
Ph
CF3
O
N
H
N
H
1e
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.94
1.00
0.97
2.02
4.04
5.03
1.04
1.01
0.94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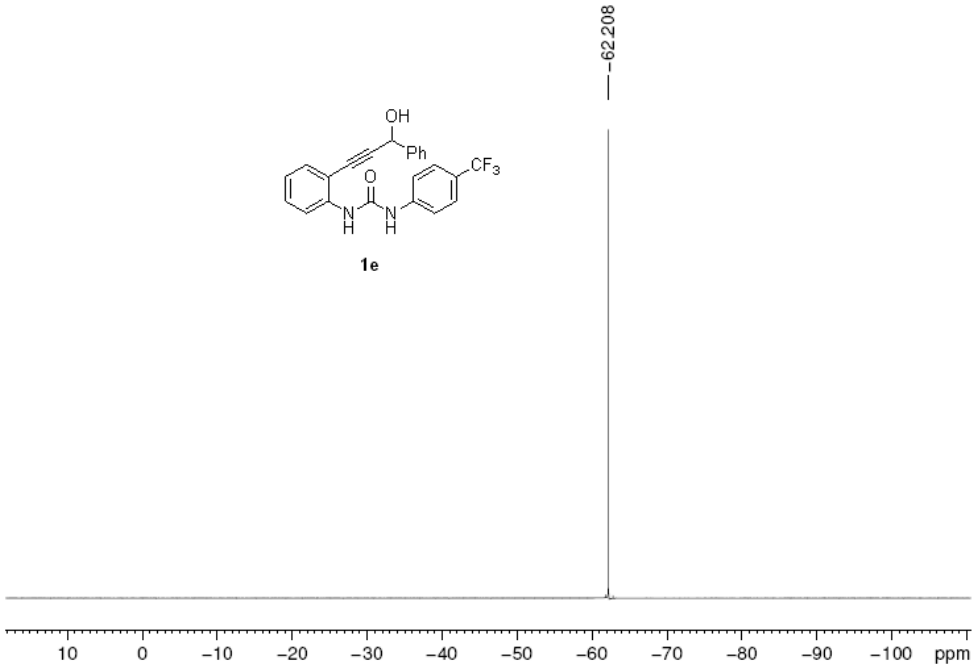
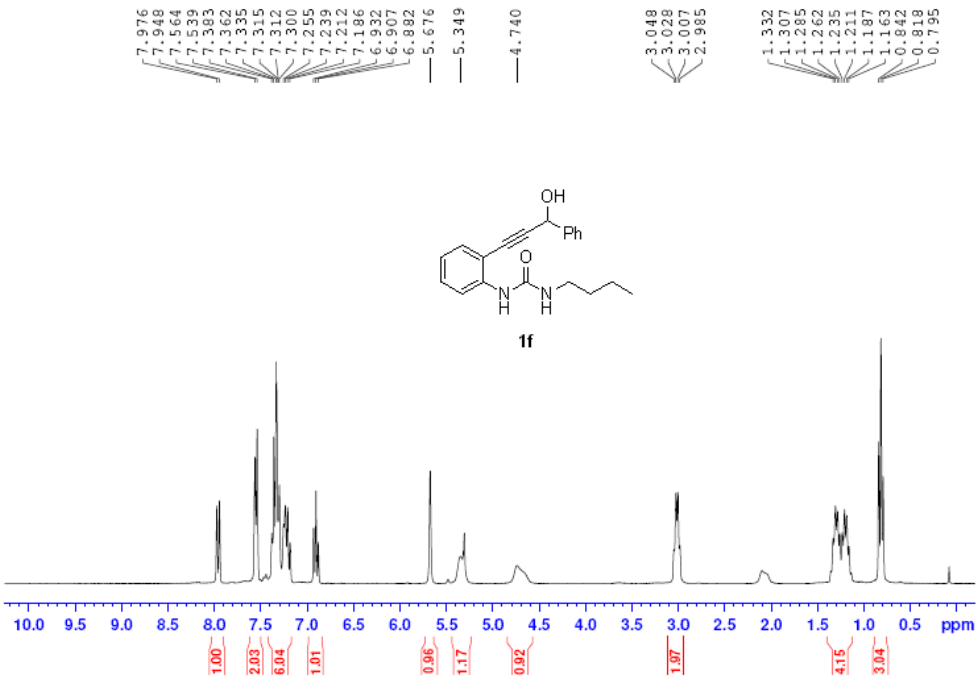
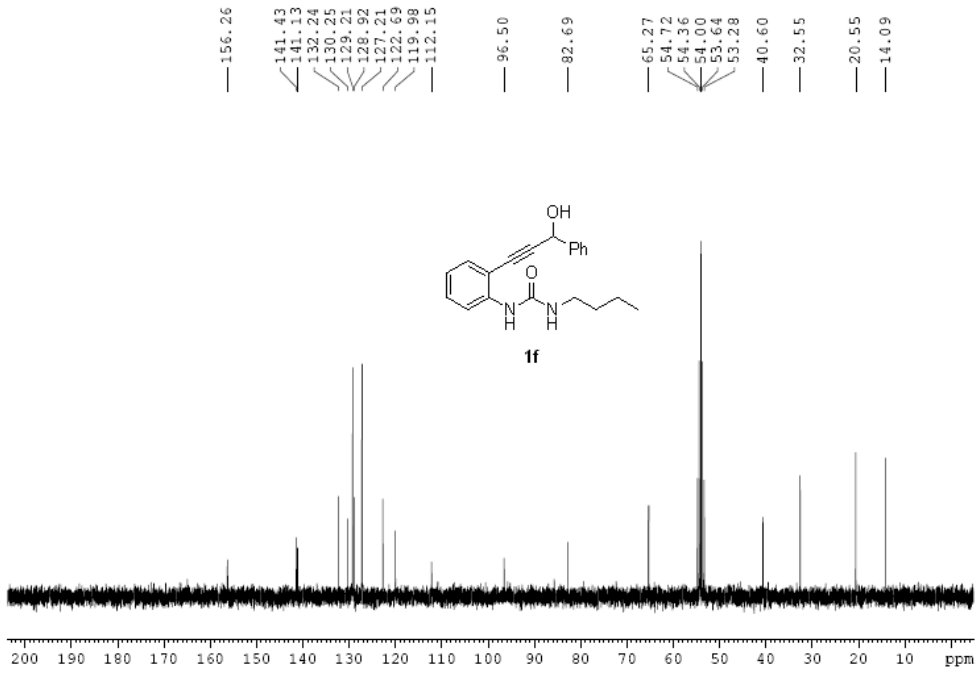
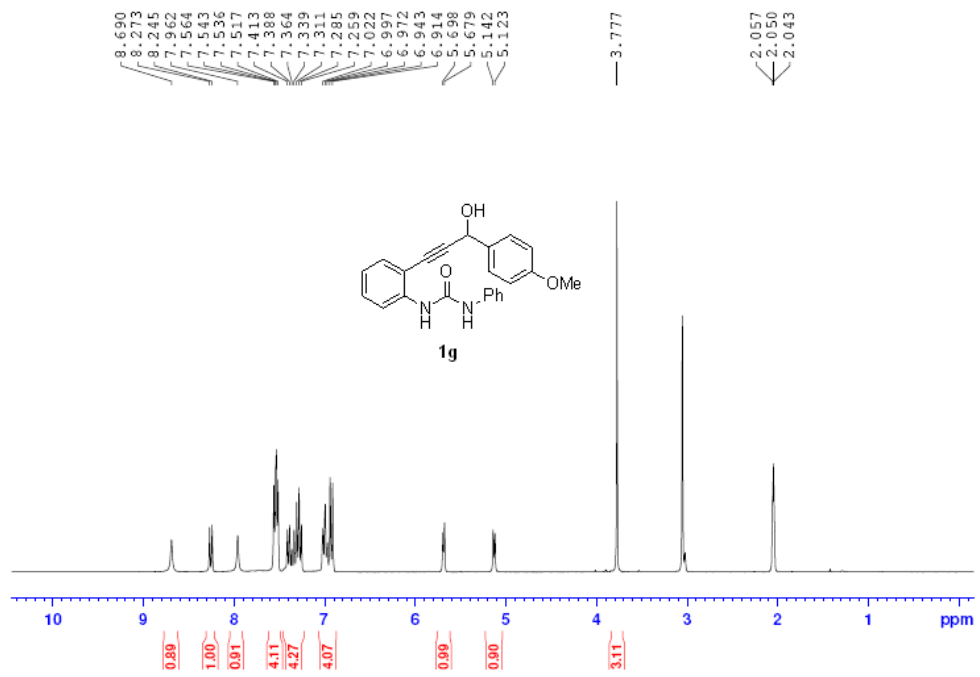
144.76
142.99
141.62
133.33
130.68
129.69
129.20
128.04
127.34
127.28
127.23
123.68
120.96
119.54
113.16
98.23
82.09
65.49
31.04
30.79
30.53
30.27
30.02
29.76
29.51
OH
Ph
CF3
O
N
H
N
H
1e
220
200
180
160
140
120
100
80
60
40
20
ppm


-62.208
OH
Ph
CF3
O
N
H
N
H
1e
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
ppm


7.976
7.948
7.564
7.539
7.383
7.362
7.335
7.315
7.312
7.300
7.255
7.239
7.212
7.186
6.932
6.907
6.882
5.676
5.349
4.740
3.048
3.028
3.007
2.985
1.332
1.307
1.285
1.262
1.235
1.211
1.187
1.163
0.842
0.818
0.795
OH
Ph
O
N
H
N
H
1f
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.03
6.04
1.01
0.96
1.17
0.92
1.97
4.15
3.04


156.26
141.43
141.13
132.24
130.25
129.21
128.92
127.21
122.69
119.98
112.15
96.50
82.69
65.27
54.72
54.36
54.00
53.64
53.28
40.60
32.55
20.55
14.09
OH
Ph
O
N
H
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1f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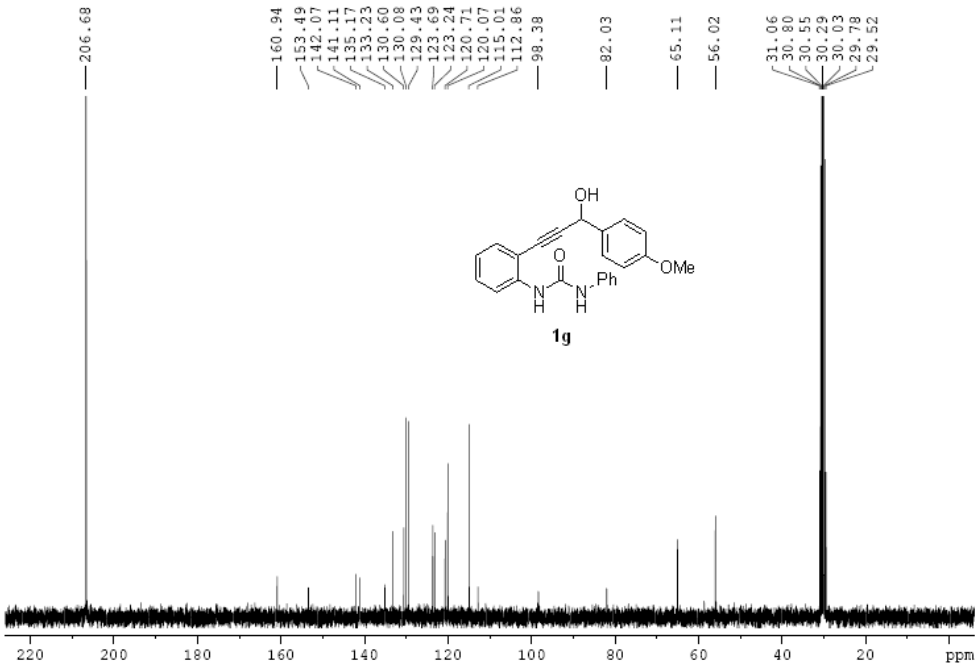
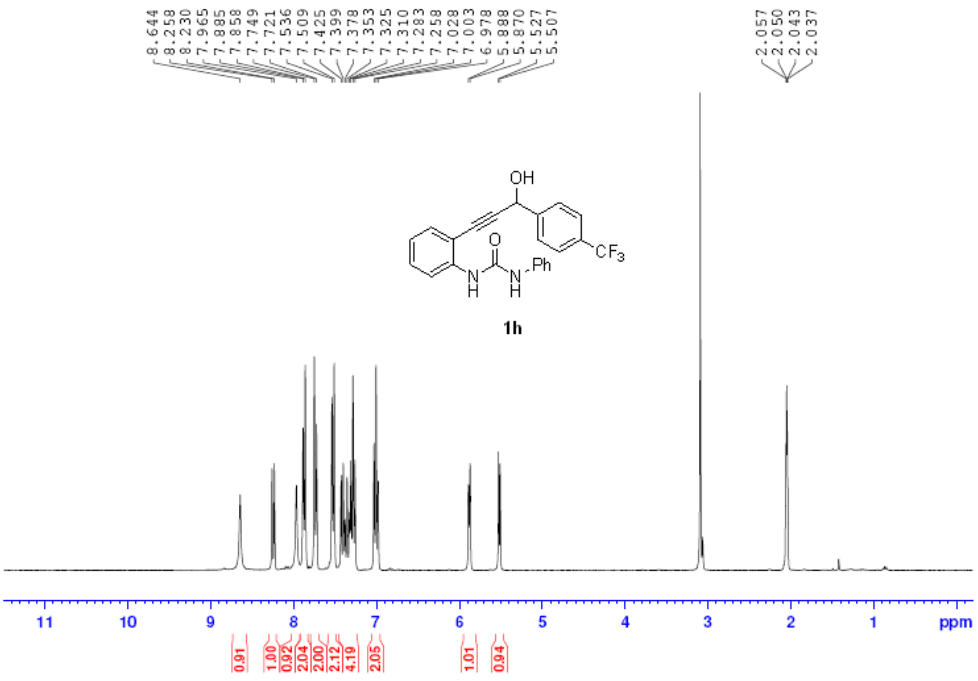
8.273
8.245
7.962
7.564
7.543
7.536
7.517
7.413
7.388
7.364
7.339
7.311
7.285
7.259
7.022
6.997
6.972
6.943
6.914
5.698
5.679
5.142
5.123
3.777
2.057
2.050
2.043
OH
O
N
H
N
H
Ph
OMe
10 9 8 7 6 5 4 3 2 1 ppm
0.89
1.00
0.91
4.11
4.27
4.07
0.99
0.90
3.11

