Catalyst-free hydroarylation of *in situ* generated *ortho*-Quinone methide (*o*-QM) with electron rich arenes in water

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Supporting Information

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General information

Reagent grade solvents were used for extraction and flash chromatography. All the reagents and chemicals were purchased from Sigma-Aldrich Chemical Co, Lancaster and were used directly without further purification.The progress of reactions was checked by analytical thin-layer chromatography (TLC, Merck silica gel 60 F-254 plates). The plates were visualized first with UV illumination followed by iodine. Flash column chromatography was performed using silica gel (100-200 mesh). ^{1}H-NMR spectra were recorded at either 200 or 300 MHz and are reported in parts per million (ppm) on the δ scale relative to tetramethylsilane as an internal standard.^{13}C-NMR spectra were recorded at either 50 or 75 MHz and are reported in parts per million (ppm) on the δ scale relative to $CDCl_3$ (δ 77.00). Mass spectra were obtained using JEOL SX-102 (ESI) instrument.

General procedure for the preparation of C3-alkylated 4-hydroxycoumarin (4a-h)

4-Hydroxycoumarin (1 mmol), formaldehyde (2 mmol) and *N*,*N*-dimethylaniline (1 mmol) in 5 mL of 2.5 M aq solution of LiCl were taken in a round-bottom flask equipped with a magnetic stirrer. The reaction mixture was then stirred at room temperature for an appropriate time given in Table 3 and the progress of the reaction was monitored by

TLC. After completion of the reaction, the reaction mixture was extracted with ethyl acetate. Evaporation of the solvent gave a crude product which was purified by column chromatography (silica gel, ethyl acetate:hexane).

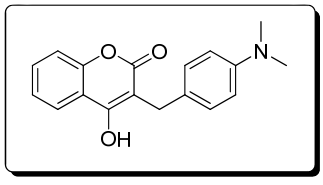
General procedure for the preparation of C3-alkylated 4-hydroxypyrone (7a-d).

4-Hydroxypyrone (1 mmol), formaldehyde (2 mmol) and *N,N*-dimethylaniline (1 mmol) in 5 mL of 2.5 M aq solution of LiCl were taken in a round-bottom flask equipped with a magnetic stirrer. The reaction mixture was then stirred at room temperature for an appropriate time given in Table 4 and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with ethyl acetate. Evaporation of the solvent gave a crude product which was purified by column chromatography (silica gel, ethyl acetate:hexane).

General procedure for the preparation of C3-alkylated 2-phenylindole (9a-f)

2-phenylindole (1 mmol), formaldehyde (2 mmol) and *N,N*-dimethylaniline (1 mmol) in 5 mL of 2.5 M aq solution of LiCl were taken in a round-bottom flask equipped with a magnetic stirrer. The reaction mixture was then stirred at room temperature for an appropriate time given in Table 5 and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with ethyl acetate. Evaporation of the solvent gave a crude product which was purified by column chromatography (silica gel, ethyl acetate:hexane).

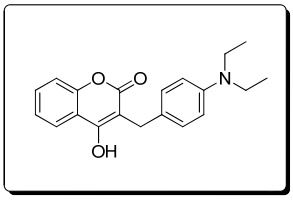
3-(4-(dimethyl-amino) benzyl)-4-hydroxy-2H-chromen-2-one: (**4a**)



Mp: 148-151 ^{0}C. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 2.85(s, 6H, -N(CH_3)$_2$, 3.86(s, 2H, -CH_2), 7.13(d, *J* = 8.3Hz, 2H, ArH), 7.18-7.25 (m, 4H, ArH), 7.40 (t, *J* = 8.6 Hz, 1H, ArH), 7.64 (d, *J* = 7.7

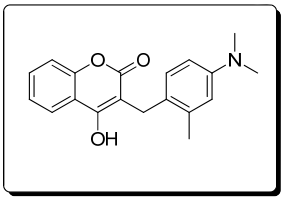
Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 29.7, 40.9, 102.9, 113.1, 116.2, 116.4, 123.7, 123.8, 128.5, 129.6, `131.4, 132.6, 134.9, 139.5, 144.1, 152.6,166.6; IR (cm^{-1}): 3764, 3416, 2926, 2367, 1613,1220, 768, 678; ESIMS: m/z 296 (M+H), calcd for $C_{18}H_{17}NO_3$ is C, 73.20; H, 5.80; N, 4.74. Found; C, 73.22; H, 5.81; N, 4.72.

3-(4-(diethylamino) benzyl)-4-hydroxy-2H-chromen-2-one: (4b)



Mp: 152-156 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.00 (t, *J* = 6.9 Hz, 6H, -N($CH_2\underline{CH_3}$)$_2$, 3.19 (q, *J* = 6.9 Hz, 4H,-N$\underline{CH_2}CH_3$)$_2$, 3.88 (s, 2H, -CH_2), 6.64 (d, *J* = 8.5 Hz, 2H, ArH), 7.13-7.22 (m, 4H, ArH), 7.73 (t, *J* = 7.1 Hz, 1H, ArH), 7.88 (d, *J* = 6.9 Hz, 1H, ArH). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 17.3, 33.1, 34.3, 49.2, 110.2, 117.1, 120.9, 121.6, 128.3, 128.4, 131.70, 134.0, 136.1, 150.6, 157.1, 165.2, 168.4; IR (cm^{-1}): 3762, 3572, 2929, 2365, 1665, 1656, 1619, 1106, 758, 670; ESIMS: m/z 324 (M+H), calcd for $C_{20}H_{21}NO_3$ is C, 74.28; H, 6.55; N, 4.33. Found; C, 74.26; H, 6.53; N, 4.31.

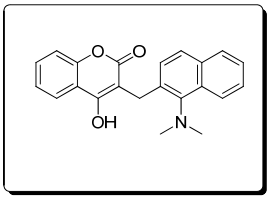
3-(4-(dimethylamino)-2-methylbenzyl)-4-hydroxy-2H-chromen-2-one: (4c)



Mp: 150-155 ^{0}C.^{1}H NMR (200 MHz, $CDCl_3$+DMSO-d_6) δ (ppm): 2.30 (s, 3H, -CH_3) 2.80 (s, 6H, -NCH_3)$_2$, 3.79 (s, 2H, -CH_2), 6.41 (d, *J* = 8.2 Hz, 1H, ArH), 6.54 (s, 1H, ArH), 6.86 (d, *J* = 8.2 Hz, 1H,

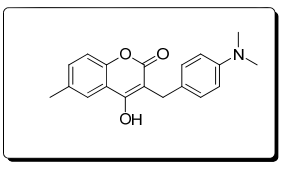
ArH), 7.17-7.24 (m, 2H, ArH), 7.41 (t, J = 7.1 Hz, 1H, ArH), 7.82 (d, J = 7.1 Hz, ArH). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 19.8, 28.6, 40.3, 102.7, 102.7, 115.2, 115.8, 116.1, 121.7, 122.6, 123.5, 129.6, 131.3, 138.3, 150.0, 152.2, 160.7, 163.5; IR (cm^{-1}): 3763, 3416, 2926, 2367, 1611, 1219, 767, 677; ESIMS: m/z 310 (M+H), calcd for $C_{19}H_{19}NO_3$ is C, 73.77; H, 6.19; N, 4.53. Found; C, 73.76; H, 6.17; N, 4.52

3-((1-(dimethylamino) naphthalen-2-yl) methyl)-4-hydroxy-2H-chromen-2-one: (4d)



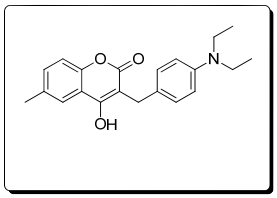
Mp: 170-173 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.88 (s, 6H, -NCH_3)$_2$, 4.36 (s, 2H, -CH_2), 6.97 (d, J = 7.5 Hz, 1H, ArH), 7.18-7.32 (m, 2H, ArH), 7.40-7.52 (m, 4H, ArH), 7.64-7.66 (m, 1H, ArH), 7.98-8.01 (m,1H, ArH), 8.25-8.28 (m, 1H ArH). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 31.1, 49.8, 99.7, 107.3, 118.2, 120.8, 121.2, 128.1, 128.1, 128.2, 128.8, 129.1, 129.4, 130.3, 133.6, 133.6, 136.0, 137.9, 154.1, 157.2, 166.5, 168.7; IR (cm^{-1}): 3775, 3408, 3010, 2936, 2365, 1608, 1218, 767, 670; ESIMS: m/z 347 (M+H), calcd for $C_{22}H_{19}NO_3$ is C, 76.50; H, 5.54; N, 4.06; Found; C, 76.51; H, 5.52; N, 4.05.

3-(4-(dimethylamino) benzyl)-4-hydroxy-6-methyl-2H-chromen-2-one: (4e)



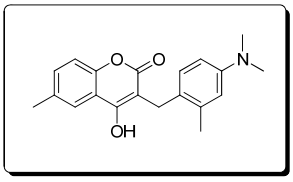
Mp: 148-150 ^{0}C.^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 2.30 (s, 3H, -CH_3), 2.86 (s, 6H, -N(CH_3)$_2$), 3.87(s, 2H, -CH_2), 6.65 (d, *J* = 8.5 Hz, 2H, ArH), 7.13-7.26 (m, 4H, ArH), 7.40-7.48 (m, 1H, ArH), . IR (cm^{-1}): 3771, 3420, 2927, 2364, 1889, 1720, 1663, 1219, 771, 677; ESIMS: m/z 310 (M+H), calcd for $C_{19}H_{19}NO_3$ is C, 73.77; H, 6.19; N, 4.53. Found; C, 73.77; H, 6.19; N, 4.53.

3-(4-(diethylamino) benzyl)-4-hydroxy-6-methyl-2H-chromen-2-one: (4f)



Mp: 146-150 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6) δ (ppm): 0.97 (t, *J* = 6.1 Hz, 6H, -N(CH_2<u>CH_3</u>)$_2$, 2.26(s, 3H, CH_3), 3.16 (q, *J* = 6.5 Hz, 4H,-N<u>CH_2</u>CH_3)$_2$, 3.75 (s, 2H, -CH_2), 6.43 (d, *J* = 7.1 Hz, 2H, ArH),7.00-7-12 (m, 3H, ArH), 7.42 (s, 1H, ArH),7.75 (s, 1H, ArH), ^{13}C NMR (75 MHz,$CDCl_3$+ DMSO-d_6) δ (ppm): 17.2, 25.7, 33.3, 49.2, 108.3, 117.1, 120.4, 123.8, 128.7, 133.4, 134.1, 136.1, 137.1, 150.6, 155.6, 170.4; IR (cm^{-1}): 3762, 3571, 2928, 2366, 1657, 1620, 1108, 758, 653; ESIMS: m/z 338 (M+H), calcd for $C_{21}H_{23}NO_3$ is C, 74.75; H, 6.87; N, 4.15. Found; C, 74.74; H, 6.86; N, 4.16.

