Supplementary Information

Fe_3O_4 supported acidic ionic liquid: An efficient and recyclable magnetic nanoparticles catalyst for one-pot synthesis of Bis(indolyl)methanes

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Table of Content	**Page No**

Single Crystal of 3,3'-((4-bromophenyl)methylene)bis(2-methyl-1*H*-indole) (4g):

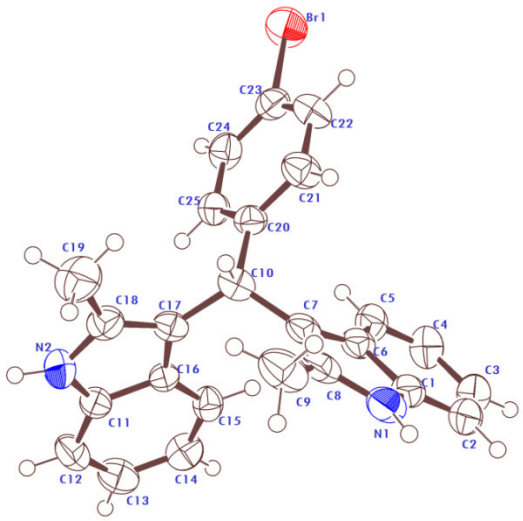
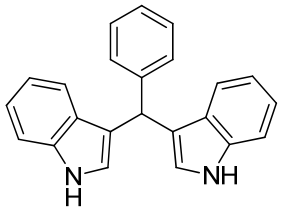


Table 1: X-ray crystallography data of **4g** (CCDC 1857237).

Empirical formula	$C_{25}H_{21}BrN_2$
Formula weight	429.36
Temperature/K	294.9(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	16.3699(8)
b/Å	13.8479(9)
c/Å	18.1112(11)
α/°	90
β/°	94.894(5)
γ/°	90
Volume (Å^3)	4090.6(4)
Z	8
ρ (calculated) (g cm^{-3})	1.3942
Absorption coefficient (mm^{-1})	2.022
Θ range (^{o})	6.3 to 52.74
Total Reflections collected	8158
Independent reflections	4173
Refinement parameters	255
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R1 = 0.0572
Final R indexes [all data]	R1 = 0.0964

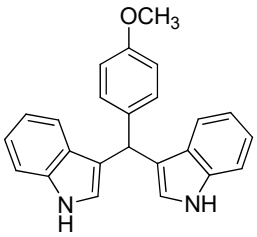
Analytical Data:

3,3'-(phenylmethylene)bis(1*H*-indole)(3a)



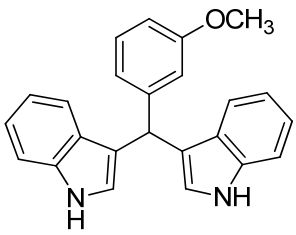
M.p 145-147 °C; IR (KBr): ν_{max} 3395, 3054, 1617, 1455, 1123, 1094, 747 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.82 (s, 2H, NH), 7.35 (t, *J*=7.2 Hz, 4H, Ar-H), 7.26 (t, *J*=7.6 Hz, 4H, Ar-H), 7.16 (t, *J*=7.2 Hz, 1H, Ar-H), 7.02 (t, *J*=7.6 Hz, 2H, Ar-H), 6.85 (t, *J*=7.2 Hz, 2H, Ar-H), 6.82 (s, 2H, N-CH=C), 5.82 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 144.9, 136.5, 128.2, 127.9, 126.5, 125.7, 123.5, 120.8, 119.0, 118.1, 118.0, 111.4, 39.6. ESI-MS: *m/z* 322 $[M]^+$. Anal.Calcd for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69; Found: C, 85.20; H, 5.36; N, 8.55.

3,3'-((4-methoxyphenyl)methylene)bis(1*H*-indole)(3b)



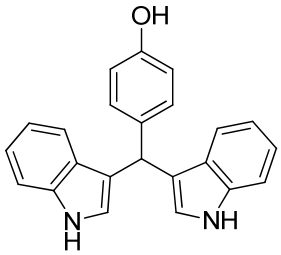
M.p 186-188 °C; IR (KBr): ν_{max} 3395, 3318, 3155, 1611, 1400, 1122, 749 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$): δ 10.05 (s, 2H, NH), 7.28-7.23 (m, 4H, Ar-H), 7.17 (d, *J*=8.8 Hz, 2H, Ar-H), 6.99 (t, *J*=7.6 Hz, 2H, Ar-H), 6.81 (t, *J*=7.6 Hz, 2H, Ar-H), 6.71 (d, *J*=8.8 Hz, 2H, Ar-H), 6.62 (s, 2H, N-CH=C), 5.71 (s,1H, CH), 3.68 (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 157.2, 136.4, 129.0, 126.5, 123.4, 120.7, 119.0, 118.5, 117.9, 112.9, 111.0, 54.6, 38.9. ESI-MS: *m/z* 352 $[M]^+$. Anal.Calcd for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95; Found: C, 81.66; H, 5.63; N, 8.18.

3,3'-((3-methoxyphenyl)methylene)bis(1*H*-indole)(3c)



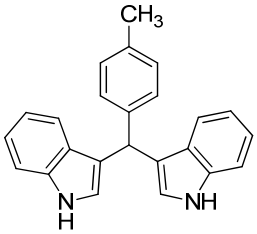
M.p 184-186 °C; IR (KBr): ν_{max} 3405, 3366, 3056, 2931, 2854, 1610, 1456, 1259, 1099, 744 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.01 (s, 2H, NH), 7.25 (t, *J*=8.4 Hz, 4H, Ar-H), 7.08 (d, *J*=8 Hz, 1H, Ar-H), 7.00-6.96 (m, 2H, Ar-H), 6.86-6.79 (m, 4H, Ar-H), 6.64 (s, 2H, N-CH=C), 6.62-6.61 (m, 1H, Ar-H), 5.71 (s, 1H, CH), 3.63 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.9, 146.0, 136.4, 128.5, 126.5, 123.47, 120.7, 118.9, 118.0, 114.2, 110.9, 110.3, 54.5, 39.8. ESI-MS: *m/z* 352 $[M]^+$. Anal.Calcd for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95; Found: C, 81.98; H, 5.83; N, 7.49.

3,3'-((-hydroxyphenyl)methylene)bis(1*H*-indole)(3d)



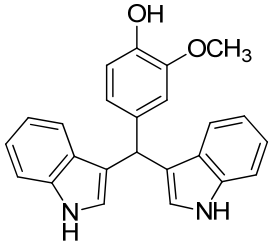
M.p 125-127 °C; IR (KBr): ν_{max} 3492, 3431, 3075, 2980, 1610, 1532, 1476, 1093, 746 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.76 (s, 2H, NH), 9.14 (s, 1H, OH), 7.31 (d, *J*=8 Hz, 2H, Ar-H), 7.24 (d, *J*=7.6 Hz, 2H, Ar-H), 7.11 (d, *J*=8.8 Hz, 2H, Ar-H), 7.02-6.98 (m, 2H, Ar-H), 6.85-6.81 (m, 2H, Ar-H), 6.76 (d, *J*=1.6 Hz, 2H, N-CH=C), 6.64 (td, *J*=8.8, 2.8 Hz, 2H, Ar-H), 5.68 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.2, 143.9, 136.5, 135.1, 130.0, 129.0, 127.9, 126.4, 123.5, 120.9, 118.9, 118.6, 118.2, 117.5, 114.6, 111.4, 38.9. ESI-MS: *m/z* 338 $[M]^+$. Anal.Calcd for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28; Found: C, 81.70; H, 5.28; N, 8.45.

3,3'-(p-tolylmethylene)bis(1*H*-indole)(3e)



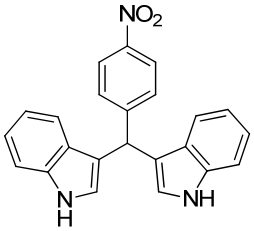
M.p 91-93 °C; IR (KBr): ν_{max} 3412, 3051, 2922, 1615, 1455, 1092, 742 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.79 (s, 2H, NH), 7.32 (d, *J*=8 Hz, 2H, Ar-H), 7.25-7.20 (m, 4H, Ar-H), 7.06-6.99 (m, 4H, Ar-H), 6.83 (t, *J*=6.8 Hz, 2H, Ar-H), 6.78 (d, *J*=2.4 Hz, 2H, N-CH=C), 5.75 (s, 1H, CH), 2.23 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.8, 136.5, 134.5, 129.6, 128.5, 128.1, 126.5, 123.4, 120.7, 119.0, 118.1, 118.0, 111.3, 30.9, 20.5. ESI-MS: *m/z* 359 $[M+Na]^+$. Anal.Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33; Found: C, 85.11; H, 5.70; N, 8.18.

3,3'-((4-hydroxy3-methoxyphenyl)methylene)bis(1*H*-indole)(3f)



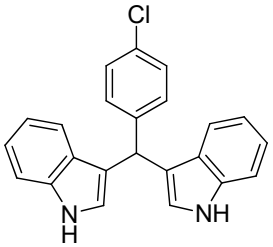
M.p 103-105 °C; IR (KBr): ν_{max} 3488, 3411, 3057, 2961, 1600, 1509, 1456, 1120, 744 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.76 (s, 2H, NH), 8.71 (s, 1H, OH), 7.33-7.26 (m, 4H, Ar-H), 7.01 (t, *J*=6.8 Hz, 2H, Ar-H), 6.94 (d, *J*=1.6 Hz, 1H, Ar-H), 6.84 (d, *J*=6.8 Hz, 2H, Ar-H), 6.78 (d, *J*=2.4 Hz, 2H, N-CH=C), 6.71-6.63 (m, 2H, Ar-H), 5.71 (s, 1H, CH), 3.64 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.1, 144.4, 136.5, 135.8, 126.6, 123.3, 120.7, 119.1, 118.5, 118.0, 114.9, 112.7, 111.4, 56.0, 39.2. ESI-MS: *m/z* 368 $[M]^+$. Anal.Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60; Found: C, 78.51; H, 5.53; N, 7.93.

3,3'-((4-nitrophenyl)methylene)bis(1*H*-indole)(3g)



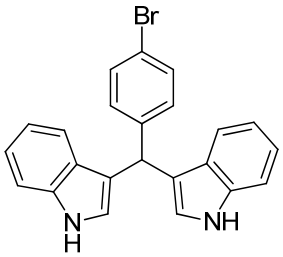
M.p 226-228 °C; IR (KBr): ν_{max} 3456, 3423, 3338, 1592, 1507, 1339, 1094, 746 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.89 (s, 2H, NH), 8.09 (d, *J*=8.4 Hz, 2H, Ar-H), 7.55 (d, *J*=8.4 Hz, 2H, Ar-H), 7.31 (d, *J*=8.4 Hz, 2H, Ar-H), 7.23 (d, *J*=8 Hz, 2H, Ar-H), 7.00 (t, *J*=8 Hz, 2H, Ar-H), 6.84 (s, 2H, N-CH=C), 6.82 (t, *J*=7.2 Hz, 2H, Ar-H), 5.97 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.0, 145.7, 136.5, 129.4, 126.3, 123.8, 123.3, 121.0, 118.8, 118.4, 116.6, 111.5, 39.4. ESI-MS: *m/z* 357 $[M]^+$. Anal.Calcd for $C_{23}H_{17}N_3O_2$: C, 75.19; H, 4.66; N, 11.44; Found: C, 75.40; H, 4.54; N, 11.37.

3,3'-((4-chlorophenyl)methylene)bis(1*H*-indole)(3h)



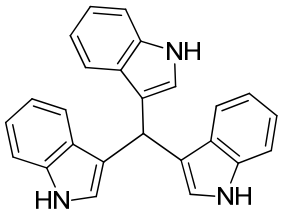
M.p 82-84 °C; IR (KBr): ν_{max} 3409, 3051, 2926, 2857, 1616, 1487, 1089, 743 cm^{-1}.^1H NMR (400 MHz, DMSO-d_6): δ 10.85 (s, 2H, NH), 7.35-7.29 (m, 6H, Ar-H), 7.25 (d, *J*=7.6 Hz, 2H, Ar-H), 7.02 (t, *J*=7.2 Hz, 2H, Ar-H), 6.85 (t, *J*=7.2 Hz, 2H, Ar-H), 6.81 (d, *J*=1.6 Hz, 2H, N-CH=C), 5.83 (s, 1H, CH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.9, 136.5, 130.1, 130.0, 127.9, 126.4, 123.5, 120.9, 118.9, 118.2, 117.4, 111.4, 38.9. ESI-MS: *m/z* 357 $[M+1]^+$. Anal.Calcd for $C_{23}H_{17}N_2Cl$: C, 77.41; H, 4.80; N, 7.85; Found: C, 77.62; H, 4.89; N, 7.41.

3,3'-((4-bromophenyl)methylene)bis(1*H*-indole) (3i)



M.p 130-132 °C; IR (KBr): ν_{max} 3412, 3055, 2926, 1617, 1485, 1456, 1093, 1010, 743 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.85 (s, 2H, NH), 7.43 (d, *J*=8.8 Hz, 2H, Ar-H), 7.33 (d, *J*=8 Hz, 2H, Ar-H), 7.29-7.24 (m, 4H, Ar-H), 7.20 (t, *J*=7.2 Hz, 2H, Ar-H), 6.87 (t, *J*=7.6 Hz, 2H, Ar-H), 6.82 (s, 2H, N-CH=C), 5.81 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 144.3, 136.5, 130.8, 130.4, 126.4, 123.5, 120.9, 118.9, 118.7, 118.2, 117.4, 111.4, 38.9. ESI-MS: *m/z* 401 $[M]^+$, 403 $[M+2]^+$. Anal.Calcd for $C_{23}H_{17}N_2Br$: C, 68.84; H, 4.27; N, 6.98; Found: C, 69.15; H, 4.18; N, 6.72.

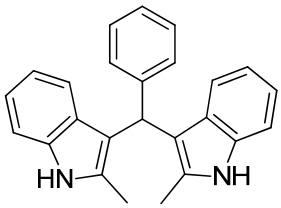
tri(1*H*-indol-3-yl)methane (3j)



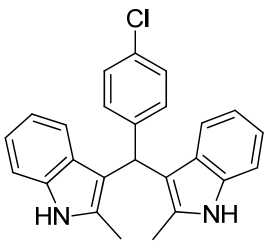
M.p 240-242 °C; IR (KBr): ν_{max} 3410, 3047, 2830, 1604, 1454, 1417, 1337, 1087, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.71 (s, 3H, NH), 7.37 (d, *J*=7.2 Hz, 3H, Ar-H), 7.31 (d, *J*=8 Hz, 3H, Ar-H), 6.99 (t, *J*=7.2 Hz, 3H, Ar-H), 6.91 (s, 3H, N-CH=C), 6.83 (t, *J*=8 Hz, 3H, Ar-H), 6.03 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.5, 126.5, 123.1, 120.5, 119.2, 118.2, 117.8, 111.3, 30.8. ESI-MS: *m/z* 360 $[M-1]^+$. Anal.Calcd for $C_{25}H_{19}N_3$: C, 83.08; H, 5.30; N, 11.63; Found: C, 82.89; H, 5.25; N, 11.56.

3,3'-(phenylmethylene)bis(2-methyl-1*H*-indole)(4a)

M.p 244-246 °C; IR (KBr): ν_{max} 3395, 3055, 2922, 1617, 1460, 1113, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.58 (s, 2H, NH), 7.09-7.00 (m, 7H, Ar-H), 6.70 (t, *J*=8 Hz, 2H, Ar-H), 6.61 (d, *J*=8 Hz, Ar-H), 6.49 (t, *J*=8 Hz, 2H, Ar-H), 5.74 (s, 1H, CH), 1.89 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 144.2, 135.0, 132.0, 128.6, 128.2, 127.8, 125.7, 119.4, 118.4, 117.8, 112.1, 110.2, 38.5, 11.8. ESI-MS: *m/z* 350 $[M]^+$. Anal.Calcd for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99; Found: C, 85.55; H, 6.39; N, 8.04.

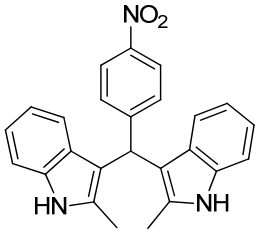


3,3'-((4-chlorophenyl)methylene)bis(2-methyl-1*H*-indole)(4b)



M.p 234-236 °C; IR (KBr): ν_{max}3381, 3047, 2918, 1617, 1486, 1459, 1305, 1125, 1101, 1087, 746 cm^{-1};^1H NMR (400 MHz, DMSO-d_6): δ 10.80 (s, 2H, NH), 7.43 (d, *J*=6.8 Hz, 2H, Ar-H), 7.20 (d, *J*=8 Hz, 2H, Ar-H), 7.11 (d, *J*=7.6 Hz, 2H, Ar-H), 6.88 (t, *J*=8 Hz, 2H, Ar-H), 6.79 (d, *J*=8 Hz, 2H, Ar-H), 6.68 (t, *J*=7.6 Hz, 2H, Ar-H), 5.88 (s, 1H, CH), 2.07 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.7, 135.0, 132.1, 130.8, 130.7, 127.9, 119.5, 118.6, 118.3, 118.0, 111.5, 110.3, 38.0, 11.8. ESI-MS: *m/z* 385 $[M+1]^+$. Anal.Calcd for $C_{25}H_{21}N_2Cl$: C, 78.01; H, 5.50; N, 7.28; Found: C, 77.95; H, 5.49; N, 7.36.

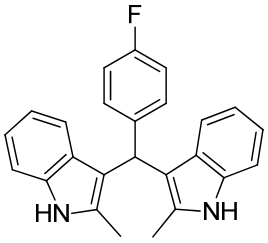
3,3'-((4-nitrophenyl)methylene)bis(2-methyl-1*H*-indole)(4c)



M.p 241-243 °C; IR (KBr): ν_{max}3397, 3068, 2921, 1587, 1499, 1339, 1125, 748 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 10.88 (s, 2H, NH), 8.15 (d, *J*= 8.4 Hz, 2H, Ar-H), 7.41 (d, *J*= 8.4 Hz, 2H, Ar-H), 7.22 (d, *J*= 8 Hz, 2H, Ar-H), 6.90 (t, *J*=7.6 Hz, 2H, Ar-H), 6.78 (d, *J*= 8 Hz, 2H, Ar-H), 6.69 (t, *J*=7.6 Hz, 2H, Ar-H), 6.06 (s, 1H, CH), 2.09 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.8, 145.6, 135.0, 132.5, 129.8, 127.8, 123.2, 119.7, 118.1, 110.8, 110.4, 38.6, 11.9. ESI-MS: *m/z* 395 $[M]^+$. Anal.Calcd for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63; Found: C, 76.08; H, 5.27; N, 10.50.

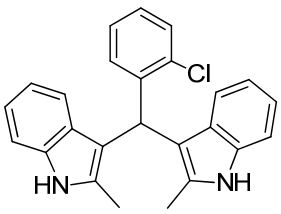
3,3'-((4-fluorophenyl)methylene)bis(2-methyl-1*H*-indole)(4d)

M.p 258-260 °C; IR (KBr): ν_{max}3920, 3082, 2912, 2866, 1615, 1503, 1459, 1302, 1214, 1156, 1126, 1097, 750 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.77 (s, 2H, NH), 7.21-7.16 (m, 4H, Ar-H), 7.07 (t, *J*=8.4 Hz, 2H, Ar-H), 6.88 (t, *J*=8 Hz, 2H, Ar-H), 6.79 (d, *J*=8 Hz, 2H, Ar-H), 6.67 (t, *J*=7.2 Hz, 2H, Ar-H), 5.90 (s, 1H, CH), 2.06 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.6, 159.2, 140.3, 135.0, 132.0, 130.3, 128.0, 119.5, 118.3, 117.9, 114.6, 112.0, 110.3, 37.8, 11.8. ESI-MS: *m/z* 368 $[M]^+$. Anal.Calcd for $C_{25}H_{21}N_2F$: C, 81.50; H, 5.74; N, 7.60; Found: C, 81.73; H, 5.63: N, 7.51.

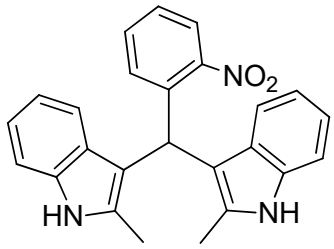


3,3'-((2-chlorophenyl)methylene)bis(2-methyl-1*H*-indole)(4e)

M.p 218-220 °C; IR (KBr): ν_{max}3391, 3060, 2902, 1638, 1459, 1135, 1124, 1102, 741 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.79 (s, 2H, NH), 7.42 (d, *J*=7.2 Hz, 1H, Ar-H), 7.28-7.20 (m, 5H, Ar-H), 6.88 (t, *J*=8 Hz, 2H, Ar-H), 6.73 (d, *J*=7.2 Hz, 2H, Ar-H), 6.66 (t, *J*=8 Hz, 2H, Ar-H), 6.04 (s, 1H, CH), 1.99 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.5, 134.9, 133.4, 132.1, 130.7, 129.2, 128.2, 127.9, 126.6, 119.6, 118.1, 117.8, 110.4, 110.3, 36.7, 11.6. ESI-MS: *m/z* 384 $[M]^+$. Anal.Calcd for $C_{25}H_{21}N_2Cl$: C, 78.01; H, 5.50; N, 7.28; Found: C, 78.29; H, 5.35; N, 6.96.

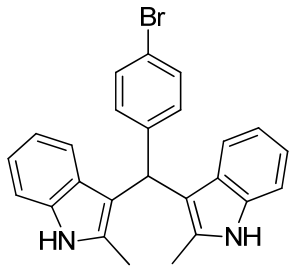


3,3'-((2-nitrophenyl)methylene)bis(2-methyl-1*H*-indole)(4f)



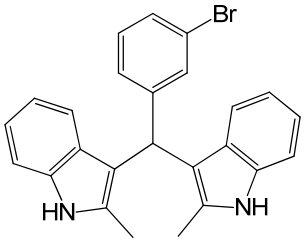
M.p 234-236 °C; IR (KBr): ν_{max}3392, 3052, 2922, 1637, 1528, 1458, 1370, 1124, 753 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.86 (s, 2H, NH), 7.83 (dd, *J*=8, 1.2 Hz, 1H, Ar-H), 7.56 (dt, *J*=7.6 Hz, *J*=1.6 Hz, 1H, Ar-H), 7.49 (dt, *J*=7.6 Hz, *J*=1.6 Hz, 1H, Ar-H), 7.25 (d, *J*=7.6 Hz, 1H, Ar-H), 7.22 (d, *J*=8 Hz, 2H, Ar-H), 6.92-6.88 (m, 2H, Ar-H), 6.73-6.67 (m, 4H, Ar-H), 6.57 (s, 1H, CH), 2.03 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.0, 137.7, 134.9, 132.6, 132.3, 130.4, 128.0, 127.6, 124.4, 119.8, 118.3, 117.6, 110.5, 109.7, 33.8, 11.5. ESI-MS: *m/z* 395 $[M]^+$. Anal.Calcd for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63; Found: C, 75.86; H, 5.28; N, 10.51.

3,3'-((4-bromophenyl)methylene)bis(2-methyl-1*H*-indole) (4g)



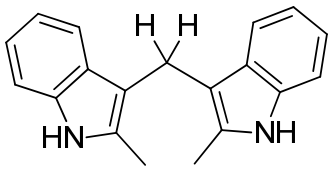
M.p 242-244 °C; IR (KBr): ν_{max}3389, 3047, 2913, 1618, 1556, 1459, 1304, 1244, 1010, 746 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.79 (s. 2H, NH), 7.30 (d, *J*=8.4 Hz, 2H, Ar-H), 7.21-7.15 (m, 4H, Ar-H), 6.88 (t, *J*=8 Hz, 2H, Ar-H), 6.79 (d, *J*=8 Hz, 2H, Ar-H), 6.68 (t, *J*=8 Hz, 2H, Ar-H), 5.90 (s, 1H, CH), 2.07 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.3, 135.0, 132.1, 130.4, 130.1, 128.0, 127.8, 119.5, 118.3, 118.0, 111.6, 110.3, 37.9, 11.8. ESI-MS: *m/z* 428 $[M-1]^+$, 430 $[M+1]^+$. Anal.Calcd for $C_{25}H_{21}N_2Br$: C, 69.94; H, 4.93; N, 6.52; Found: C, 70.02; H, 4.86; N, 6.45.

3,3'-((3-bromophenyl)methylene)bis(2-methyl-1*H*-indole)(4h)



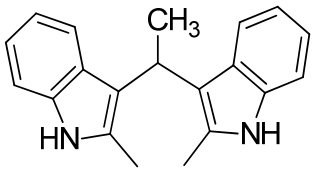
M.p 278-280 °C; IR (KBr): ν_{max}3380, 3063, 2932, 1590, 1461, 1127, 1105, 741 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.82 (s, 2H, NH), 7.40 (d, *J*=8 Hz, 1H, Ar-H), 7.31 (s, 1H, Ar-H), 7.24-7.16 (m, 4H, Ar-H), 6.91-6.87 (m, 2H, Ar-H), 6.78 (d, *J*=8 Hz, 2H, Ar-H), 6.70-6.67 (m, 2H, Ar-H), 5.94 (s, 1H, CH), 2.08 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.3, 135.0, 132.2, 131.2, 130.1, 128.6, 127.9, 127.7, 121.3, 119.6, 118.2, 118.0, 111.3, 110.4, 38.2, 11.8. ESI-MS: *m/z* 429 $[M]^+$, 431 $[M+2]^+$.Anal.Calcd for $C_{25}H_{21}N_2Br$: C, 69.94; H, 4.93; N, 6.52; Found: C, 70.01; H, 4.89; N, 6.42.

bis(2-methyl-1*H*-indol-3-yl)methane(4i)



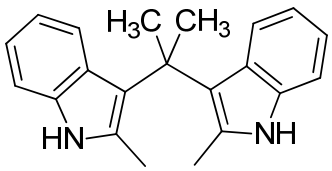
M.p 110-112 °C; IR (KBr): ν_{max}3408, 2973, 1652, 1480, 1149, 1115, 744 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.65 (s, 2H, NH), 7.24 (d, *J*=7.6 Hz, 2H, Ar-H), 7.19 (d, *J*=8 Hz, 2H, Ar-H), 6.91 (t, *J*=7.2 Hz, 2H, Ar-H), 6.80 (d, *J*=7.2 Hz, 2H, Ar-H), 3.98 (s, 2H, CH), 2.38 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 135.0, 131.1, 128.4, 119.6, 117.7, 117.6, 110.1, 109.6, 18.8, 11.5. ESI-MS: *m/z* 274 $[M]^+$. Anal.Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21; Found: C, 83.04; H, 6.55; N, 10.12.

3,3'-(ethane-1,1-diyl)bis(2-methyl-1*H*-indole)(4j)



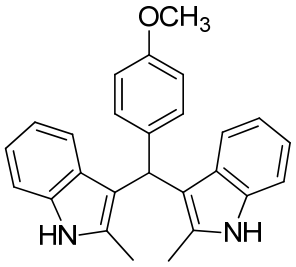
M.p 179-181 °C; IR (KBr): ν_{max} 3395, 2953, 1638, 1456, 1135, 1124, 1105, 743 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.63 (s, 2H, NH), 7.40 (d, *J*=7.6 Hz, 2H, Ar-H), 7.19 (d, *J*=7.6 Hz, 2H, Ar-H), 6.90 (t, *J*=7.2 Hz, 2H, Ar-H), 6.79 (t, *J*=7.2 Hz, 2H, Ar-H), 4.60 (q, *J*=7.2 Hz, 1H, CH), 2.33 (s, 6H, $2CH_3$), 1.82 (d, *J*=8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 134.9, 130.4, 127.7, 119.3, 118.3, 117.8, 114.5, 110.2, 28.2, 21.3, 12.1. ESI-MS: *m/z* 288 $[M]^+$. Anal.Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71; Found: C, 83.15; H, 7.13; N, 9.82.

3,3'-(propane-2,2-diyl)bis(2-methyl-1*H*-indole)(4k)



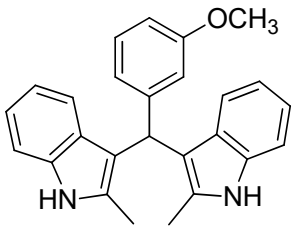
M.p 188-190 °C; IR (KBr): ν_{max} 3401, 2983, 2961, 1638, 1453, 1116, 740 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.54 (s, 2H, NH), 7.22 (d, *J*=7.6 Hz, 2H, Ar-H), 7.16 (d, *J*=8 Hz, 2H, Ar-H), 6.84 (d, *J*=8 Hz, 2H, Ar-H), 6.67 (d, *J*=8 Hz, 2H, Ar-H), 2.27 (s, 6H, $2CH_3$), 1.91 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 134.8, 129.5, 127.7, 119.6, 119.0, 118.8, 117.5, 110.1, 37.1, 31.6, 14.0. ESI-MS: *m/z* 302 $[M]^+$. Anal.Calcd for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33; N, 9.26; Found: C, 83.22; H, 7.25; N, 9.12.

3,3'-((4-methoxyphenyl)methylene)bis(2-methyl-1*H*-indole)(4l)



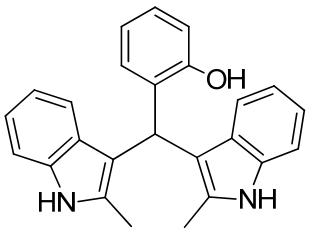
M.p 196-198 °C; IR (KBr): ν_{max}3395, 3049, 1606, 1509, 1457, 1300, 1237, 1125, 1034, 741 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 10.72 (s, 2H, NH), 7.19 (d, J=7.6 Hz, 2H, Ar-H), 7.07 (d, J=8 Hz, 2H, Ar-H), 6.87 (d, J=7.6 Hz, 2H, Ar-H), 6.81 (d, J=8.4 Hz, 4H, Ar-H), 6.66 (t, J=7.2 Hz, 2H, Ar-H), 5.84 (s, 1H, CH), 3.71 (s, 3H, OCH_3), 2.05 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.2, 136.0, 135.0, 131.8, 129.5, 128.2, 119.4, 118.4, 117.8, 113.3, 112.4, 110.2, 54.8, 37.7, 11.8. ESI-MS: *m/z* 380 $[M]^+$. Anal.Calcd for $C_{26}H_{24}N_2O$: C, 82.07; H, 6.36; N, 7.36; Found: C, 82.20; H, 6.31; N, 7.34.