1g


206.68
160.94
153.49
142.07
141.11
135.17
133.23
130.60
130.08
129.43
123.69
123.24
120.71
120.07
115.01
112.86
98.38
82.03
65.11
56.02
31.06
30.80
30.55
30.29
30.03
29.78
29.52
OH
OMe
O
N
H
N
Ph
H
220
200
180
160
140
120
100
80
60
40
20
ppm

1g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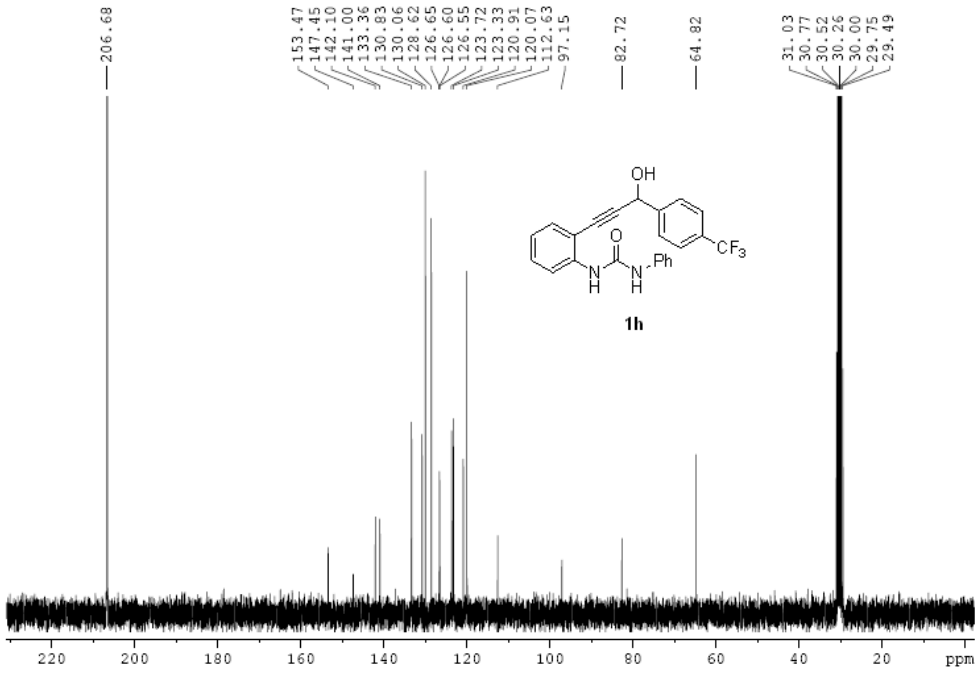
8.258
8.230
7.965
7.885
7.858
7.749
7.721
7.536
7.509
7.425
7.399
7.378
7.353
7.325
7.310
7.283
7.258
7.028
7.003
6.978
5.888
5.870
5.527
5.507
2.057
2.050
2.043
2.037
OH
CF3
O
N
H
N
Ph
H
11
10
9
8
7
6
5
4
3
2
1
ppm
0.91
1.00
0.92
2.04
2.00
2.12
4.19
2.05
1.01
0.94

1h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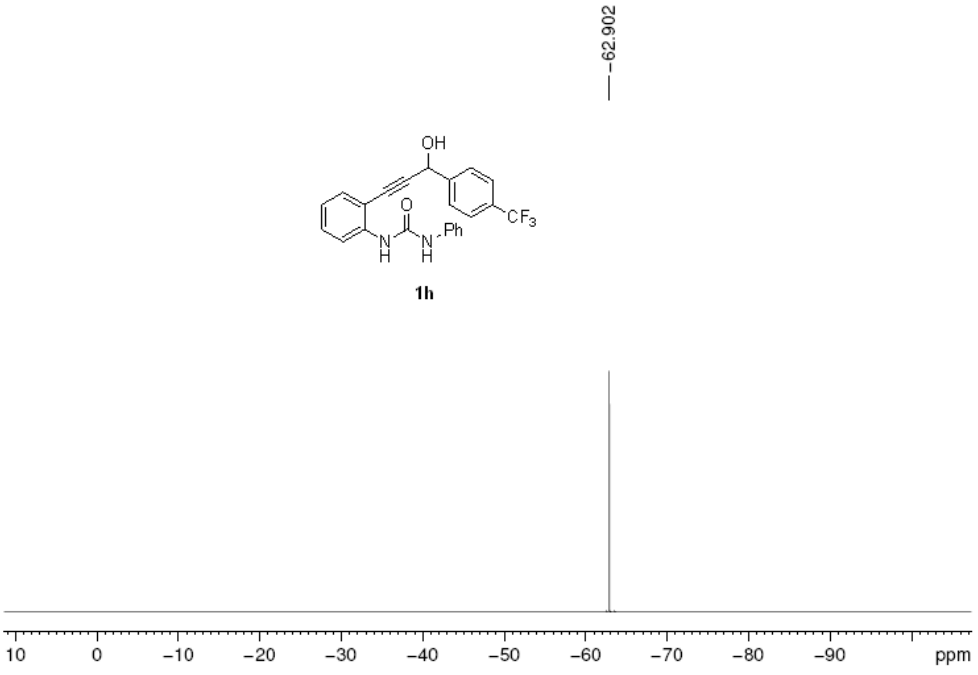
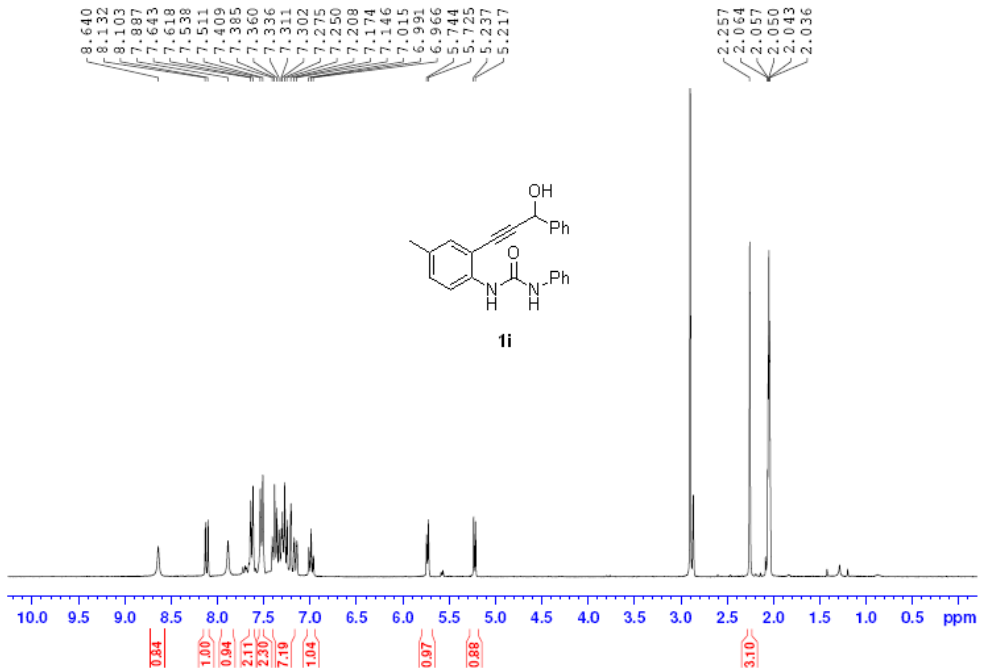
153.47
147.45
142.10
141.00
133.36
130.83
130.06
128.62
126.65
126.60
126.55
123.72
123.33
120.91
120.07
112.63
97.15
82.72
64.82
31.03
30.77
30.52
30.26
30.00
29.75
29.49
OH
O
N
H
N
H
Ph
CF3
1h
220
200
180
160
140
120
100
80
60
40
20
ppm


62.902
OH
O
N
H
N
H
Ph
CF3
1h
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
ppm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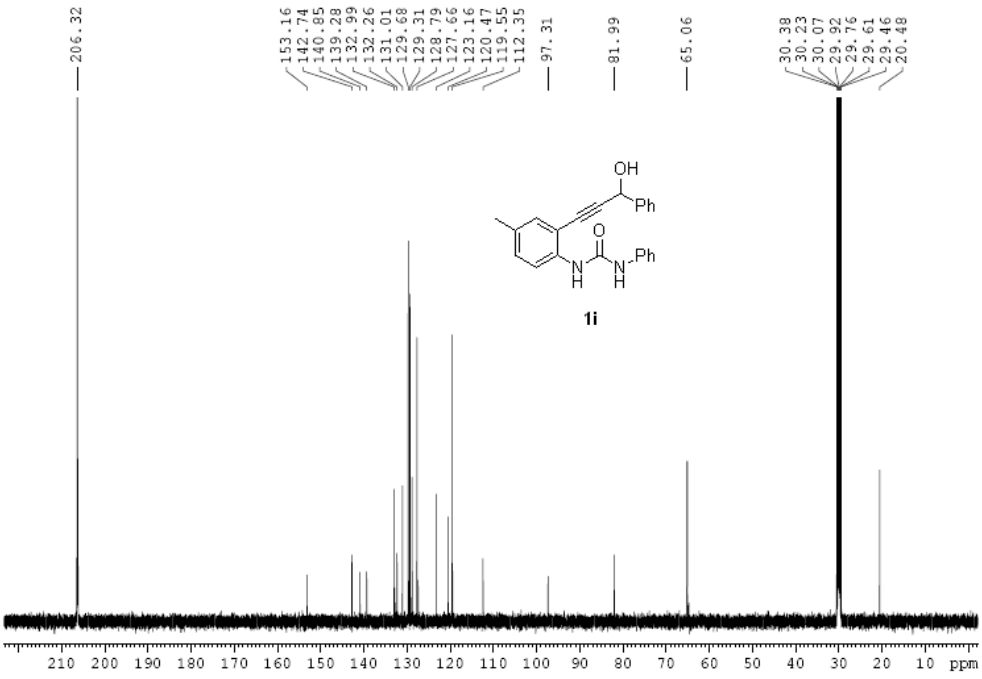
8.132
8.103
7.887
7.643
7.618
7.538
7.511
7.409
7.385
7.360
7.336
7.311
7.302
7.275
7.250
7.208
7.174
7.146
7.015
6.991
6.966
5.744
5.725
5.237
5.217
2.257
2.064
2.057
2.050
2.043
2.036
OH
Ph
O
N
H
N
H
Ph
1i
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.84
1.00
0.94
2.11
2.30
7.19
1.04
0.97
0.88
3.10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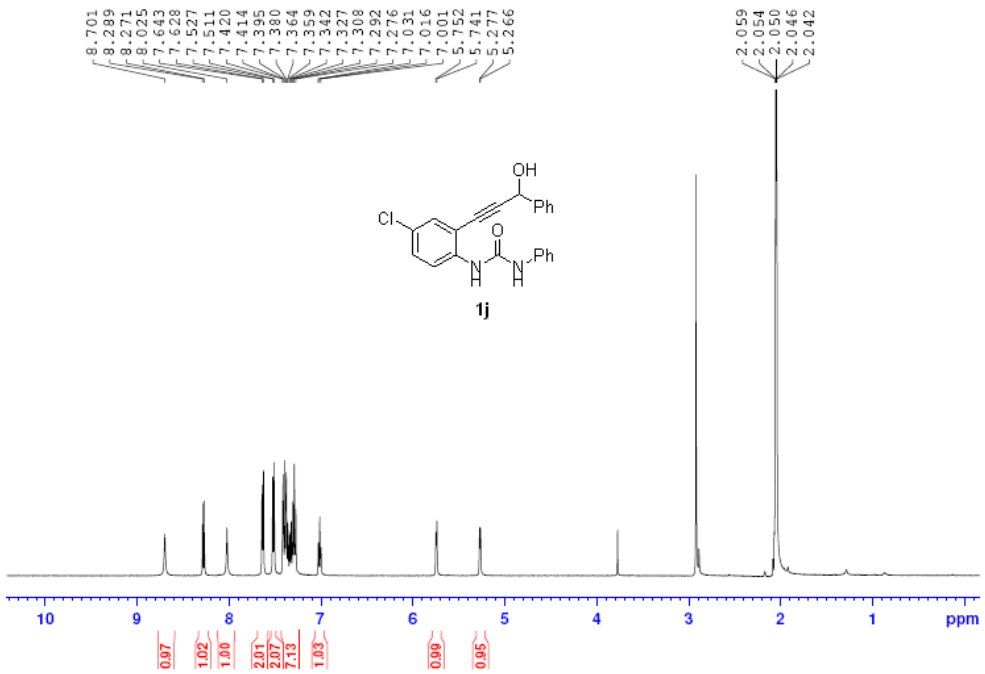
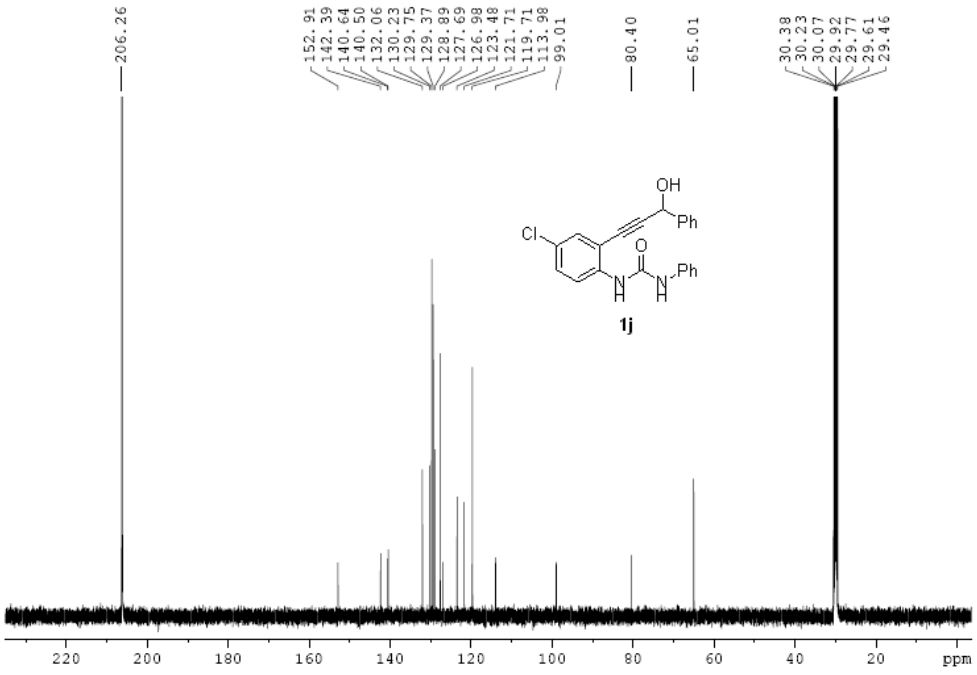
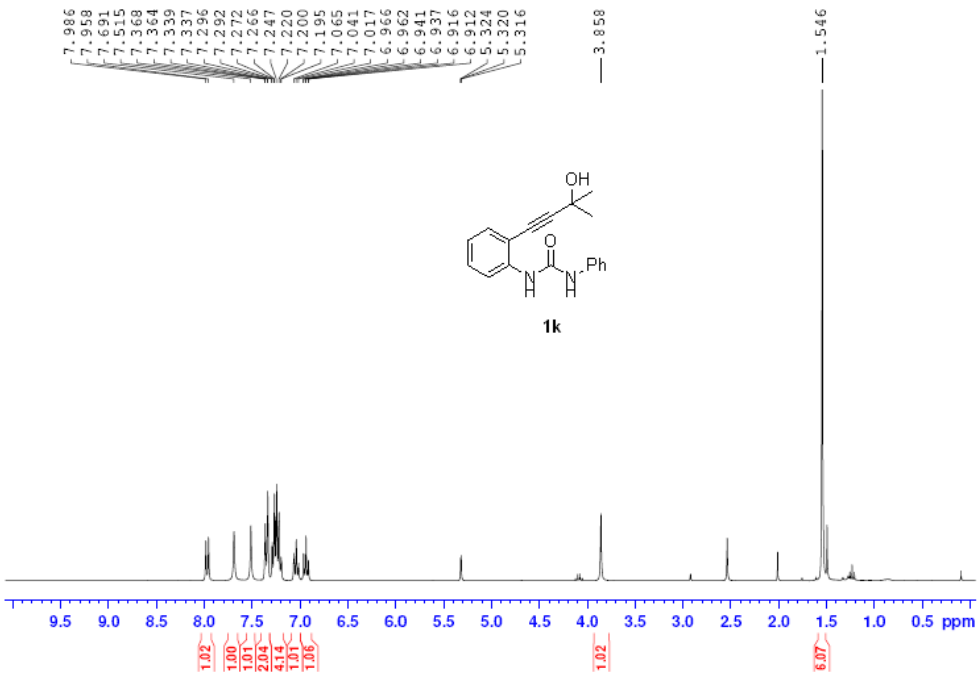
140.85
139.28
132.99
132.26
131.01
129.68
129.31
128.79
127.66
123.16
120.47
119.55
112.35
97.31
81.99
65.06
30.38
30.23
30.07
29.92
29.76
29.61
29.46
20.48
OH
Ph
O
N
H
N
H
Ph
1i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.701
8.289
8.271
8.025
7.643
7.628
7.527
7.511
7.420
7.414
7.395
7.380
7.364
7.359
7.342
7.327
7.308
7.292
7.276
7.031
7.016
7.001
5.752
5.741
5.277
5.266
2.059
2.054
2.050
2.046
2.042
OH
Ph
Cl
O
N
H
N
H
Ph
1j
10
9
8
7
6
5
4
3
2
1
ppm
0.97
1.02
1.00
2.01
2.07
7.13
1.03
0.99
0.95