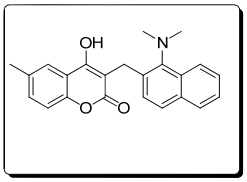
3-(4-(dimethylamino)-2-methylbenzyl)-4-hydroxy-6-methyl-2H-chromen-2-one: (4g)



Mp: 150-155 ^{0}C.^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 2.29 (s, 3H, -CH_3), 2.33 (s, 3H, -CH_3), 2.80 (s, 6H, -N(CH_3)$_2$), 3.73 (s, 2H, -CH_2), 6.39-6.51 (m, 2H, ArH), 6.74 (d, *J* = 8.3 Hz, 1H, ArH), 7.07-7.36

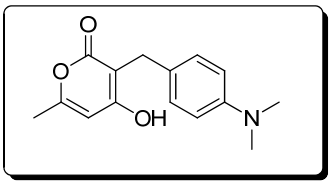
(m, 2H, ArH), 7.64-7.65 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$+ DMSO-d_6) δ (ppm): 24.7, 25.4, 30.9, 41.4, 108.2, 115.2, 119.7, 120.5, 127.5, 129.8, 132.1, 136.7, 137.6, 141.6, 155.2, 165.6; IR (cm^{-1}): 3764, 3415, 2928, 2366, 1612, 1219, 768, 677; ESIMS: m/z 325 (M+H), calcd for $C_{20}H_{21}NO_3$ is C, 74.28; H, 6.55; N, 4.33 Found; C, 74.27; H, 6.53; N, 4.32.

3-((1-(dimethylamino) naphthalen-2-yl) methyl)-4-hydroxy-6-methyl-2H-chromen-2-one: (4h)



Mp: 170-172 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.33 (s, 3H, -CH_3), 2.84 (s, 6H, -$NCH_3)_2$, 4.27 (s, 2H, -CH_2), 6.92 (d, *J* = 7.5 Hz, 1H, ArH), 7.19 (d, *J* = 5.6 Hz, 1H, ArH), 7.25-7.32 (m, 2H, ArH), 7.42-7.48 (m, 3H, ArH), 7.97 (d, *J* = 7.5 Hz, 1H, ArH), 8.24 (d, *J* = 7.5 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 20.6, 28.1, 44.9, 102.7, 113.2, 115.3, 115.9, 122.4, 124.2, 124.6, 125.2, 125.4, 126.3, 127.7, 129.2, 132.5, 132.8, 133.3, 150.4, 150.7, 161.6, 163.8; IR (cm^{-1}): 3775, 34510, 3012, 2936, 2366, 1609, 1218, 767, 671; ESIMS: m/z 360 (M+H), calcd for $C_{23}H_{21}NO_3$ is C, 76.86; H, 5.89; N, 3.90 Found; C, 76.85; H, 5.87; N, 3.91.

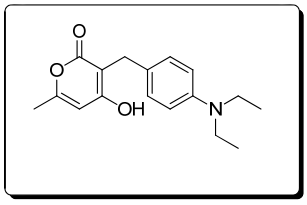
3-(4-(dimethylamino) benzyl)-4-hydroxy-6-methyl-2H-pyran-2-one: (7a)



Mp: 140-142 ^{0}C.^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 2.15 (s, 3H, -CH_3, 2.91 (s, 6H, -$N(CH_3)_2$), 3.75 (s, 2H, -CH_2), 5.99 (s, 1H, ArH), 6.68 (d, *J* = 8.7 Hz, 2H, ArH), 7.23-7.30 (m, 2H, ArH). ^{13}C NMR

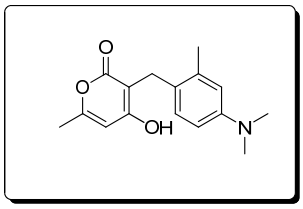
(75 MHz, $CDCl_3$) δ (ppm): 27.5, 29.2, 40.6, 102.1, 102.1, 112.9, 127.9, 128.8, 148.5, 159.6, 166.5, 167.0; IR (cm^{-1}): 3762, 3573, 2926, 2365, 1878, 1666, 1583, 770, 772; ESIMS: m/z 260 (M+H), calcd for $C_{15}H_{17}NO_3$ is C, 69.48; H, 6.61; N, 5.40.Found; C, 69.47; H, 6.60; N, 5.41.

3-(4-(diethylamino)benzyl)-4-hydroxy-6-methyl-2H-pyran-2- one: (7b)



Mp: 135-140 ^{0}C.^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 0.93 (t, *J* = 7.1 Hz, 6H, -N($CH_2\underline{CH_3}$)$_2$), 1.98 (s, 3H, -CH_3), 3.13 (q, *J* = 6.9 Hz, 4H, -N($\underline{CH_2}CH_3$)$_2$), 3.60 (s, 2H, -CH_2), 5.91 (s, 1H, ArH), 6.54 (d, *J* = 8.6 Hz, 2H, ArH), 7.11 (s, 2H, ArH) . ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 12.1, 19.6, 28.0, 46.3, 101.8, 102.8, 114.2, 129.7, 143.6, 159.6, 167.8, 169.6; IR (cm^{-1}): 3777, 3693, 3020, 2928, 2363, 1661, 1587, 1405, 1217, 767, 671; ESIMS: m/z 288 (M+H), calcd for $C_{17}H_{21}NO_3$ is C, 71.06; H, 7.37; N, 4.87. Found; C, 71.04; H, 7.36; N, 4.84.

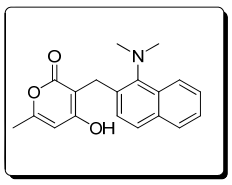
3-(4-(dimethylamino)-2-methylbenzyl)-4-hydroxy-6-methyl-2H-pyran-2-one: (7c)



Mp: 150-152 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.13 (s, 3H, -CH_3), 2.32 (s, 3H, -CH_3), 2.82 (s, 6H, -N (CH_3)$_2$), 3.58 (s, 2H, -CH_2), 5.89 (s, 1H, ArH), 6.43-6.50 (m, 2H, ArH), 6.94 (d, *J* = 8.2 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 24.5, 24.8, 30.1, 34.3, 47.7, 105.1, 105.2, 118.1, 122.2,

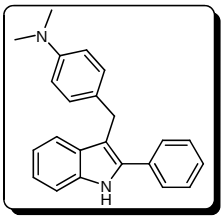
133.6, 136.8, 142.1, 150.5, 164.7, 170.5, 171.0; IR (cm^{-1}): 3773, 3406, 2928, 2362, 1812, 1666, 1583, 769, 678**;** ESIMS: m/z 274 (M+H), calcd for $C_{16}H_{19}NO_3$ is C, 70.31; H, 7.01; N, 5.12. Found; C, 70.30; H, 7.03; N, 5.10.

3-((1-(dimethylamino) naphthalen-2-yl) methyl)-4-hydroxy-6-methyl-2H-pyran-2-one: (7d)



Mp: 160-162 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.12 (s, 3H, $-CH_3$), 2.79 (s, 6H, $-N(CH_3)_2$), 4.09 (s, 2H, $-CH_2$), 5.89 (s, 1H, ArH), 6.91 (d, *J* = 7.6 Hz, 1H, ArH), 7.16 (d, *J* = 7.6 Hz, 1H, ArH), 7.40-7.45 (m, 2H, ArH), 8.20-8.23 (m, 2H, ArH). IR (cm^{-1}): 3777, 3409, 3012, 2936, 2366, 1612, 1220, 768, 671; ESIMS: m/z 310 (M+H), calcd for $C_{19}H_{19}NO_3$ is C, 73.77; H, 6.19; N, 4.53. Found; C, 73.76; H, 6.20; N, 4.54.

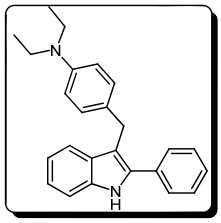
***N,N*-dimethyl-4-((2-phenyl-1H-indol-3-yl)methyl)aniline: (9a)**



Mp: 175-176 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.91 (s, 6H, $-NCH_3)_2$, 4.45 (s, 2H, $-CH_2$), 6.89 (d, *J* = 8.4 Hz, 2H, ArH), 7.11-7.32 (m, 4H, ArH), 7.35-7.59 (m, 7H, ArH), 8.13 (s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 29.4, 41.1, 110.7, 111.9, 113.2, 119.7, 119.8, 122.3, 127.6, 127.8, 128.8,

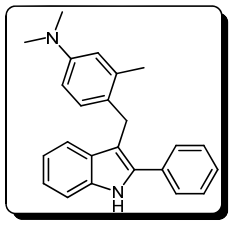
128.8. 129.6, 130.0, 133.1, 135.2, 136.1, 148.8; IR (cm^{-1}): 3375, 2922, 2845, 1413, 765; ESIMS: m/z 327 (M+H), calcd for $C_{23}H_{22}N_2$ is C, 84.63; H, 6.79; N, 8.58. Found; C, 84.61; H, 6.80; N, 8.59.

***N,N*-diethyl-4-((2-phenyl-1H-indol-3-yl)methyl)aniline: (9b)**



Mp: 192-194 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.06 (t, *J* = 7.0 Hz, 6H, -N($CH_2\underline{CH_3}$)$_2$), 3.25 (q, *J* = 7.0 Hz, 4H, -N($\underline{CH_2}CH_3$)$_2$), 4.10 (s, 2H, -CH_2), 6.55 (d, *J* = 8.4 Hz, 2H, ArH), 7.02 (d, *J* = 8.4 Hz, 3H, ArH), 7.15-7.11 (m, 1H, ArH), 7.28-7.36 (m, 3H, ArH), 7.42 (d, *J* = 7.2 Hz, 1H, ArH), 7.47(d, *J* = 7.8 Hz, 3H, ArH), 8.01(s, 1H, NH) .^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 12.9, 29.7, 45.2, 111.1, 112.5, 113.1, 120.1, 120.2, 122.7, 128.0, 128.2, 129.2, 129.4, 130.1, 133.5, 135.5, 136.4; IR (cm^{-1}): 3265, 2855, 3020, 2928, 1415, 755; ESIMS: m/z 355 (M+H), calcd for $C_{25}H_{26}N_2$ is C, 84.70; H, 7.39; N, 7.90 Found; C, 84.69; H, 7.37; N, 7.91

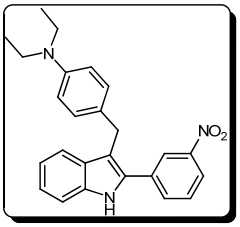
***N,N*,3-trimethyl-4-((2-phenyl-1H-indol-3-yl)methyl)aniline: (9c)**



Mp: 185-188 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.26 (s, 3H,-CH_3), 2.79 (s, 6H, -N(CH_3)$_2$), 3.99 (s, 2H, -CH_2), 6.36-6.23 (m, 1H, ArH), 6.57-6.56 (br, 1H, ArH), 6.77 (d, *J* =

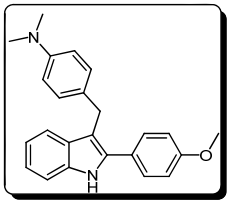
8.4 Hz, 1H, ArH),6.98 (t, *J* = 7.5 Hz, 1H, ArH), 7.19-7.07(m, 2H, ArH), 7.36-7.22(m, 4H, ArH), 7.39(d, *J* = 1.4 Hz, 2H, ArH), 8.04(s, 1H, NH). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 20.5, 29.9, 41.4, 110.9, 111.6, 115.1, 119.8, 120.0, 122.5, 127.7, 127.8, 127.9, 128.9, 129.0, 130.1, 133.2, 125.5, 136.3, 136.8, 149.2; IR (cm^{-1}): 3206, 2925, 2856, 1453, 739, 692; ESIMS: m/z 341 (M+H), calcd for $C_{24}H_{24}N_2$ is C, 84.67; H, 7.11; N, 8.23. Found; C, 84.66; H, 7.12; N, 8.25.