3,3'-((3-methoxyphenyl)methylene)bis(2-methyl-1*H*-indole)(4m)



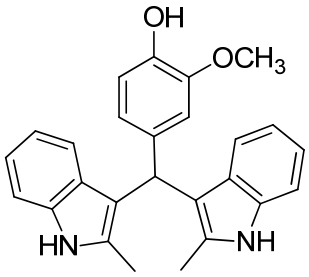
M.p 150-152 °C; IR (KBr): ν_{max}3385, 3057, 2998, 2915, 1596, 1487, 1460, 1428, 1304, 1242, 1158, 1040, 742 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 10.73 (s, 2H, NH), 7.20-7.14 (m, 3H, Ar-H), 6.87 (t, J= 7.6 Hz, 2H, Ar-H), 6.81-6.75 (m, 4H, Ar-H), 6.71 (s, 1H, Ar-H), 6.66 (t, J= 7.6 Hz, 2H, Ar-H), 5.86 (s, 1H, CH), 3.61 (s, 3H, OCH_3), 2.06 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.0, 145.8, 134.9, 131.9, 128.8, 128.1, 121.2, 119.5, 118.4, 117.8, 114.9, 112.0, 110.4, 110.2, 54.7, 38.5, 11.8. ESI-MS: *m/z* 380 $[M]^+$. Anal.Calcd for $C_{26}H_{24}N_2O$: C, 82.07; H, 6.36; N, 7.36; Found: C, 81.89; H, 6.30; N, 7.63.

3,3'-((2-hydroxyphenyl)methylene)bis(2-methyl-1*H*-indole)(4n)



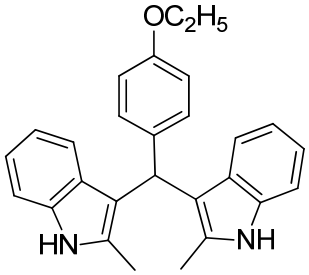
M.p 228-230 °C; IR (KBr): ν_{max}3495, 3390, 2912, 1639, 1484, 1459, 1127, 746 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.63 (s, 2H, NH), 9.13 (s, 1H, OH), 7.17 (d, J=8 Hz, 2H, Ar-H), 7.02 (t, J=8 Hz, 1H, Ar-H), 6.97 (d, J=7.6 Hz, 1H, Ar-H), 6.85 (t, J=7.6 Hz, 2H, Ar-H), 6.78 (d, J=8 Hz, 3H, Ar-H), 6.63 (t, J=7.6 Hz, 3H, Ar-H), 6.03 (s, 1H, CH), 1.99 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.0, 134.9, 131.5, 130.4, 129.7, 128.6, 126.8, 119.2, 118.2, 117.7, 114.7, 112.1, 110.1, 32.6, 11.7. ESI-MS: *m/z* 367 $[M+1]^+$. Anal.Calcd for $C_{25}H_{22}N_2O$: C, 81.94; H, 6.05; N, 7.64; Found: C, 81.82; H, 5.86; N, 7.76.

3,3'-((4-hydroxy-3-methoxyphenyl)methylene)bis(2-methyl-1*H*-indole)(4o)



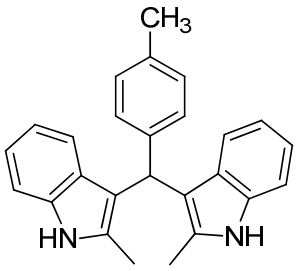
M.p 228-230 °C; IR (KBr): ν_{max} 3552, 3383, 3053, 2969, 2939, 2915, 1614, 1509, 1460, 1255, 1120, 1024, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.69 (s, 2H, NH), 8.74 (s, 1H, OH), 7.18 (d, *J*=7.6 Hz, 2H, Ar-H), 6.88-6.80 (m, 5H, Ar-H), 6.69-6.10 (m, 3H, Ar-H), 6.50 (d, *J*=8 Hz, 1H, Ar-H), 5.80 (s, 1H, CH), 3.55 (s, 3H, OCH_3), 2.04 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.2, 144.5, 134.9, 131.7, 128.3, 120.8, 119.4, 118.4, 117.8, 114.8, 113.3, 112.7, 110.2, 55.5, 38.1, 11.9. ESI-MS: *m/z* 395 $[M-1]^+$. Anal.Calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07; Found: C, 78.97; H, 6.23; N, 7.01.

3,3'-((4-ethoxyphenyl)methylene)bis(2-methyl-1*H*-indole)(4p)



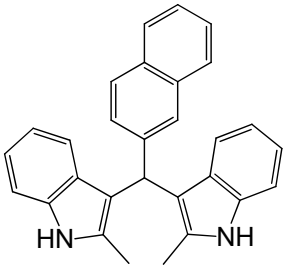
M.p 184-186 °C; IR (KBr): ν_{max} 3409: 3041, 2957, 1637, 1454, 1123, 1089, 746 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.70 (s, 2H, NH), 7.18 (d, *J*=7.6 Hz, 2H, Ar-H), 7.05 (d, *J*=8 Hz, 2H, Ar-H), 6.86 (t, *J*=7.6 Hz, 2H, Ar-H), 6.79 (t, *J*=8 Hz, 4H, Ar-H), 6.65 (t, *J*=8 Hz, 2H, Ar-H), 5.83 (s,1H, CH), 3.95 (q, *J*=6.4 Hz, 2H, CH_2), 2.04 (s, 6H, $2CH_3$), 1.29 (t, *J*=6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.5, 135.9, 135.0, 131.8, 129.5, 128.2, 119.4, 118.4, 117.8, 113.7, 112.5, 110.2, 62.7, 37.7, 14.6, 11.8. ESI-MS: *m/z* 394 $[M]^+$. Anal.Calcd for $C_{27}H_{26}N_2O$: C, 82.20; H, 6.64; N, 7.10; Found: C, 82.32; H, 6.48; N, 7.15.

3,3'-(p-tolylmethylene)bis(2-methyl-1*H*-indole)(4q)



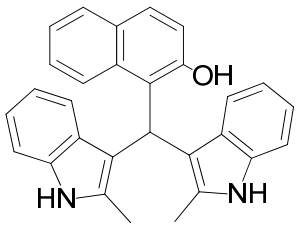
M.p 179-181 °C; IR (KBr): ν_{max}3384, 3052, 2912, 1638, 1459, 1305, 1126, 1105, 746 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.73 (s, 2H, NH), 7.20 (d, J=8 Hz, 2H, Ar-H), 7.05 (s, 4H, Ar-H), 6.88 (t, J=7.6 Hz, 2H, Ar-H), 6.82 (d, J=8 Hz, 2H, Ar-H), 6.67 (t, J=8 Hz, 2H, Ar-H), 5.87 (s, 1H, CH), 2.06 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.1, 135.0, 134.4, 131.9, 128.5, 128.4, 128.2, 119.4, 118.5, 117.8, 112.3, 110.2, 38.1, 20.6, 11.9. ESI-MS: *m/z* 364 $[M]^+$. Anal.Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69; Found: C, 86.02; H, 6.81; N, 7.90.

3,3'-(naphthalen-2-ylmethylene)bis(2-methyl-1*H*-indole)(4r)



M.p 204-206 °C; IR (KBr): ν_{max}3402, 3048, 2914, 2851, 1594, 1461, 1295, 1218, 1011, 748 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.76 (s, 2H, NH), 7.96-7.90 (m, 2H, Ar-H), 7.81 (d, J=7.6 Hz, 1H, Ar-H), 7.43 (t, *J*=7.6 Hz, 1H, Ar-H), 7.35 (q, J=8.4 Hz, 2H, Ar-H), 7.19 (t, *J*=8.8 Hz, 3H, Ar-H), 6.87 (t, *J*=8 Hz, 2H, Ar-H), 6.78 (t, 2H, Ar-H), 6.63 (t, *J*=8 Hz, 2H, Ar-H), 6.50 (s, 1H, CH), 1.96 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 139.8, 134.9, 133.3, 132.0, 131.7, 128.4, 126.8, 125.7, 125.3, 125.1, 123.8, 119.5, 118.0, 117.9, 111.8, 110.3, 35.7, 11.7. ESI-MS: *m/z* 400 $[M]^+$. Anal.Calcd for $C_{29}H_{24}N_2$: C, 86.97; H, 6.04; N, 6.99; Found: C, 87.18; H, 5.98; N, 7.14.

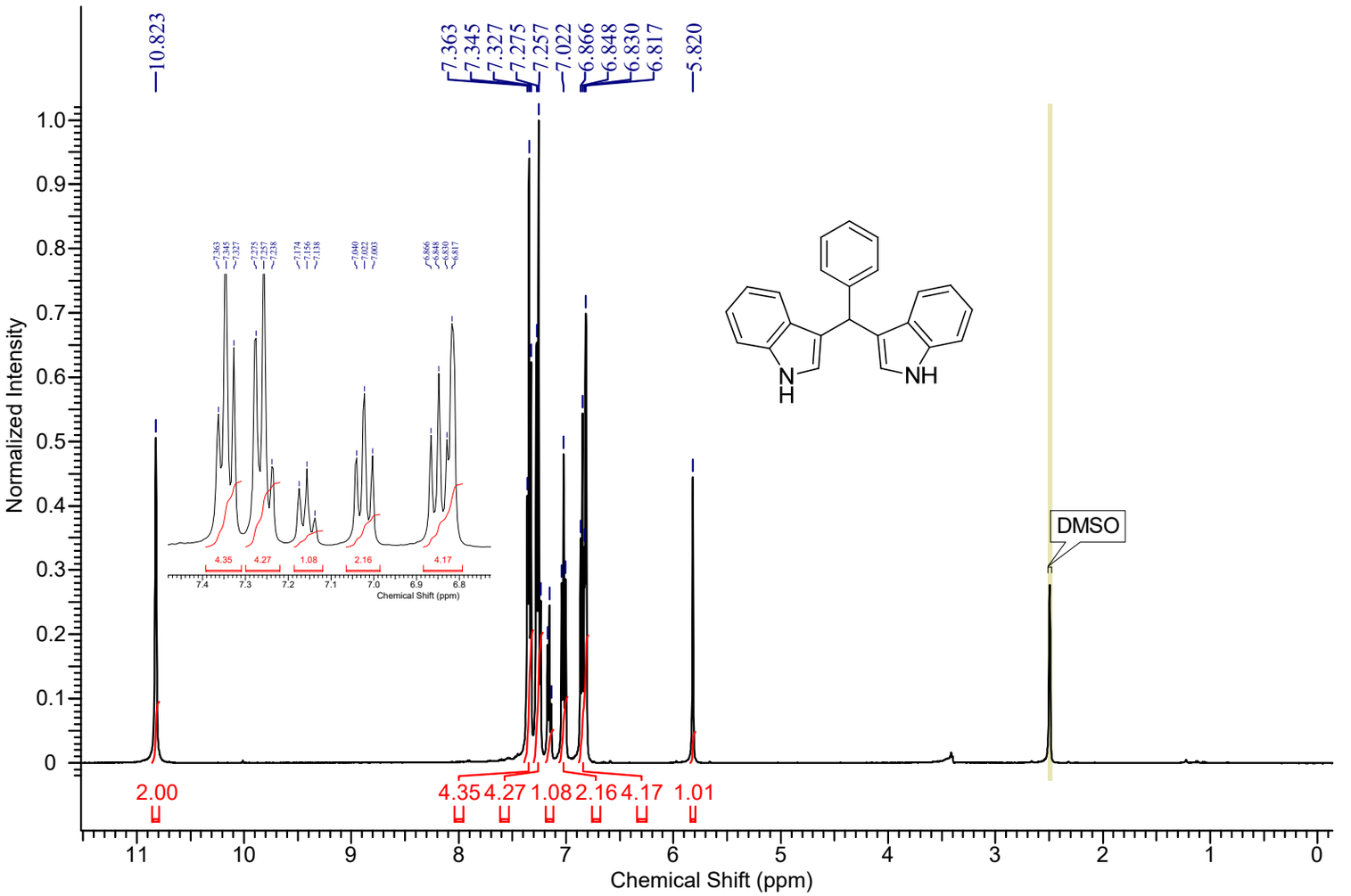
1-(bis(2-methyl-1*H*-indol-3-yl)methyl)naphthalen-2-ol (4s)



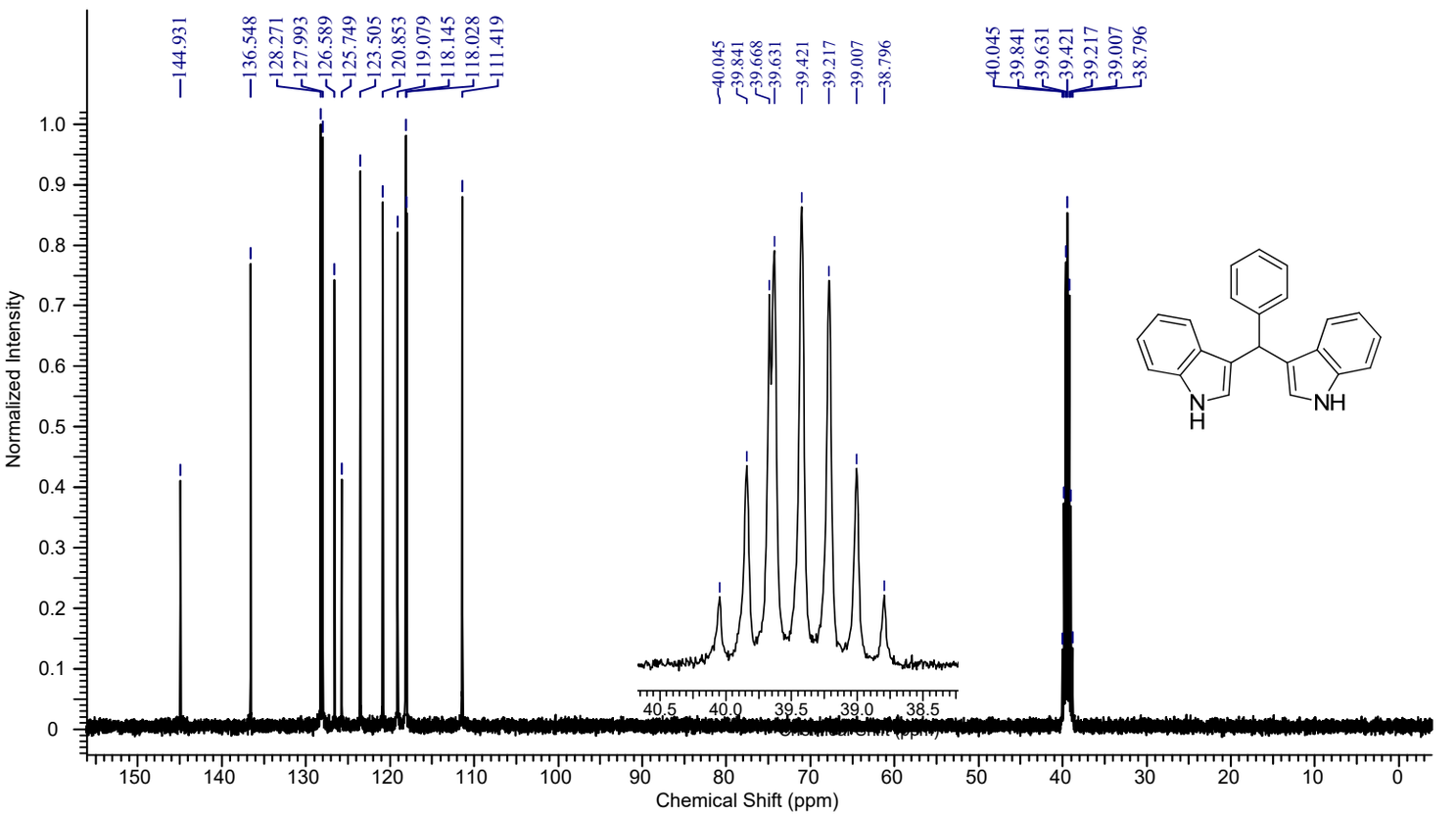
M.p 249-251 °C; IR (KBr): ν_{max}3410, 3394, 3047, 2969, 2923, 1618, 1513, 1460, 1216, 753 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.65 (s, 2H, NH), 9.14 (s, 1H, OH), 8.00 (d, *J*=9.2 Hz, 1H, Ar-H), 7.73 (d, *J*=8.8 Hz, 1H, Ar-H), 7.67 (d, *J*=9.2 Hz, 1H, Ar-H), 7.19-7.12 (m, 5H, Ar-H), 6.85 (d, *J*=8 Hz, 2H, Ar-H), 6.75 (d, *J*=8.8 Hz, 3H, Ar-H), 6.60 (brs, 2H, Ar-H and CH), 1.85 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.9, 134.8, 132.1, 128.7, 128.3, 127.9, 121.8, 119.4, 118.5, 118.2, 117.8, 110.1, 56.0, 31.6, 11.8. ESI-MS: *m/z* 416 $[M]^+$, 455 $[M+K]^+$.Anal.Calcd for $C_{29}H_{24}N_2O$: C, 83.63; 5.81; N, 6.73; Found: C, 83.80; H, 5.69; N, 6.63.