206.26
152.91
142.39
140.64
140.50
132.06
130.23
129.75
129.37
128.89
127.69
126.98
123.48
121.71
119.71
113.98
99.01
80.40
65.01
30.38
30.23
30.07
29.92
29.77
29.61
29.46
OH
Ph
Cl
O
N
H
N
H
Ph
1j
220
200
180
160
140
120
100
80
60
40
20
ppm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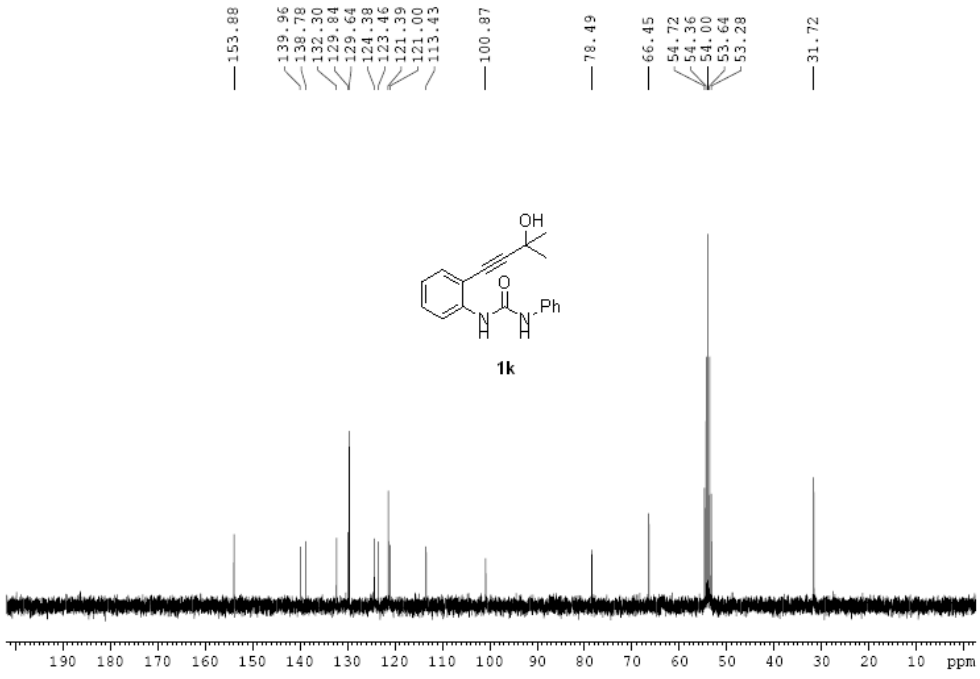
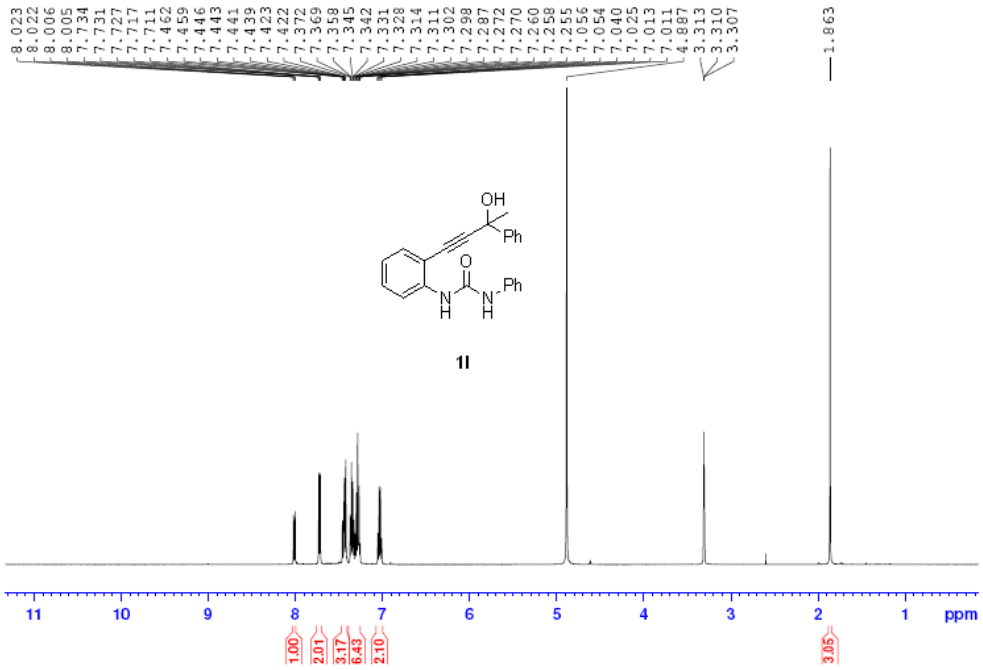
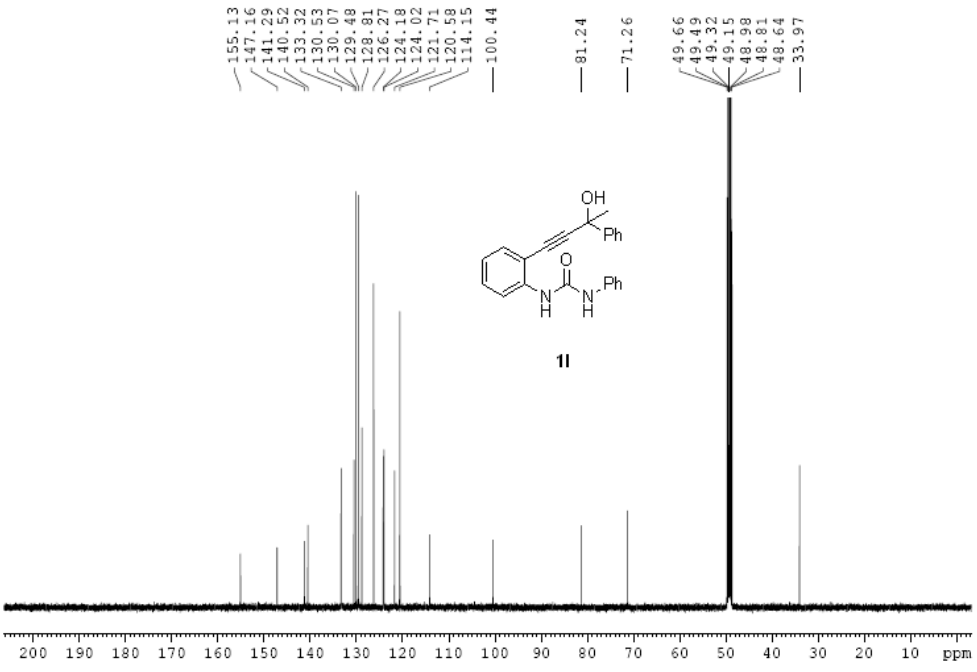
7.691
7.515
7.368
7.364
7.339
7.337
7.296
7.292
7.272
7.266
7.247
7.220
7.200
7.195
7.065
7.041
7.017
6.966
6.962
6.941
6.937
6.916
6.912
5.324
5.320
5.316
3.858
1.546
OH
O
N
H
N
H
Ph
1k
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02
1.00
1.01
2.04
4.14
1.01
1.06
1.02
6.07

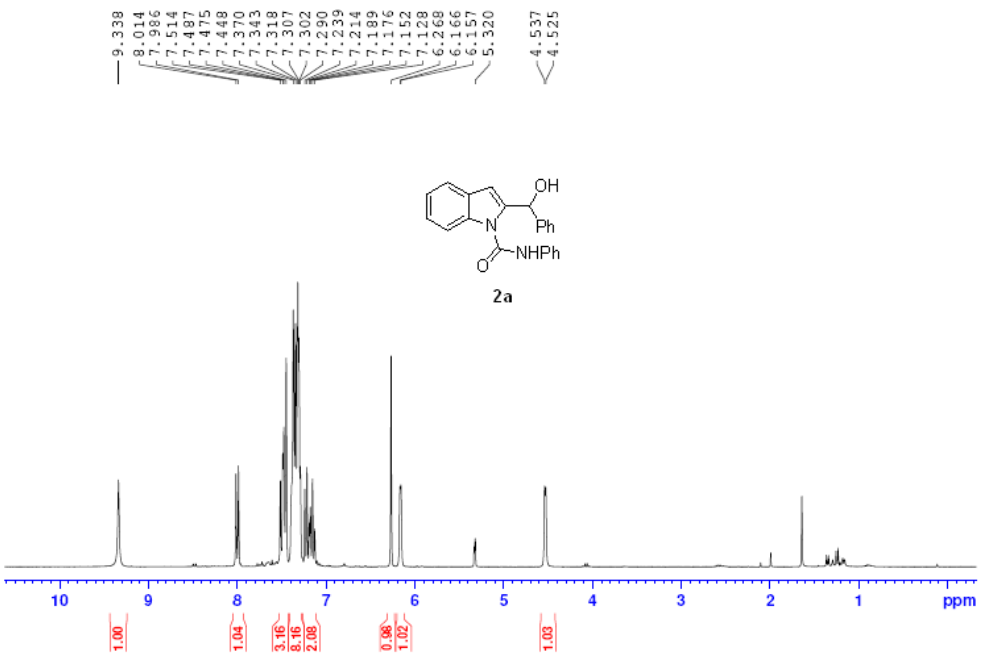

153.88
139.96
138.78
132.30
129.84
129.64
124.38
123.46
121.39
121.00
113.43
100.87
78.49
66.45
54.72
54.36
54.00
53.64
53.28
31.72
OH
O
N
H
N
H
Ph
1k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.023
8.022
8.006
8.005
7.734
7.731
7.727
7.717
7.711
7.462
7.459
7.446
7.443
7.441
7.439
7.423
7.422
7.372
7.369
7.358
7.345
7.342
7.331
7.328
7.314
7.311
7.302
7.298
7.287
7.272
7.270
7.260
7.258
7.255
7.056
7.054
7.040
7.025
7.013
7.011
4.887
3.313
3.310
3.307
1.863
OH
Ph
O
N
H
Ph
N
H
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.01
3.17
6.43
2.10
3.05