***N,N*-diethyl-4-((2-(3-nitrophenyl)-1H-indol-3-yl)methyl)aniline: (9d)**



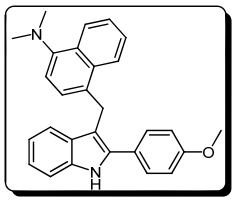
Mp: 180-184 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.16 (t, *J* = 6.9 Hz, 6H, -N($CH_2\underline{CH_3}$)$_2$), 3.35 (q, *J* = 6.8 Hz, 4H, -N($\underline{CH_2}CH_3$)$_2$), 4.20 (s, 2H, -CH_2), 6.63 (d, *J* = 7.5 Hz, 2H, ArH), 7.30-7.07 (m, 5H, ArH), 7.87-7.43 (m, 3H, ArH), 8.23-8.16 (m, 2H, ArH), 8.43-8.42 (br, 1H, NH). IR (cm^{-1}): 3225, 2939, 2846, 1443, 755, 682; ESIMS: m/z 400 (M+H), calcd for $C_{25}H_{25}N_3O_2$ is C, 75.16; H, 6.31; N, 10.52. Found; C, 75.17; H, 6.32; N, 10.50.

4-((2-(4-methoxyphenyl)-1H-indol-3-yl)methyl)-*N,N*-dimethylaniline: (9e)



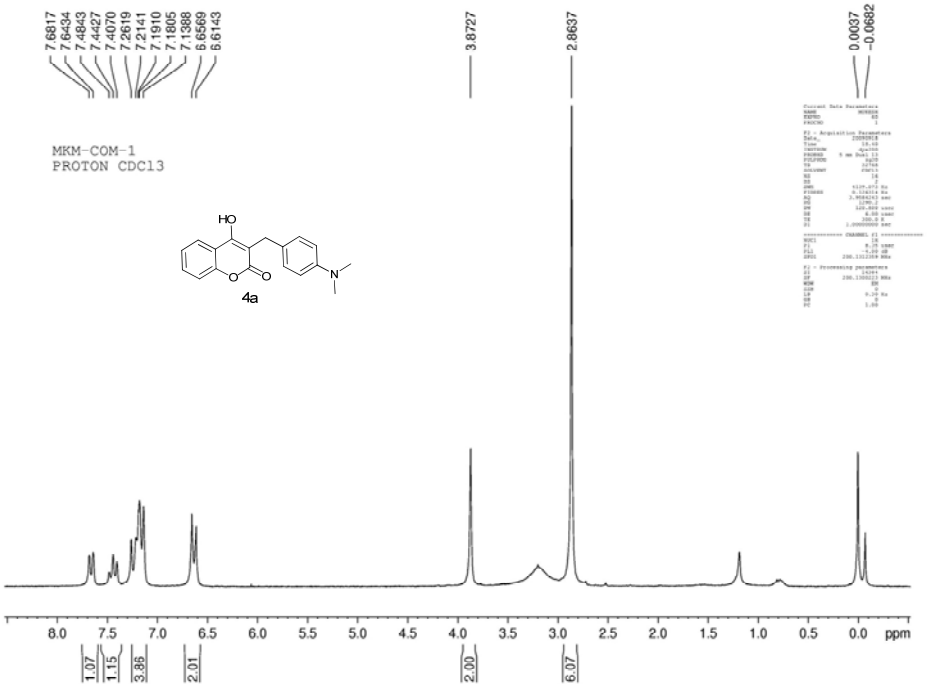
Mp: 197-199 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.89 (s, 6H, -N(CH_3)$_2$), 3.83 (s, 3H, OCH_3), 4.15 (s, 2H, -CH_2), 6.69 (d, *J* = 8.6 Hz, 2H, ArH), 6.96 (d, *J* = 8.7 Hz, 2H, ArH), 7.20-7.03 (m, 4H, ArH), 7.37 (d, *J* = 7.9 Hz, 1H, ArH), 7.47-7.44 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 29.7, 41.4, 55.8, 111.0, 111.5, 113.6, 114.7, 119.9, 120.0, 122.4, 126.1, 129.2, 129.5, 130.2, 130.4, 135.5, 136.3, 149.3, 159.6; IR (cm^{-1}): 3209, 3012, 2827, 2251, 1156, 756; ESIMS: m/z 357 (M+H), calcd for $C_{24}H_{24}N_2O$ is C, 80.87; H, 6.79; N, 7.86. Found; C, 80.85; H, 6.80; N, 7.87.

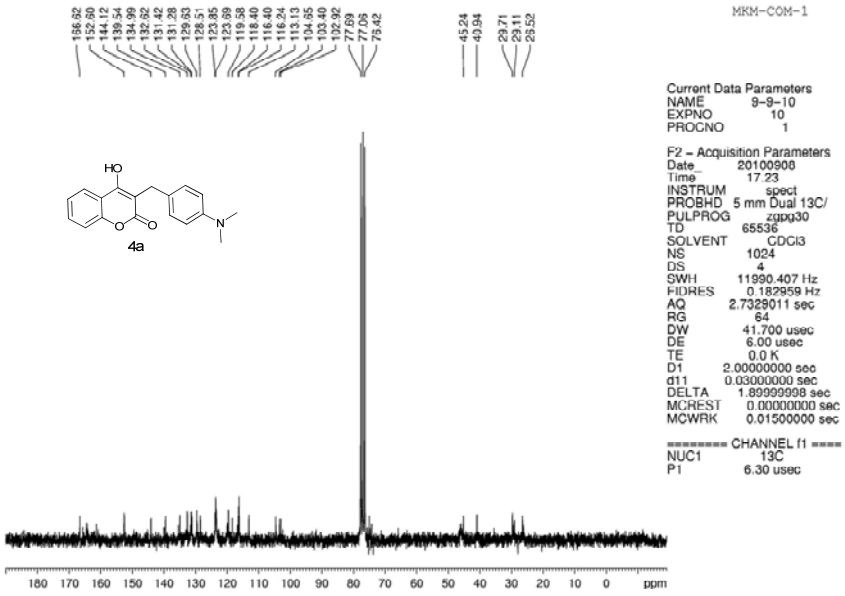
4-((2-(4-methoxyphenyl)-1H-indol-3-yl)methyl)-*N*,*N*-dimethylnaphthalen-1-amine: (9f)



Mp: 225-230 ^{0}C.^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.76 (s, 6H, -N(CH_3)$_2$), 3.68(s, 3H, OCH_3), 4.49 (s, 2H, -CH_2), 6.80 (d, *J* = 8.5 Hz, 3H, ArH),6.97-6.92(m, 2H, ArH), 7.15-7.08 (m, 1H, ArH), 7.33-7.28 (m, 3H, ArH), 7.47-7.43 (m, 2H, ArH), 8.11-8.04 (m, 2H, ArH), 8.27-8.25 (m, 1H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 26.7, 44.8, 54.7, 109.0, 110.1, 113.5, 113.8, 118.9, 119.1, 121.5, 123.3, 124.2, 124.3, 124.7, 124.8, 125.1, 128.2, 128.5, 129.2, 130.6, 132.6, 135.1, 135.4, 158.7; IR (cm^{-1}): 3460, 3020, 2927, 2361, 1216, 765, 735; ESIMS: m/z 407 (M+H), calcd for $C_{28}H_{26}N_2O$ is C, 82.73; H, 6.45; N, 6.89. Found; C, 82.71; H, 6.46; N, 6.88.

^{1}H NMR and ^{13}C NMR Spectra for Spectroscopic Data of C3-alkylated 4-hydroxycoumarin, 4-hydroxypyrone and 2-phenylindole.