Spectra

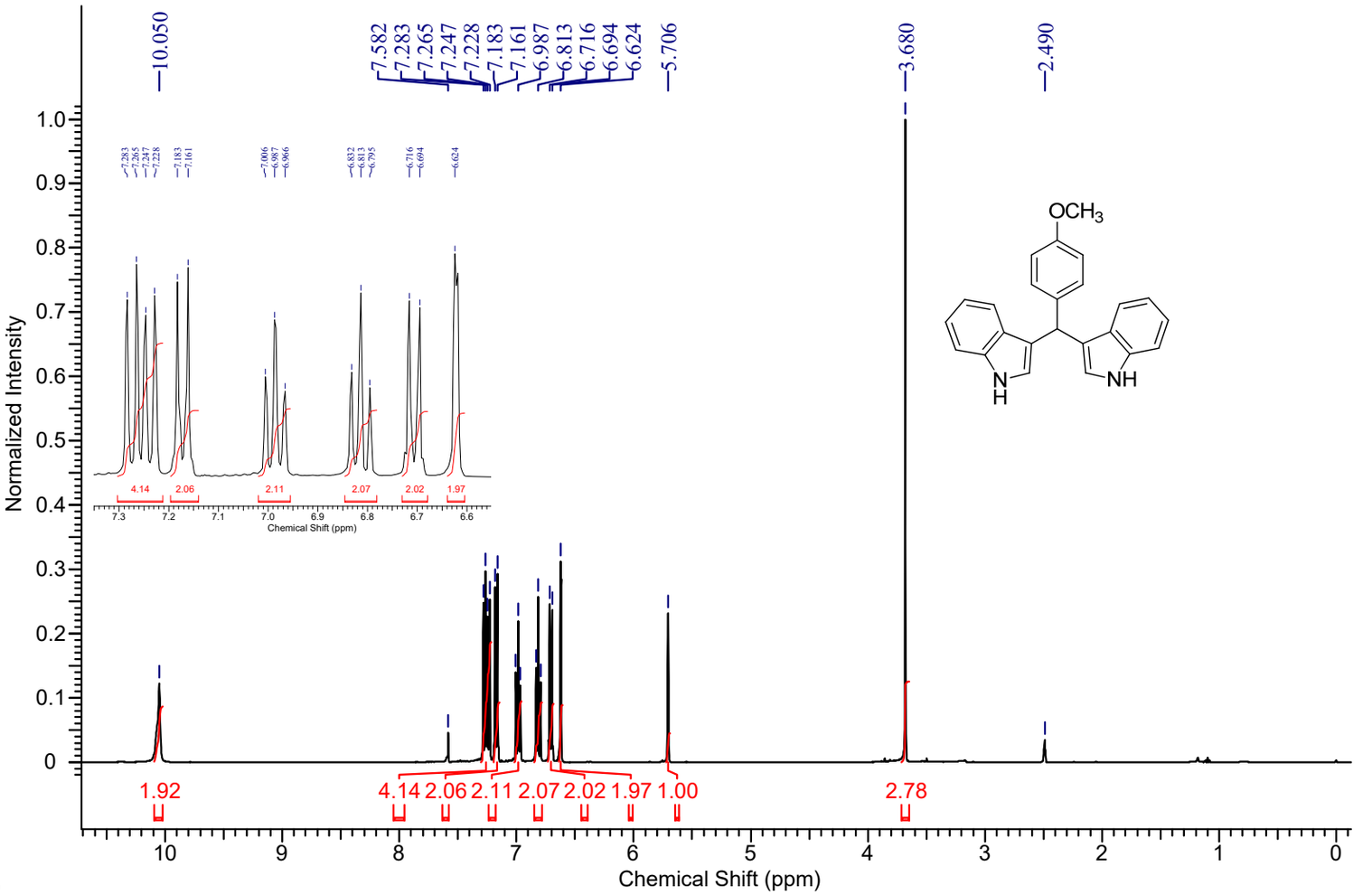
^{1}H NMR of 3a



^{13}C NMR of 3a

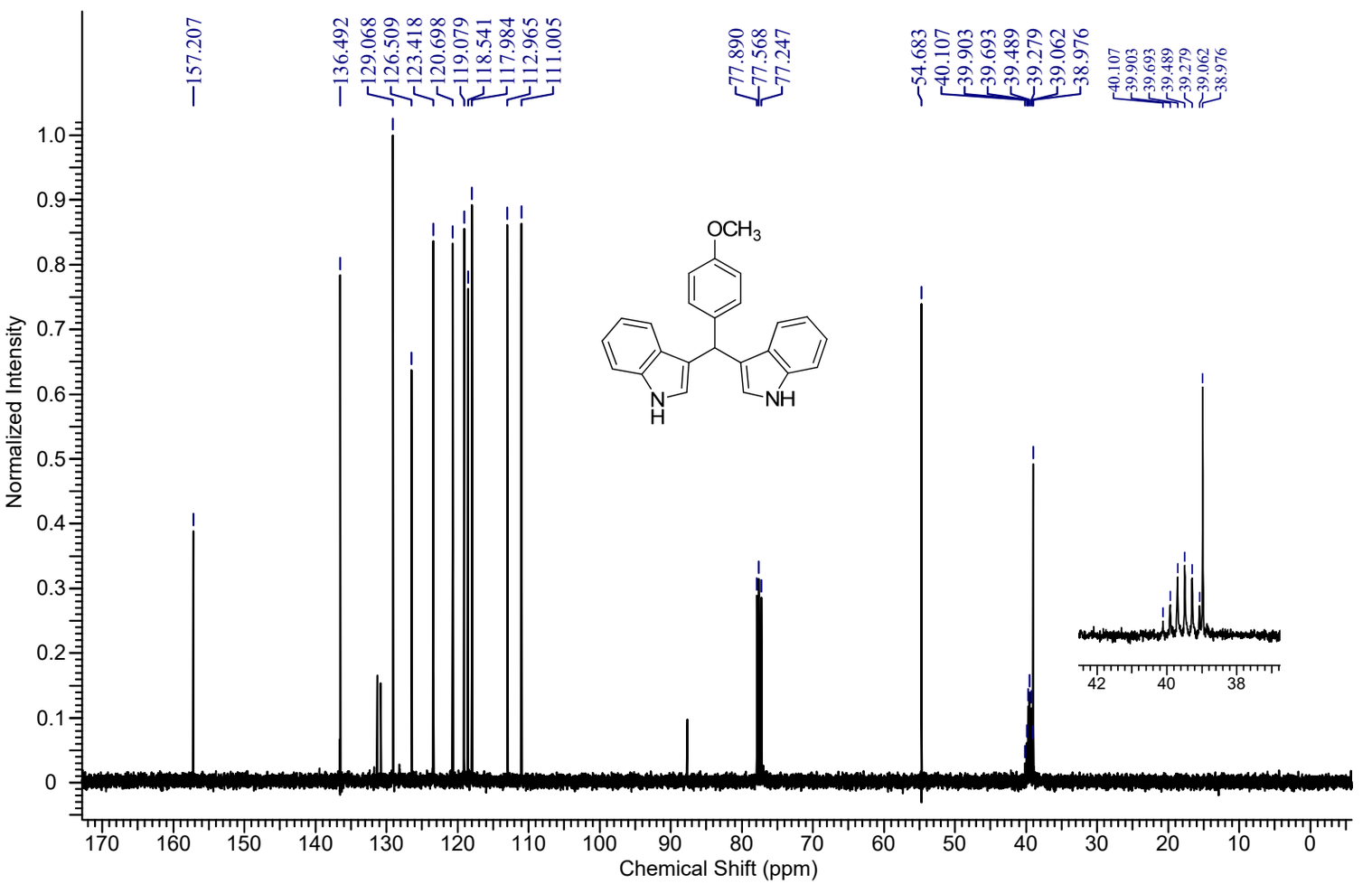


^{1}H NMR of

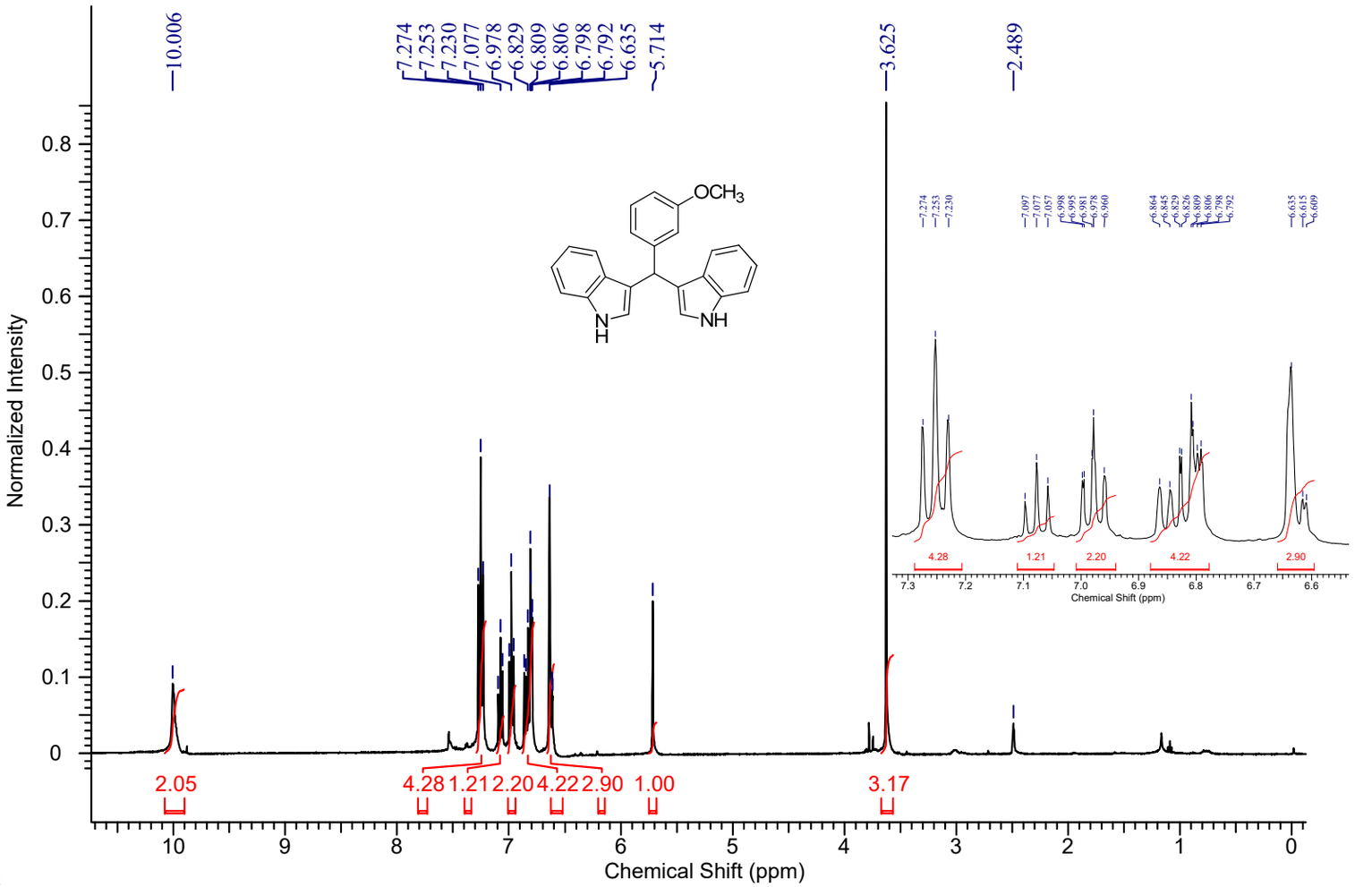


3b

^{13}C NMR of 3b

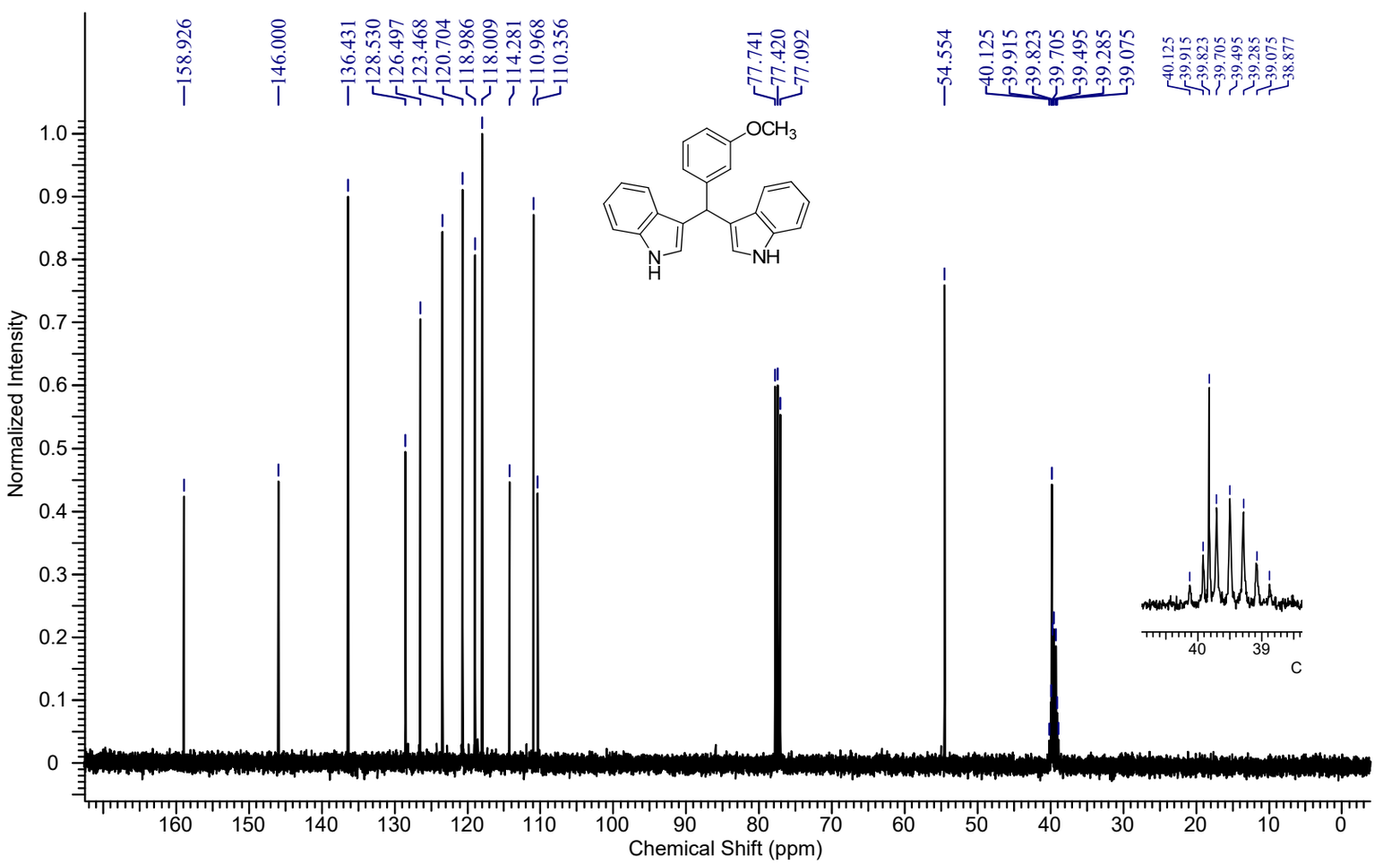


^{1}H NMR of

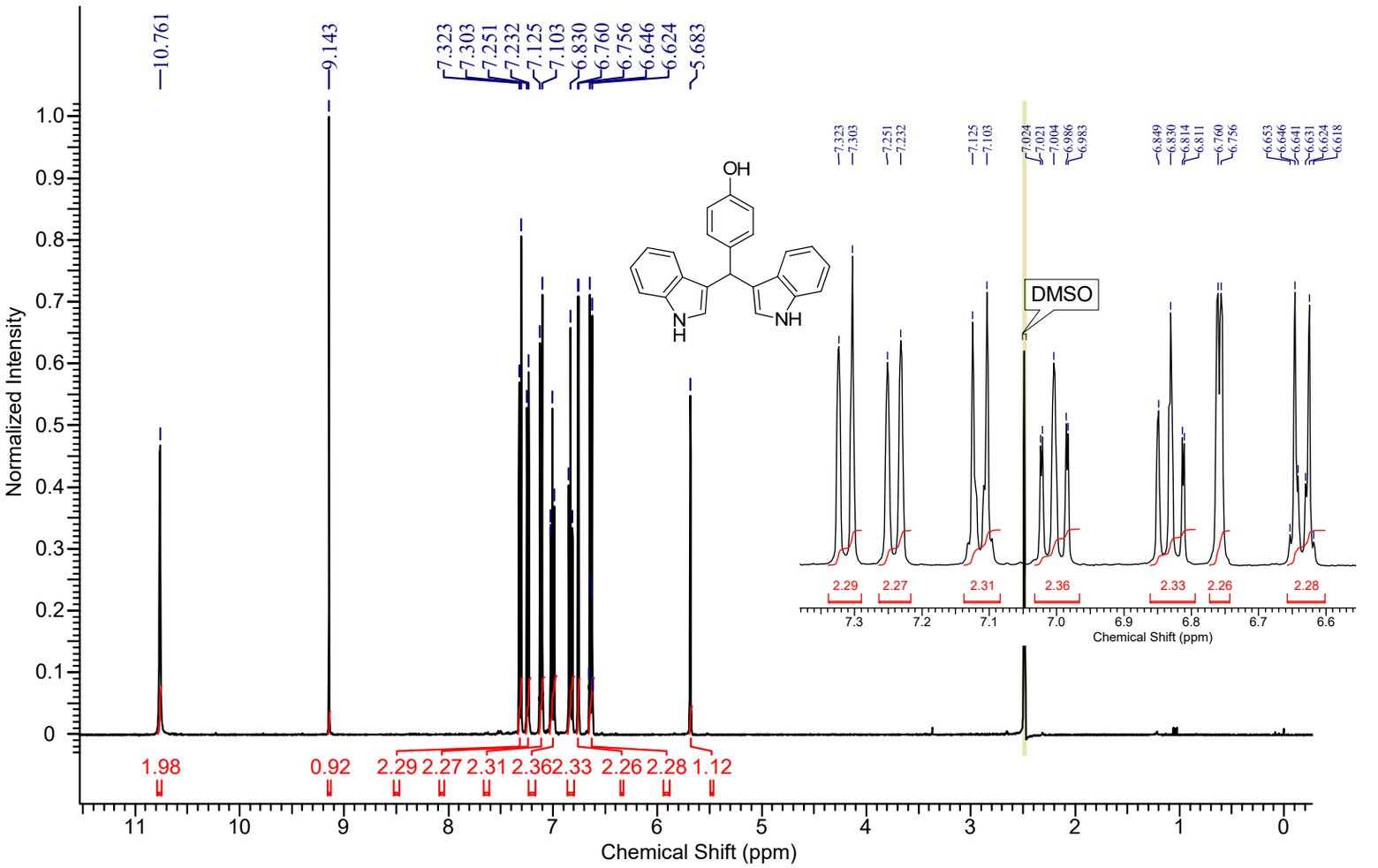


3c

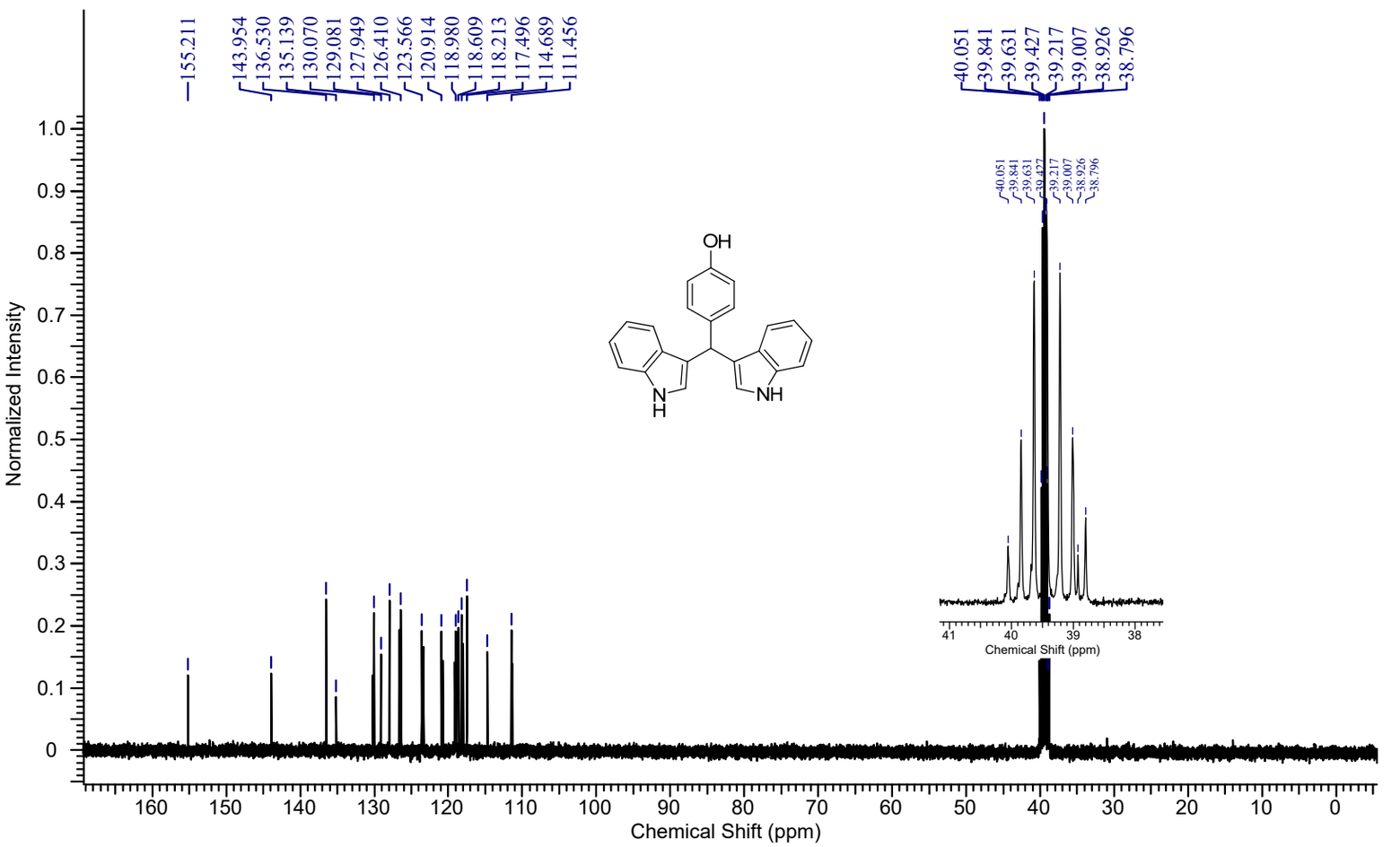
^{13}C NMR of 3c



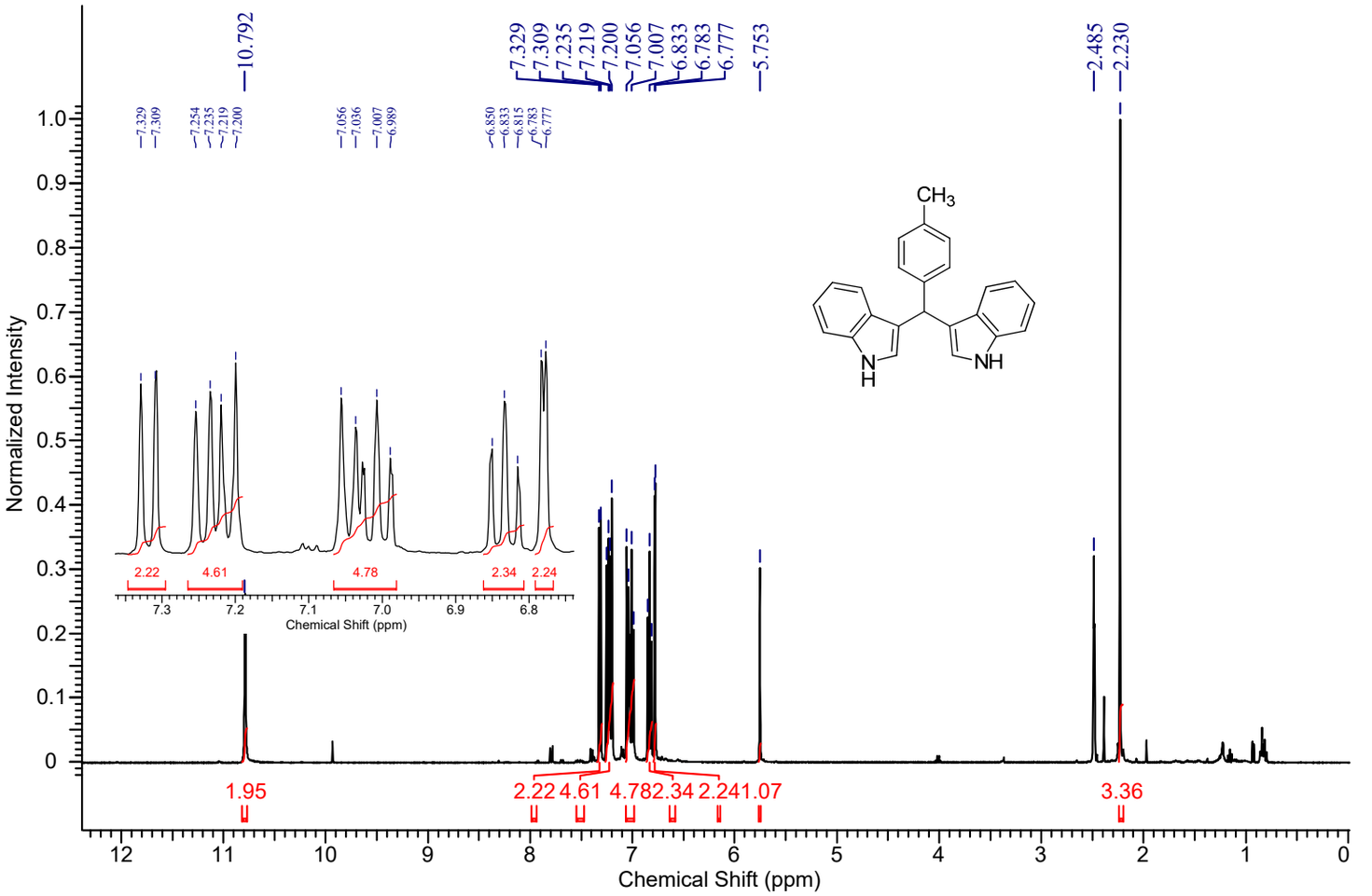
^{1}H NMR of 3d



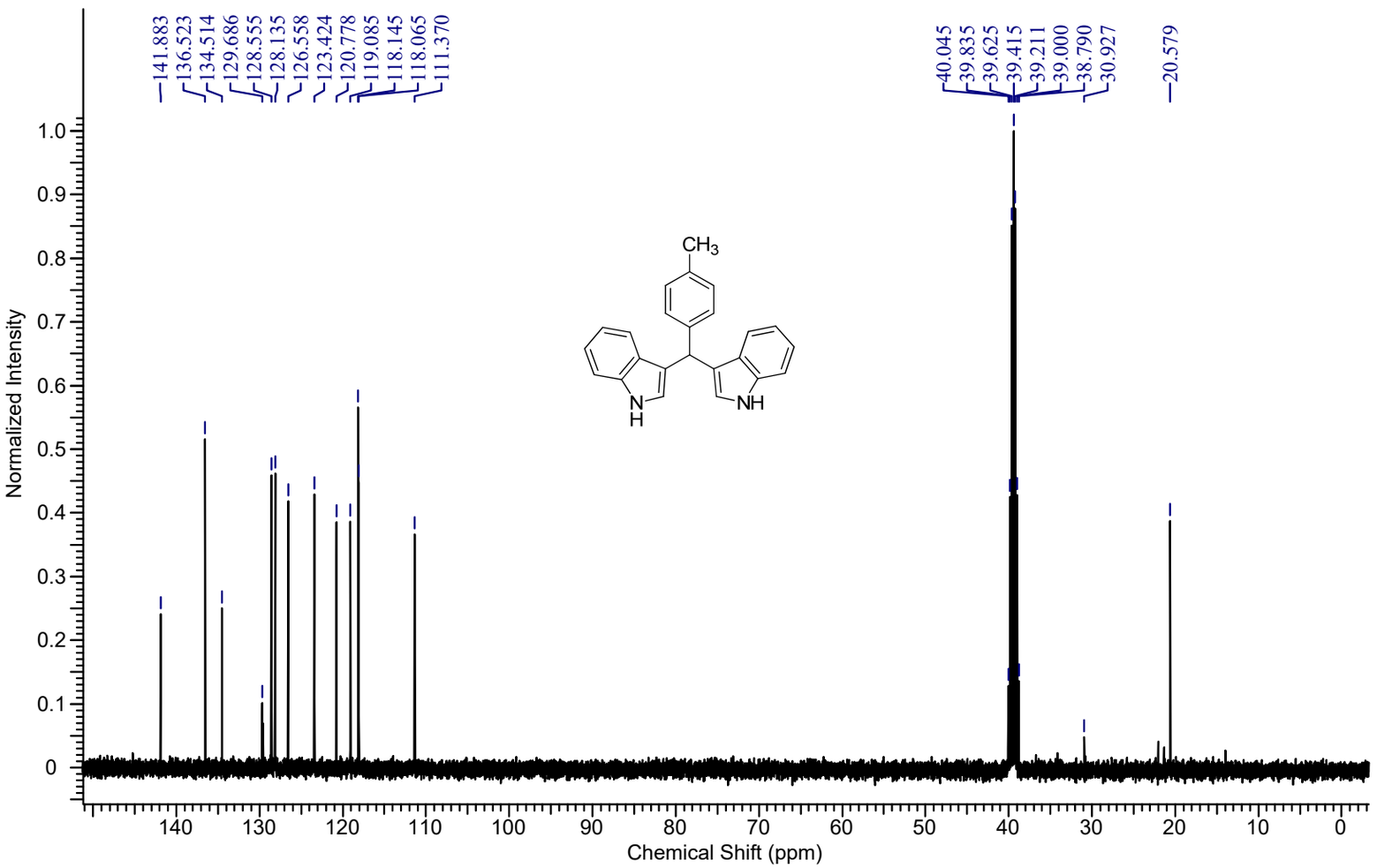
^{13}C NMR of 3d



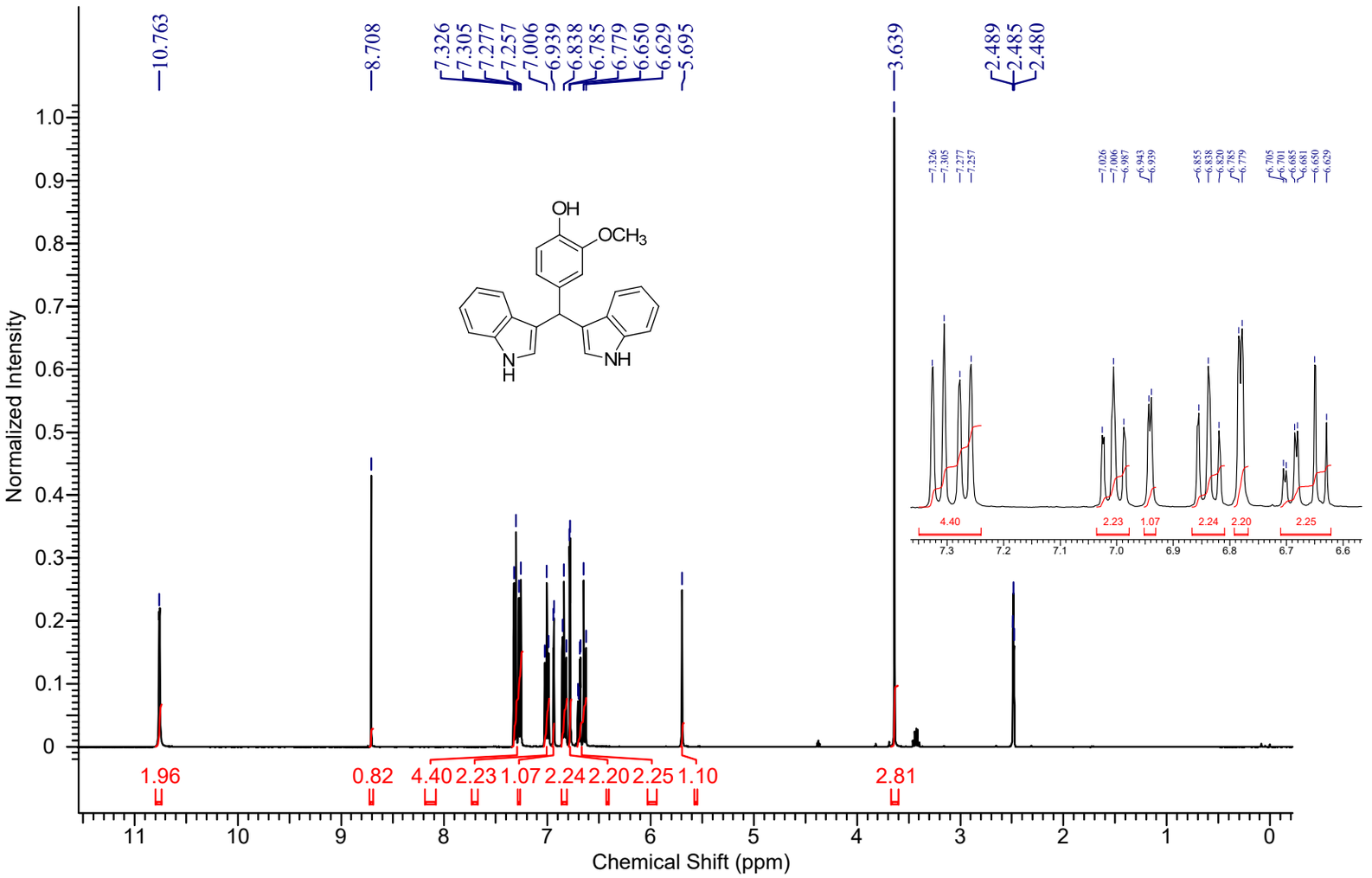
^{1}H NMR of 3e



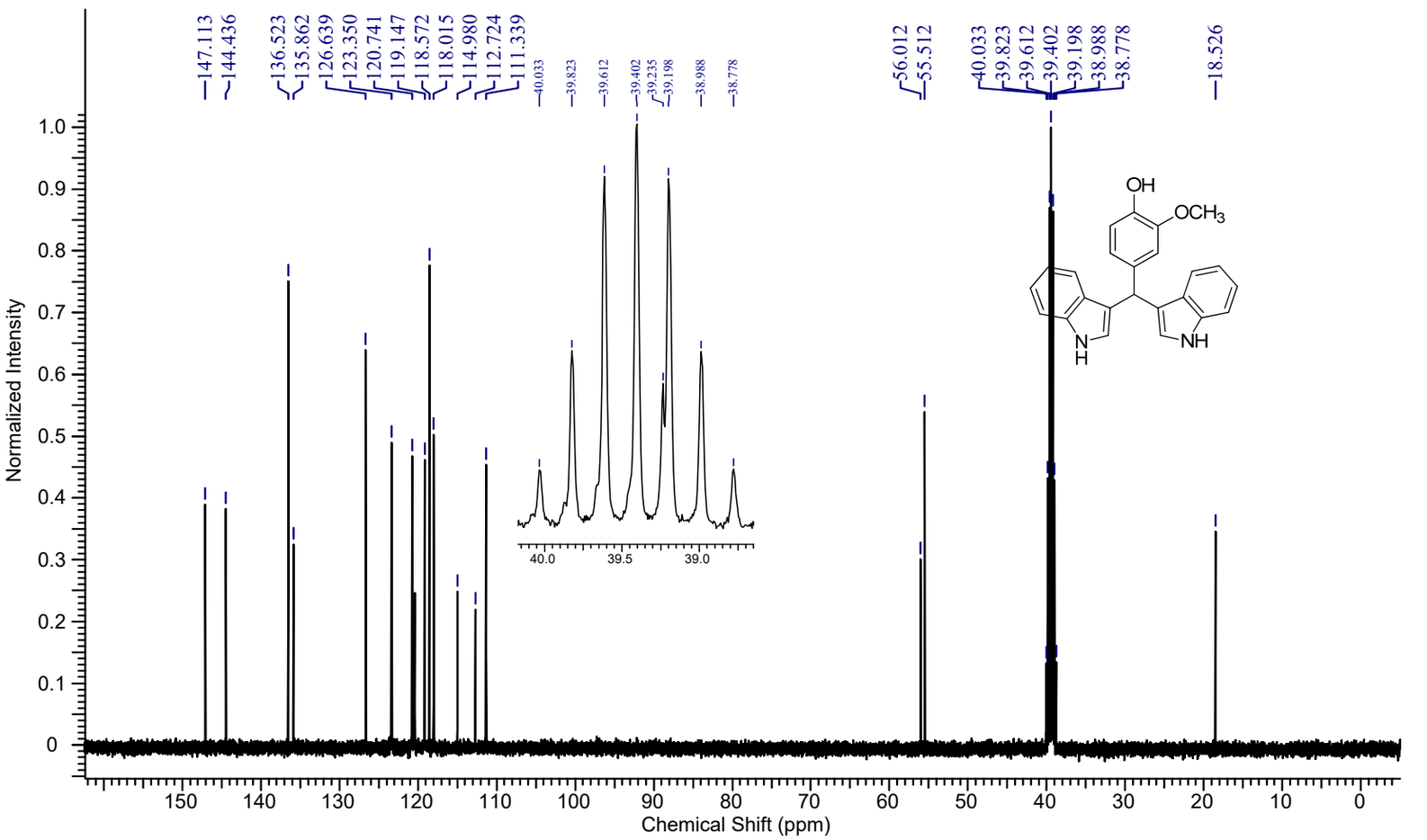
^{13}C NMR of 3e



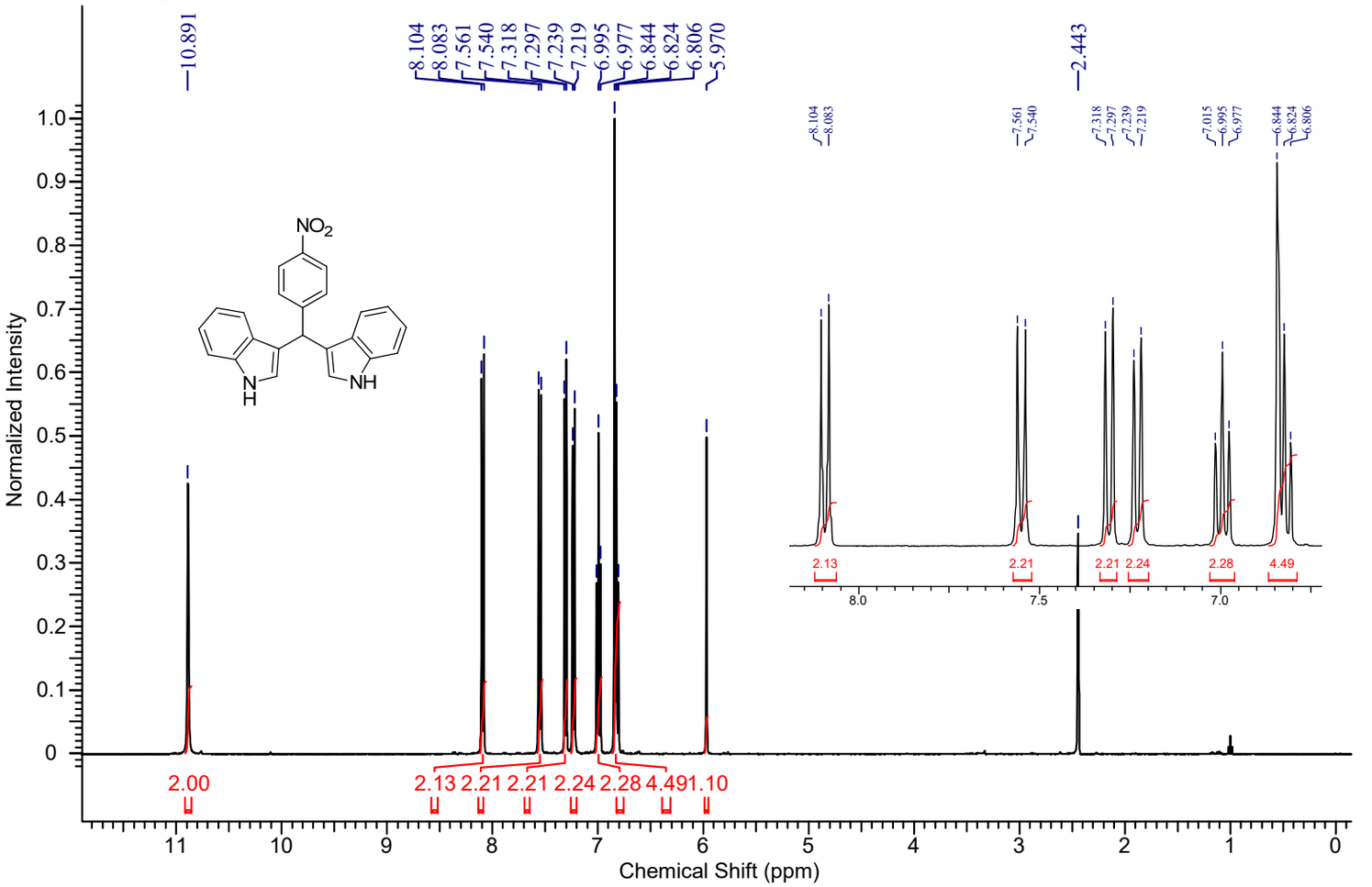