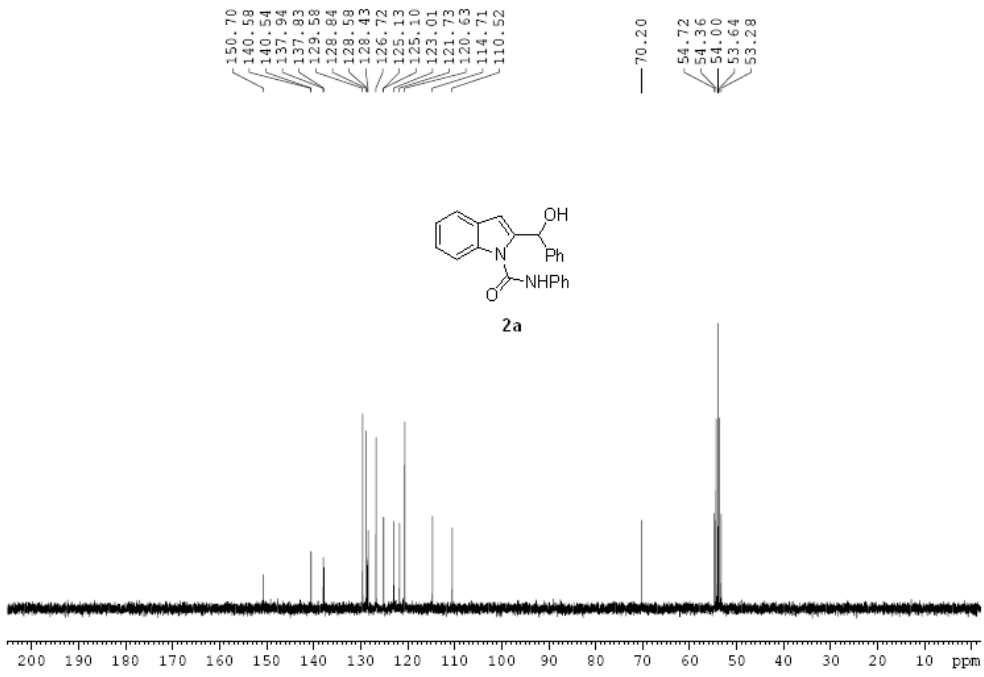
1l


155.13
147.16
141.29
140.52
133.32
130.53
130.07
129.48
128.81
126.27
124.18
124.02
121.71
120.58
114.15
100.44
81.24
71.26
49.66
49.49
49.32
49.15
48.98
48.81
48.64
33.97
OH
Ph
O
N
H
Ph
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

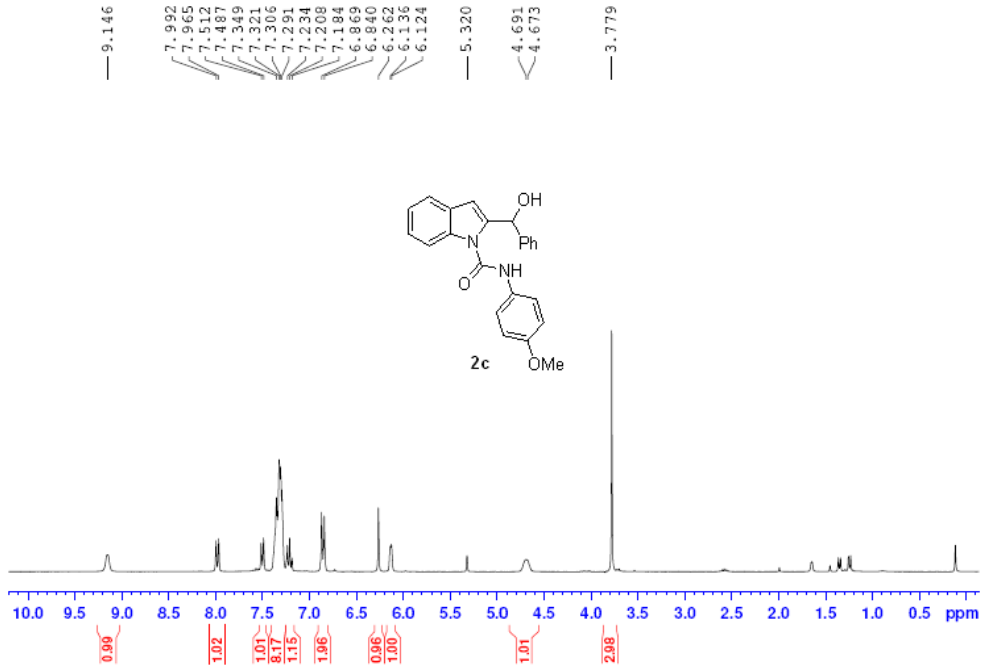
1l

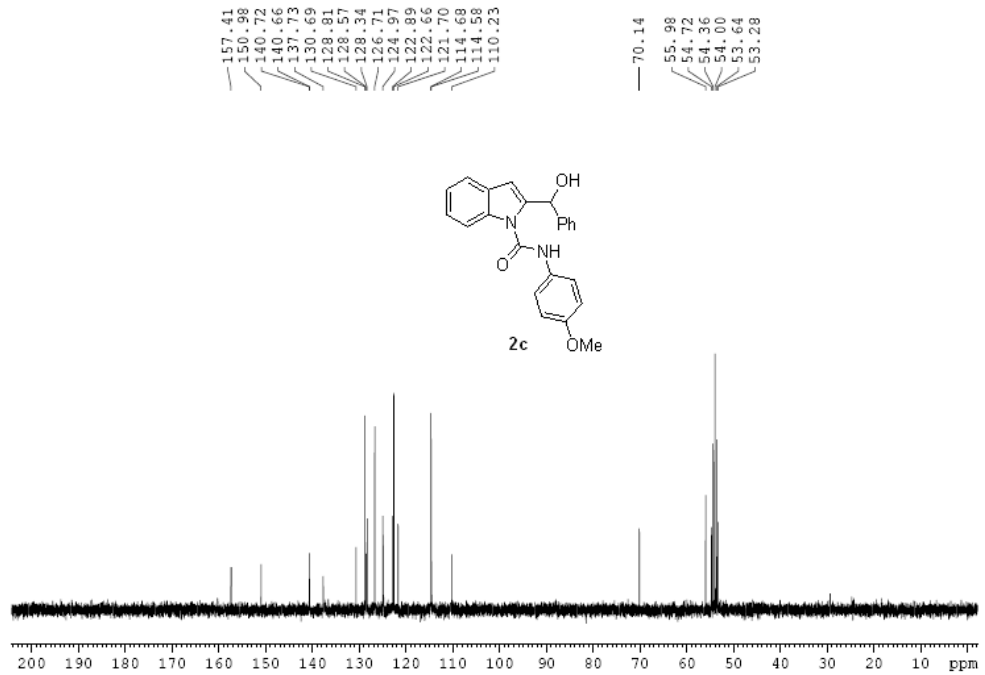

9.338
8.014
7.986
7.514
7.487
7.475
7.448
7.370
7.343
7.318
7.307
7.302
7.290
7.239
7.214
7.189
7.176
7.152
7.128
6.268
6.166
6.157
5.320
4.537
4.525
OH
Ph
N
O
NHPh
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.04
3.16
8.16
2.08
0.98
1.02
1.03

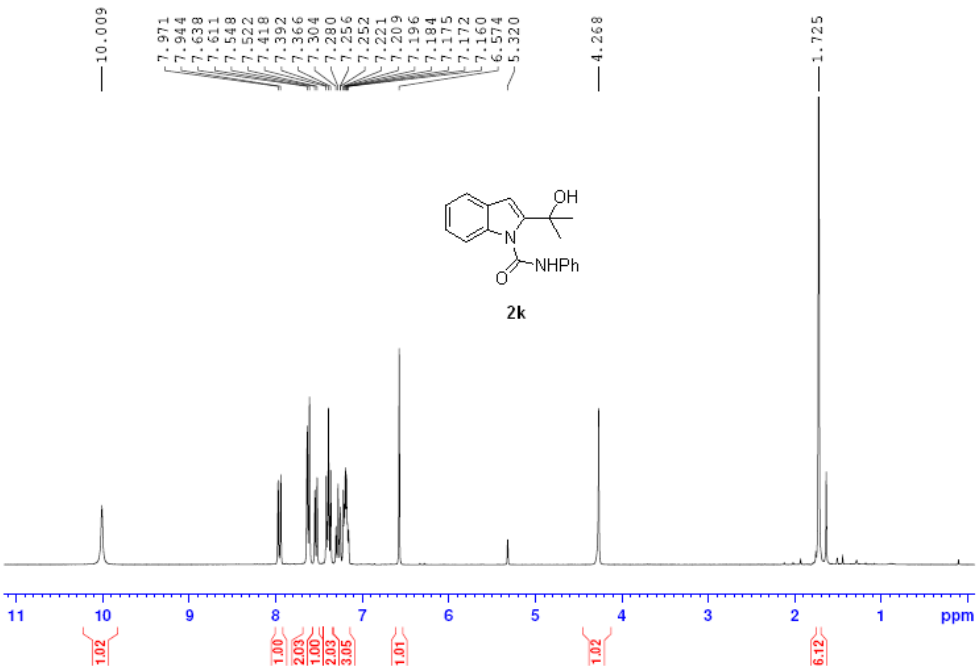
2a

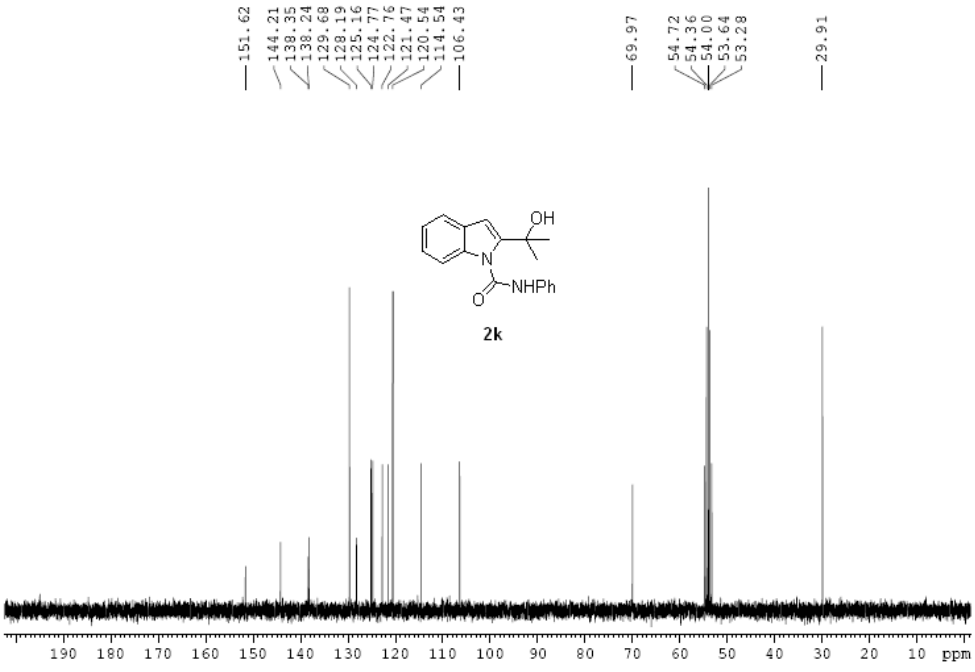

150.70
140.58
140.54
137.94
137.83
129.58
128.84
128.58
128.43
126.72
125.13
125.10
123.01
121.73
120.63
114.71
110.52
70.20
54.72
54.36
54.00
53.64
53.28
OH
Ph
N
O
NHPh
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

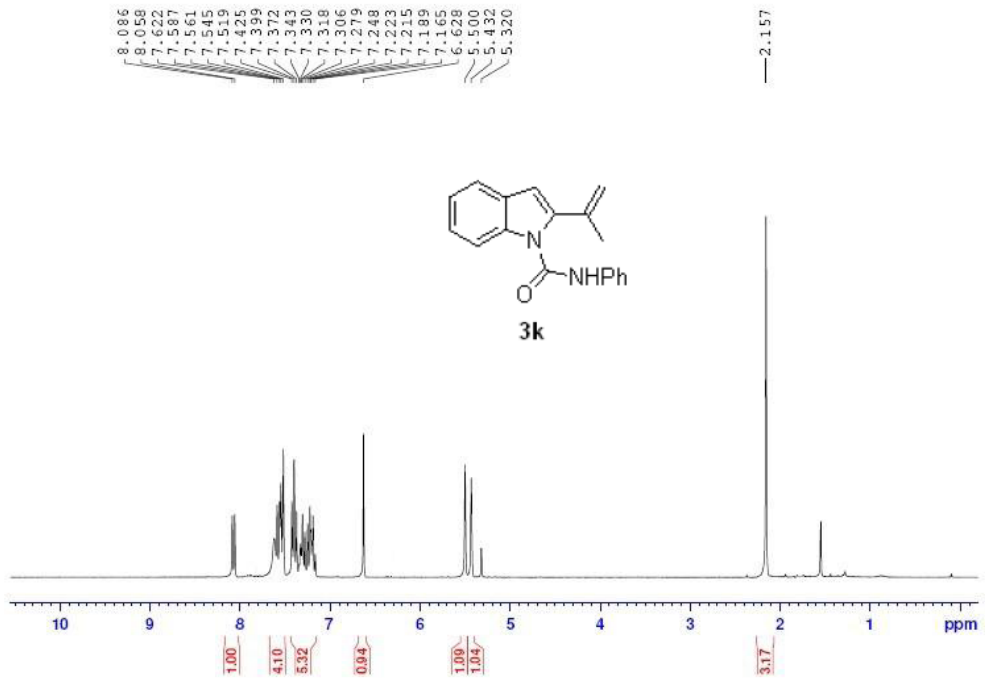
2a

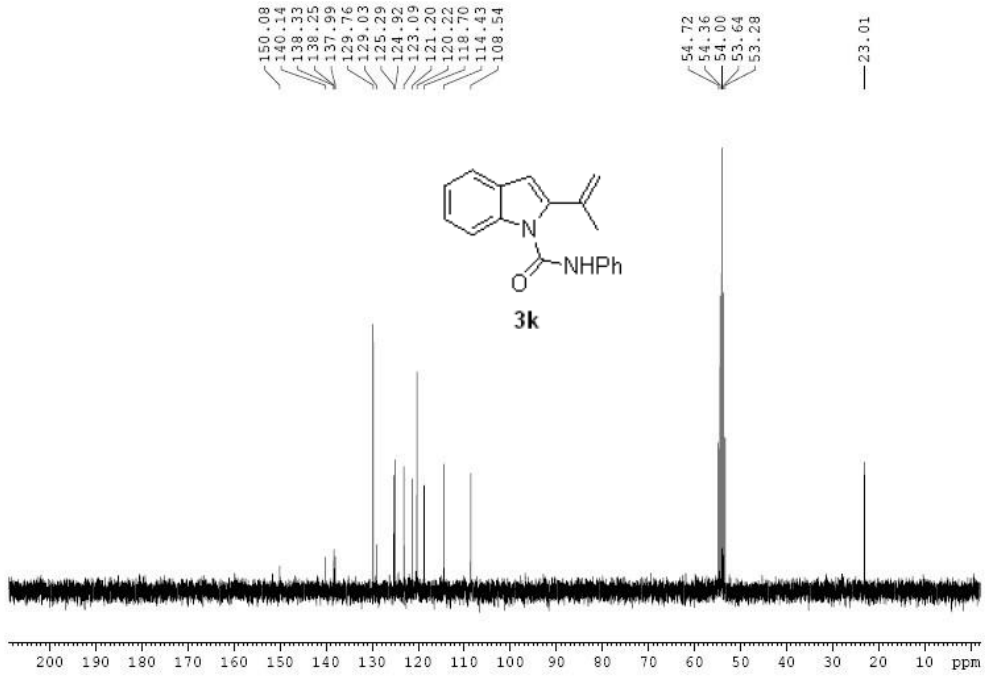

9.146
7.992
7.965
7.512
7.487
7.349
7.321
7.306
7.291
7.234
7.208
7.184
6.869
6.840
6.262
6.136
6.124
5.320
4.691
4.673
3.779
OH
Ph
N
O
NH
OMe
2c
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99
1.02
1.01
8.17
1.15
1.96
0.96
1.00
1.01
2.98