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144.12
139.54
134.99
132.82
131.42
131.28
129.63
128.51
123.85
123.69
119.58
118.40
116.40
116.24
113.13
104.85
103.40
102.92
77.69
77.05
76.42
45.24
43.94
29.71
29.11
29.52
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PROCNO 1
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Time 17.23
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 11990.407 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 64
DW 41.700 usec
DE 6.00 usec
TE 0.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ====
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O
O
N
4a
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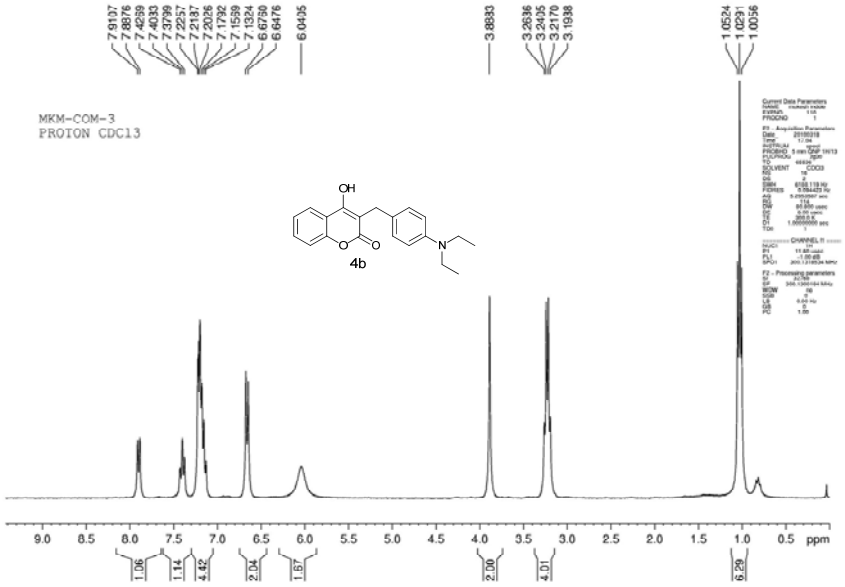
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7.4259
7.4033
7.3799
7.2257
7.2137
7.2026
7.1792
7.1559
7.1324
6.6479
6.6476
6.0495
3.8833
3.2636
3.2405
3.2170
3.1938
1.0524
1.0291
1.0056
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OH
O
O
N
4b
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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1.14
4.42
2.04
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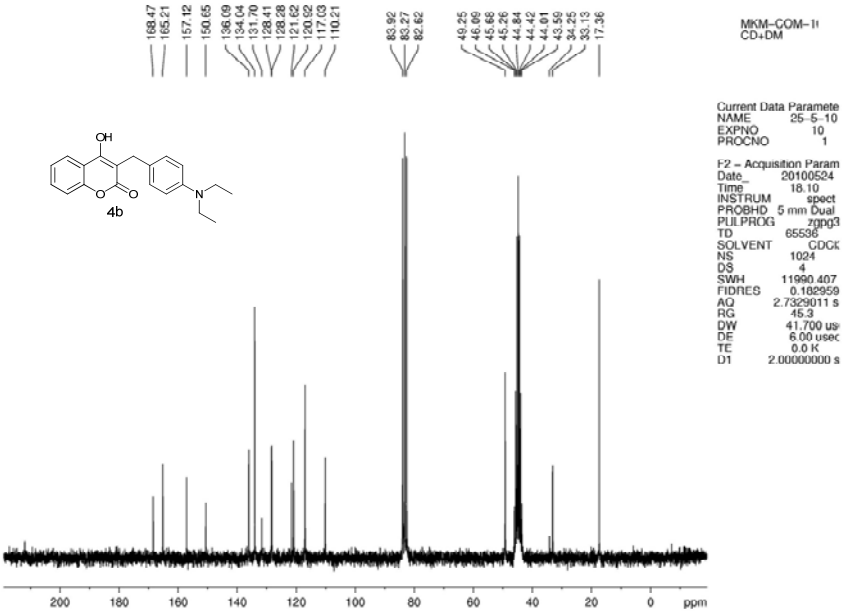
2.00
4.01
6.29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165.21
157.12
150.65
136.09
134.04
131.70
128.41
128.28
121.62
120.92
117.03
110.21
63.92
63.27
62.62
49.25
46.66
45.66
45.26
44.84
44.42
44.01
43.59
34.25
33.13
17.36
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NS 1024
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FIDRES 0.182959
AQ 2.7329011 s
RG 45.3
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DE 6.00 usec
TE 0.0 K
D1 2.00000000 s
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140
120
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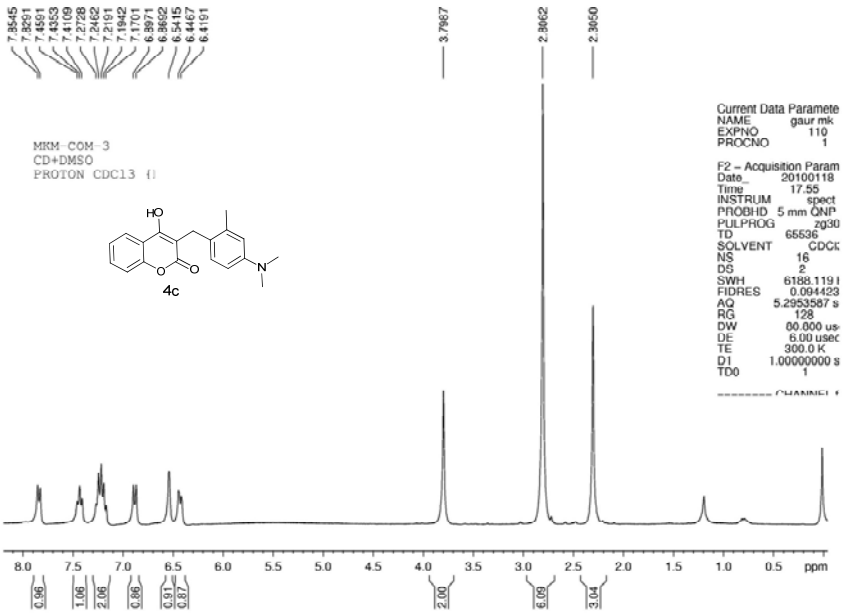
40
20
0
ppm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7.4353
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7.2728
7.2462
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7.1942
7.1701
6.8971
6.8662
6.5415
6.4467
6.4191
3.7967
2.8962
2.3950
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CD+DMSO
PROTON CDCl3 (
HO
O
O
N
4c
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PROCNO 1
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Time 17.55
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PULPROG zg30
TD 65536
SOLVENT CDCl
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DS 2
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FIDRES 0.094423
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RG 128
DW 80.800 us
DE 6.00 usec
TE 300.0 K
D1 1.00000000 s
TD0 1
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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
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ppm
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2.06
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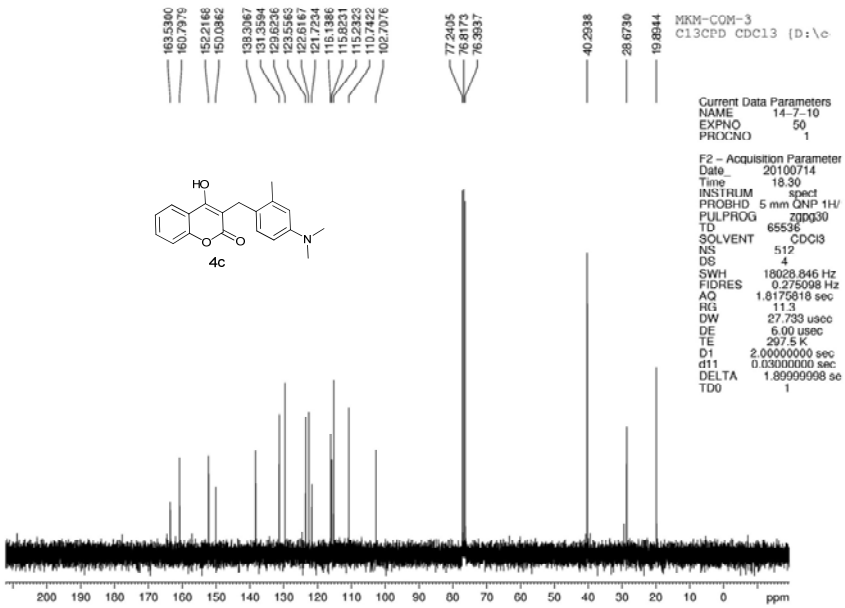
0.91
0.87
2.00
6.09
3.04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PROCNO 1
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Time 18.30
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
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FIDRES 0.275098 Hz
AQ 1.8175616 sec
RG 11.3
DW 27.733 usec
DE 6.00 usec
TE 297.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 se
TD0 1
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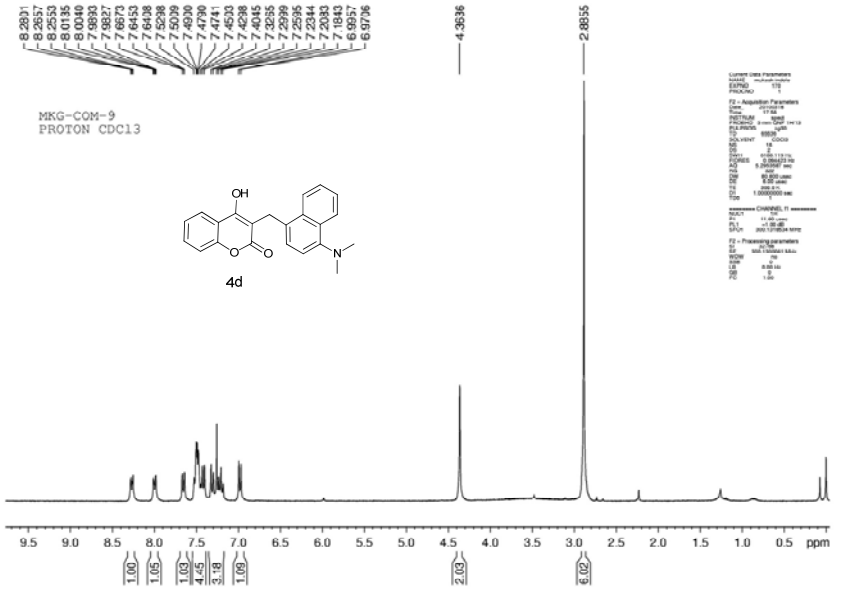
O
O
N
4c
ppm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N
4d
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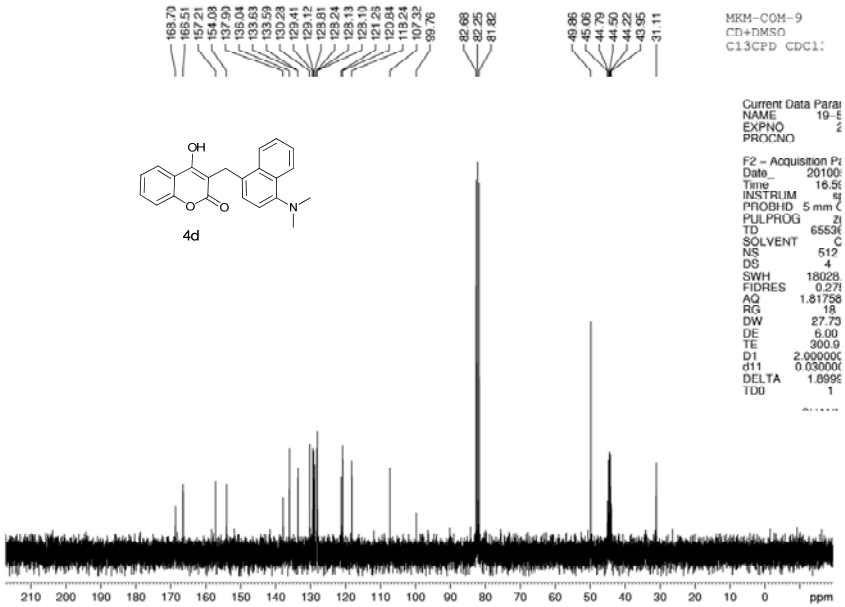
1.03
4.45
3.18
1.09
2.03
6.02
ppm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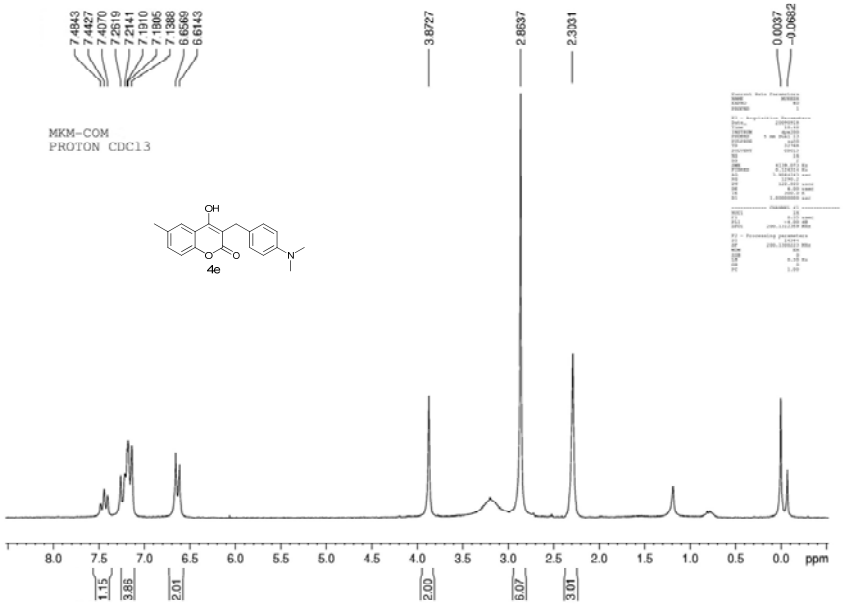
C13CPD CDCl3
4d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PROTON CDCl3
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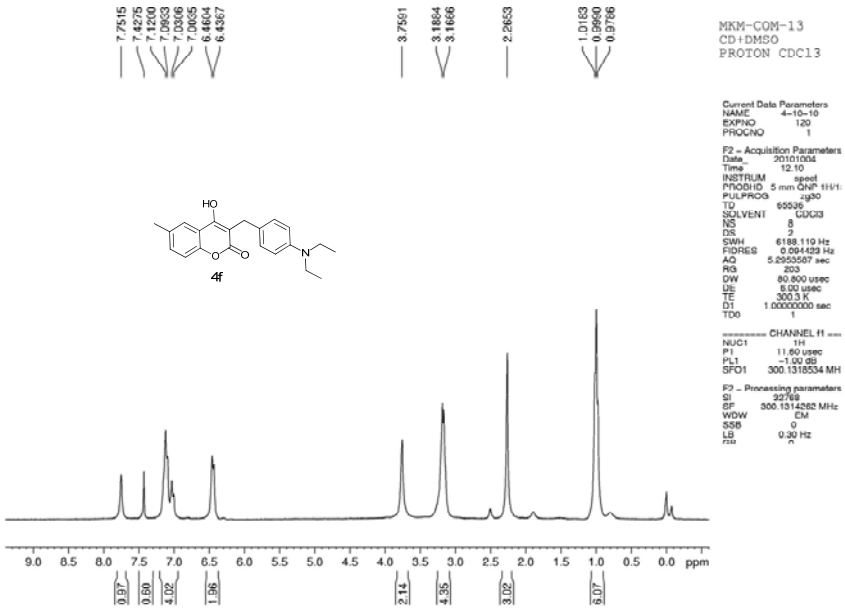
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7.0806
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3.1666
2.2653
1.0183
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PROTON CDC13
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O
O
N
4f
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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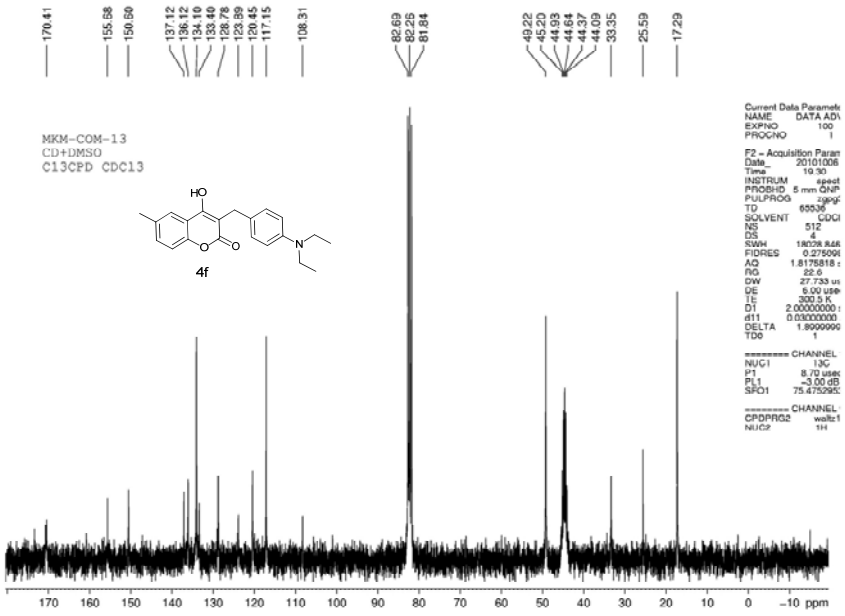
6.07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134.10
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117.15
108.31
82.69
82.25
81.84
49.22
45.20
44.93
44.64
44.37
44.09
33.35
25.59
17.29
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CD+DMSO
C13CPD CDC13
HO
O
O
N
4f