^{1}H NMR of 3f



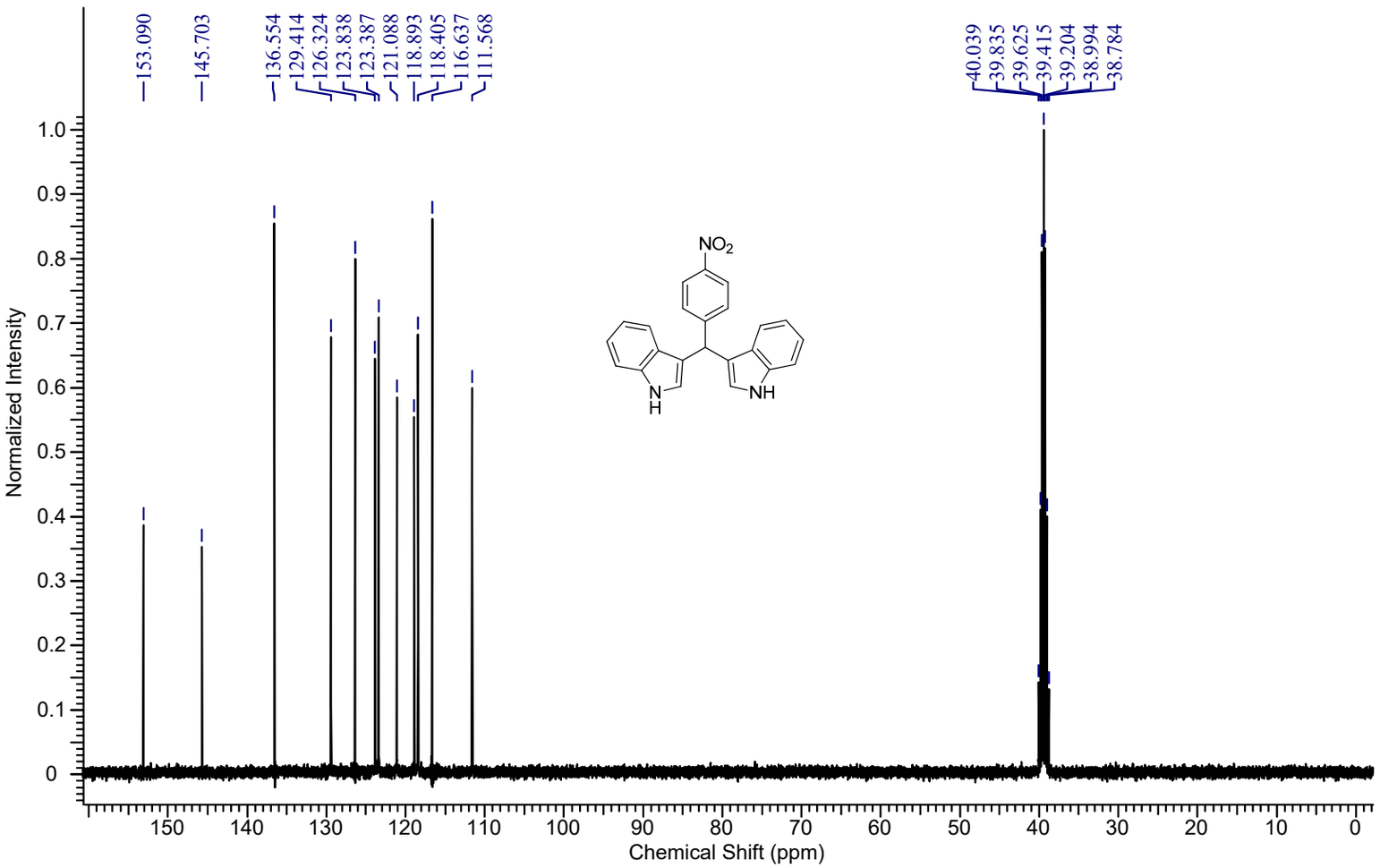
^{13}C NMR of 3f



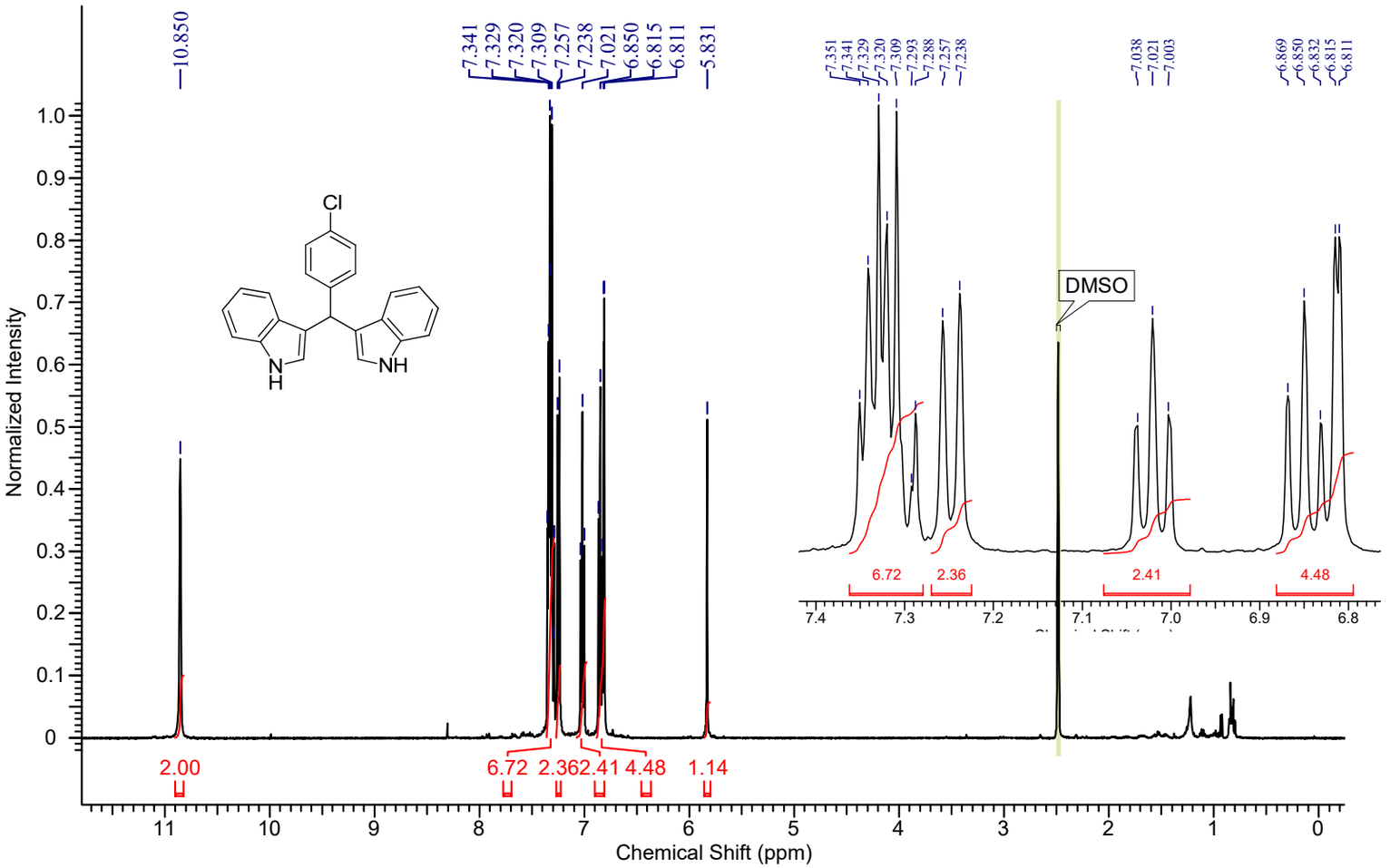
^{1}H NMR of 3g



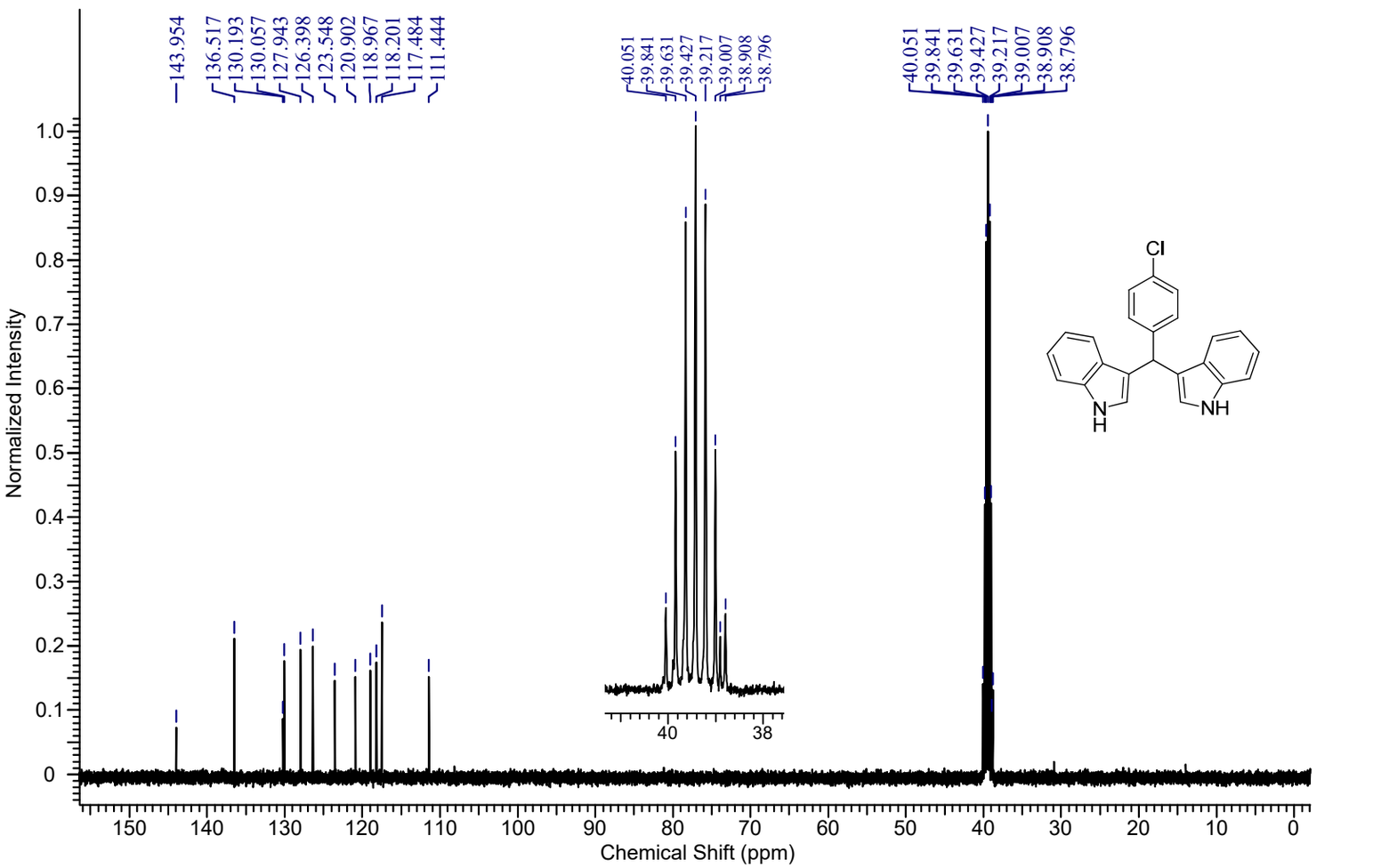
^{13}C NMR of 3g



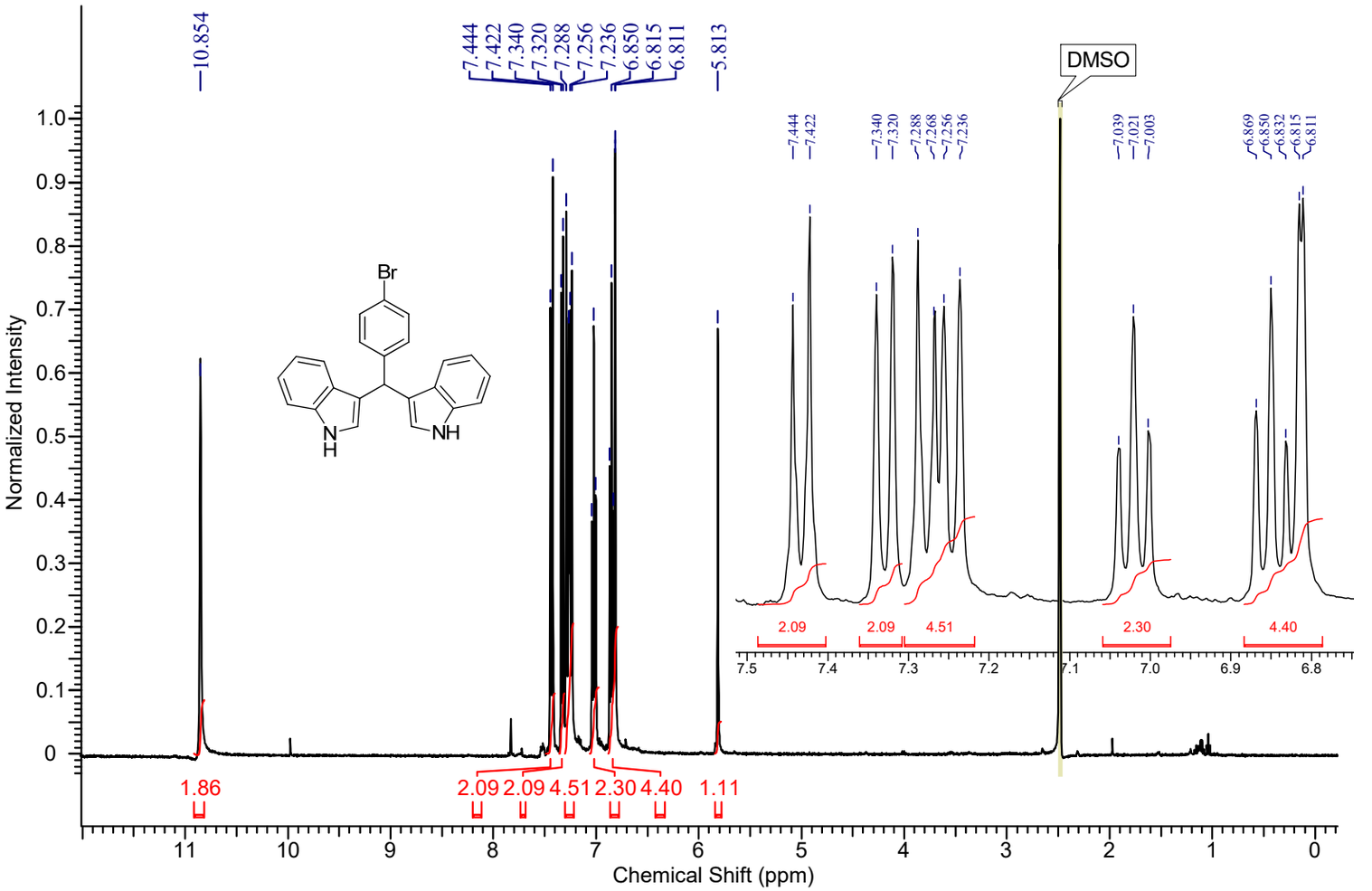
^{1}H NMR of 3h



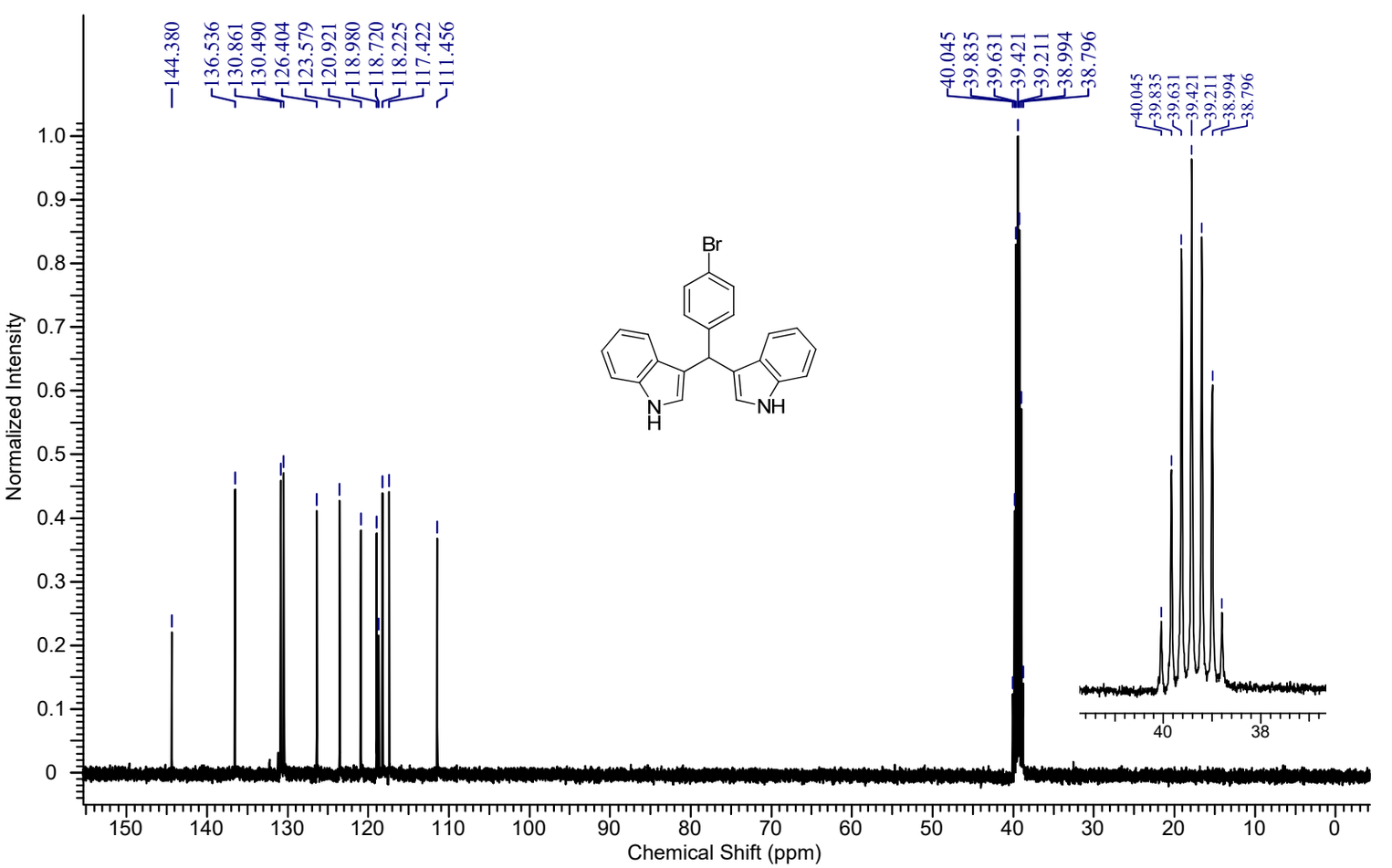
^{13}C NMR of 3h



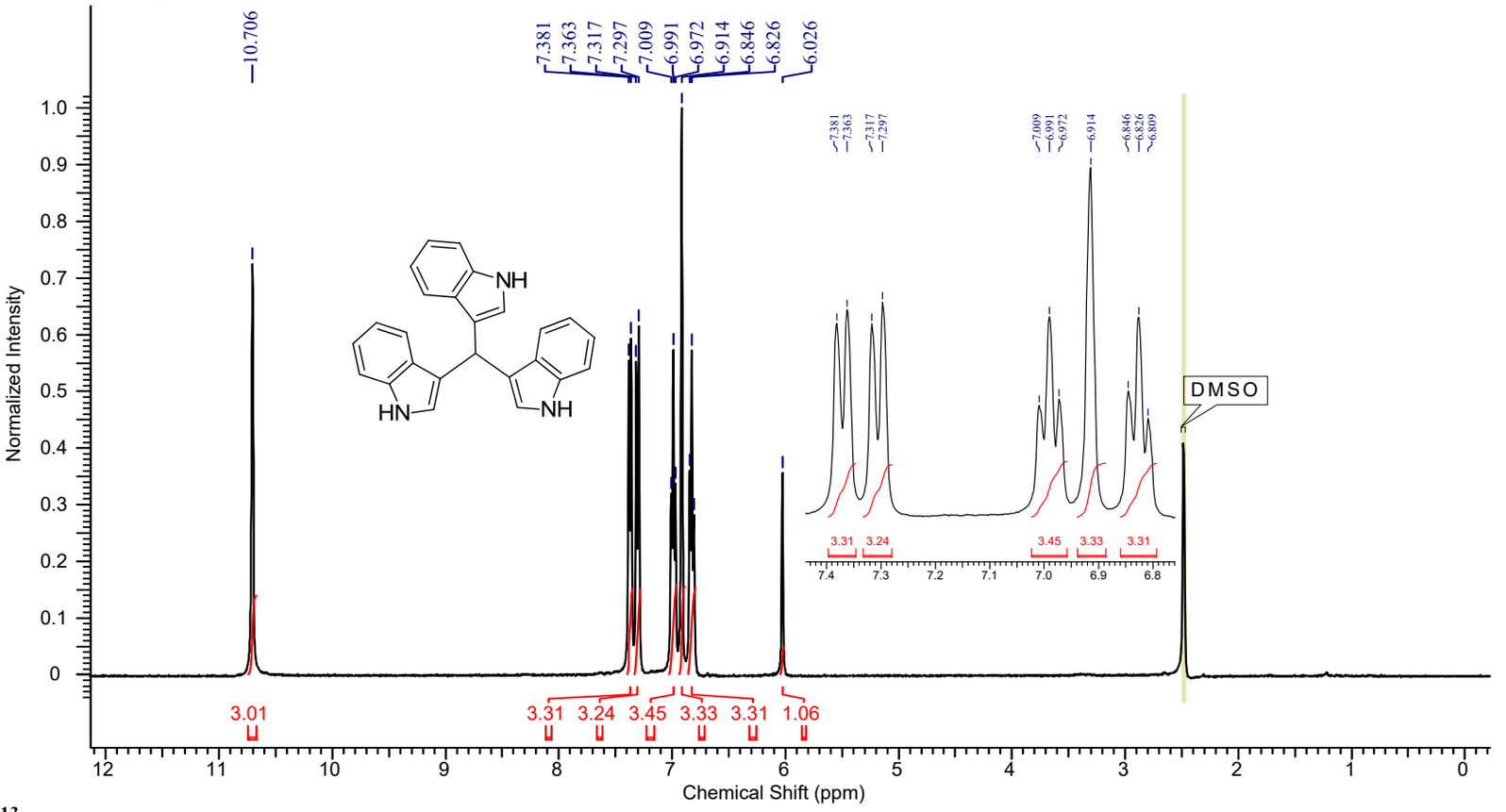
^{1}H NMR of 3i



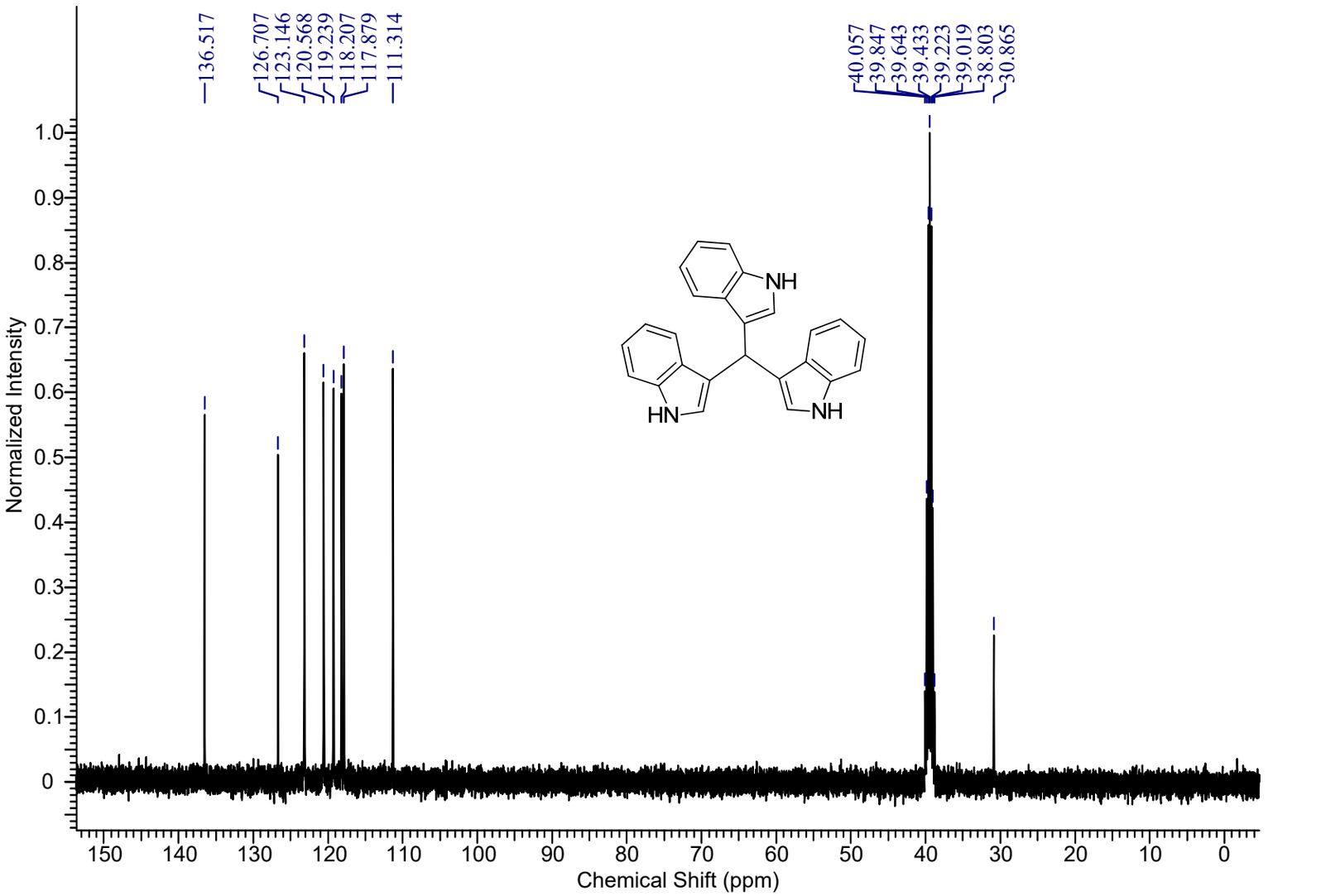
^{13}C NMR of 3i



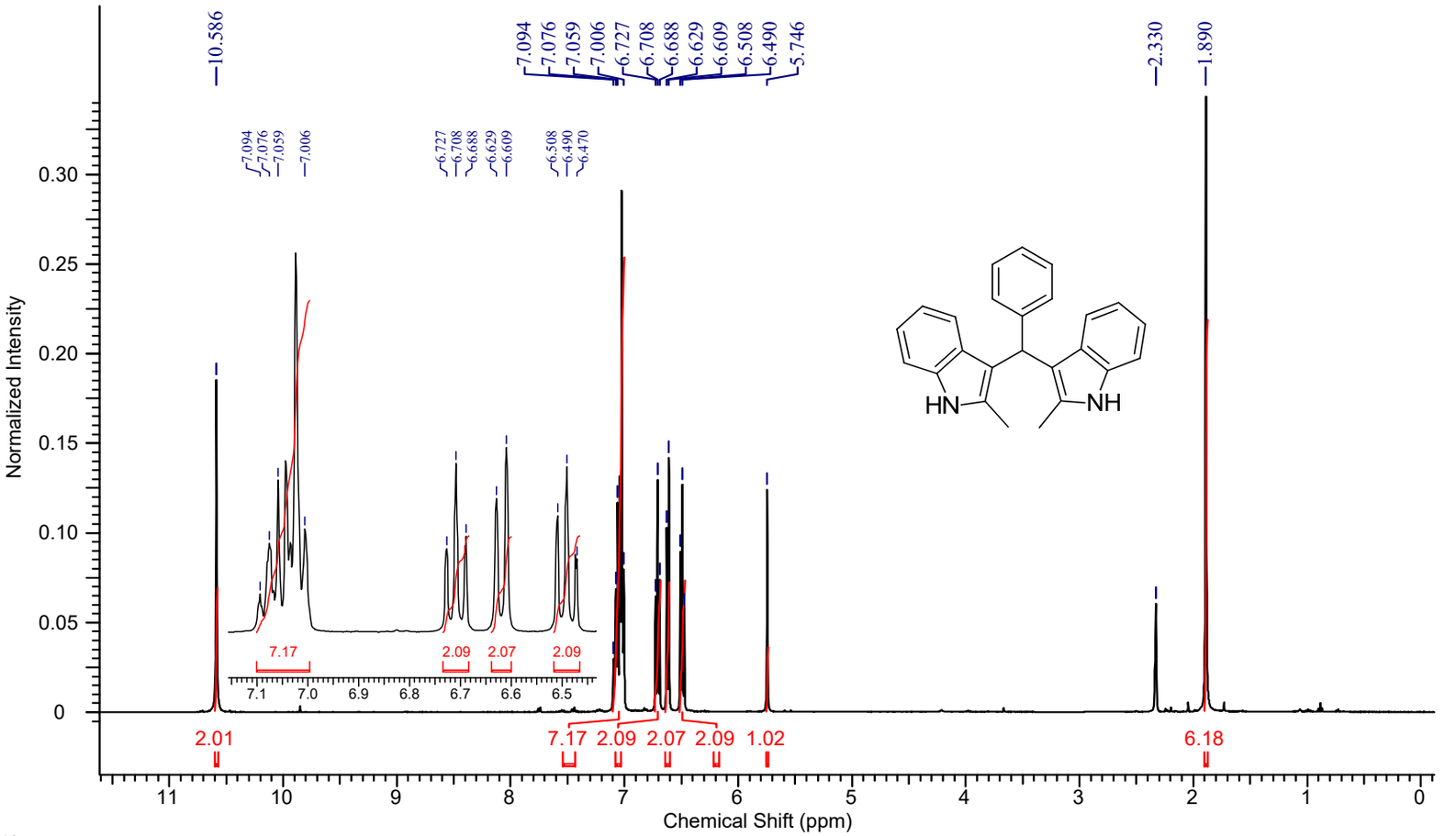
^{1}H NMR of 3j



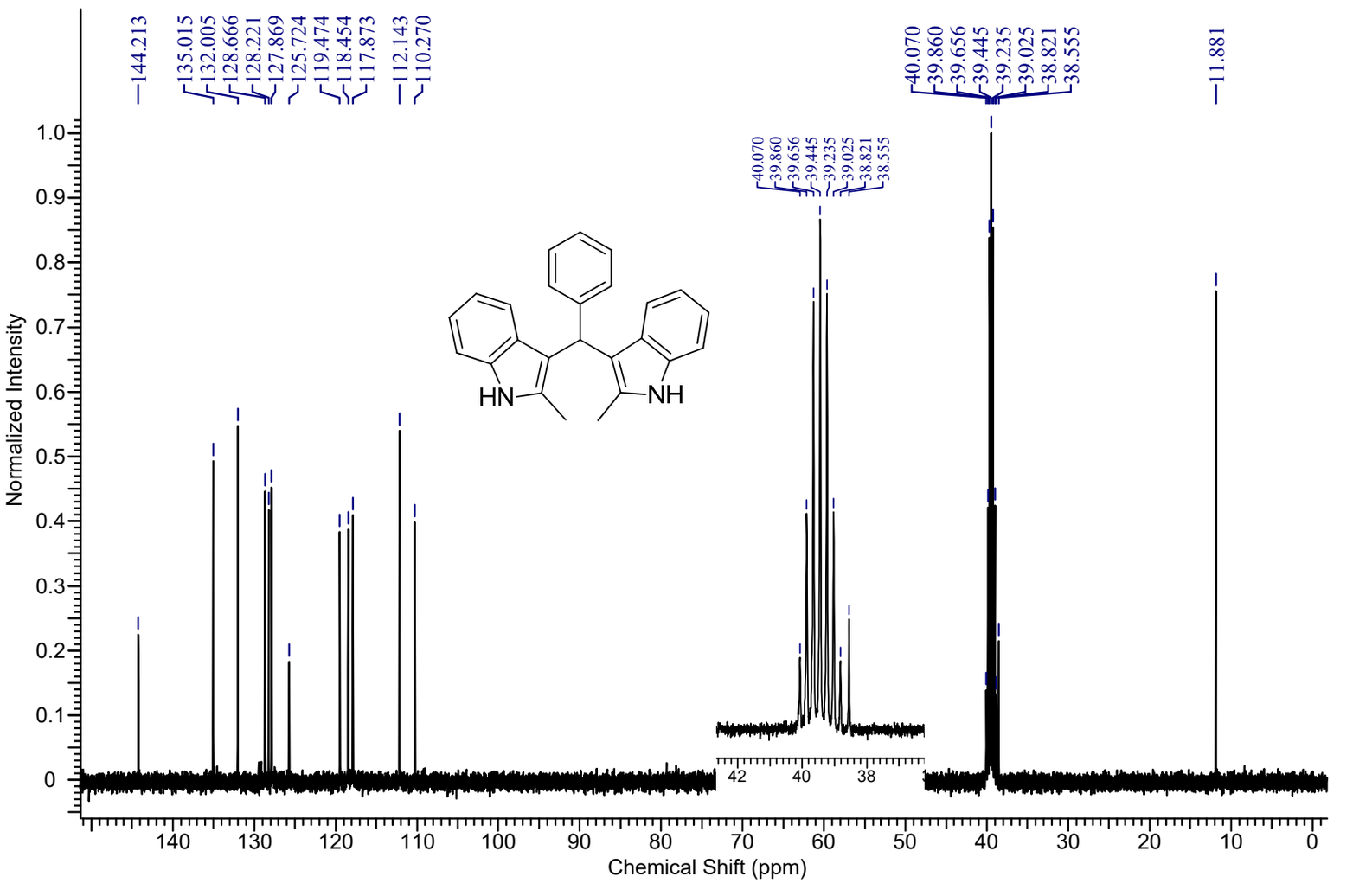
^{13}C NMR of 3j



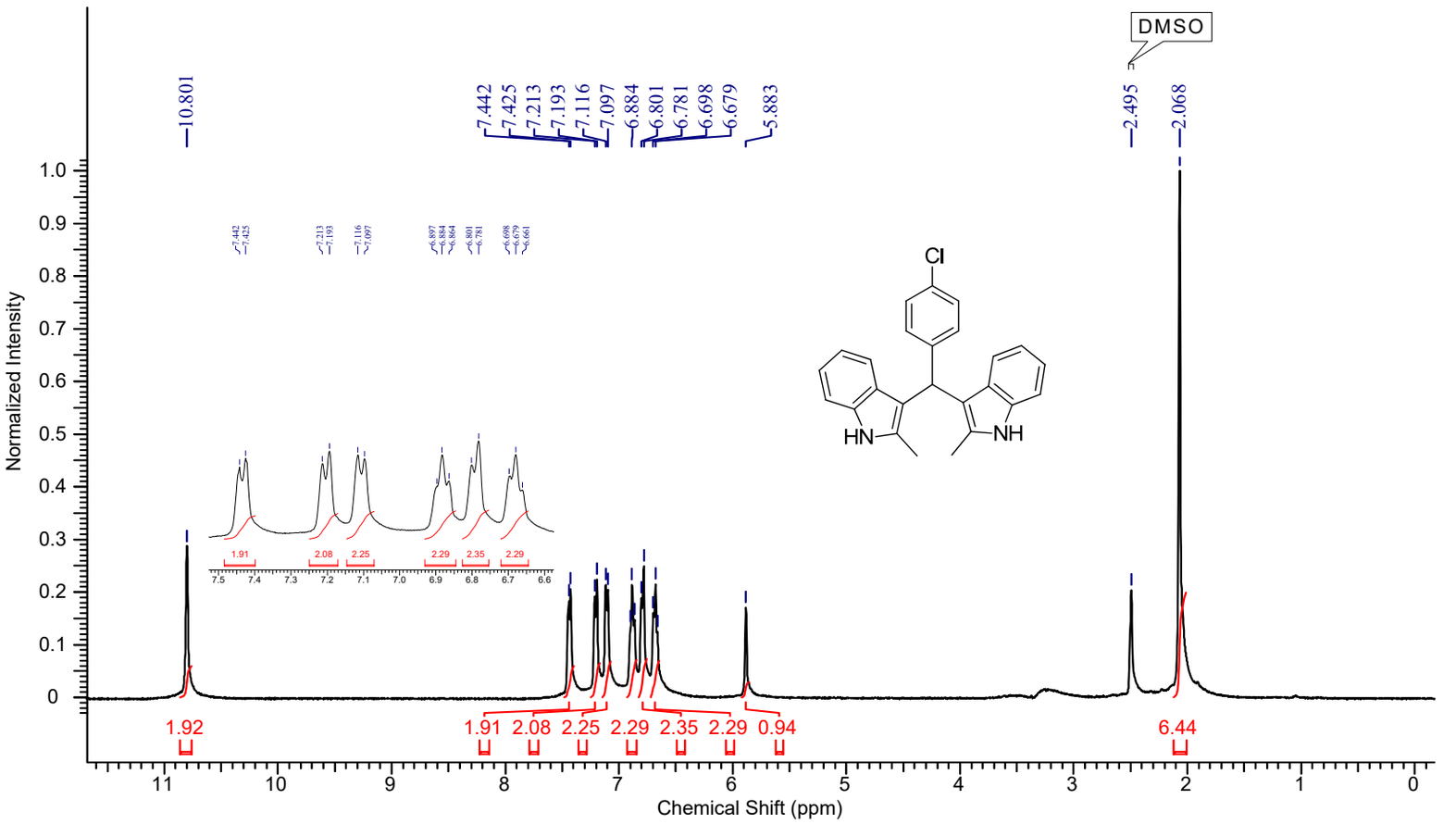
^{1}H NMR of 4a