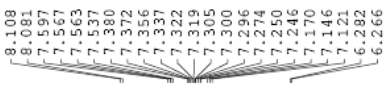

157.41
150.98
140.72
140.66
137.73
130.69
128.81
128.57
128.34
126.71
124.97
122.89
122.66
121.70
114.68
114.58
110.23
70.14
55.98
54.72
54.36
54.00
53.64
53.28
OH
Ph
N
O
NH
OMe
2c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

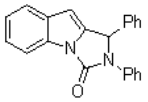

10.009
7.971
7.944
7.638
7.611
7.548
7.522
7.418
7.392
7.366
7.304
7.280
7.256
7.252
7.221
7.209
7.196
7.184
7.175
7.172
7.160
6.574
5.320
4.268
1.725
OH
N
O
NHPh
2k
11
10
9
8
7
6
5
4
3
2
1
ppm
1.02
1.00
2.03
1.00
2.03
3.05
1.01
1.02
6.12


151.62
144.21
138.35
138.24
129.68
128.19
125.16
124.77
122.76
121.47
120.54
114.54
106.43
69.97
54.72
54.36
54.00
53.64
53.28
29.91
OH
N
O
NHPh
2k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

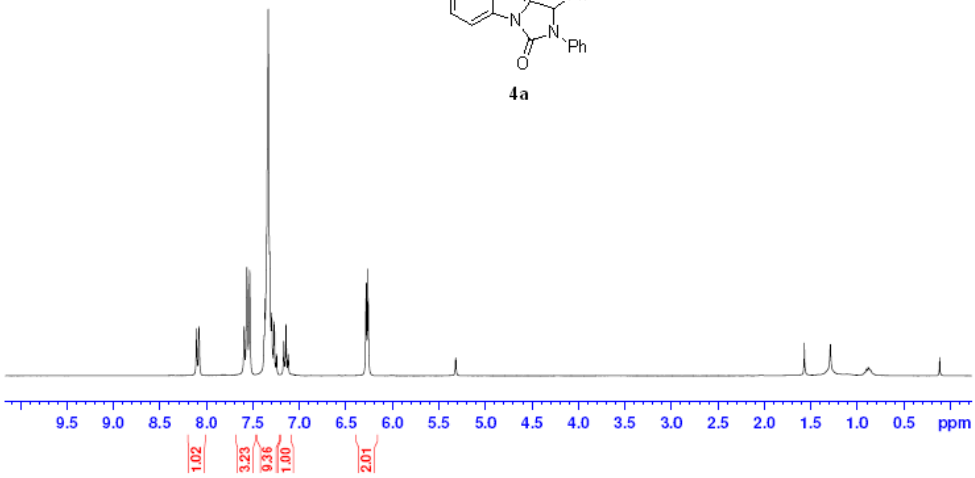

8.086
8.058
7.622
7.587
7.561
7.545
7.519
7.425
7.399
7.372
7.343
7.330
7.318
7.306
7.279
7.248
7.223
7.215
7.189
7.165
6.628
5.500
5.432
5.320
2.157
NHPh
3k
10
9
8
7
6
5
4
3
2
1
ppm
1.00
4.10
5.32
0.94
1.09
1.04
3.17

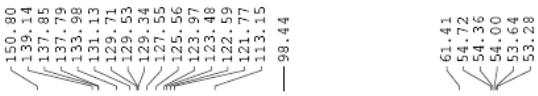

150.08
140.14
138.33
138.25
137.99
129.76
129.03
125.29
124.92
123.09
121.20
120.22
118.70
114.43
108.54
54.72
54.36
54.00
53.64
53.28
23.01
NHPh
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

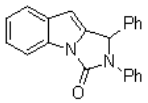

8.108
8.081
7.597
7.567
7.563
7.537
7.380
7.372
7.356
7.337
7.322
7.319
7.305
7.300
7.296
7.274
7.250
7.246
7.170
7.146
7.121
6.282
6.266


Ph
N
N
Ph
O

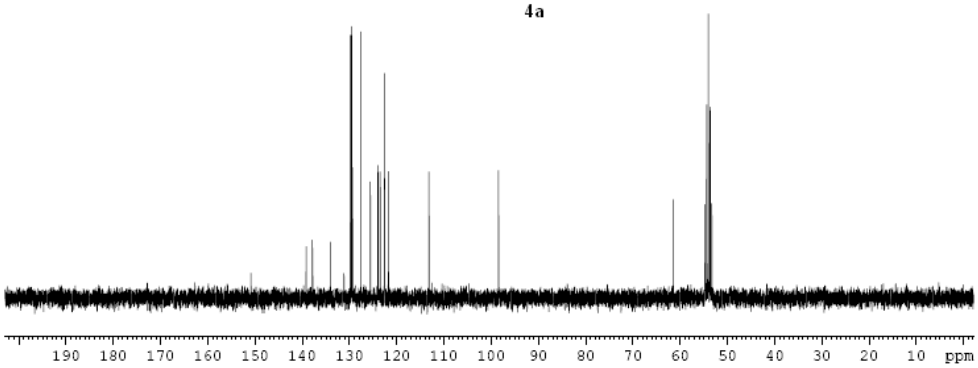
4a

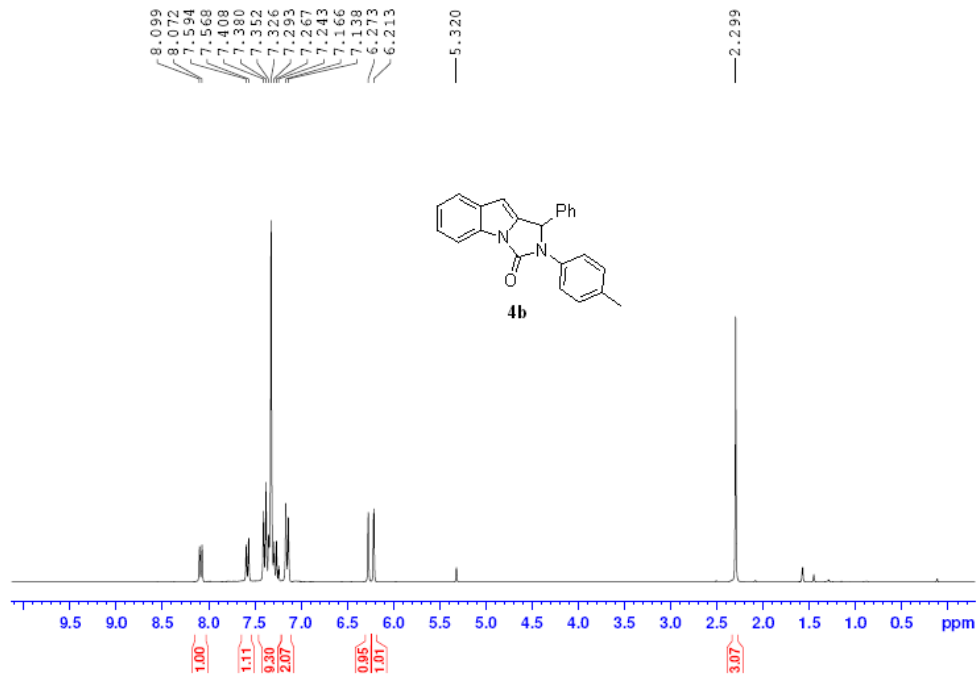

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02
3.23
9.36
1.00
2.01

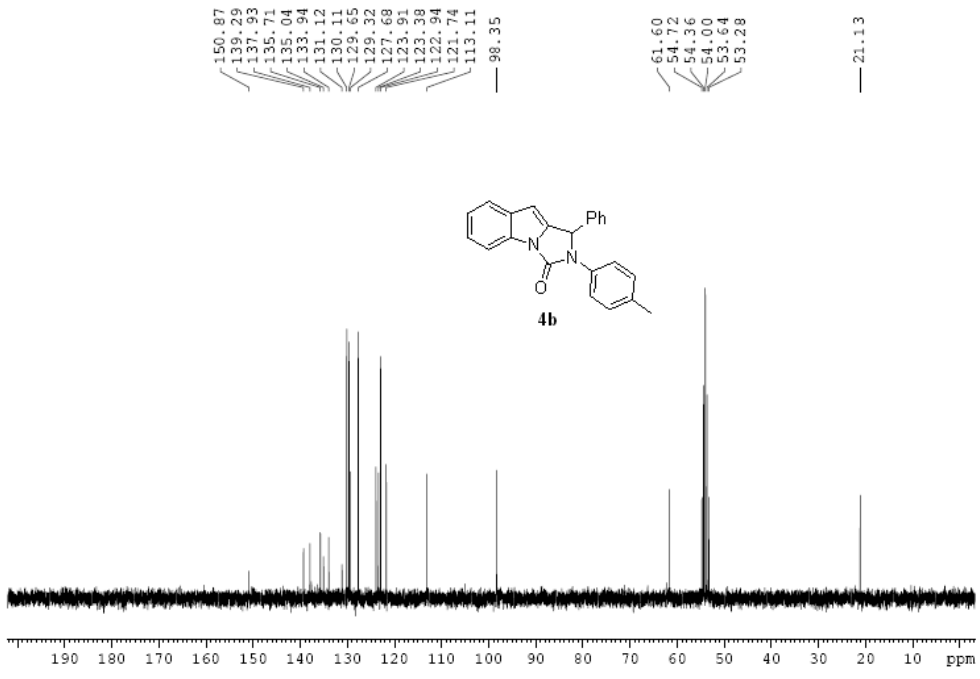

150.80
139.14
137.85
137.79
133.98
131.13
129.71
129.53
129.34
127.55
125.56
123.97
123.48
122.59
121.77
113.15
98.44
61.41
54.72
54.36
54.00
53.64
53.28