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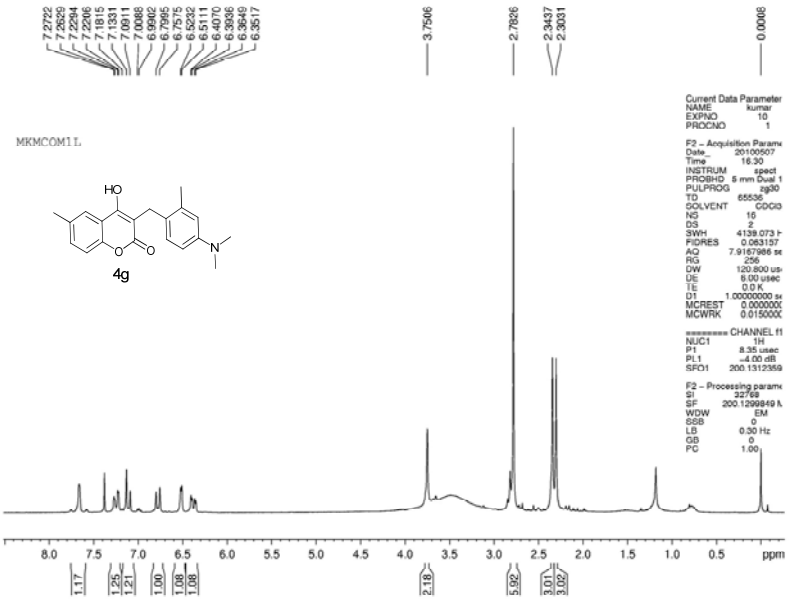
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7.2246
7.1815
7.1331
7.0911
7.0088
6.9902
6.7995
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6.5232
6.5111
6.4070
6.3936
6.3846
6.3517
3.7566
2.7826
2.3437
2.3031
0.0006
MKMCOM1L
HO
O
O
N
4g
Current Data Parameter
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EXPNO 10
PROCNO 1
F2 - Acquisition Param
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Time 16.30
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT CDCl3
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RG 256
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DE 6.00 usec
TE 0.0 K
D1 1.00000000 se
MCREST 0.000000
MCWRK 0.015000
CHANNEL f1
NUC1 1H
P1 8.35 usec
PL1 -4.00 dB
SFO1 200.1312359
F2 - Processing param
SI 32768
SF 200.1299849 M
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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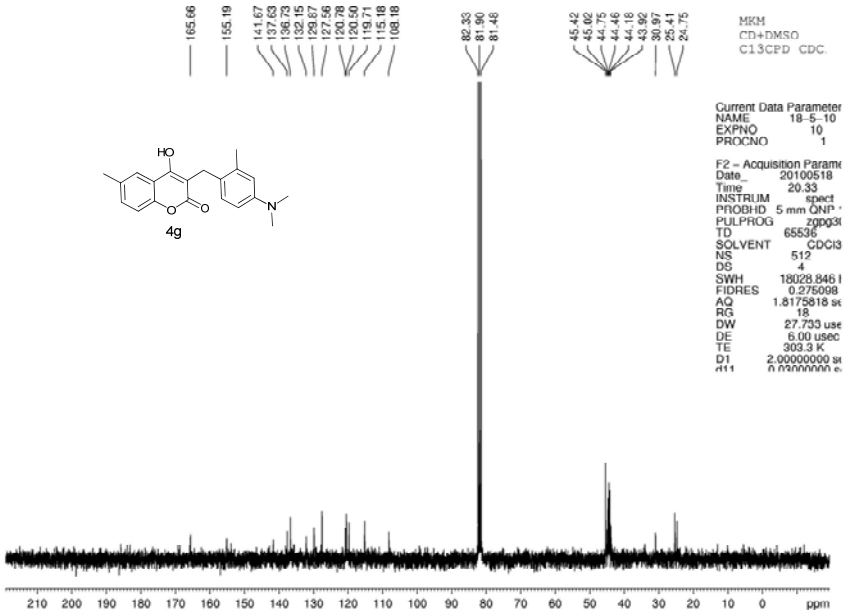
1.25
1.21
1.00
1.08
1.08
2.18
5.92
3.01
3.02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132.15
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127.56
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115.18
108.18
82.33
81.90
81.48
45.42
45.02
44.75
44.46
44.18
43.92
30.97
25.41
24.75
MKM
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C13CPD CDC.
HO
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4g
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Time 20.33
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SOLVENT CDCl3
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DE 6.00 usec
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D1 2.00000000 se
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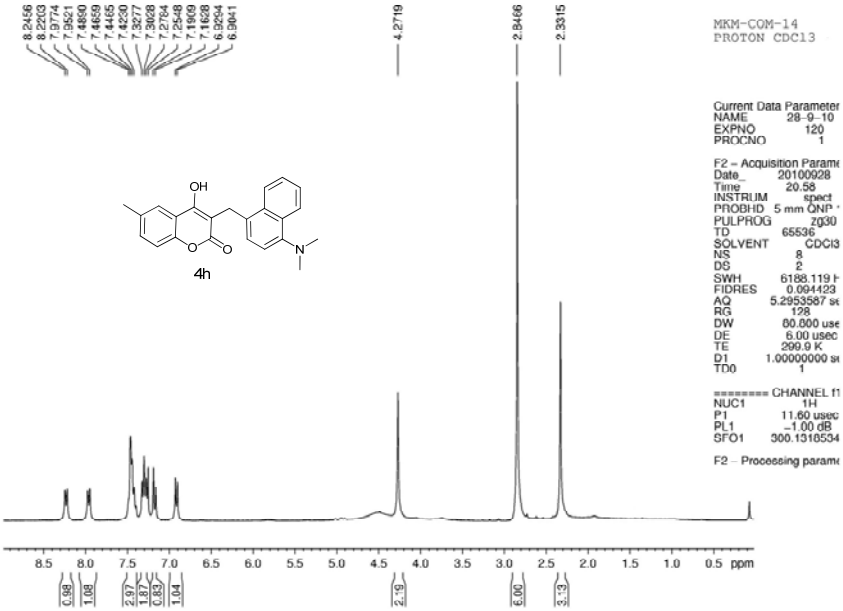
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7.1669
7.1458
6.9024
6.9041
4.2719
2.8466
2.3315
MKM-COM-14
PROTON CDCl3
OH
O
O
N
4h
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PROCNO 1
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TD 65536
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RG 128
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DE 6.00 usec
TE 299.9 K
D1 1.00000000 s
TD0 1
CHANNEL f1
NUC1 1H
P1 11.60 usec
PL1 -1.00 dB
SFO1 300.1316534
F2 - Processing parame
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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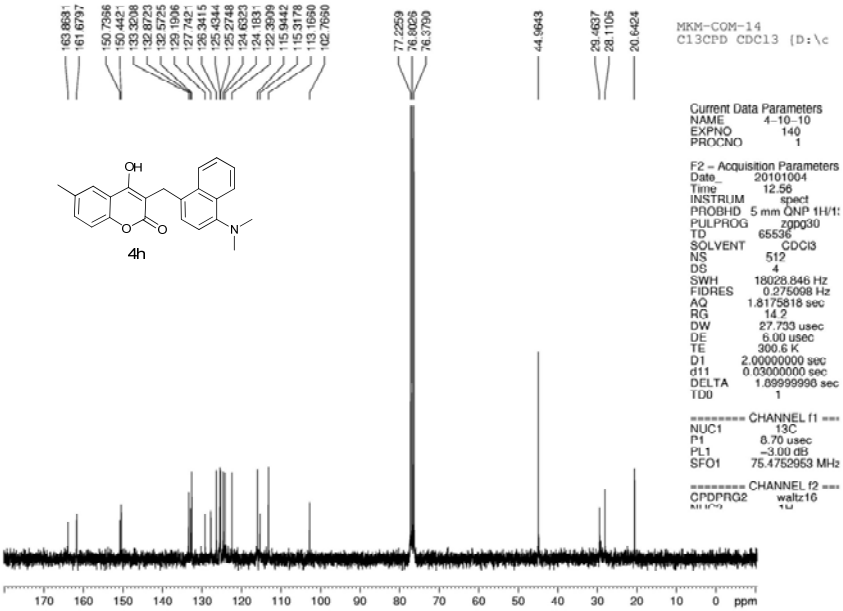
0.83
1.04
2.19
6.00
3.13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FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 14.2
DW 27.733 usec
DE 6.00 usec
TE 300.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz
CHANNEL f2
CPDPRG2 waltz16
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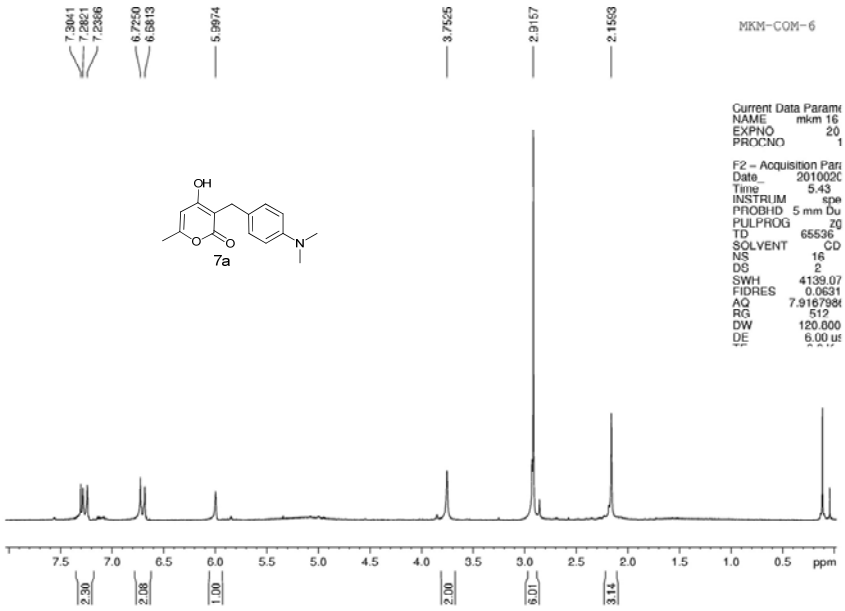
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7.2821
7.2366
6.7250
6.6813
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3.7525
2.9157
2.1563
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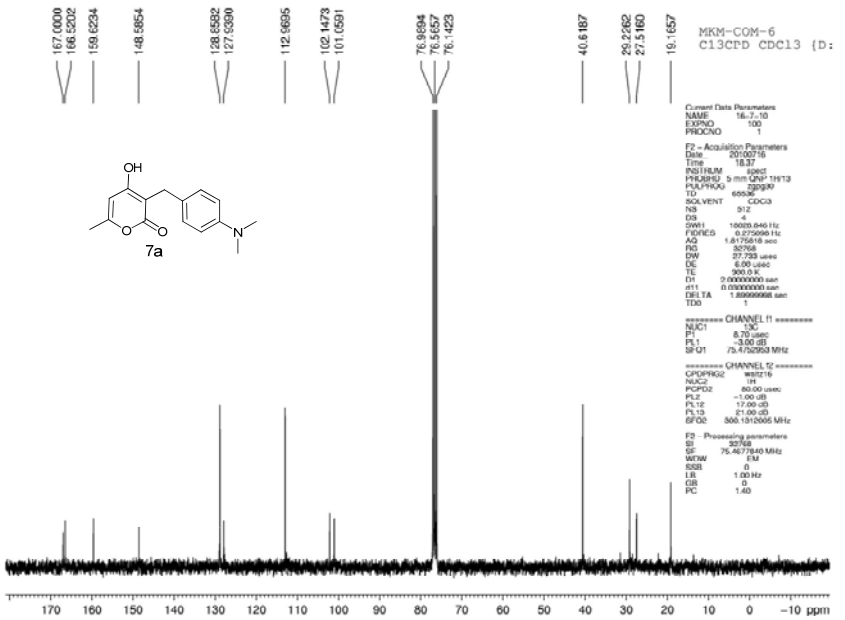
OH
O
O
N
7a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.30
2.08
1.00
2.00
6.01
3.14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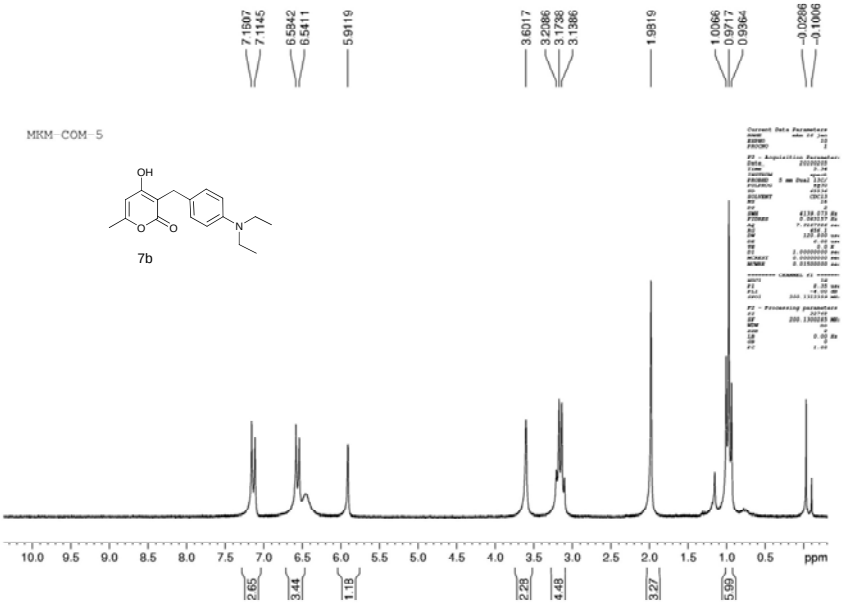
166.5202
159.6234
148.5654
128.6582
127.5390
112.9695
102.1473
101.0591
76.9894
76.5657
76.1423
40.6187
29.2262
27.5160
19.1657
MKM-COM-6
C13CPD CDCl3 {D:
OH
O
O
N
7a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10 ppm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6.5842
6.5411
5.9119
3.6017
3.2086
3.1738
3.1386
1.9819
1.0066
0.9717
0.9364
-0.0286
-0.1006
MKM-COM-5
OH
O
O
N
7b
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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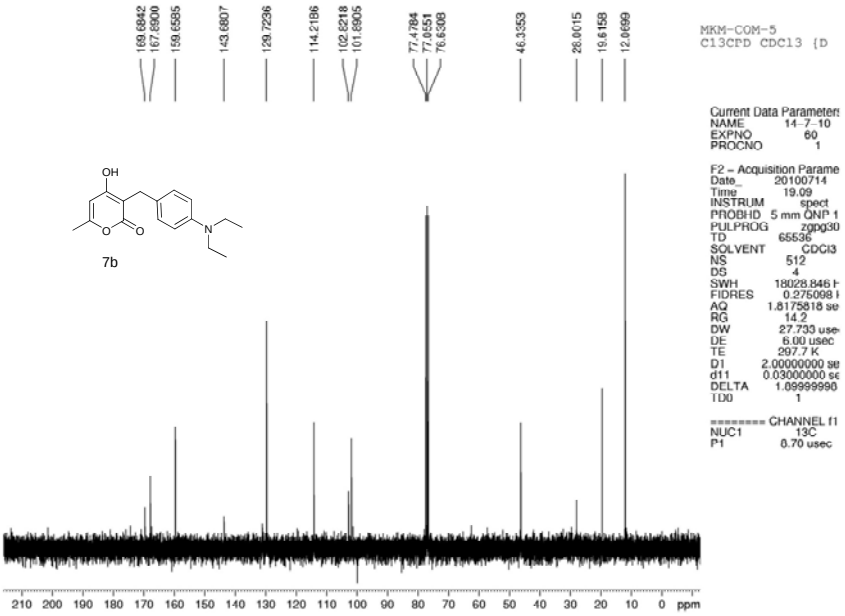
3.44
1.18
2.28
4.48
9.27
5.99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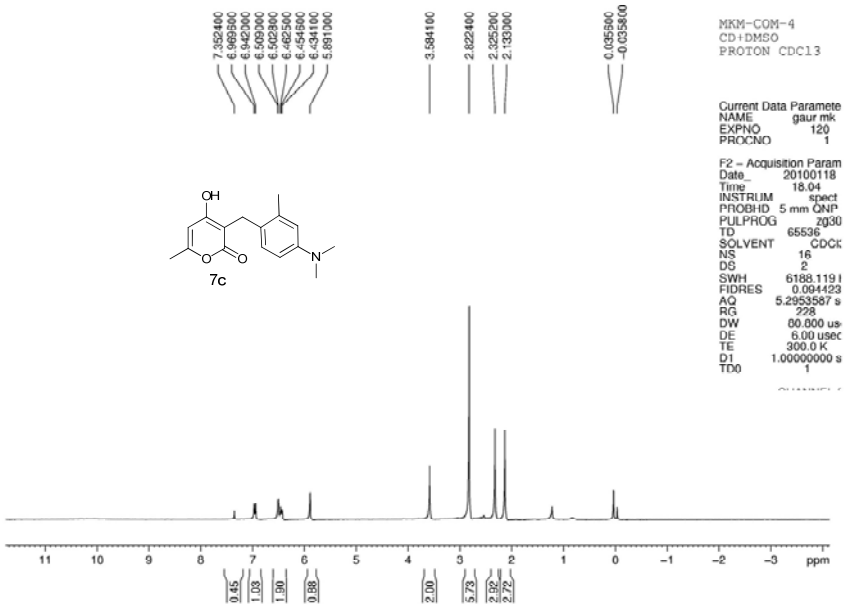
129.7236
114.2186
102.8218
101.8905
77.4784
77.0551
76.6308
46.3353
26.0015
19.6158
12.0699
MKM-COM-5
C13CPD CDCl3 {D
Current Data Parameters
NAME 14-7-10
EXPNO 60
PROCNO 1
F2 - Acquisition Parame
Date_ 20100714
Time 19.09
INSTRUM spect
PROBHD 5 mm QNP 1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 18028.846 H
FIDRES 0.275098 H
AQ 1.8175818 se
RG 14.2
DW 27.733 use
DE 6.00 usec
TE 297.7 K
D1 2.00000000 se
d11 0.03000000 se
DELTA 1.09999990
TD0 1
======== CHANNEL f1
NUC1 13C
P1 0.70 usec
OH
O
O
N
7b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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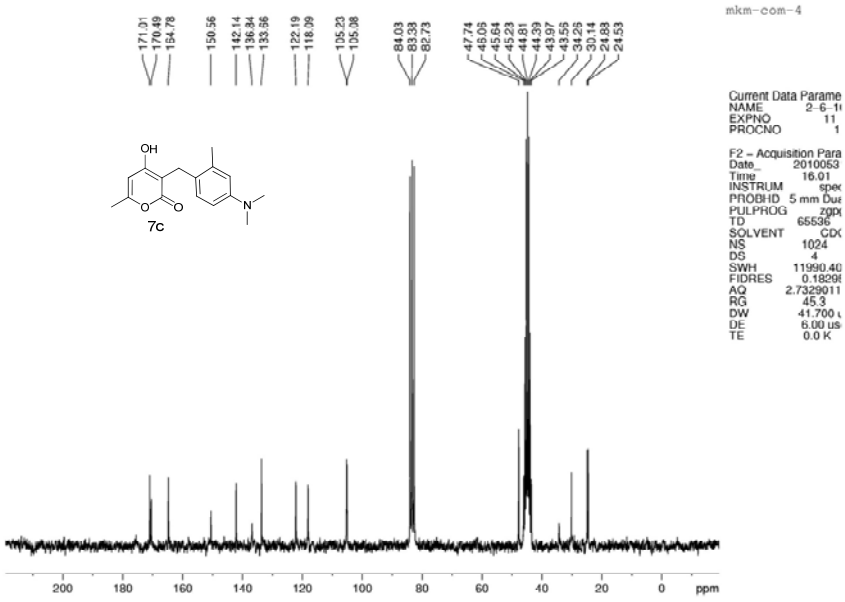
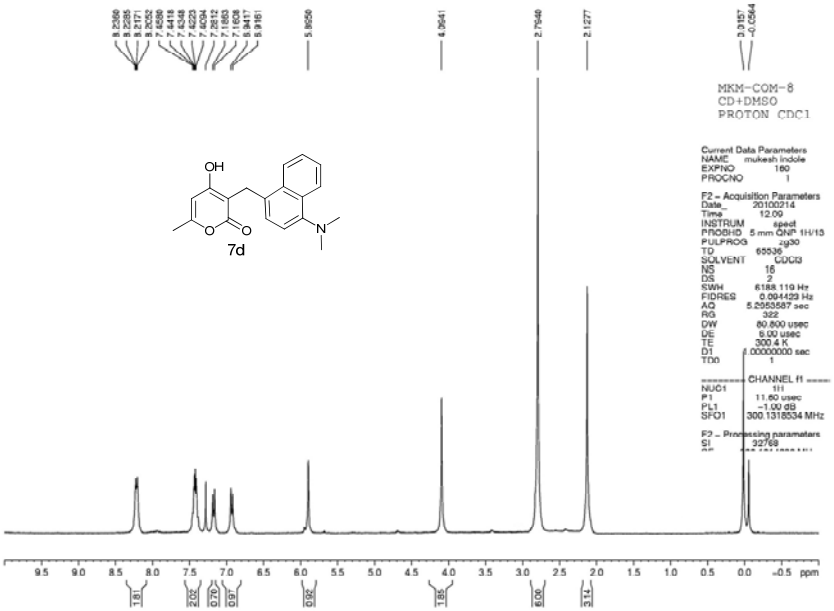
CD+DMSO
PROTON CDC13
OH
O
O
N
7c
ppm