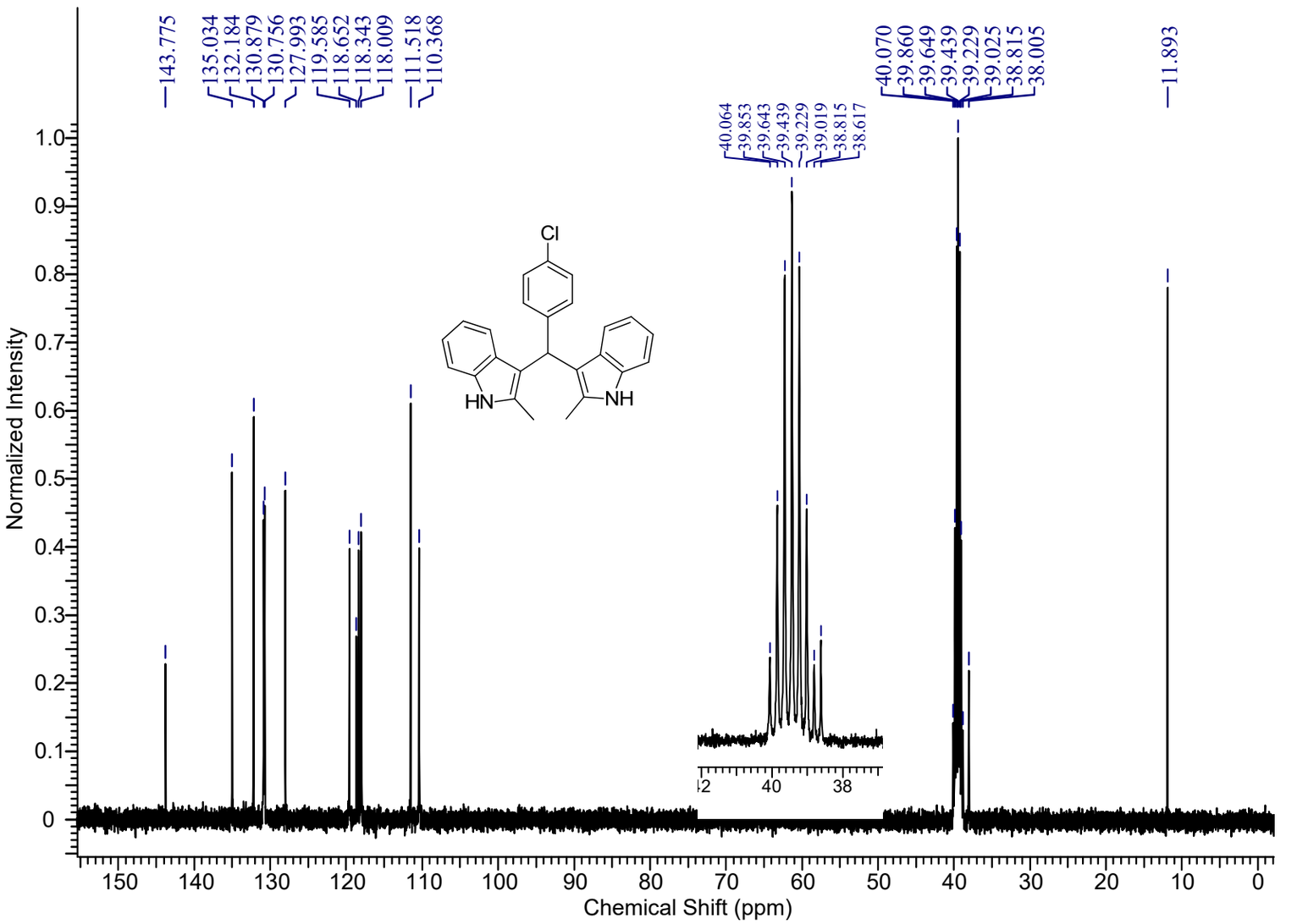
^{13}C NMR of 4a



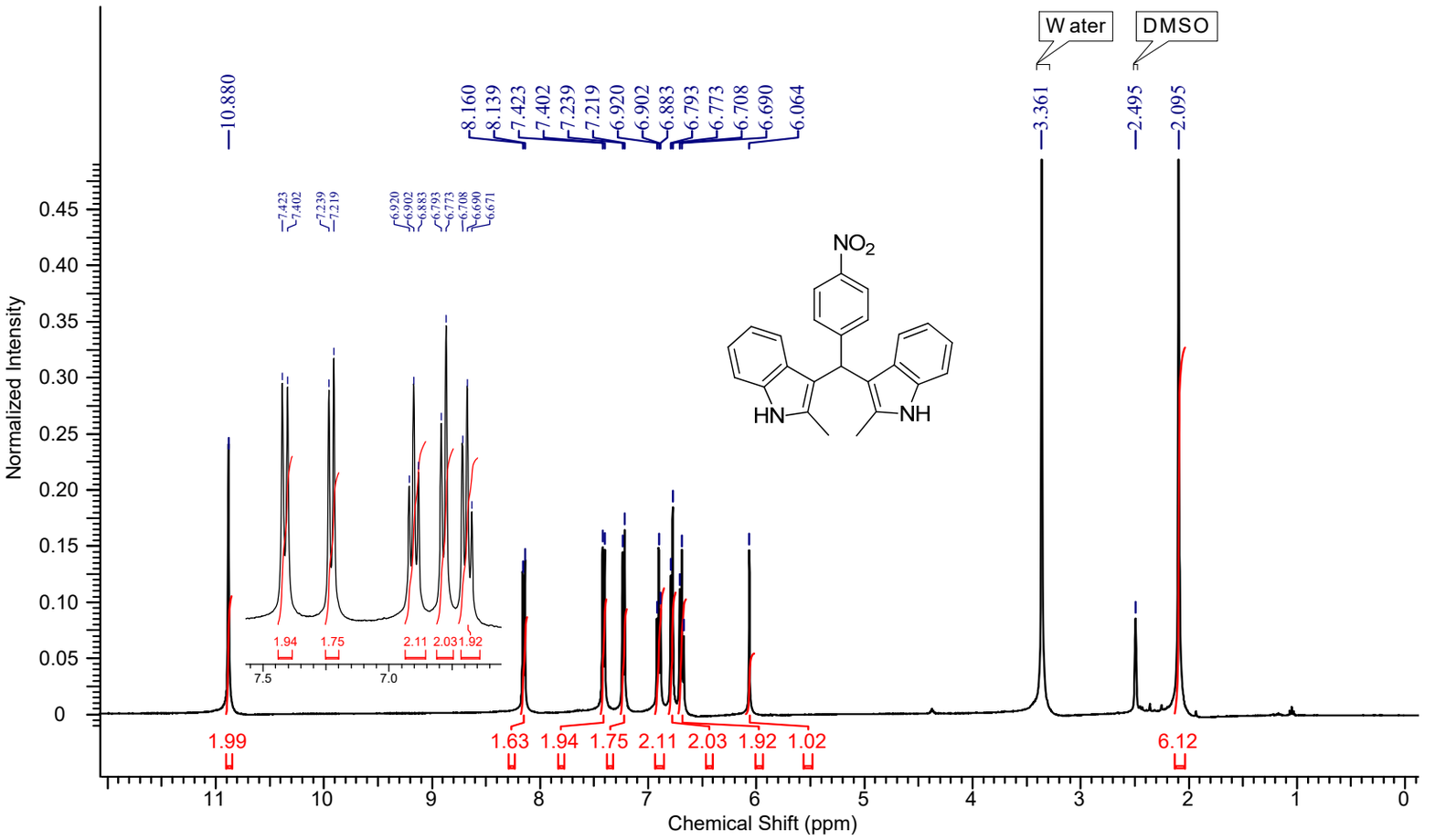
^{1}H NMR of 4b


DMSO
10.801
7.442
7.425
7.213
7.193
7.116
7.097
6.884
6.801
6.781
6.698
6.679
5.883
2.495
2.068
Cl
HN
NH
Normalized Intensity
1.92
1.91
2.08
2.25
2.29
2.35
2.29
0.94
6.44
Chemical Shift (ppm)

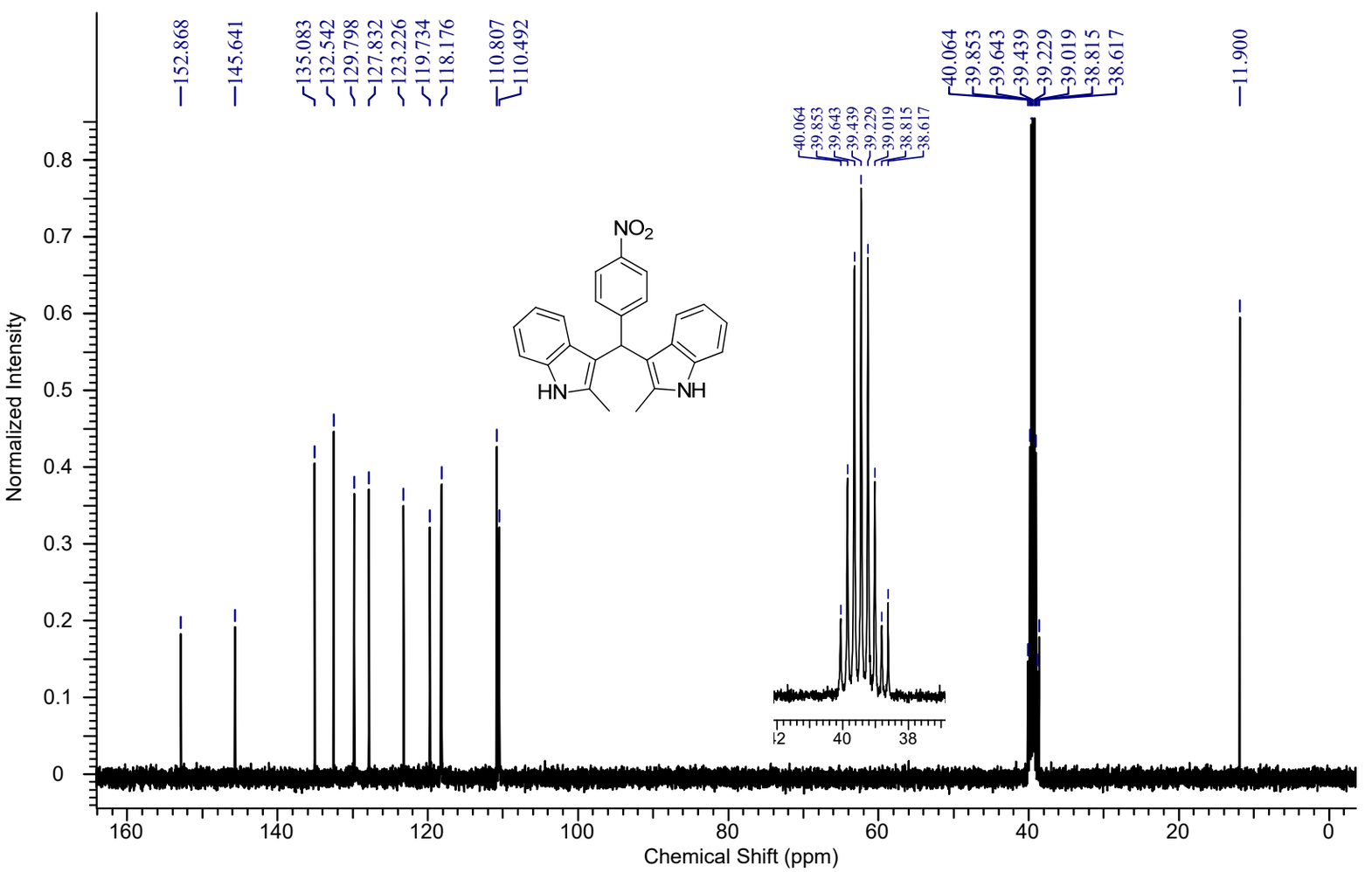
^{13}C NMR of 4b


143.775
135.034
132.184
130.879
130.756
127.993
119.585
118.652
118.343
118.009
111.518
110.368
40.070
39.860
39.649
39.439
39.229
39.025
38.815
38.005
11.893
40.064
39.853
39.643
39.439
39.229
39.019
38.815
38.617
Cl
HN
NH
Normalized Intensity
Chemical Shift (ppm)