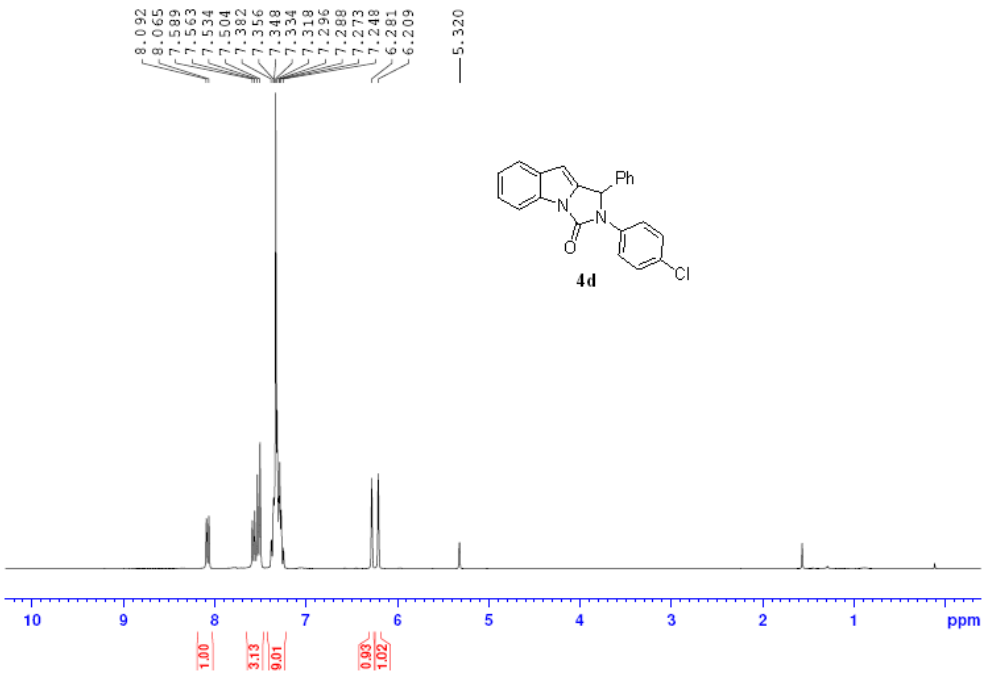

Ph
N
N
Ph
O

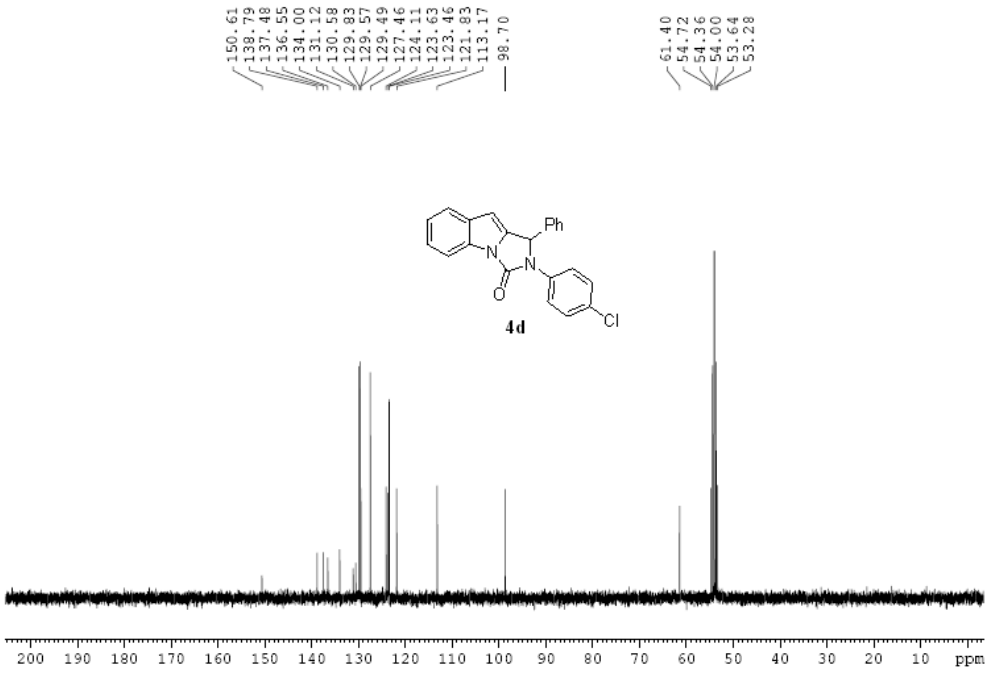
4a

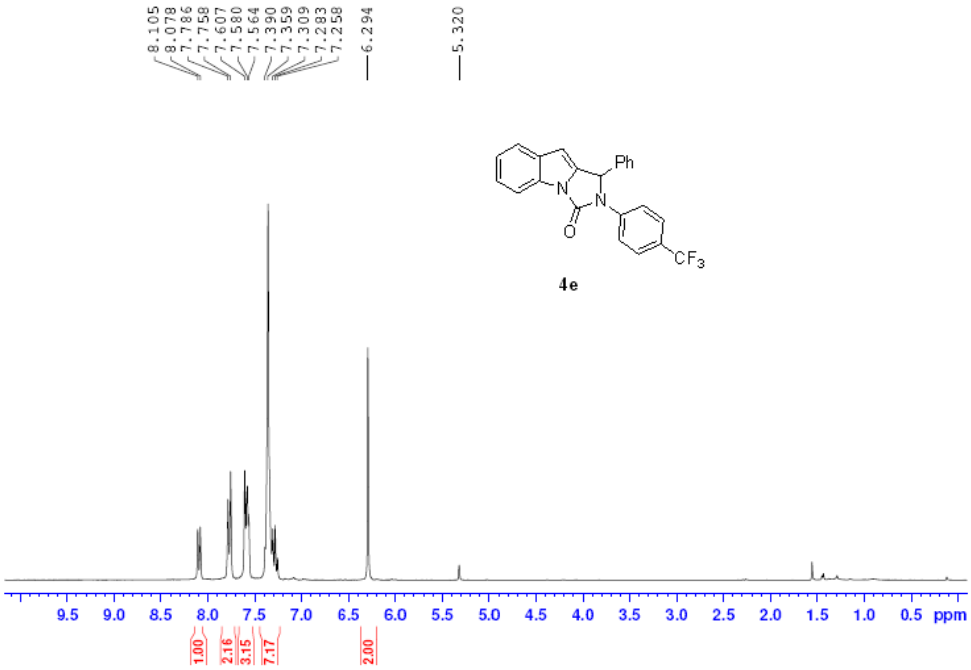

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

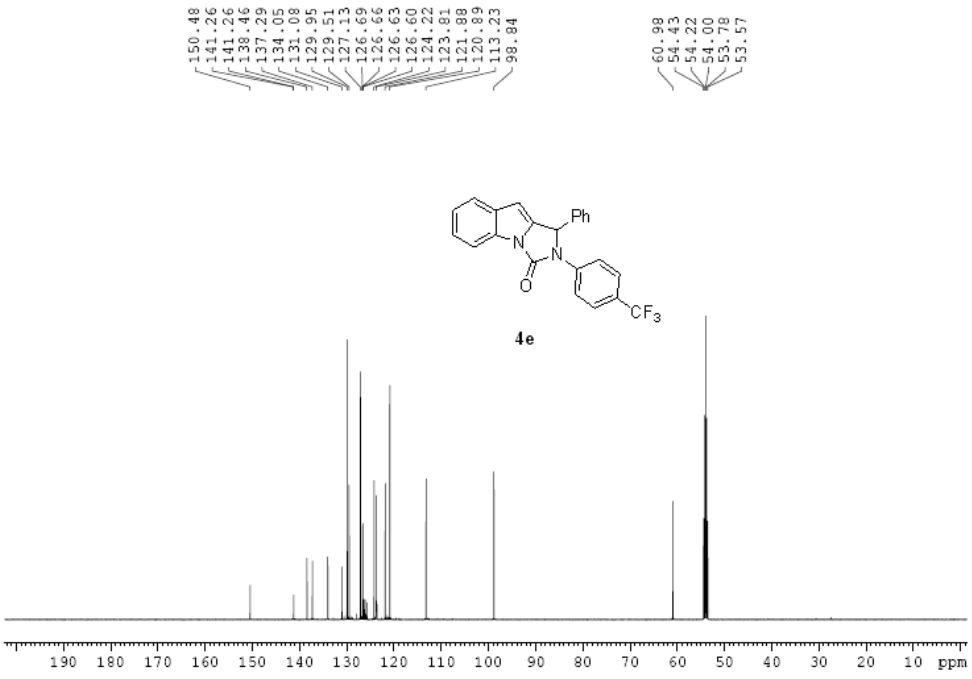

8.099
8.072
7.594
7.568
7.408
7.380
7.352
7.326
7.293
7.267
7.243
7.166
7.138
6.273
6.213
5.320
2.299
Ph
N
N
O
4b
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.11
9.30
2.07
0.95
1.01
3.07

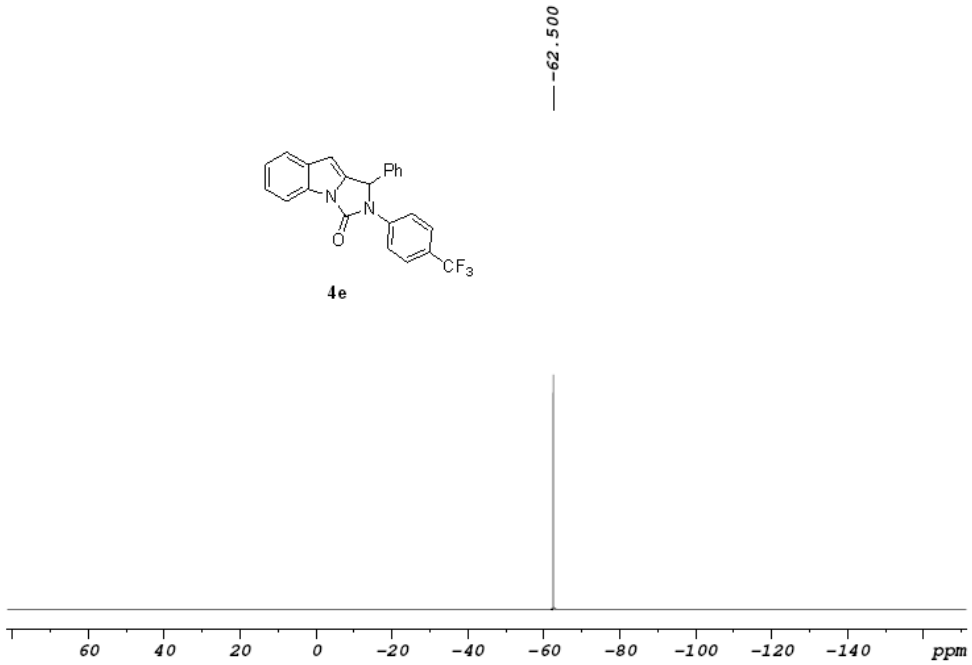

150.87
139.29
137.93
135.71
135.04
133.94
131.12
130.11
129.65
129.32
127.68
123.91
123.38
122.94
121.74
113.11
98.35
61.60
54.72
54.36
54.00
53.64
53.28
21.13
Ph
N
N
O
4b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.092
8.065
7.589
7.563
7.534
7.504
7.382
7.356
7.348
7.334
7.318
7.296
7.288
7.273
7.248
6.281
6.209
5.320
Ph
N
N
O
Cl
4d
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.13
9.01
0.93
1.02


150.61
138.79
137.48
136.55
134.00
131.12
130.58
129.83
129.57
129.49
127.46
124.11
123.63
123.46
121.83
113.17
98.70
61.40
54.72
54.36
54.00
53.64
53.28
Ph
N
N
O
Cl
4d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

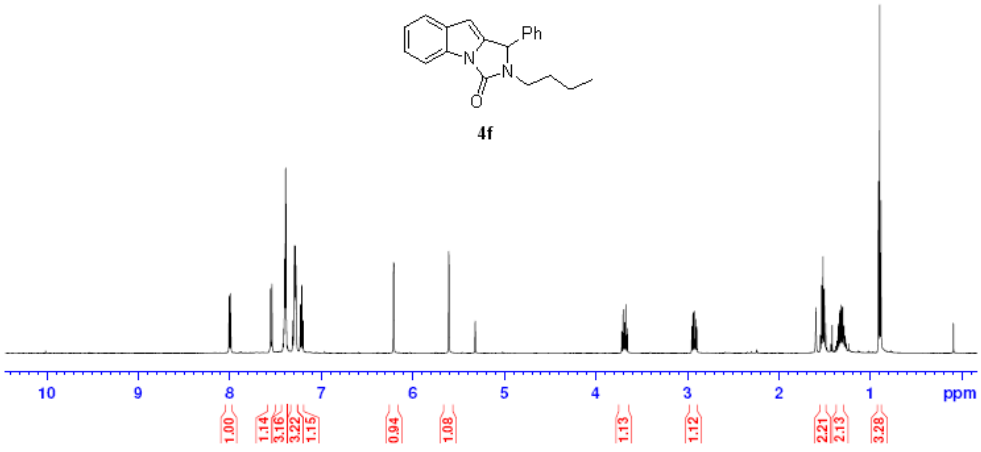

8.105
8.078
7.786
7.758
7.607
7.580
7.564
7.390
7.359
7.309
7.283
7.258
6.294
5.320
Ph
N
N
O
CF3
4e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.16
3.15
7.17
2.00


150.48
141.26
141.26
138.46
137.29
134.05
131.08
129.95
129.51
127.13
126.69
126.66
126.63
126.60
124.22
123.81
121.88
120.89
113.23
98.84
60.98
54.43
54.22
54.00
53.78
53.57
Ph
N
N
O
CF3
4e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