mkm-com-4
OH
O
O
N
7c
ppm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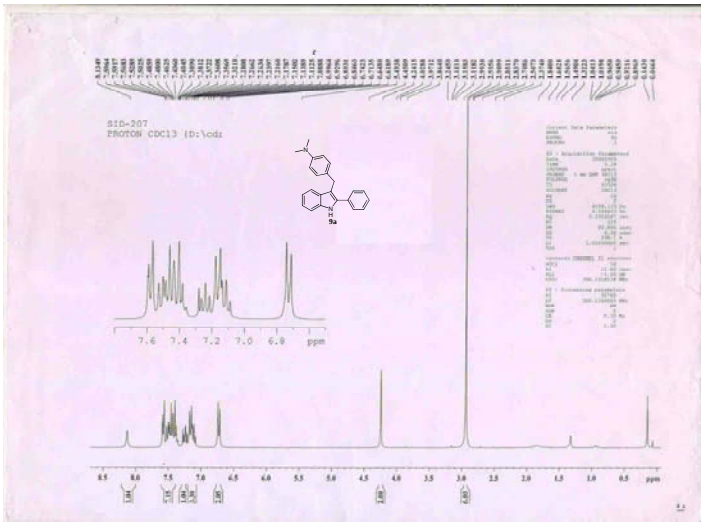
CD+DMSO
PROTON CDC1
OH
O
O
N
7d