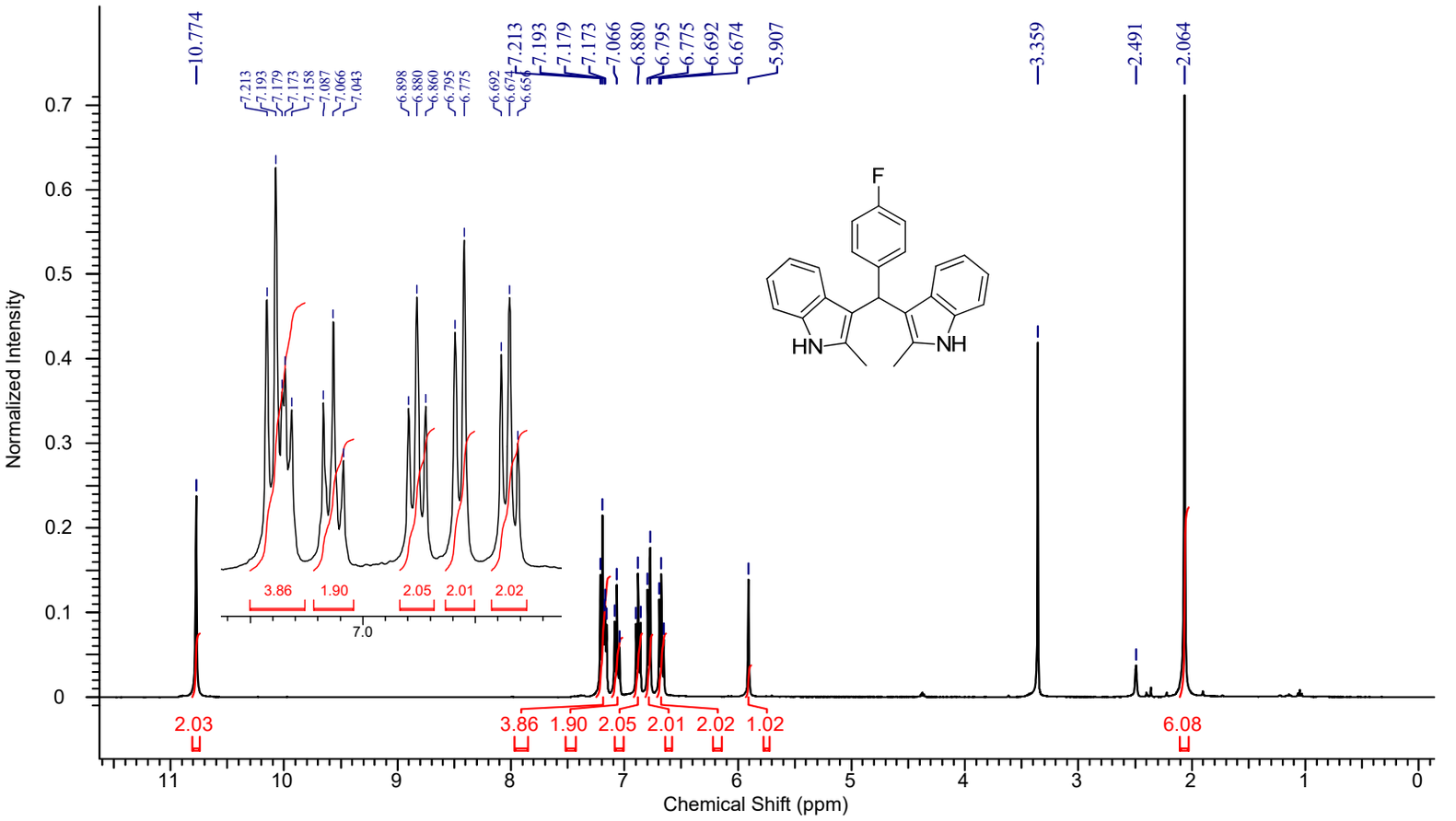
^{1}H NMR of 4c



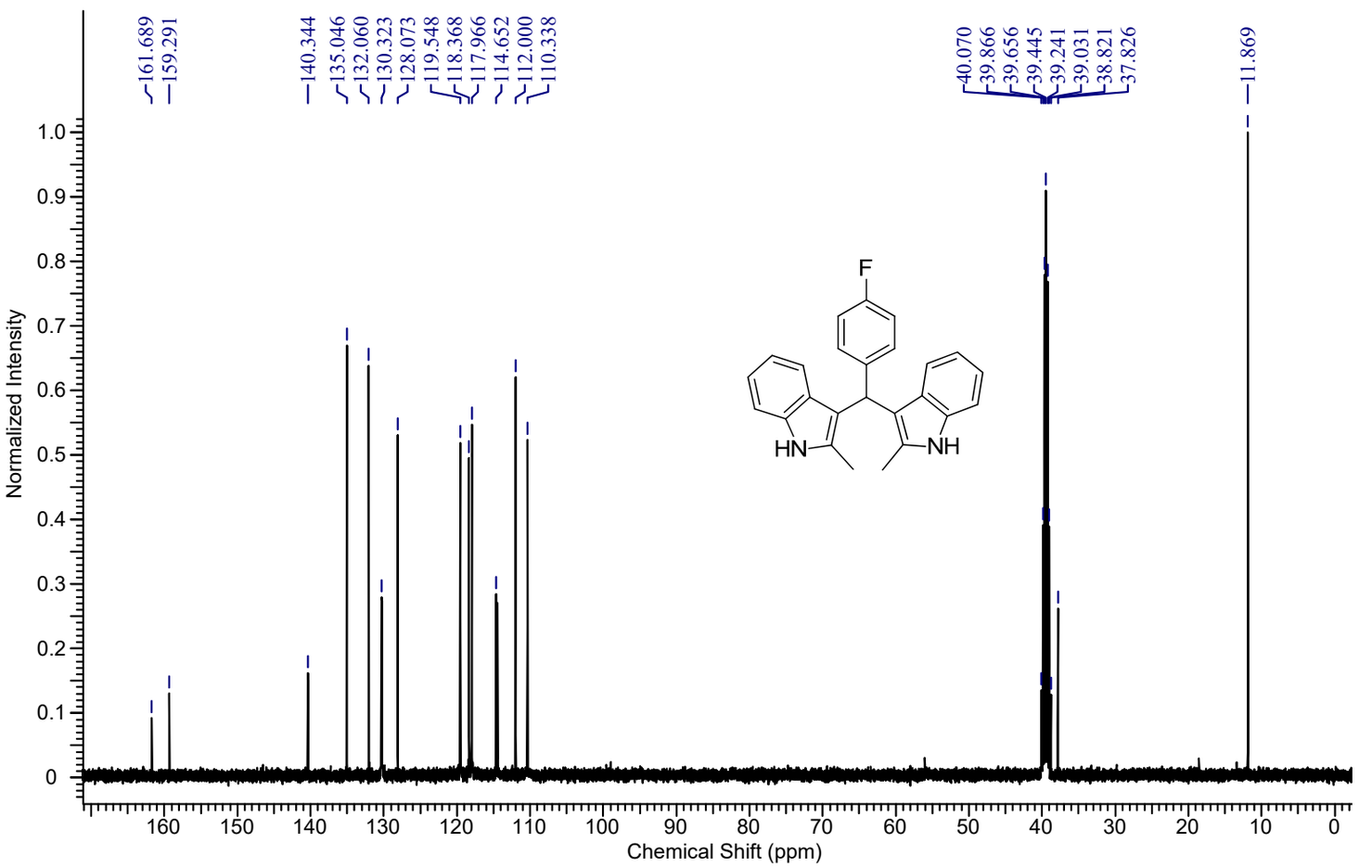
^{13}C NMR 4c



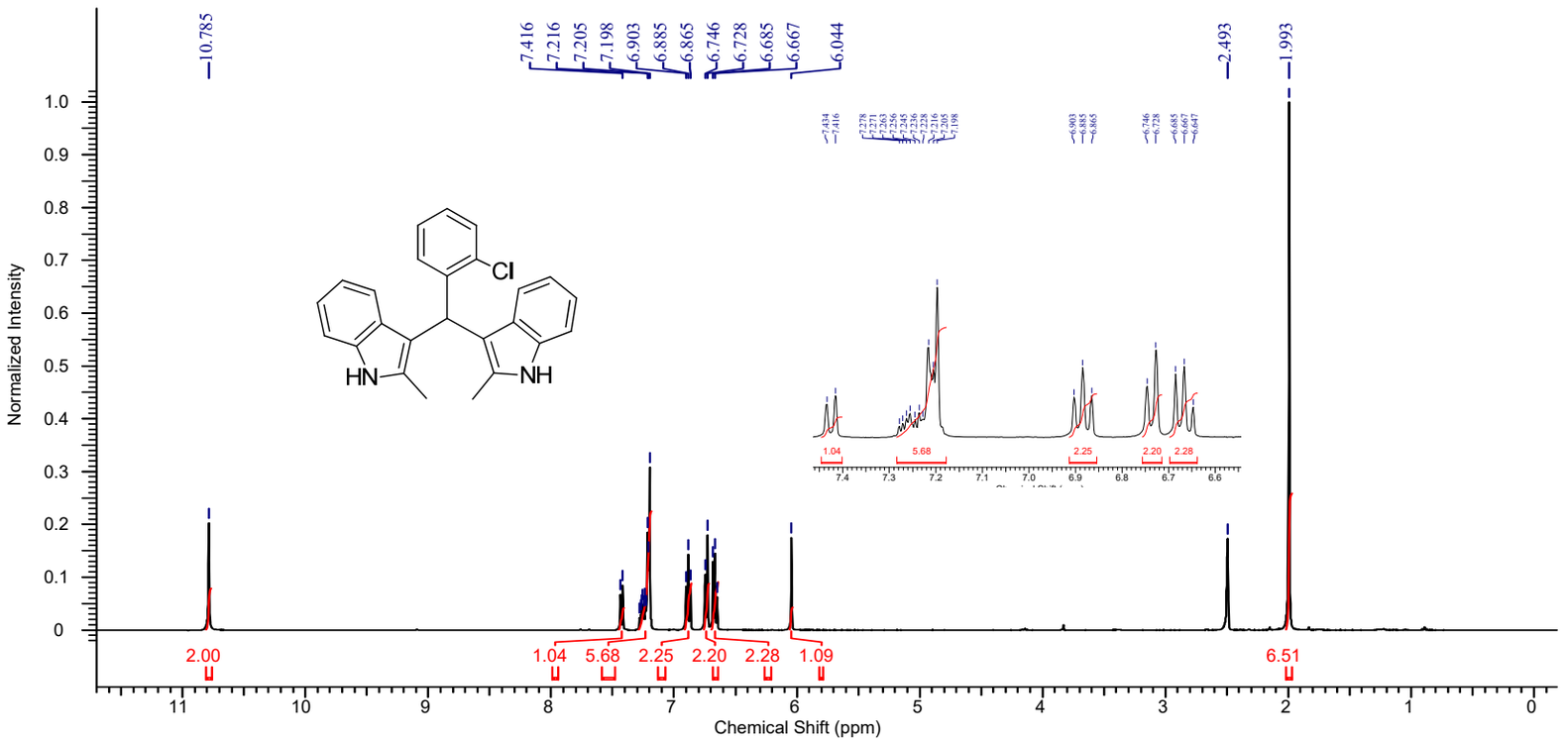
^{1}H NMR of 4d



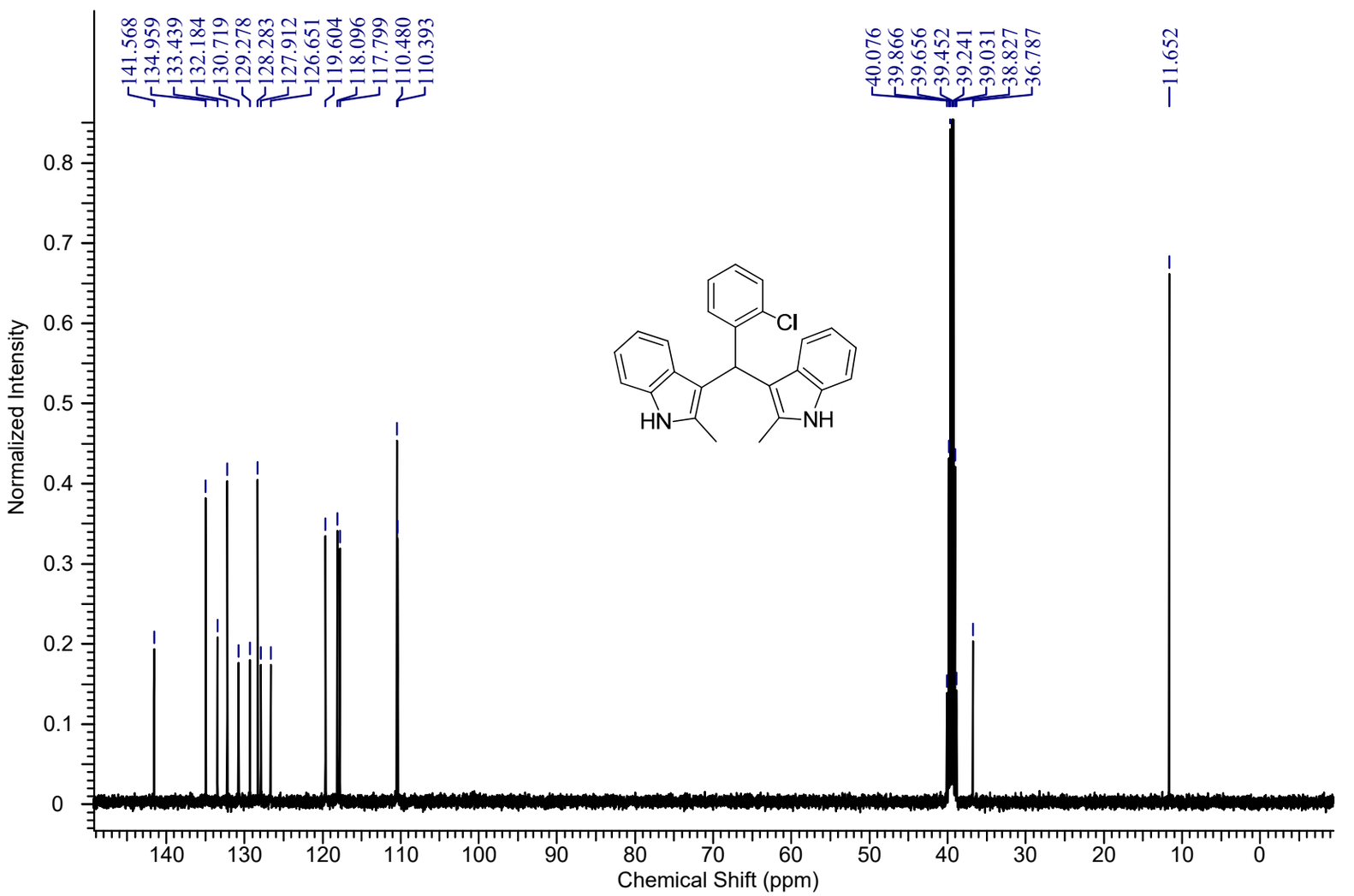
^{13}C NMR of 4d



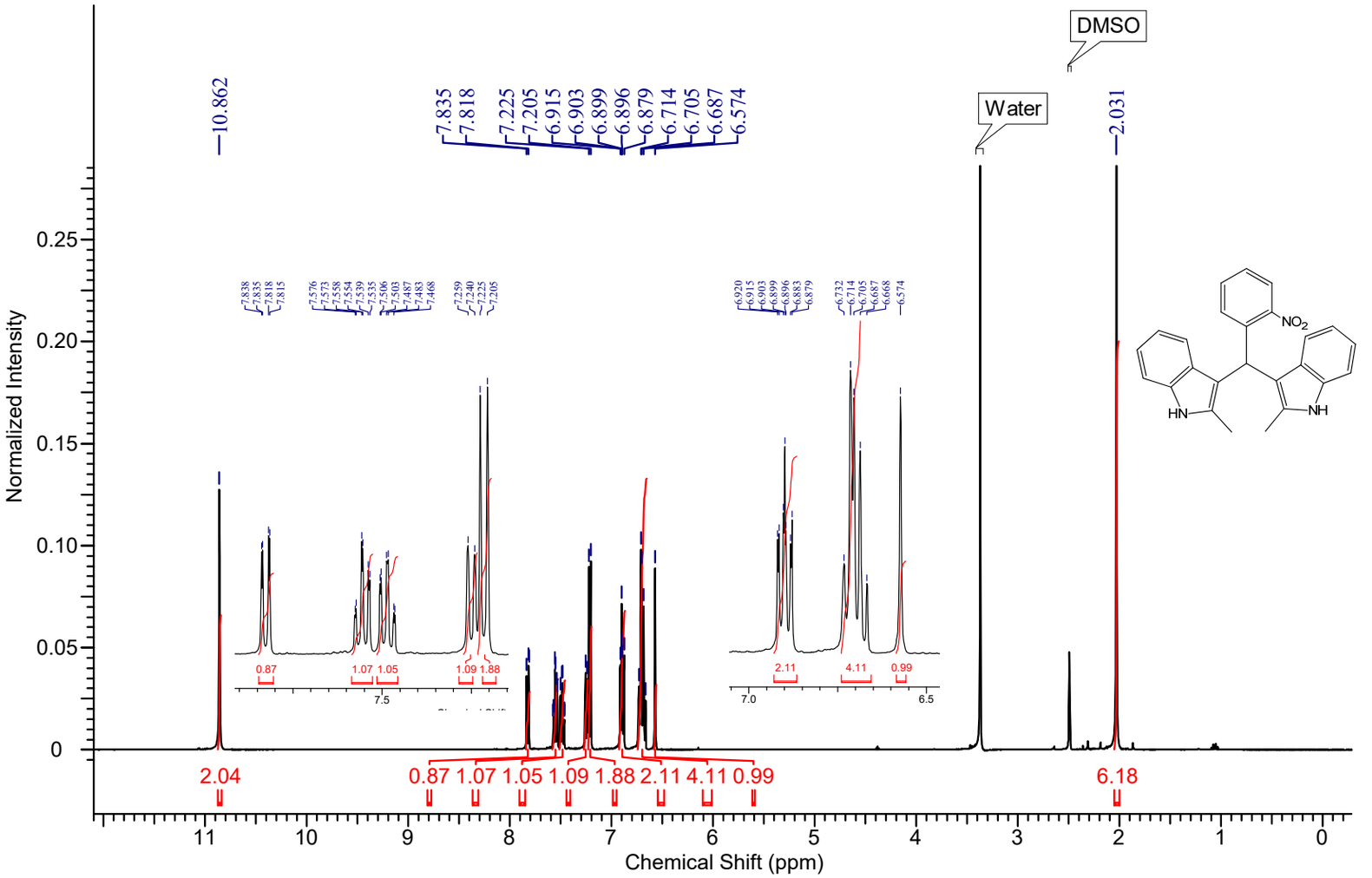
^{1}H NMR of 4e



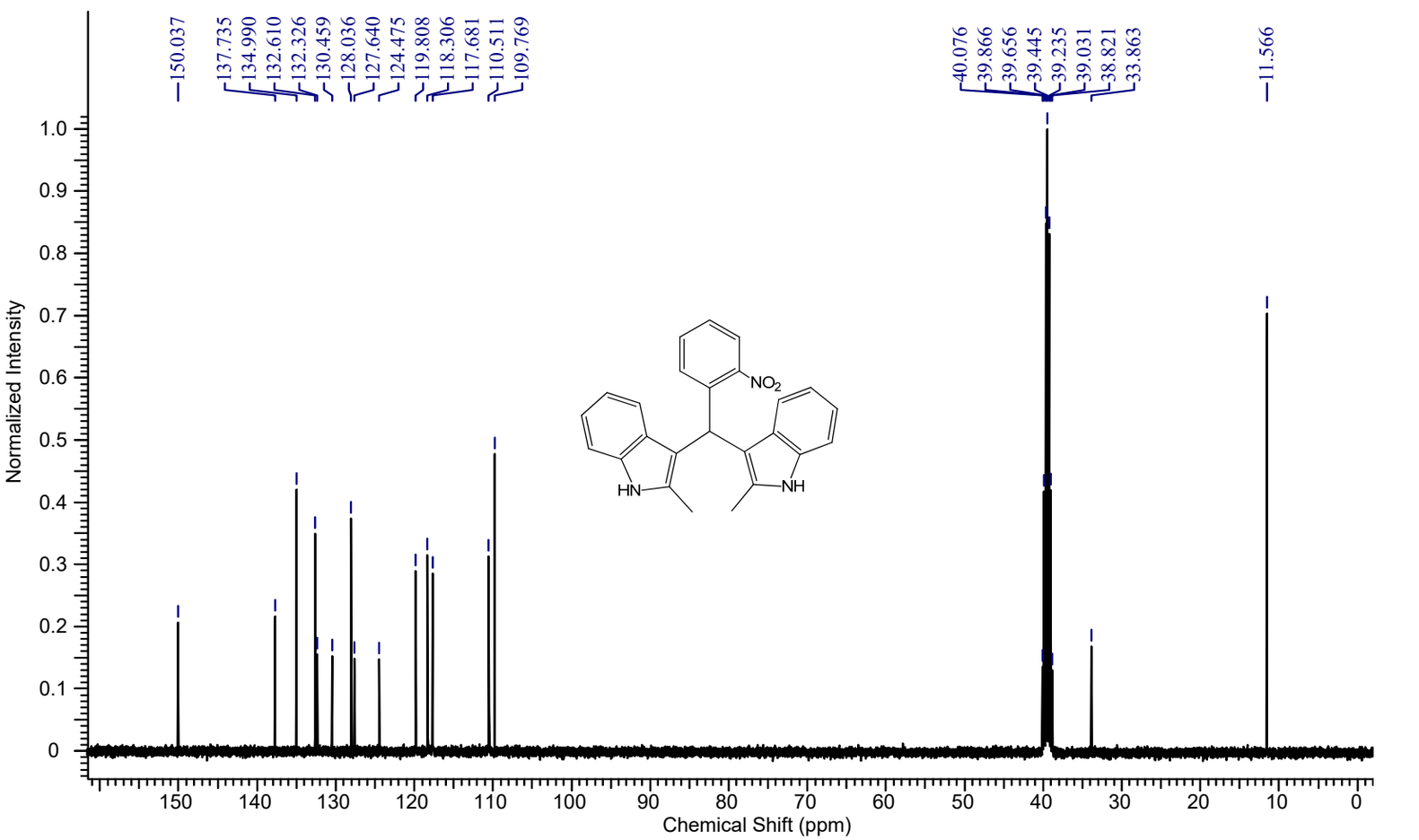
^{13}C NMR of 4e



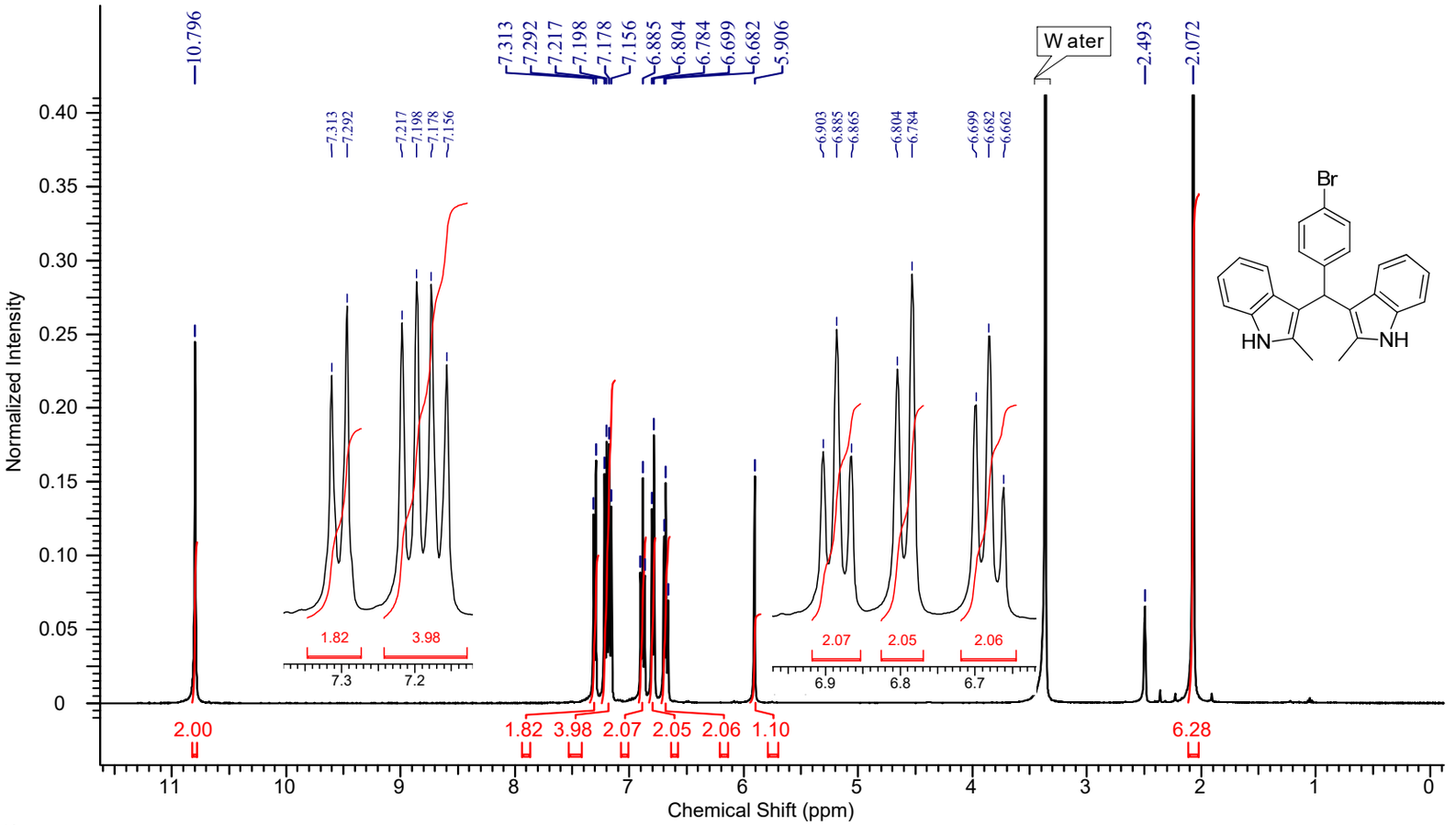
^{1}H NMR of 4f



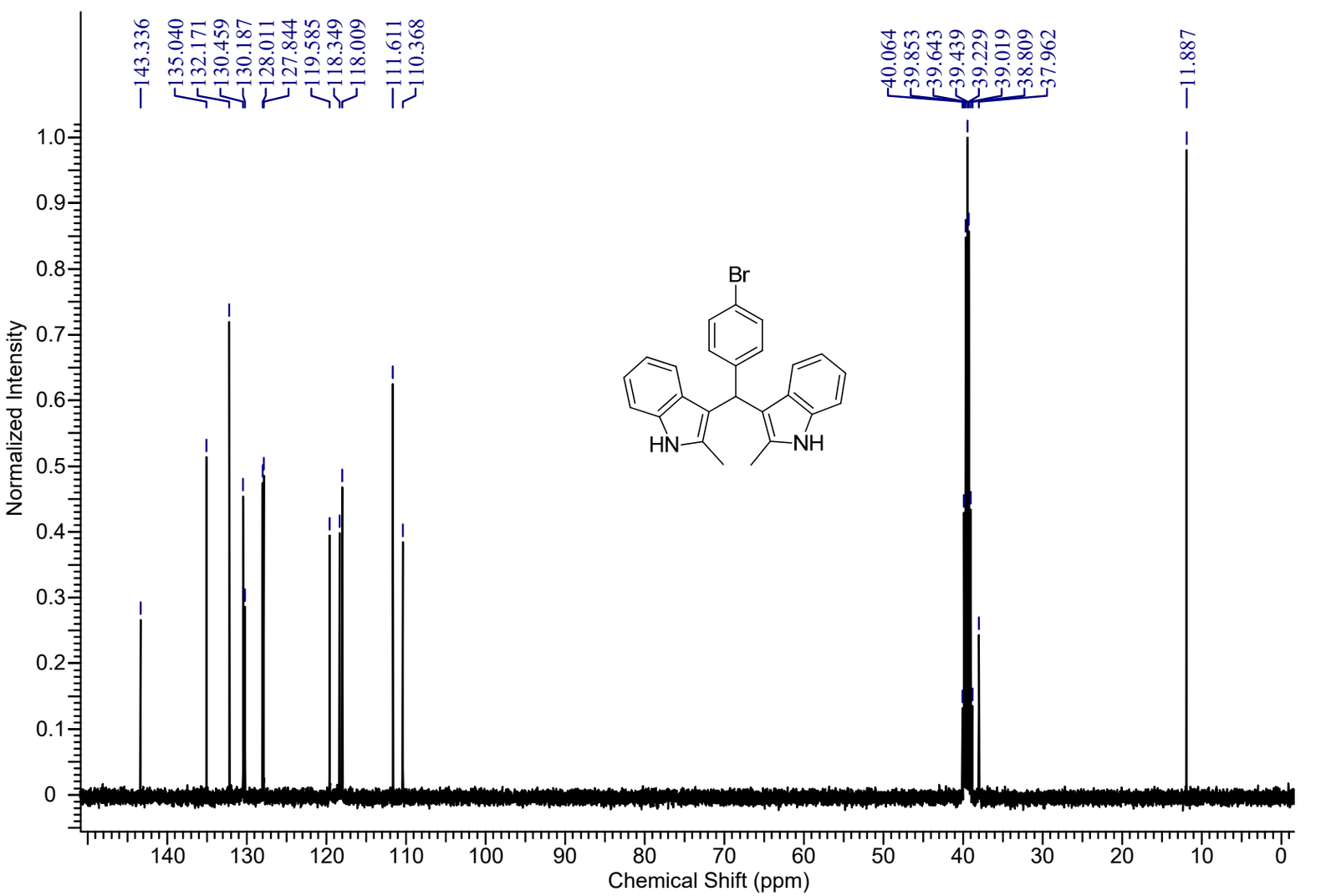
^{13}C NMR of 4f



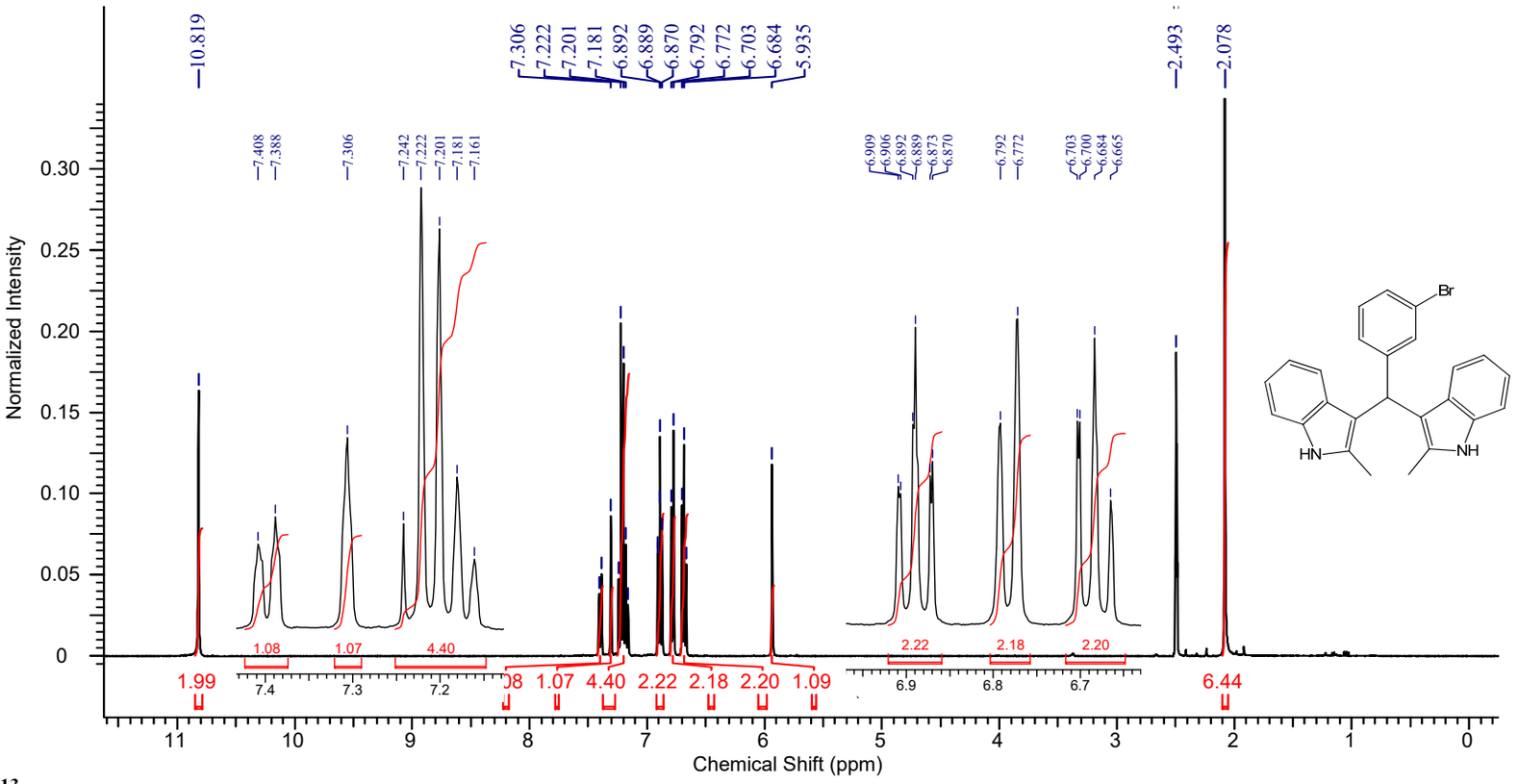
^{1}H NMR of 4g



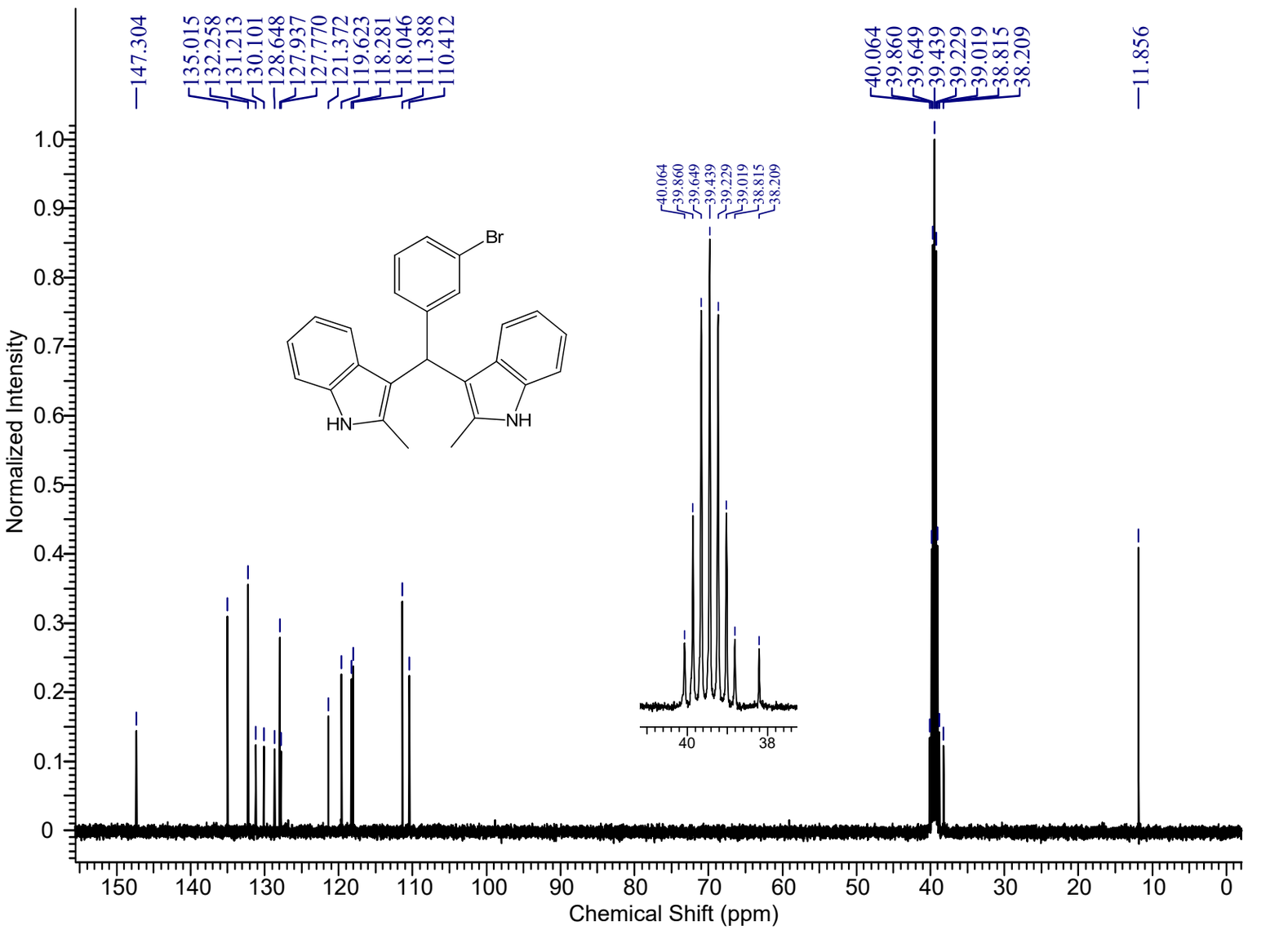