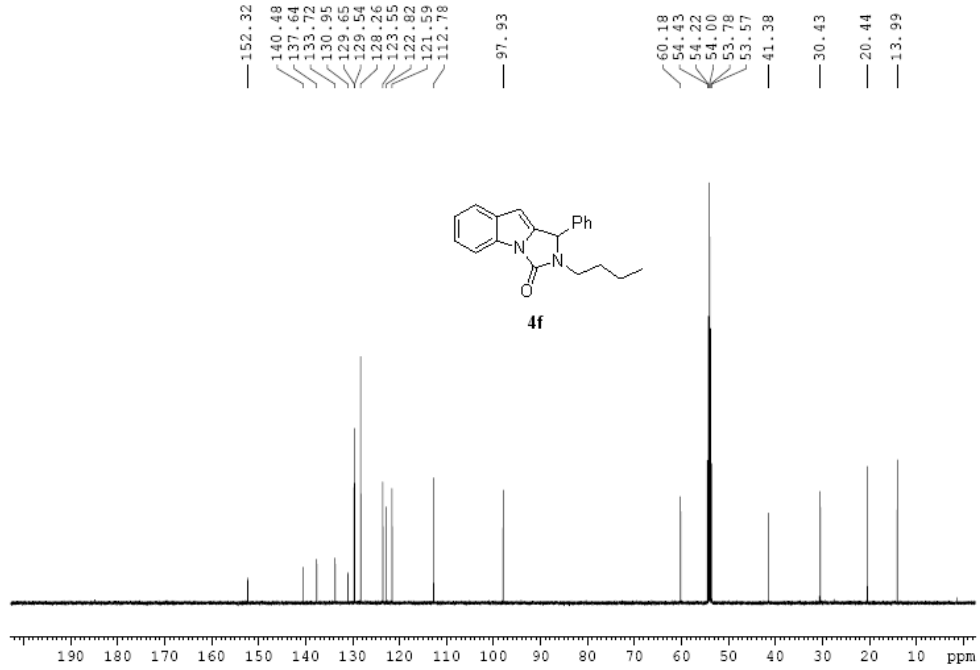

-62.500
Ph
N
N
O
CF3
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
ppm

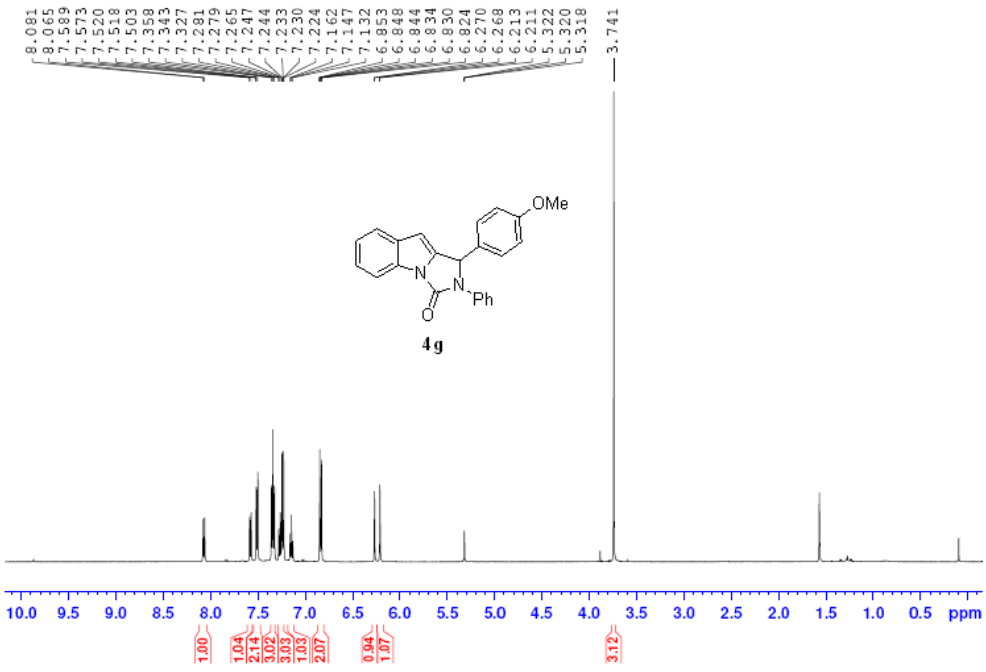
4e

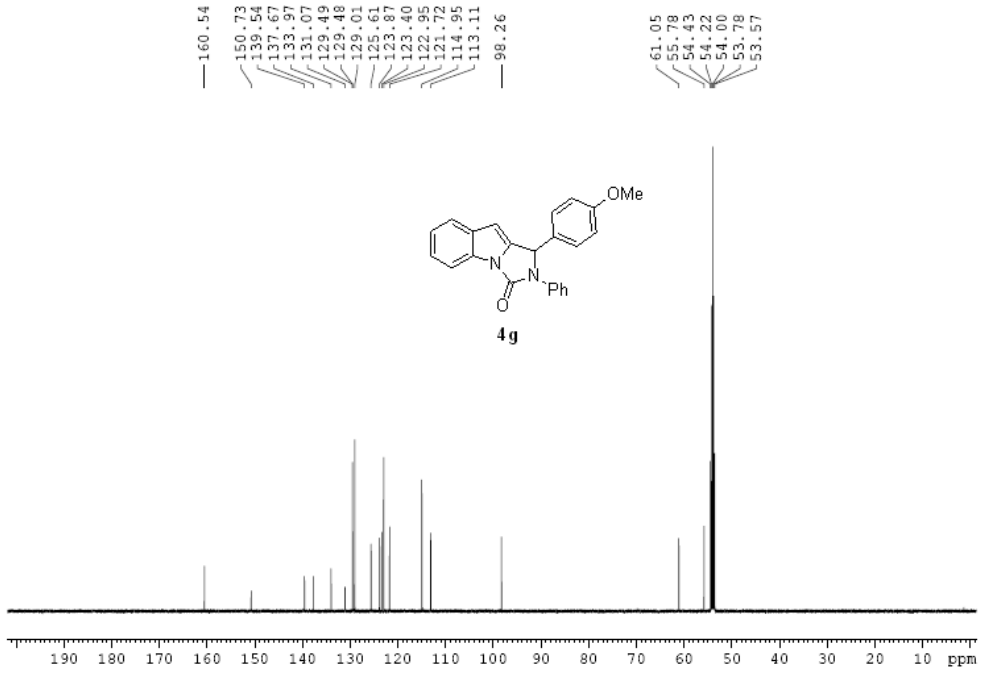

8.009
7.993
7.557
7.541
7.412
7.403
7.399
7.393
7.389
7.384
7.380
7.315
7.313
7.299
7.294
7.288
7.285
7.279
7.275
7.232
7.230
7.216
7.201
7.199
6.212
5.609
5.322
5.320
5.318
3.718
3.703
3.689
3.688
3.674
3.658
2.953
2.939
2.926
2.910
2.898
1.550
1.534
1.519
1.505
1.490
1.368
1.353
1.339
1.335
1.324
1.319
1.309
1.304
1.290
1.277
0.914
0.899
0.885


Ph
N
N
O
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.14
3.16
3.22
1.15
0.94
1.08
1.13
1.12
2.21
2.13
3.28

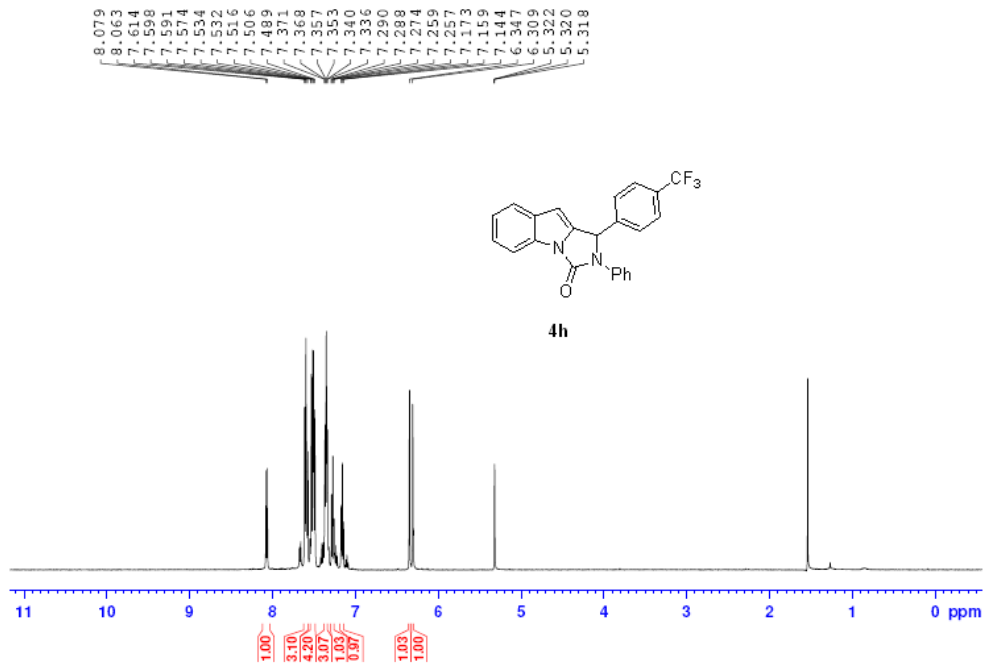
4f


152.32
140.48
137.64
133.72
130.95
129.65
129.54
128.26
123.55
122.82
121.59
112.78
97.93
60.18
54.43
54.22
54.00
53.78
53.57
41.38
30.43
20.44
13.99
Ph
N
N
O
4f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

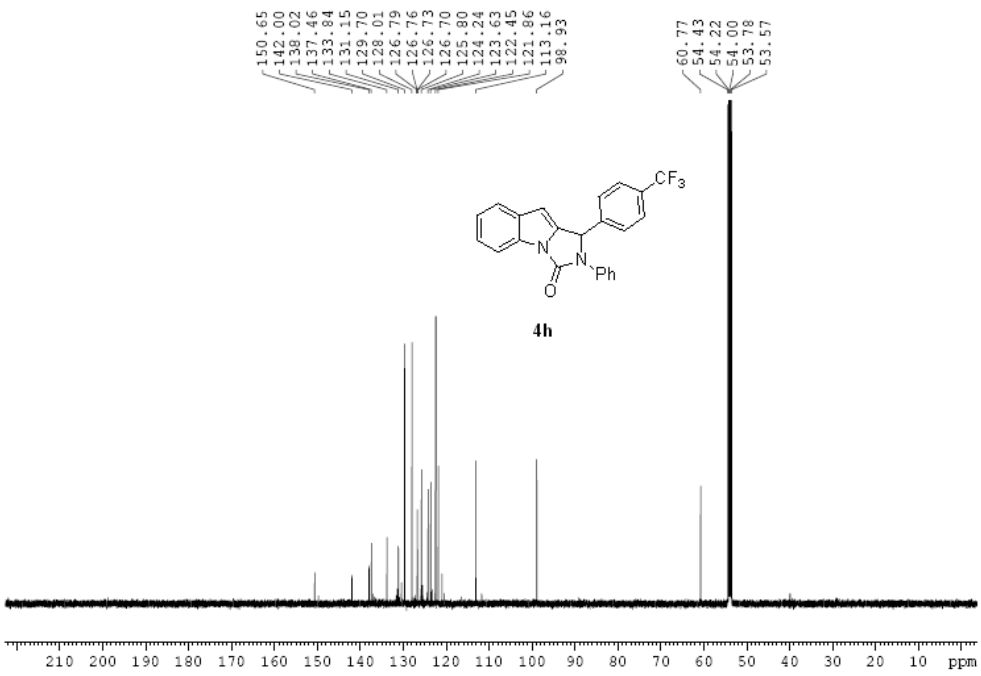

8.081
8.065
7.589
7.573
7.520
7.518
7.503
7.358
7.343
7.327
7.281
7.279
7.265
7.247
7.244
7.233
7.230
7.224
7.162
7.147
7.132
6.853
6.848
6.844
6.834
6.830
6.824
6.270
6.268
6.213
6.211
5.322
5.320
5.318
3.741
OMe
N
N
Ph
O
4g
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.04
2.14
3.02
3.03
1.03
2.07
0.94
1.07
3.12


160.54
150.73
139.54
137.67
133.97
131.07
129.49
129.48
129.01
125.61
123.87
123.40
122.95
121.72
114.95
113.11
98.26
61.05
55.78
54.43
54.22
54.00
53.78
53.57
OMe
N
N
Ph
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

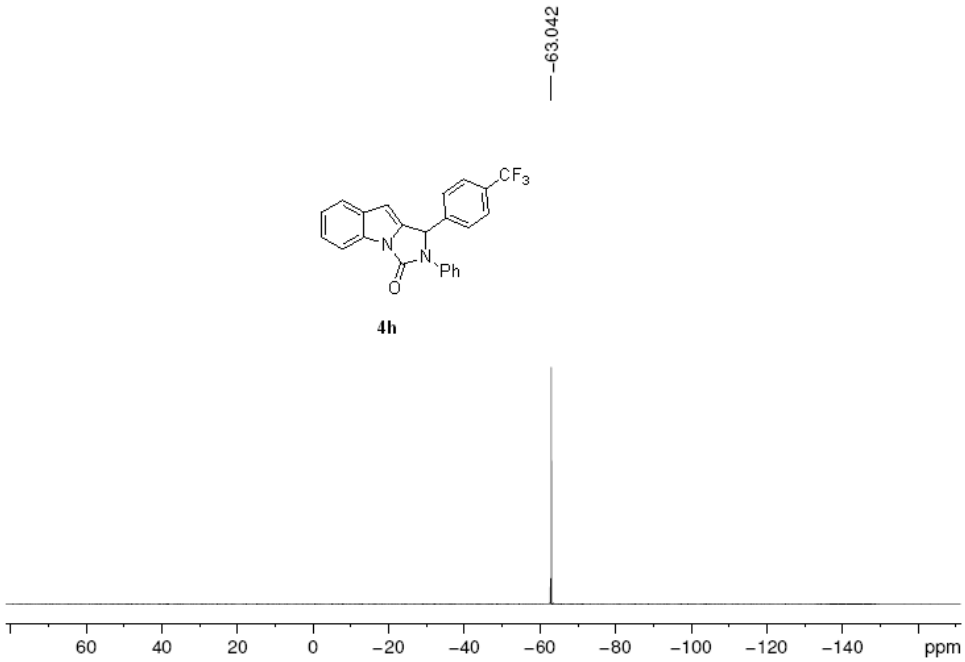
4g


8.079
8.063
7.614
7.598
7.591
7.574
7.534
7.532
7.516
7.506
7.489
7.371
7.368
7.357
7.353
7.340
7.336
7.290
7.288
7.274
7.259
7.257
7.173
7.159
7.144
6.347
6.309
5.322
5.320
5.318
CF3
N
N
Ph
O
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
3.10
4.20
3.07
1.03
0.97
1.03
1.00

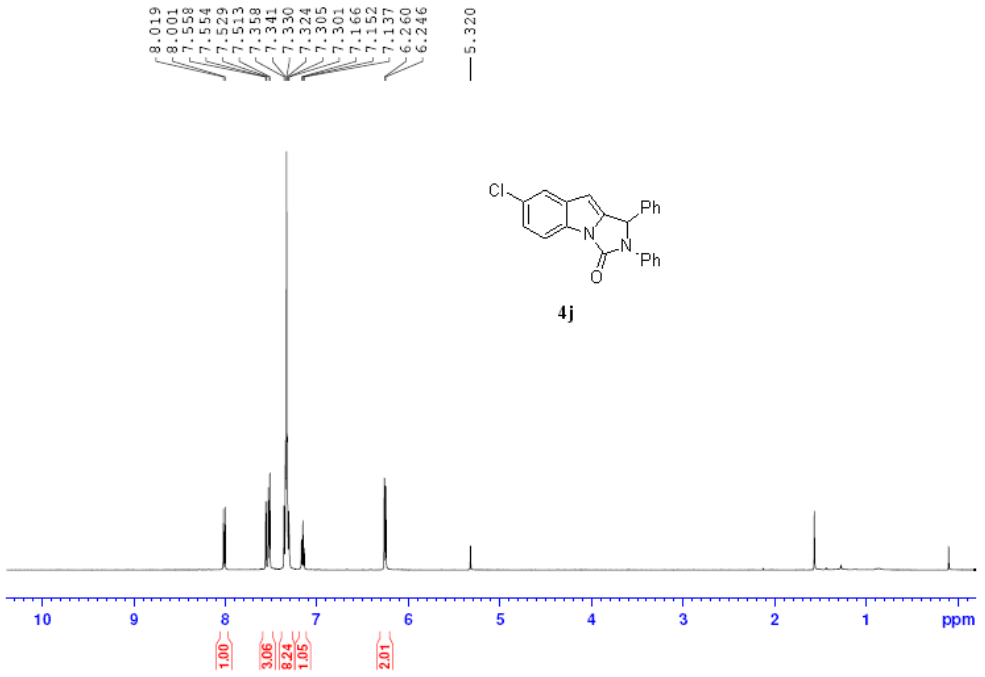
4h


150.65
142.00
138.02
137.46
133.84
131.15
129.70
128.01
126.79
126.76
126.73
126.70
125.80
124.24
123.63
122.45
121.86
113.16
98.93
60.77
54.43
54.22
54.00
53.78
53.57
CF3
N
N
Ph
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