SID-207
PROTON CDC13 ID:\odz
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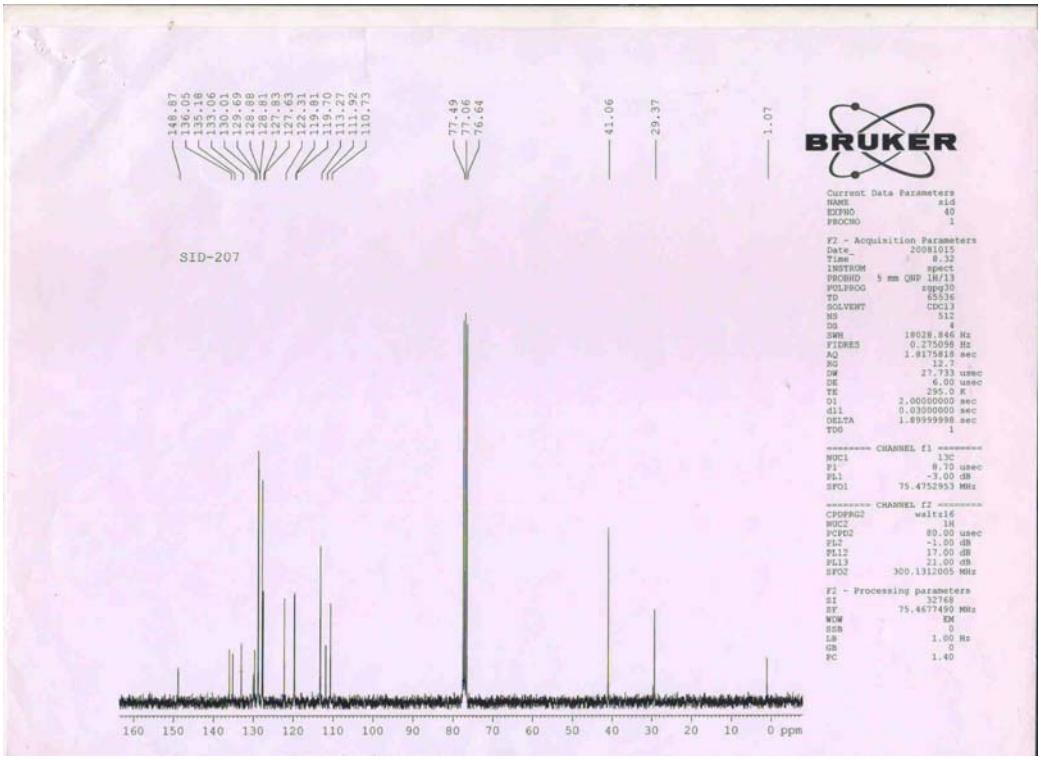
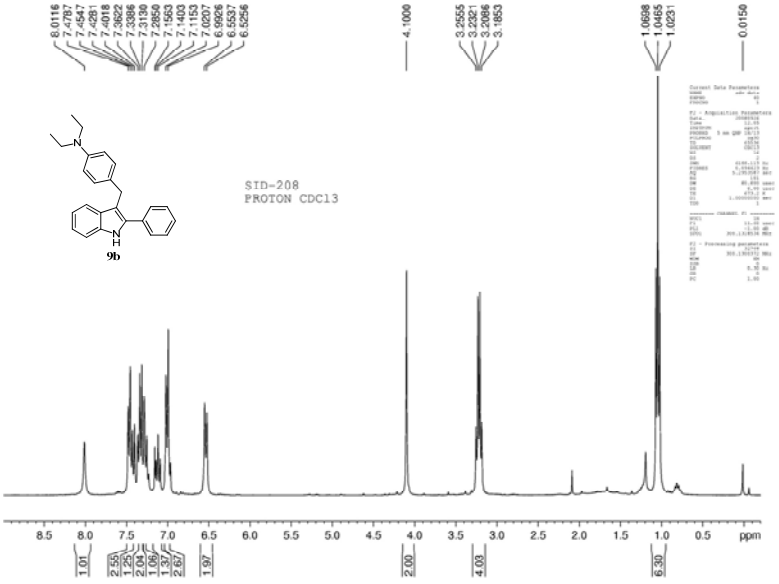
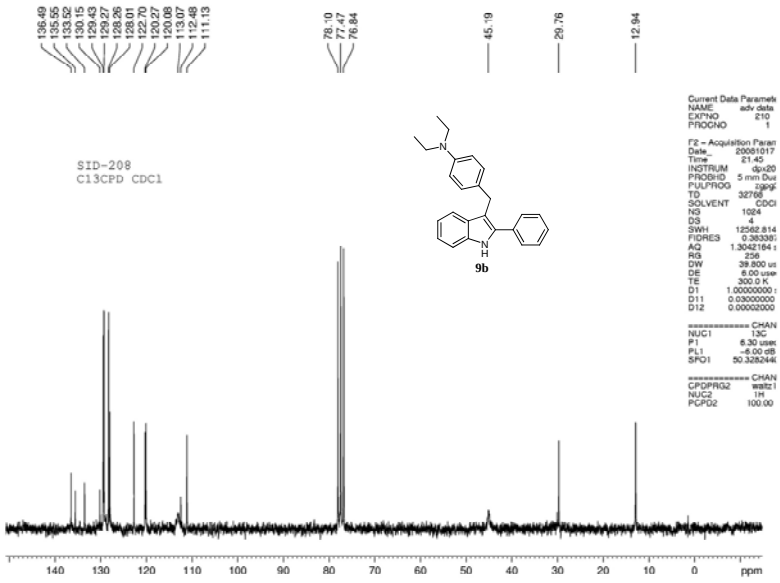