^{13}C NMR of 4g



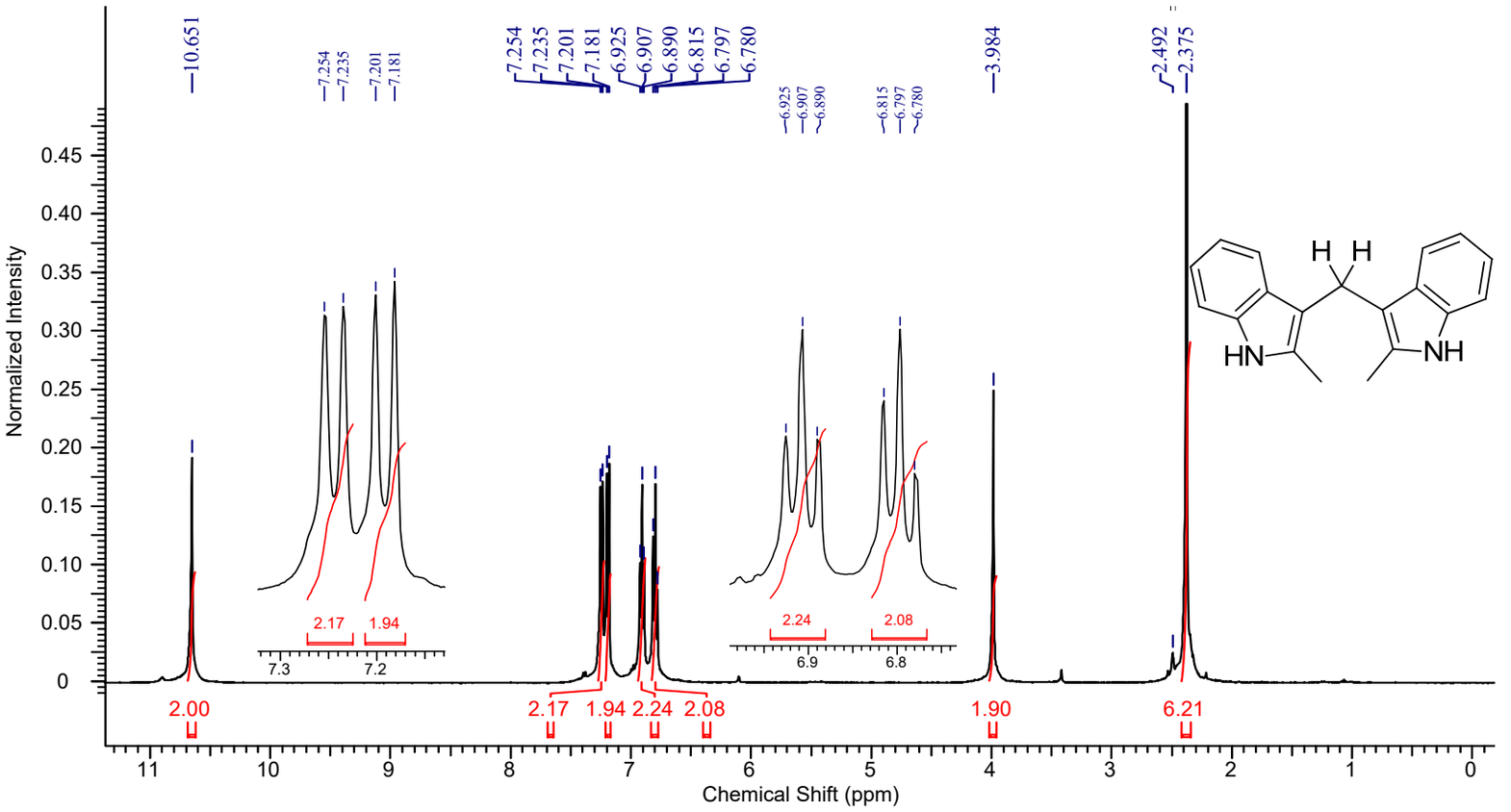
^{1}H NMR of 4h



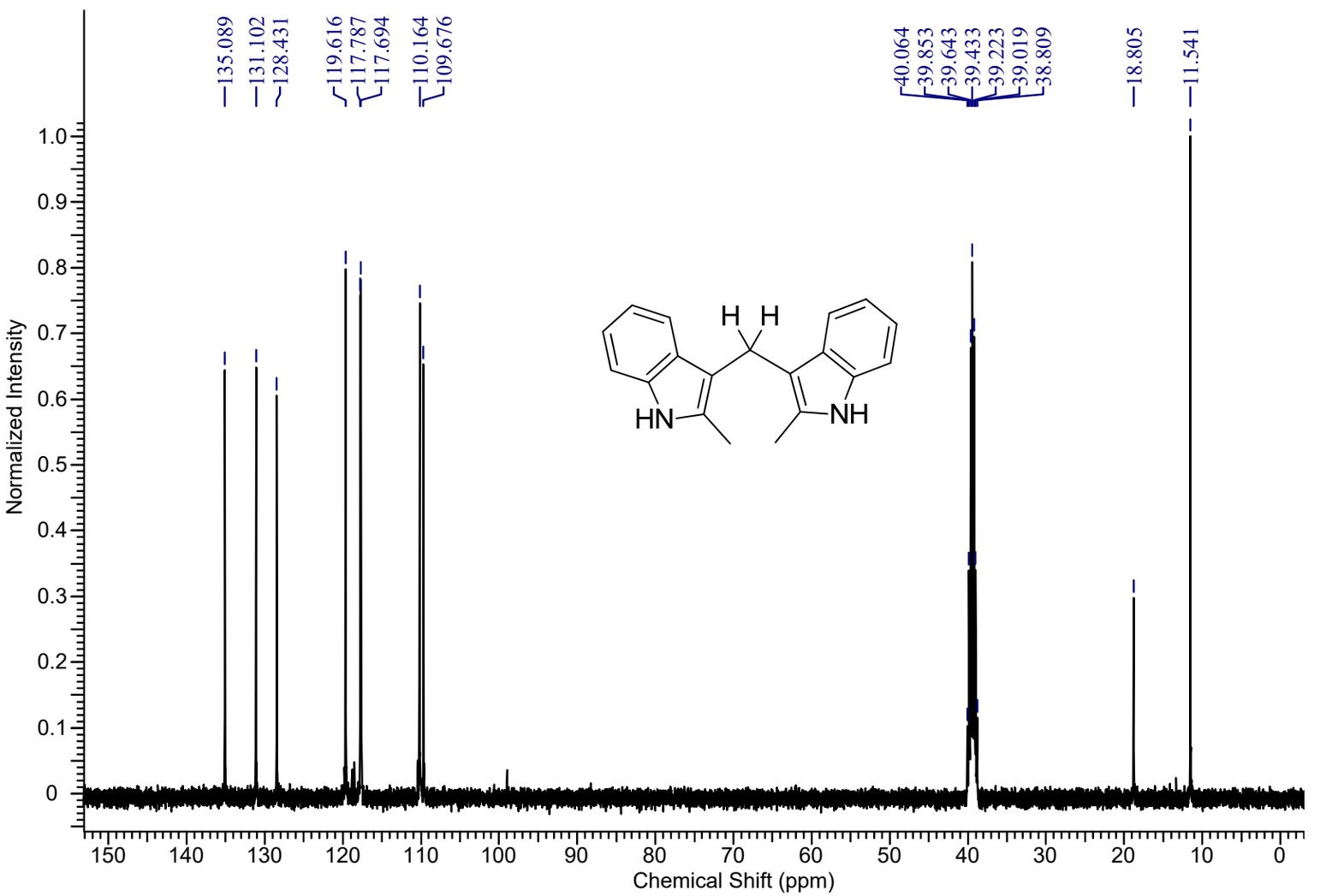
^{13}C NMR of 4h



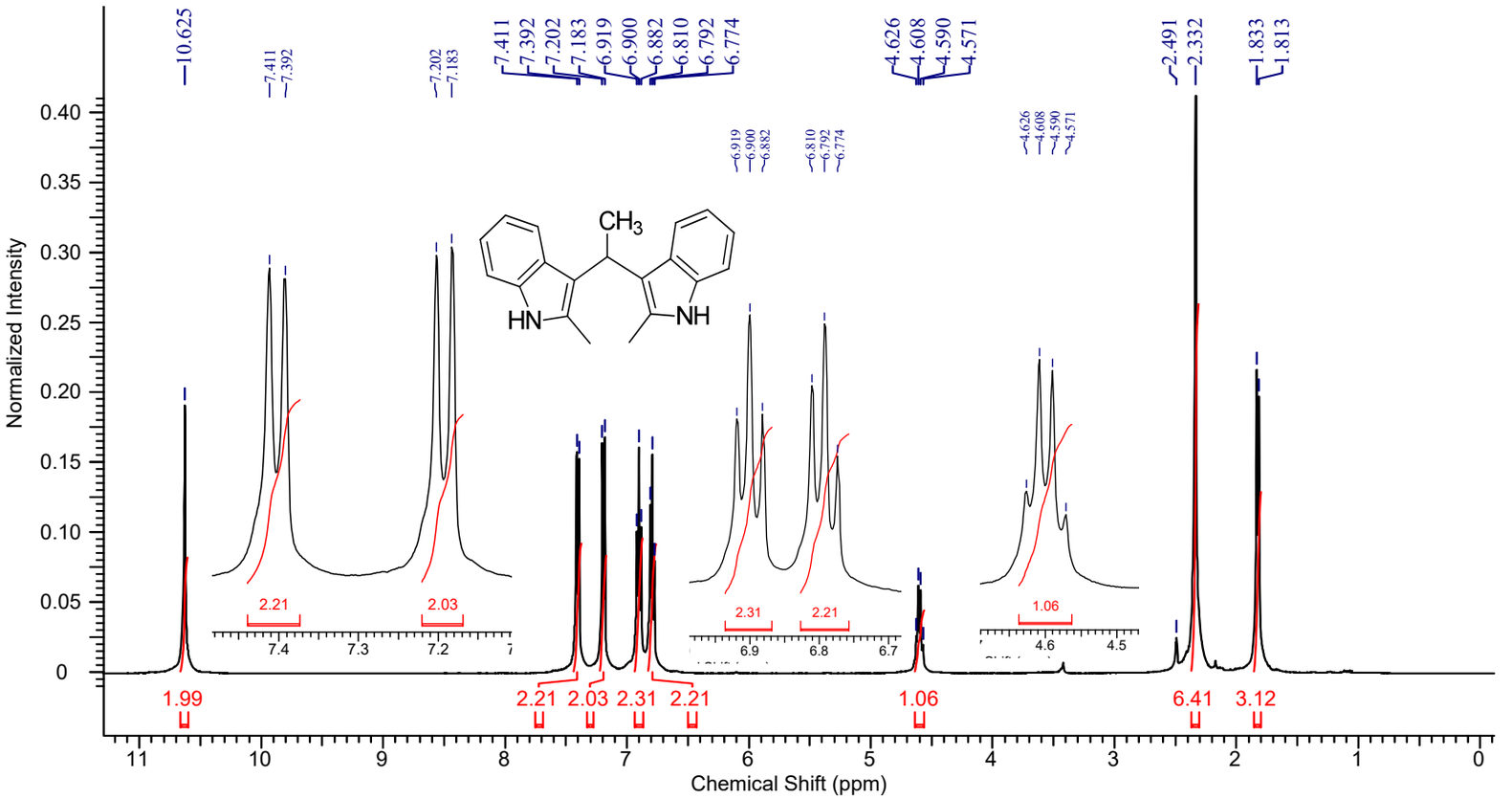
^{1}H NMR of 4i



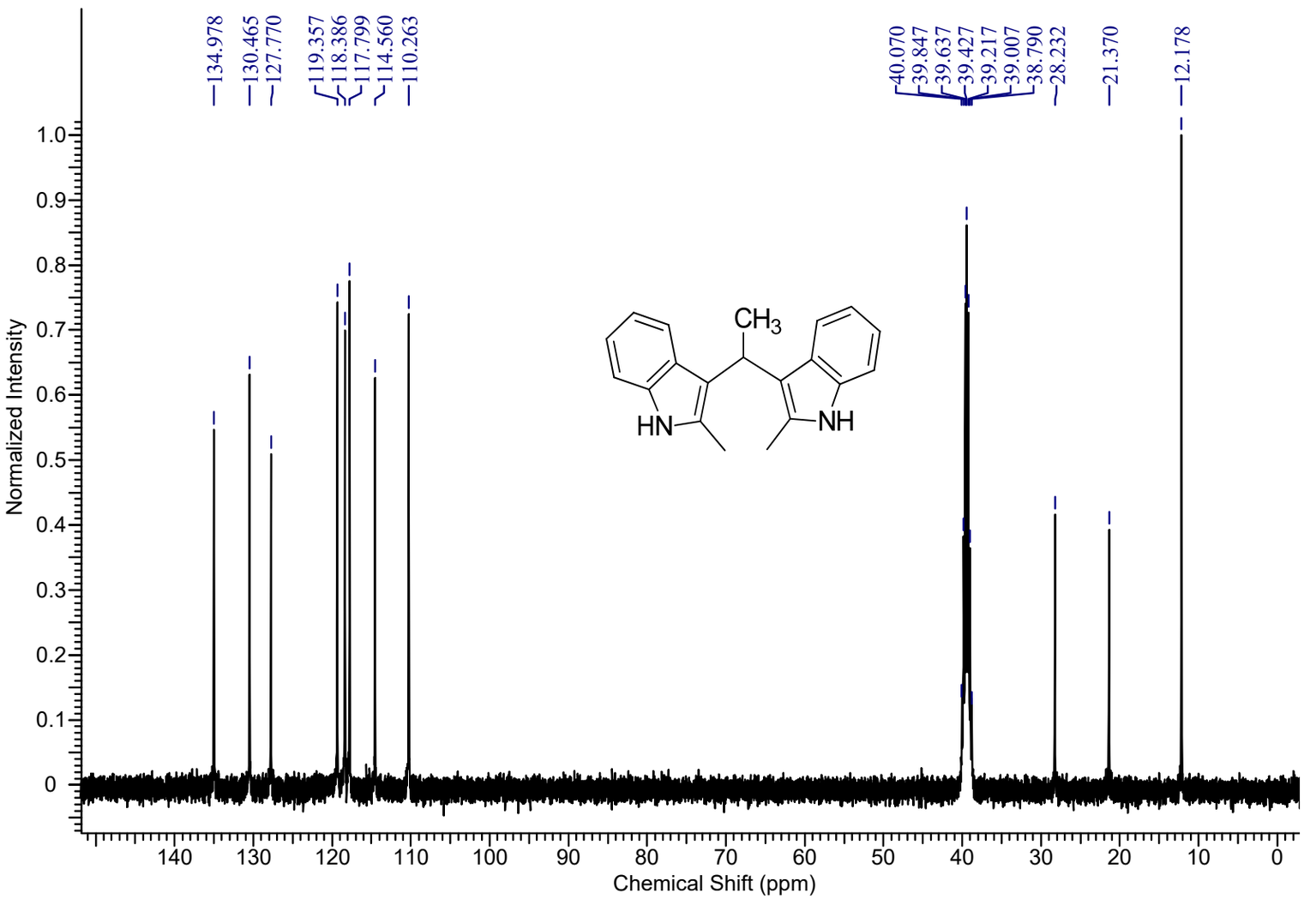
^{13}C NMR 4i



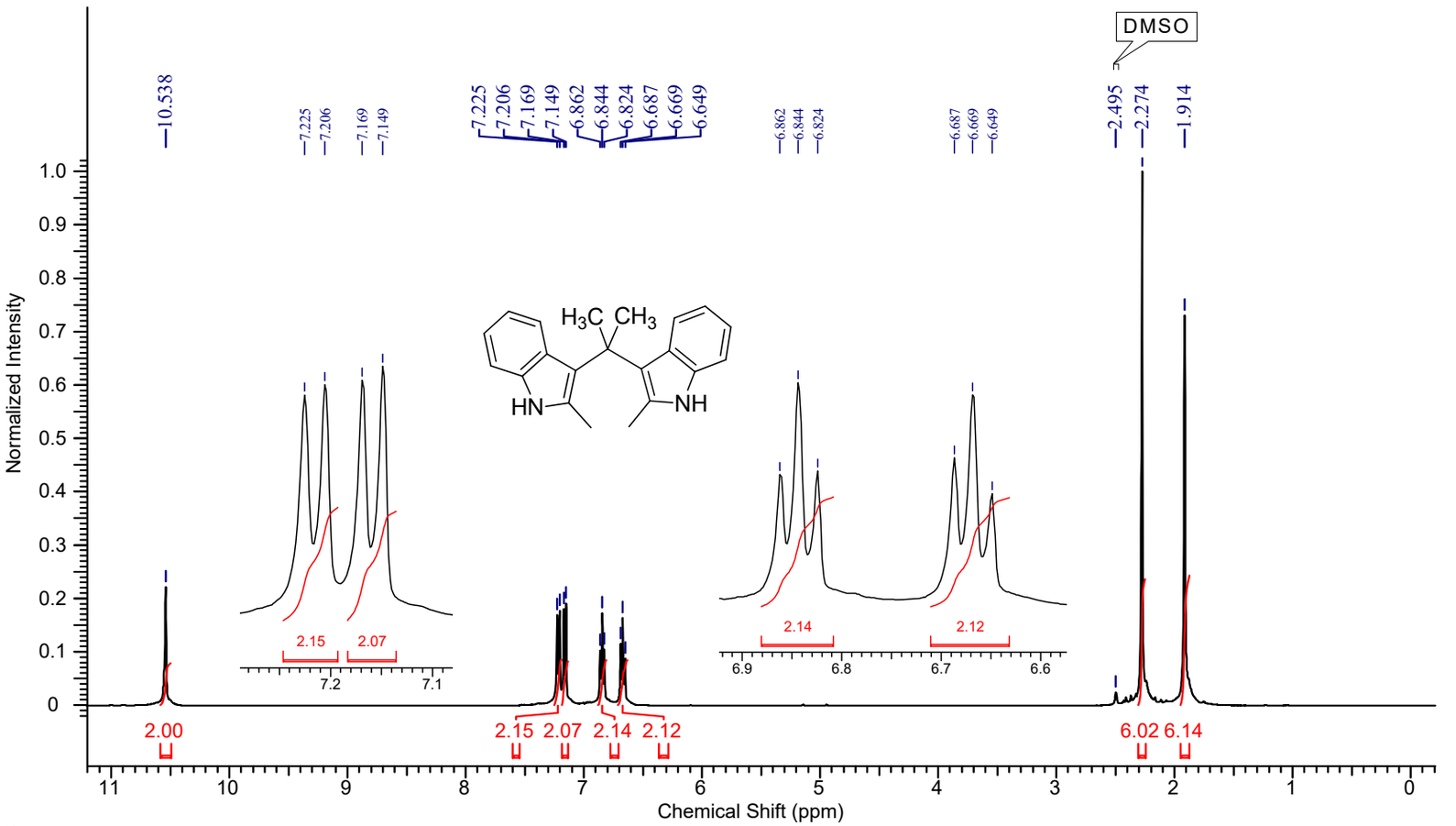
^{1}H NMR of 4j



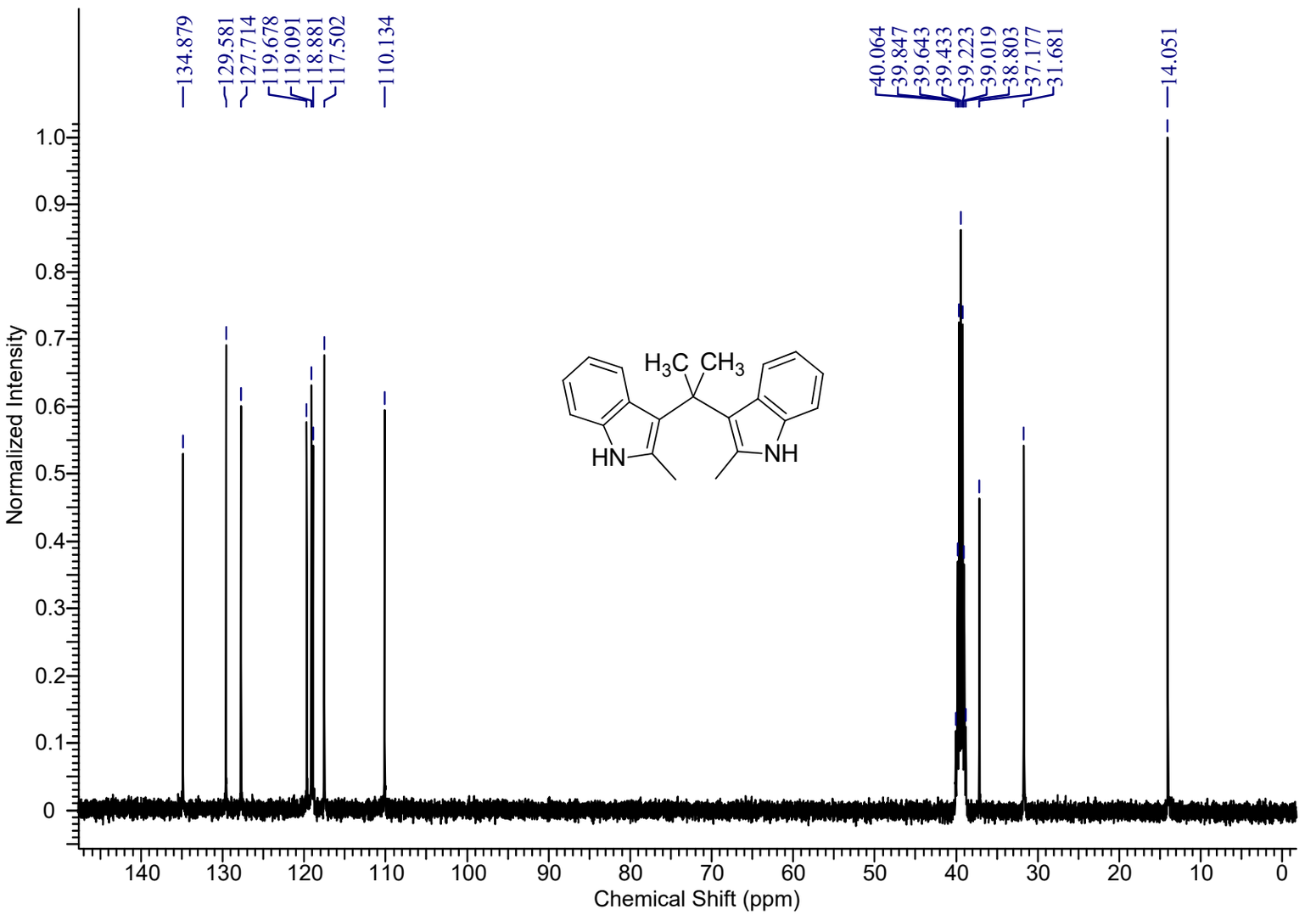
^{13}C NMR of 4j



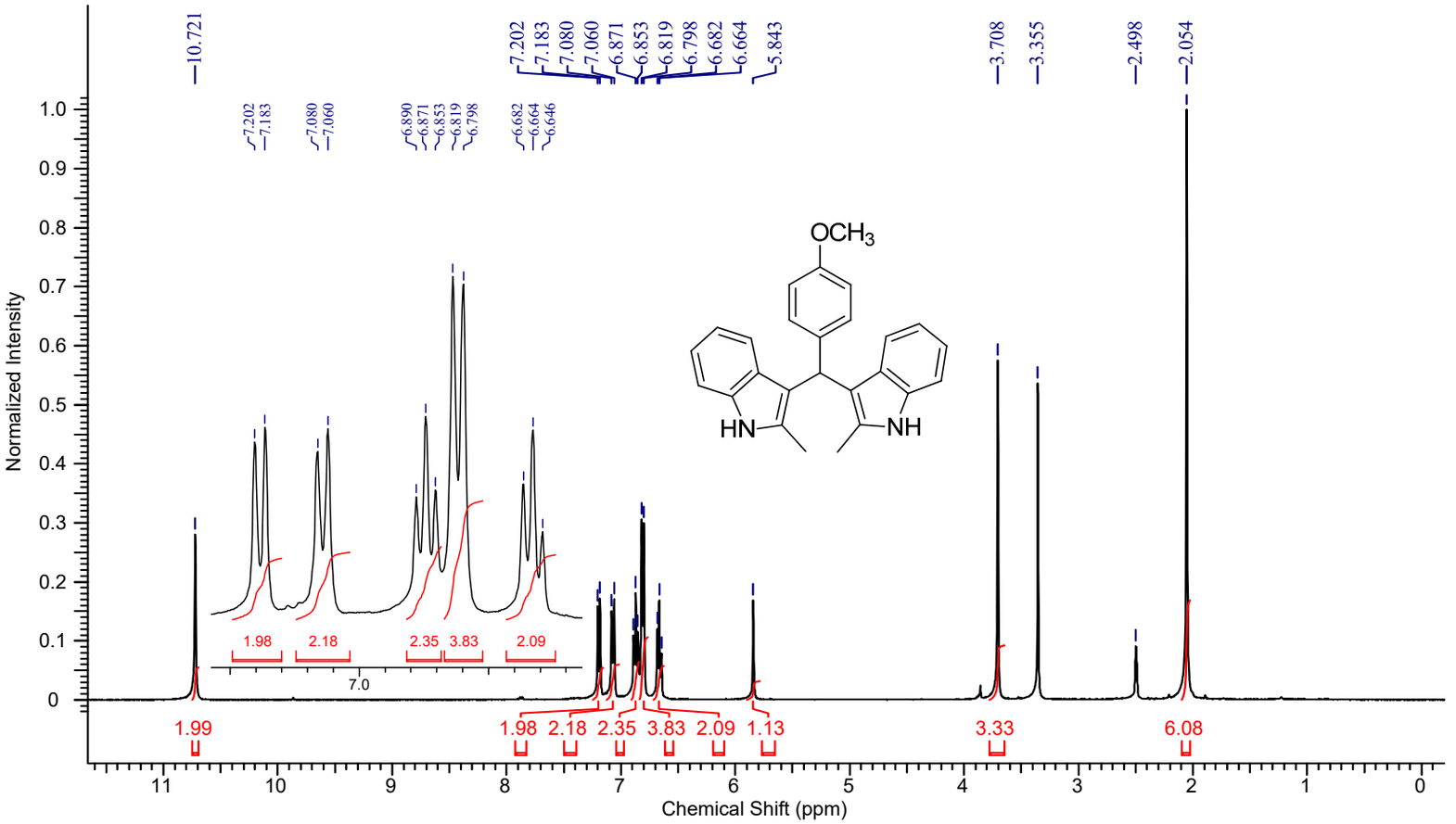
^{1}H NMR of 4k



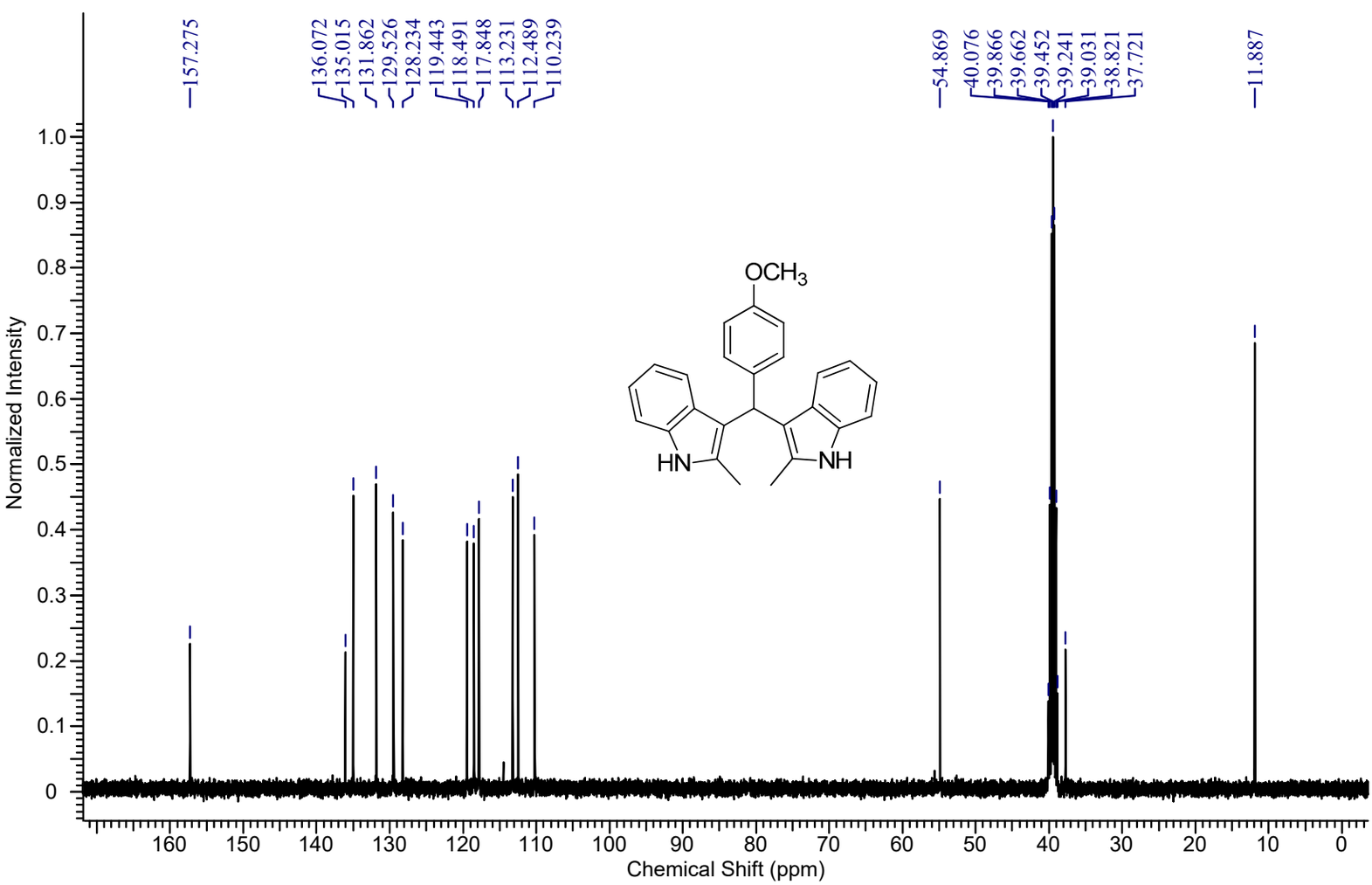
^{13}C NMR of 4k



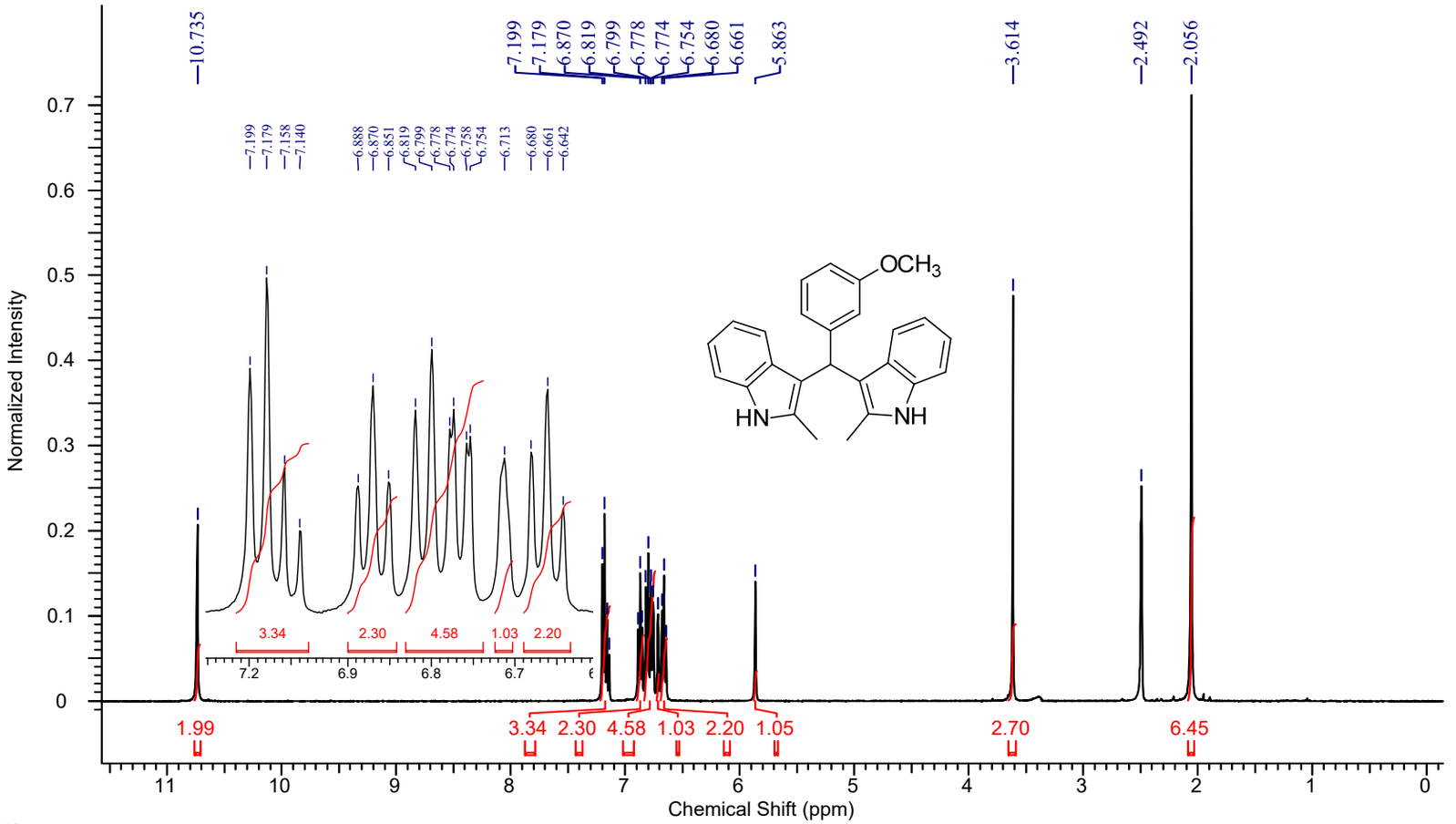
^{1}H NMR of 4l



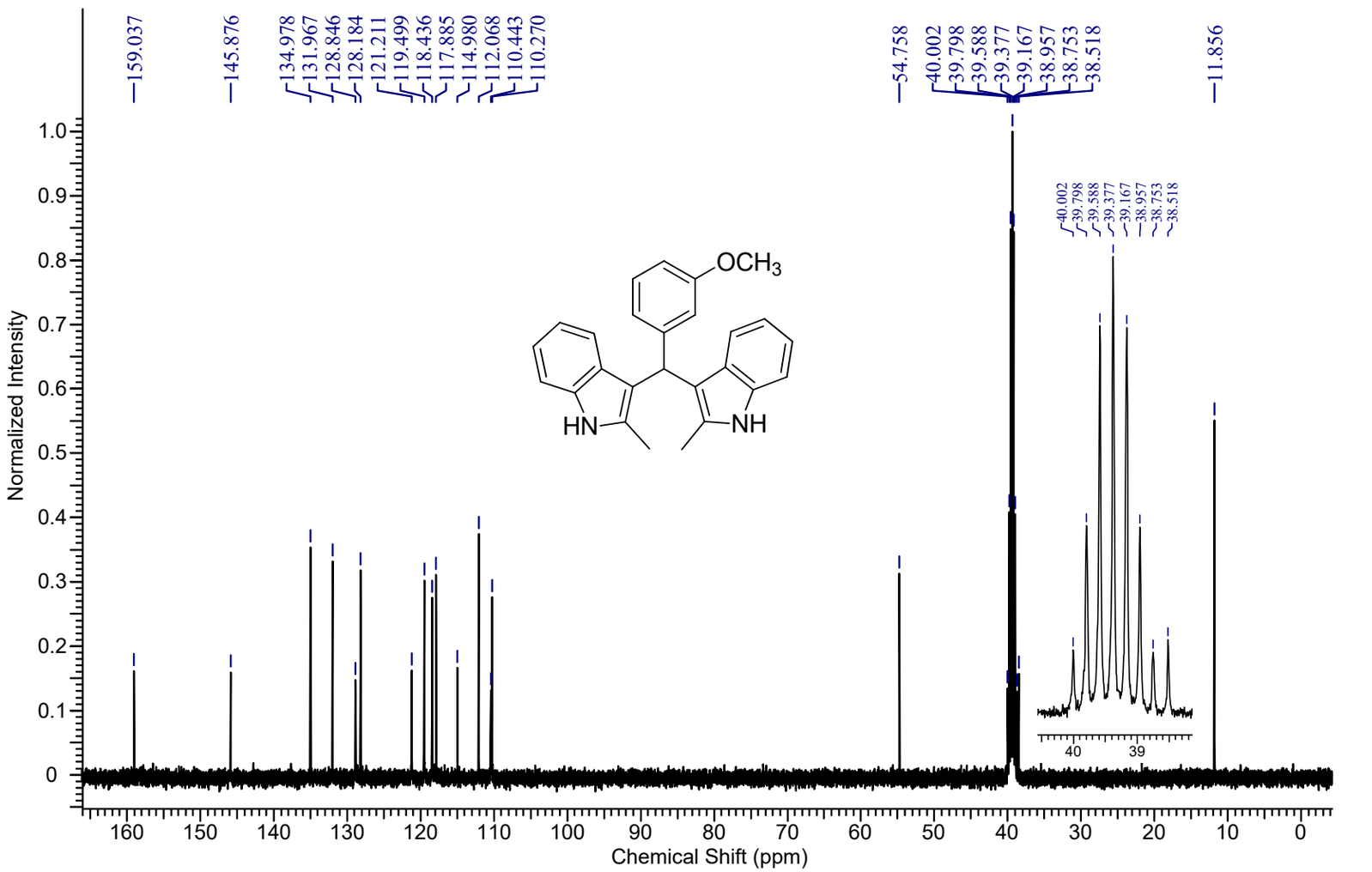