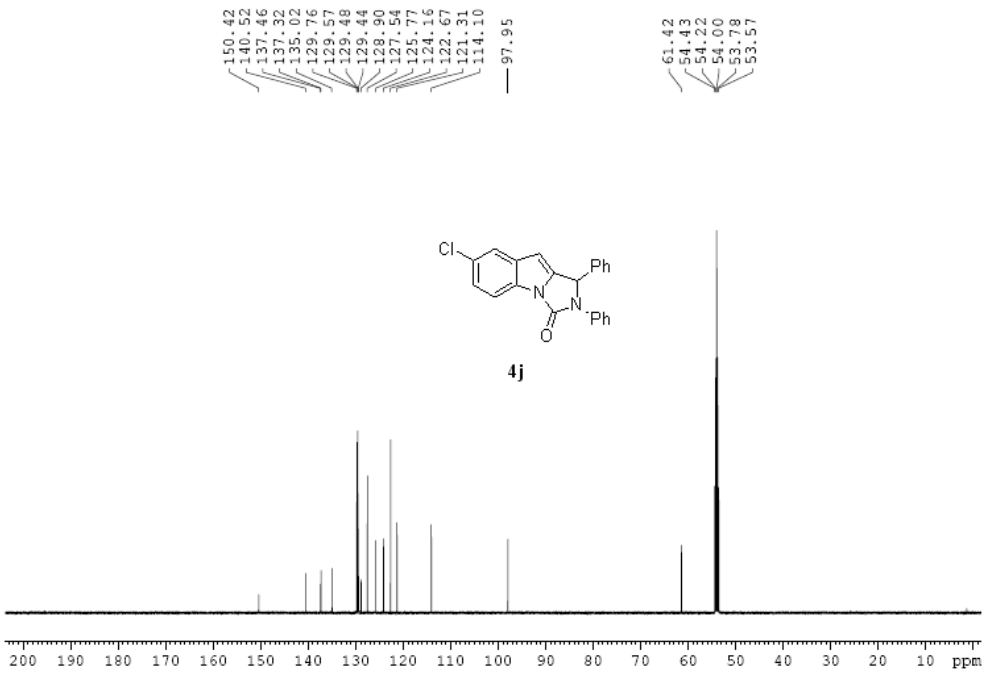
4h


-63.042
CF3
N
N
Ph
O
60 40 20 0 −20 −40 −60 −80 −100 −120 −140 ppm

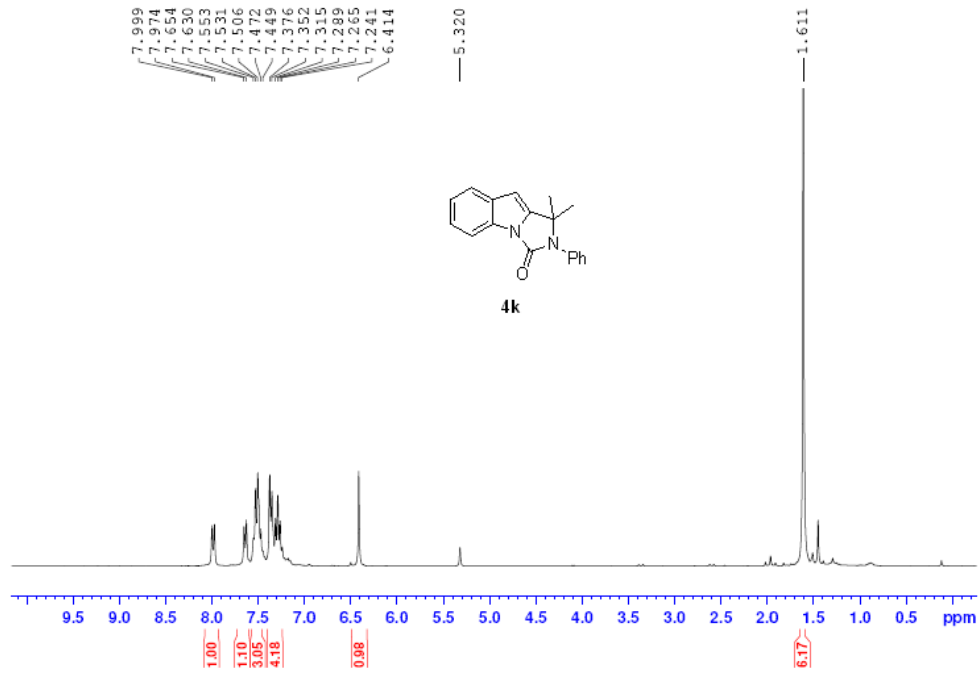
4h


8.019
8.001
7.558
7.554
7.529
7.513
7.358
7.341
7.330
7.324
7.305
7.301
7.166
7.152
7.137
6.260
6.246
5.320
Cl
Ph
N
N
Ph
O
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.06
8.24
1.05
2.01

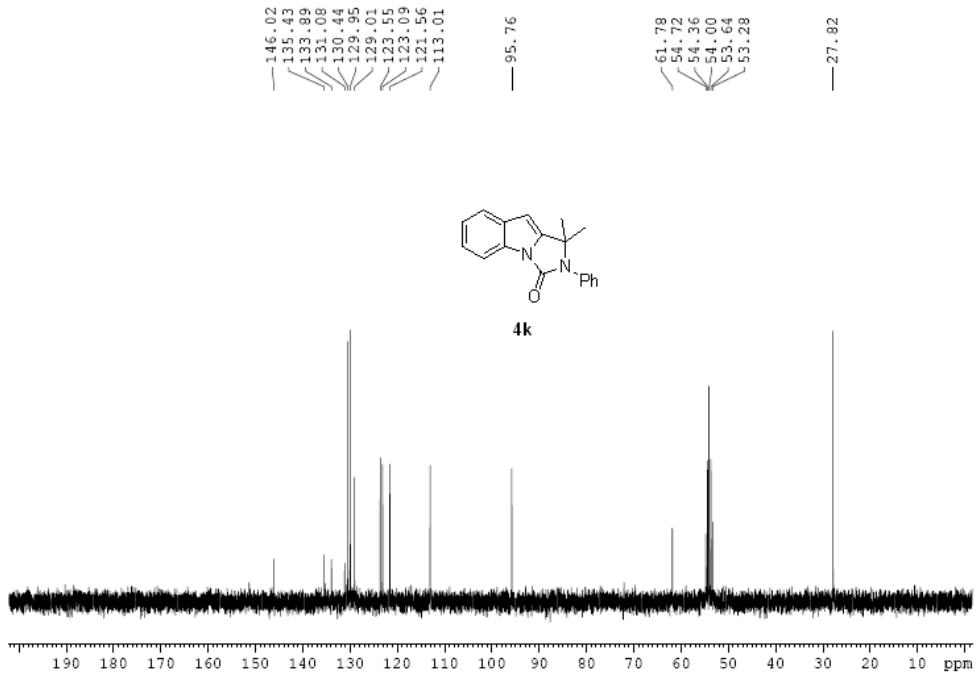
4j


150.42
140.52
137.46
137.32
135.02
129.76
129.57
129.48
129.44
128.90
127.54
125.77
124.16
122.67
121.31
114.10
97.95
61.42
54.43
54.22
54.00
53.78
53.57
Cl
Ph
N
N
Ph
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

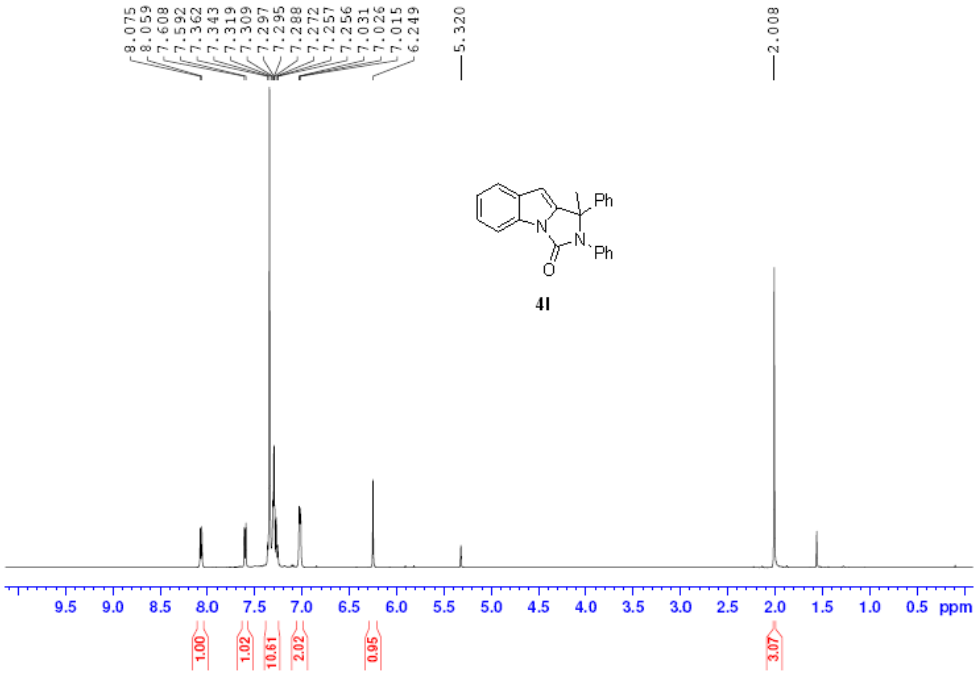
4j


7.999
7.974
7.654
7.630
7.553
7.531
7.506
7.472
7.449
7.376
7.352
7.315
7.289
7.265
7.241
6.414
5.320
1.611
Ph
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.10
3.05
4.18
0.98
6.17

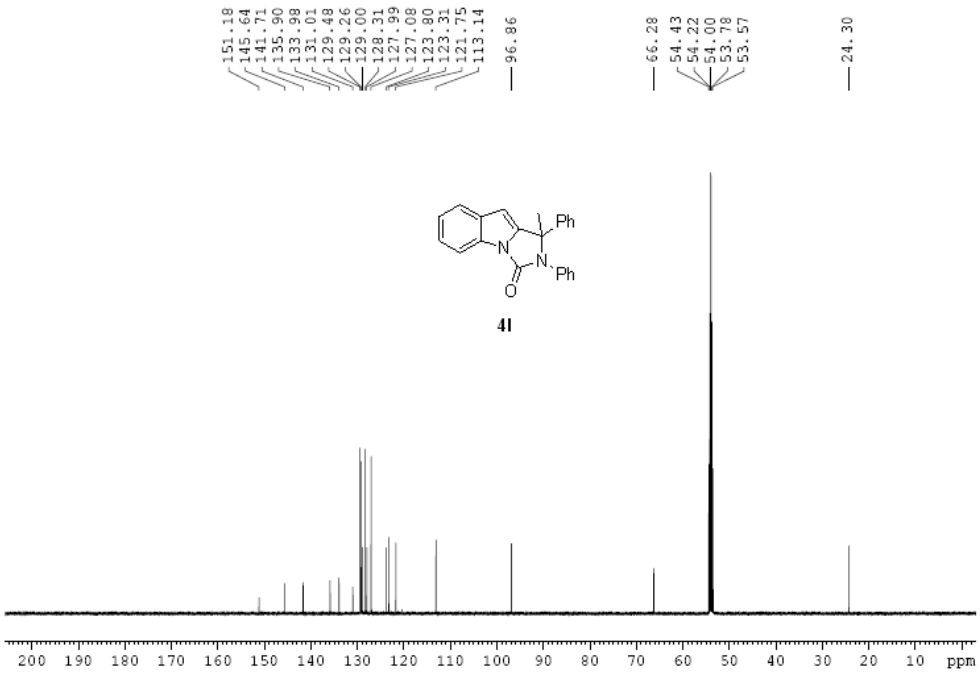
4k


146.02
135.43
133.89
131.08
130.44
129.95
129.01
123.55
123.09
121.56
113.01
95.76
61.78
54.72
54.36
54.00
53.64
53.28
27.82
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

4k


8.075
8.059
7.608
7.592
7.362
7.343
7.319
7.309
7.297
7.295
7.288
7.272
7.257
7.256
7.031
7.026
7.015
6.249
5.320
2.008
Ph
N
N
Ph
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.02
10.61
2.02
0.95
3.07

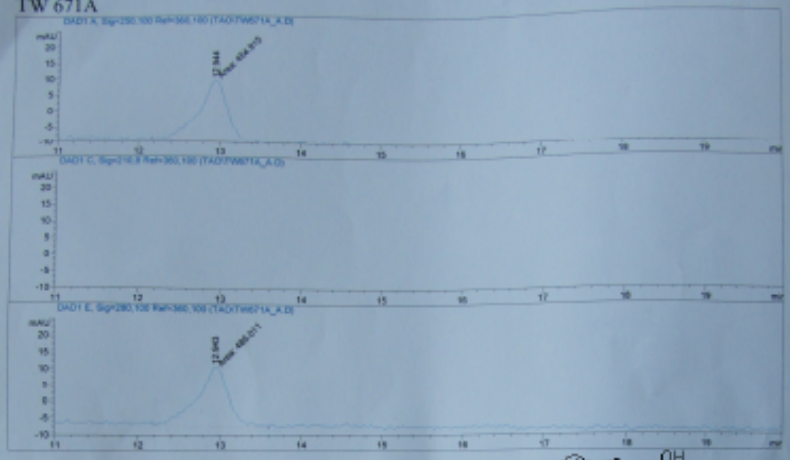
4l

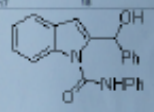

151.18
145.64
141.71
135.90
133.98
131.01
129.48
129.26
129.00
128.31
127.99
127.08
123.80
123.31
121.75
113.14
96.86
66.28
54.43
54.22
54.00
53.78
53.57
24.30
Ph
N
N
Ph
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

4l

IB, 90% Hexan, 10% 2-Propanol

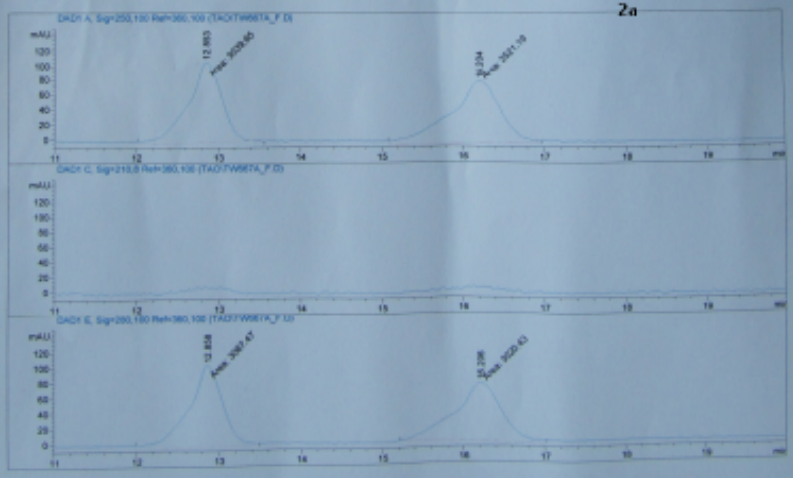
TW 671A



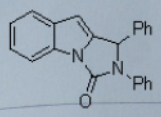


2a

TW 667A



Column: IB, 85% n-Hexan, 15% 2-Propanol



4a

TW 664B