SID-207
BRUKER


SID-208
PROTON CDCl3
9b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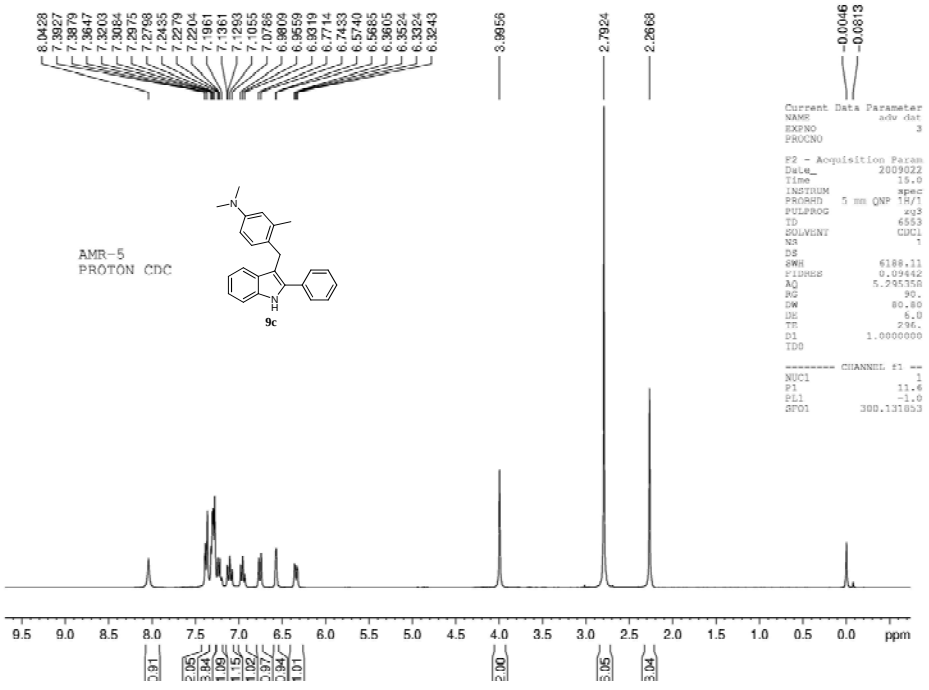
133.52
130.15
129.43
129.27
128.26
128.01
122.70
120.27
120.08
113.07
112.48
111.13
78.10
77.47
76.84
45.19
29.76
12.94
SID-208
C13CPD CDCl
9b
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.3927
7.3879
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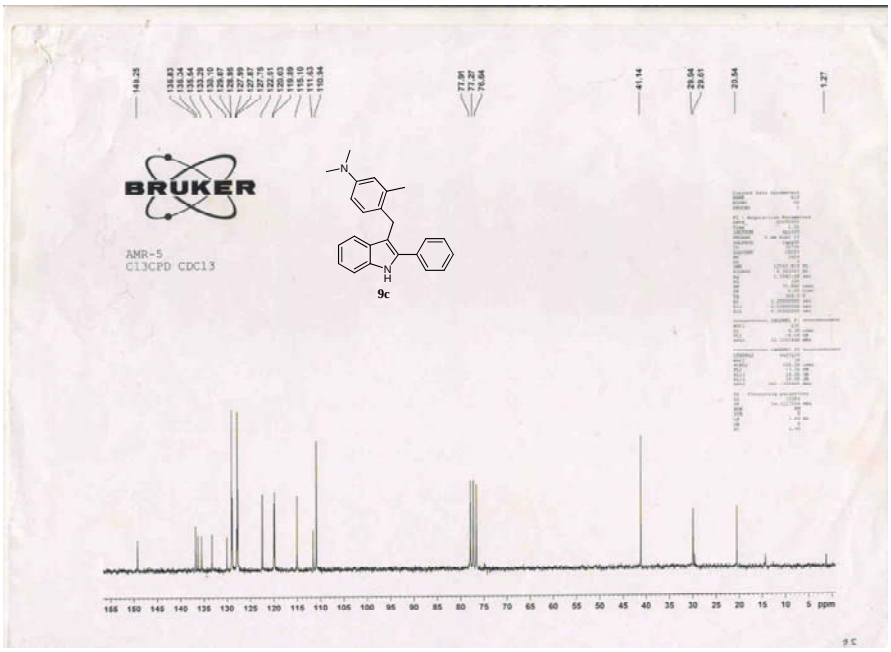
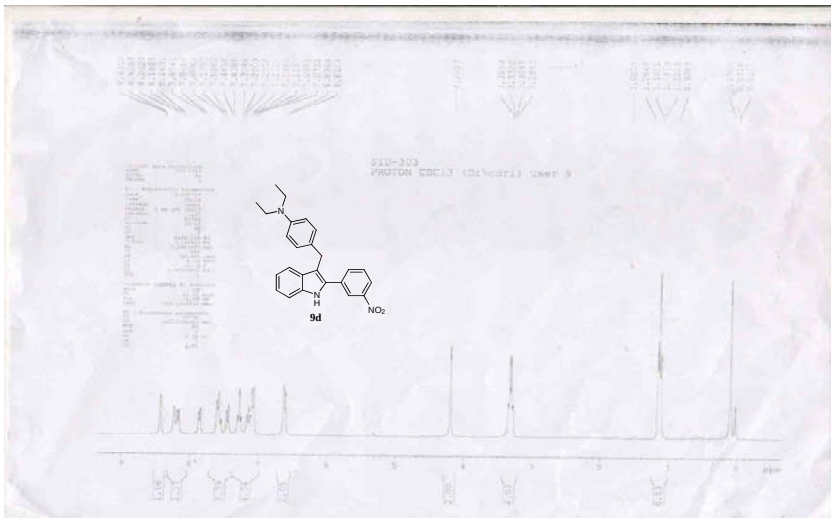
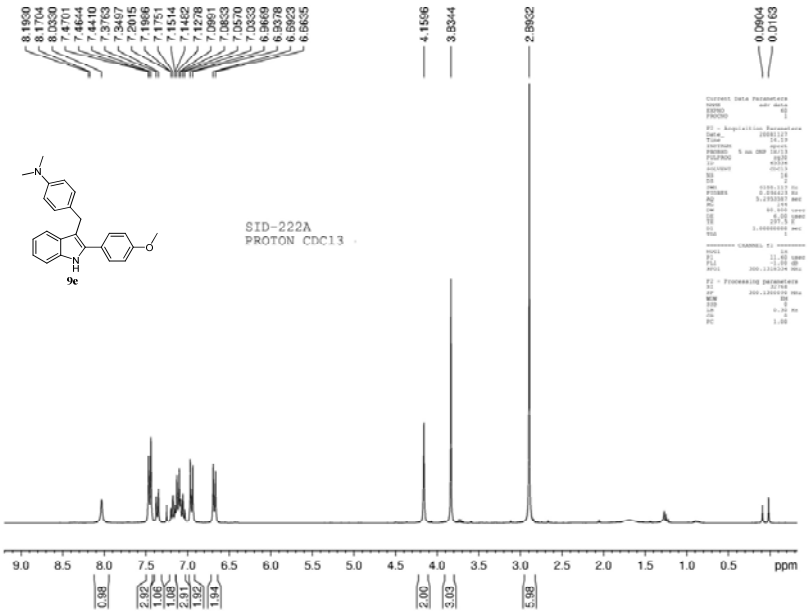
7.3203
7.3084
7.2975
7.2798
7.2435
7.2279
7.2204
7.1961
7.1961
7.1293
7.1055
7.0786
6.9809
6.9559
6.9319
6.7714
6.7433
6.5740
6.5685
6.3605
6.3524
6.3324
6.3243
3.9956
2.7924
2.2668
-0.0046
-0.0813
AMR-5
PROTON CDC
9c
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


BRUKER
AMR-5
C13CPD CDCl3
9c


9d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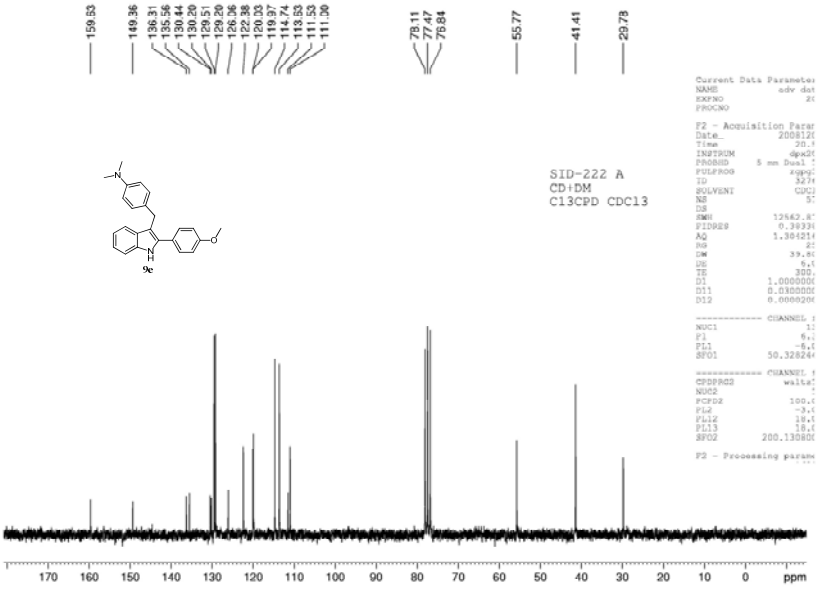
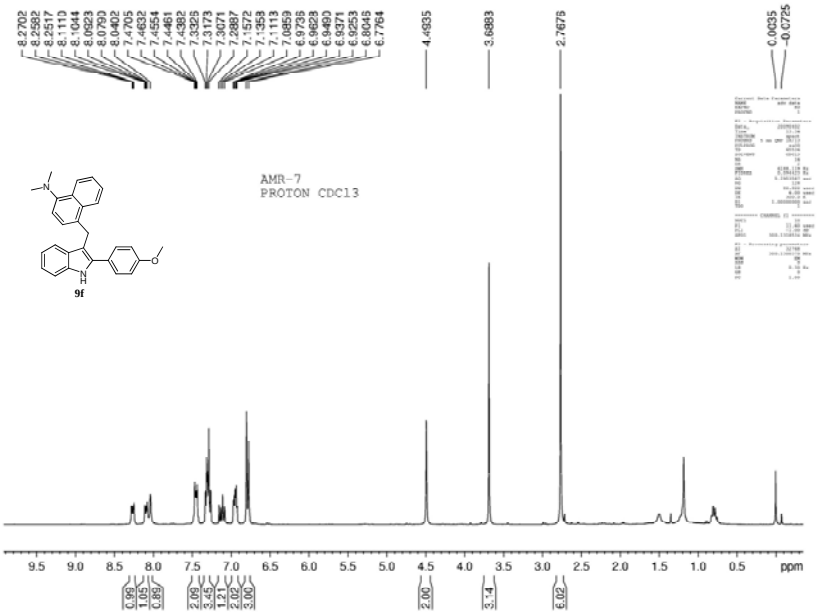
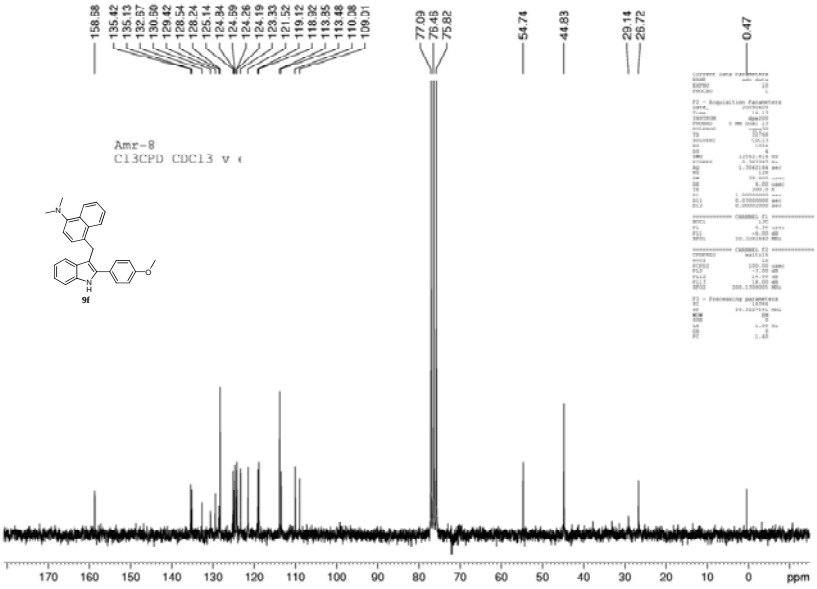
8.0330
7.4701
7.4644
7.4410
7.3763
7.3497
7.2015
7.1966
7.1751
7.1514
7.1452
7.1278
7.0961
7.0853
7.0570
7.0333
6.9669
6.9378
6.6923
6.6635
4.1596
3.8344
2.8852
0.0904
0.0163
SID-222A
PROTON CDC13
9e
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98
2.02
1.06
1.08
2.01
1.02
1.94
2.00
3.03
5.98


159.53
149.36
136.31
135.56
130.44
130.29
129.51
129.20
126.06
122.38
120.03
119.97
114.74
113.53
111.53
111.00
79.11
77.47
76.84
55.77
41.41
29.73
SID-222 A
CD+DM
C13CPD CDC13
9e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


AMR-7
PROTON CDC13
9f
ppm


Amr-8
C13CPD CDC13 v
9f
ppm