^{13}C NMR of 4l



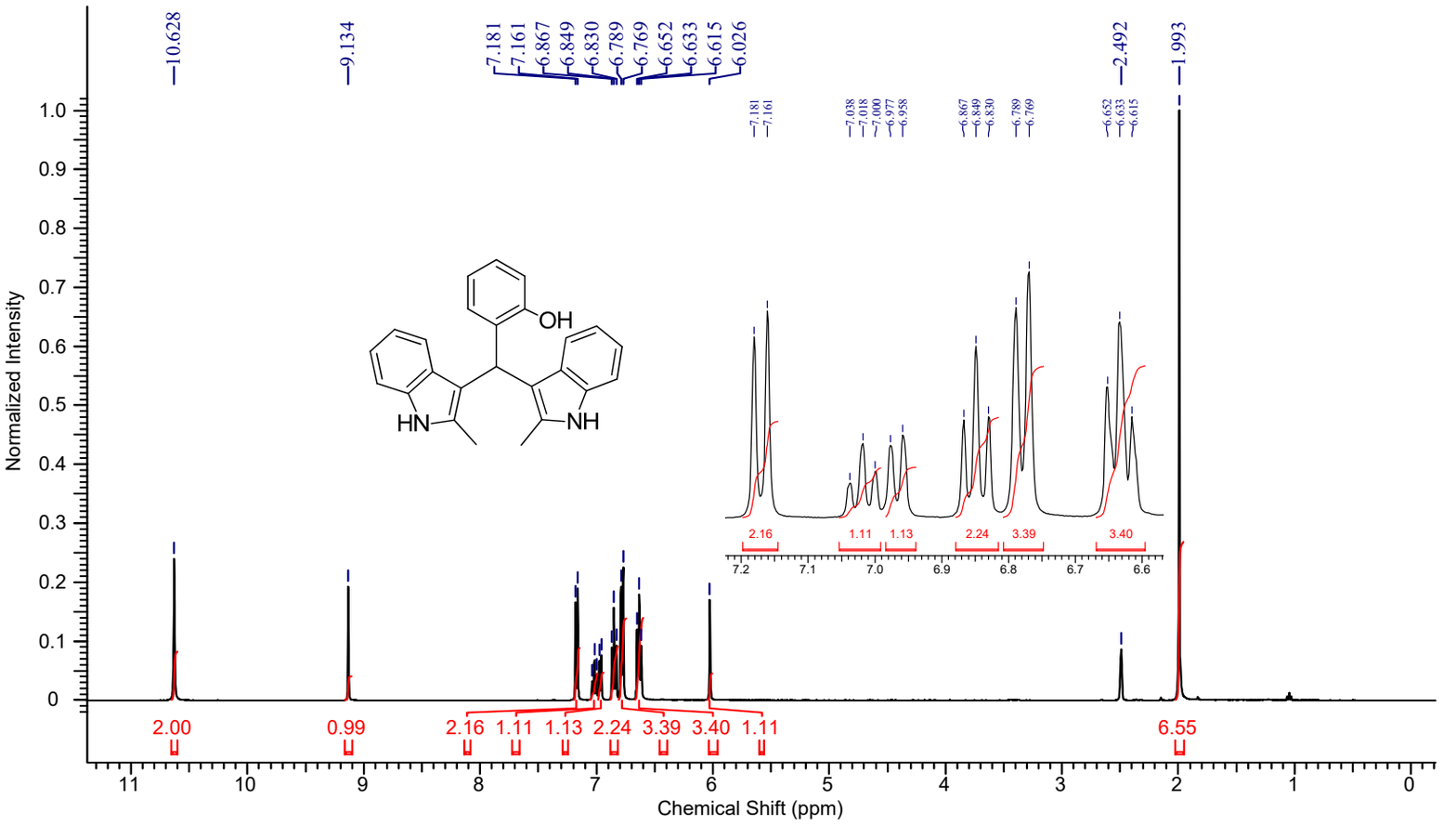
JR-293(BI-25) 1H-NMR



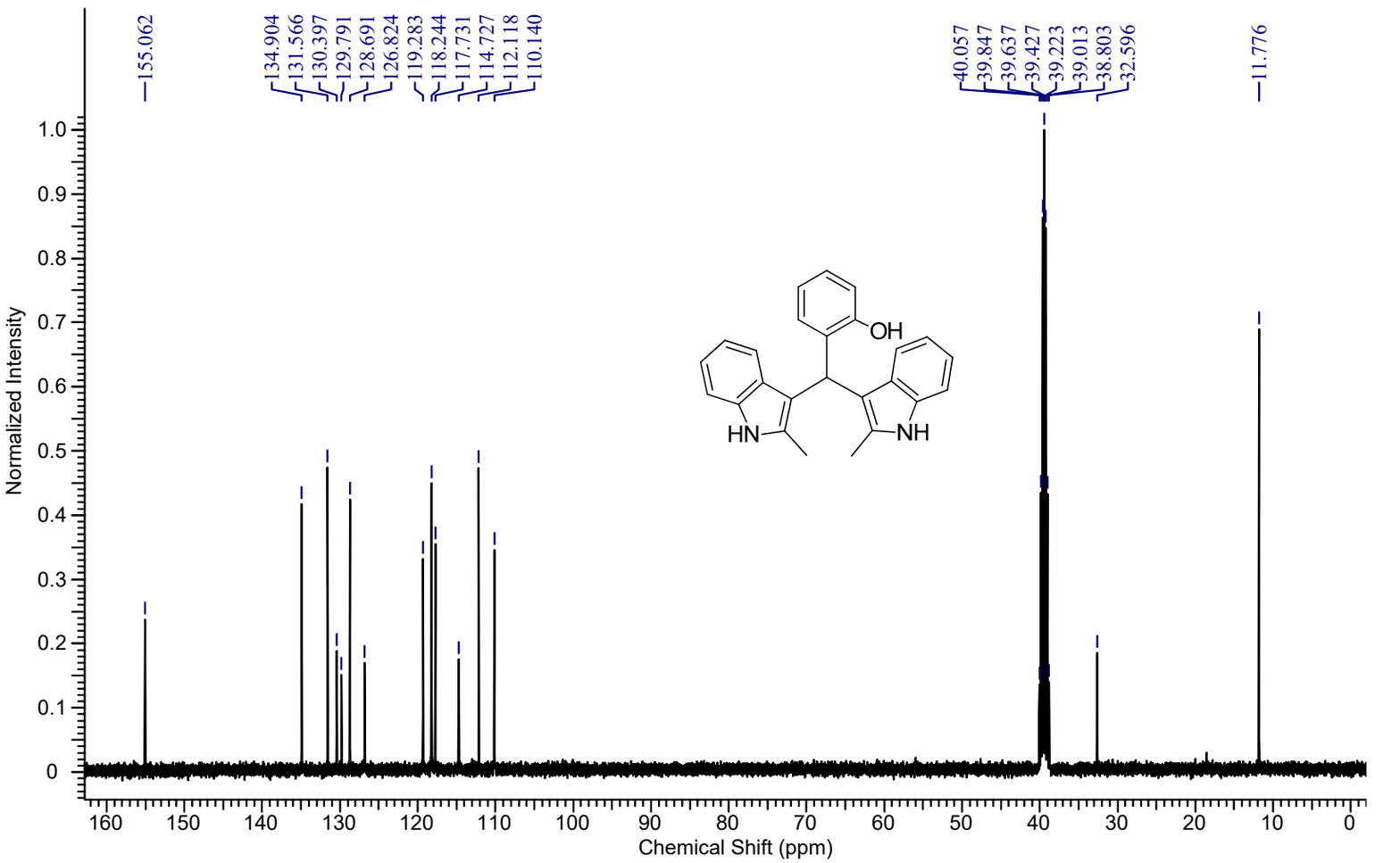
^{13}C NMR of 4m



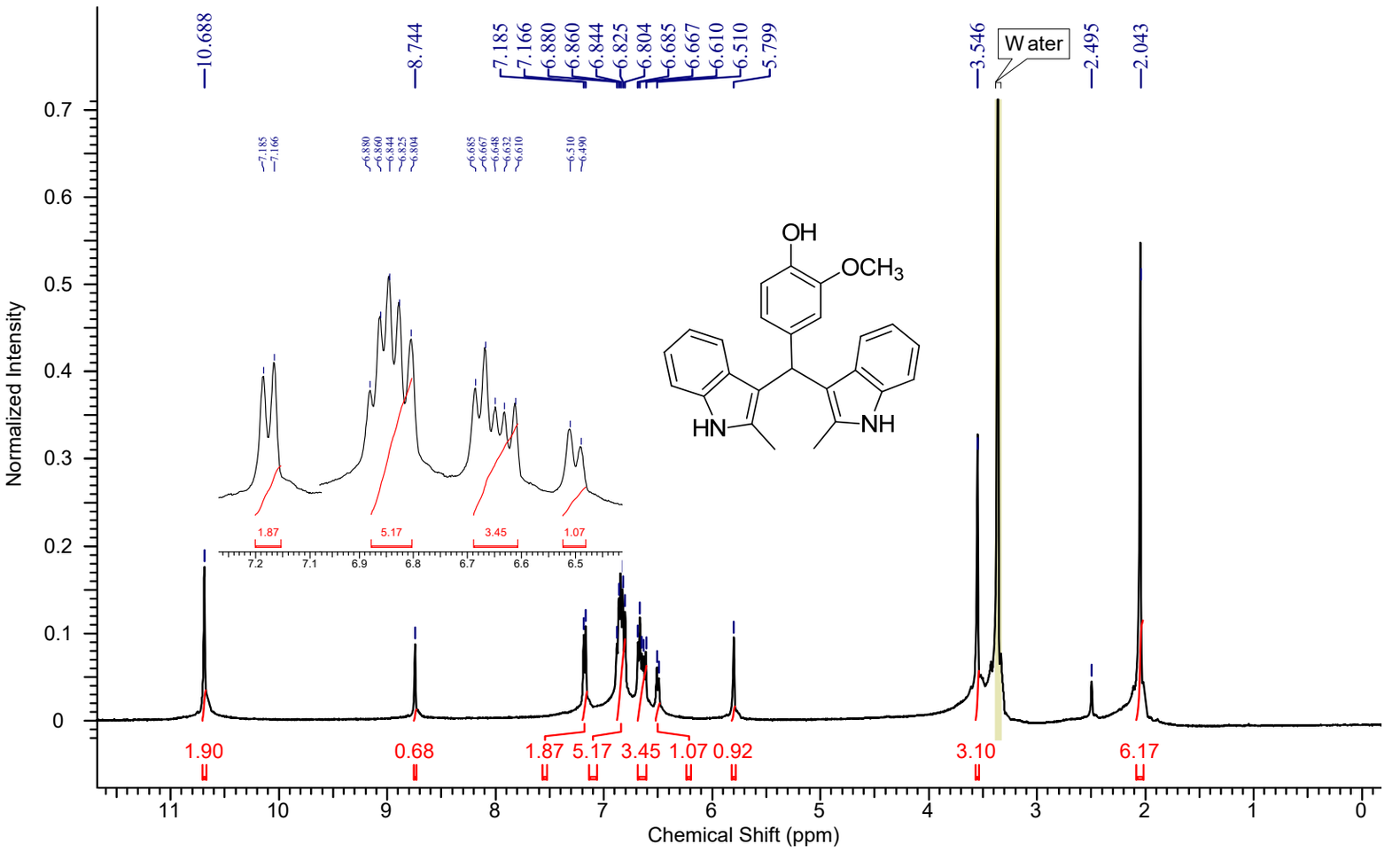
^{1}H NMR of 4n



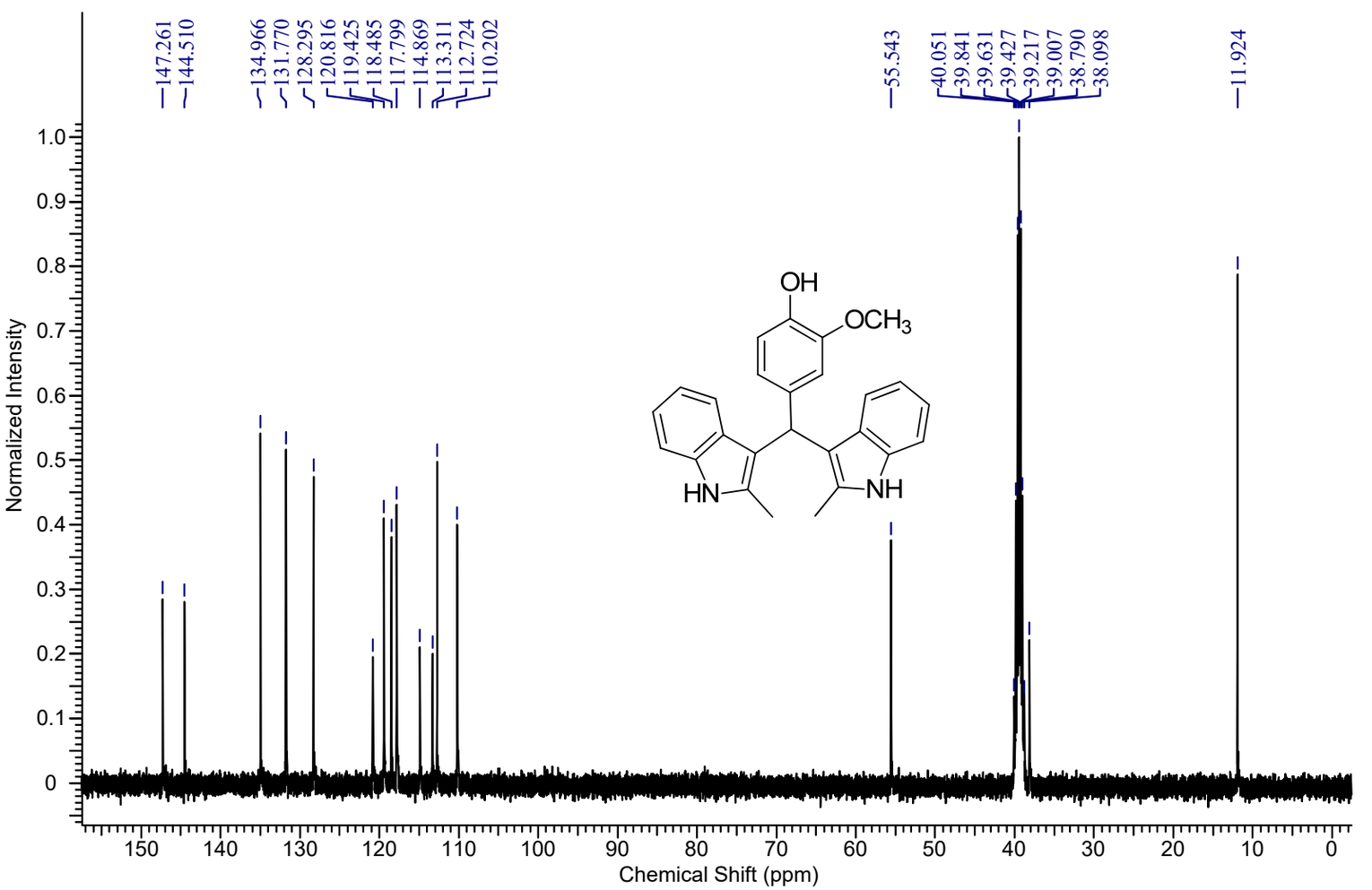
^{13}C NMR of 4n



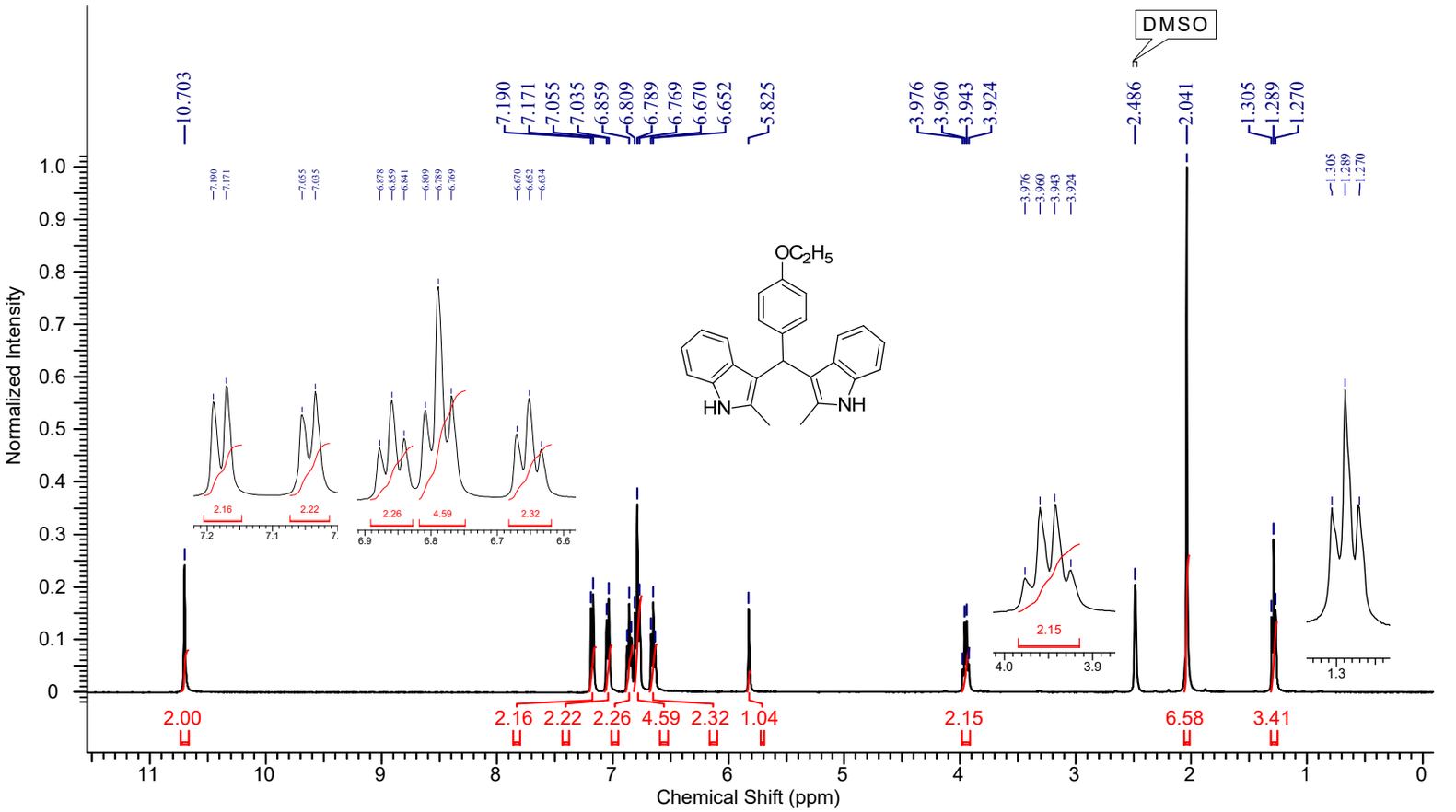
^{1}H NMR of 4o



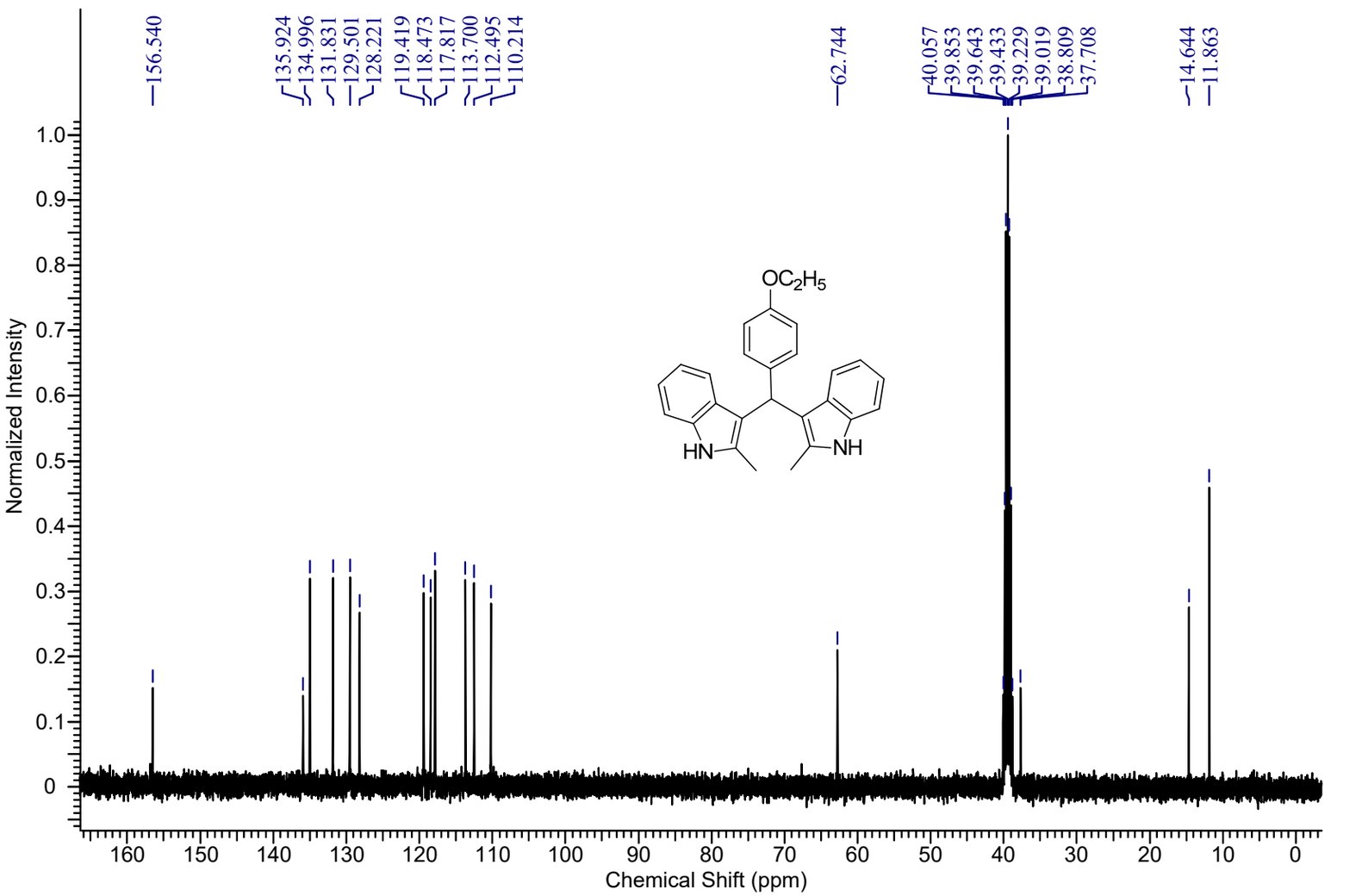
^{13}C NMR of 4o



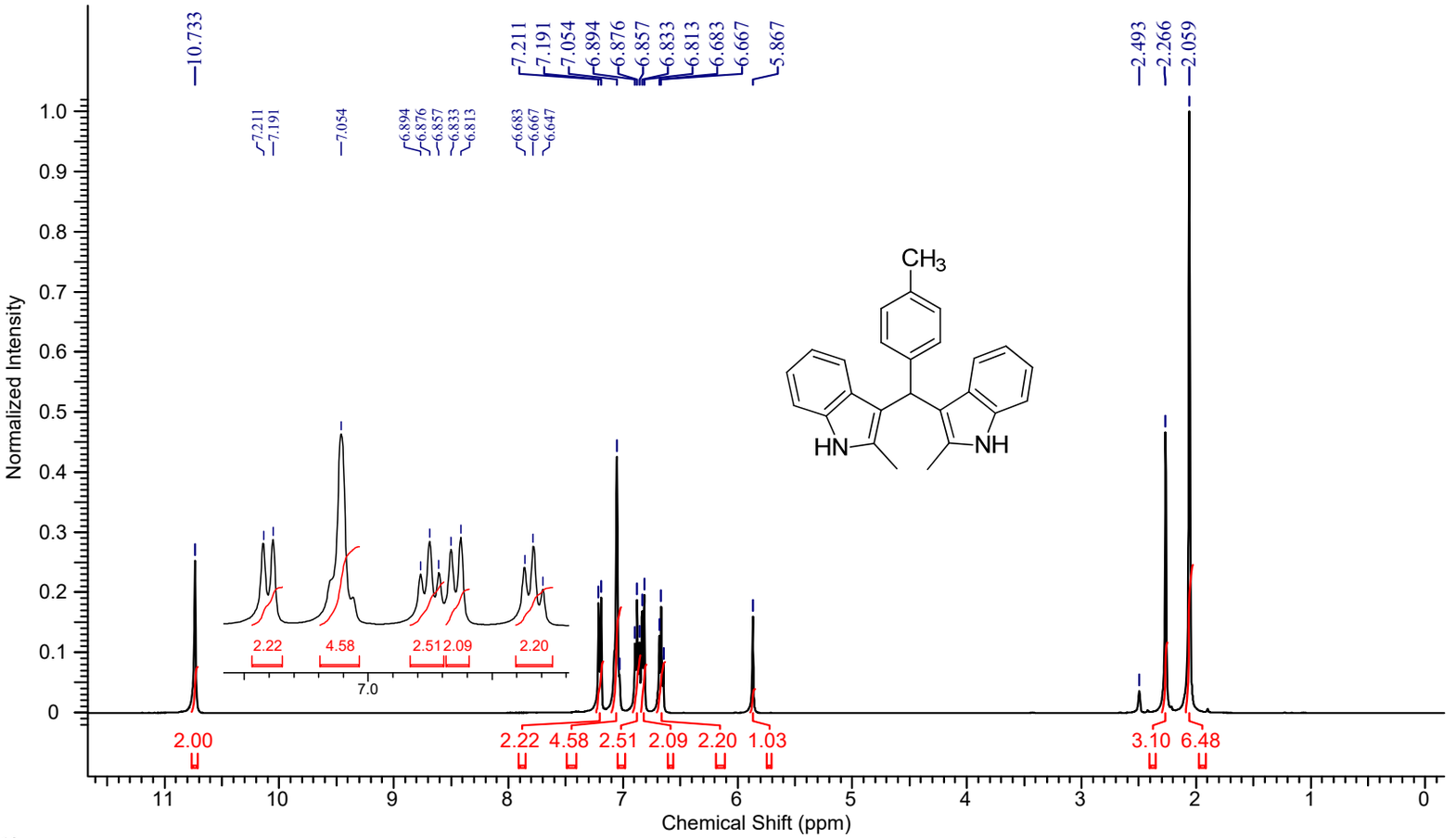
^{1}H NMR of 4p



^{13}C NMR of 4p



^{1}H NMR of 4q



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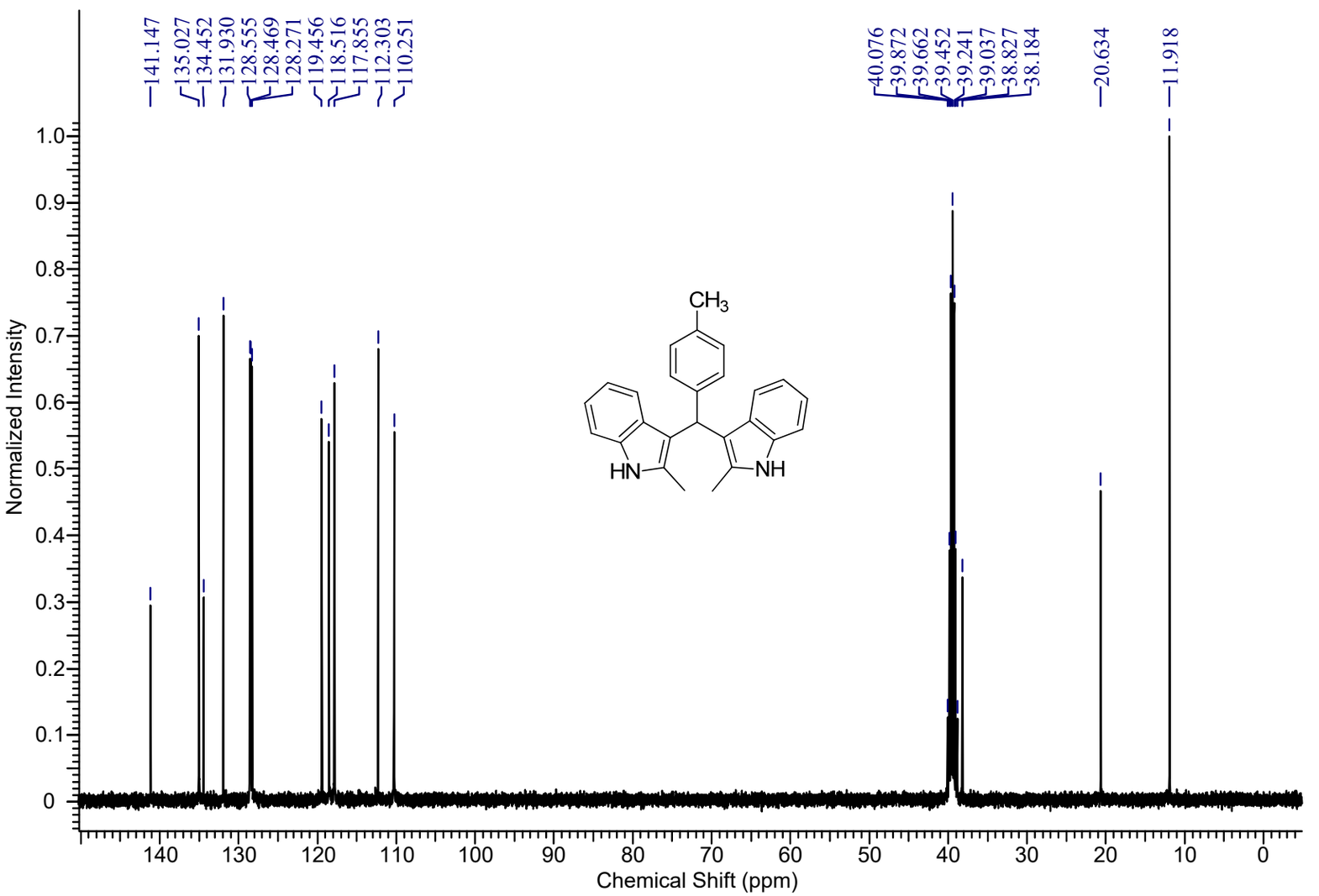
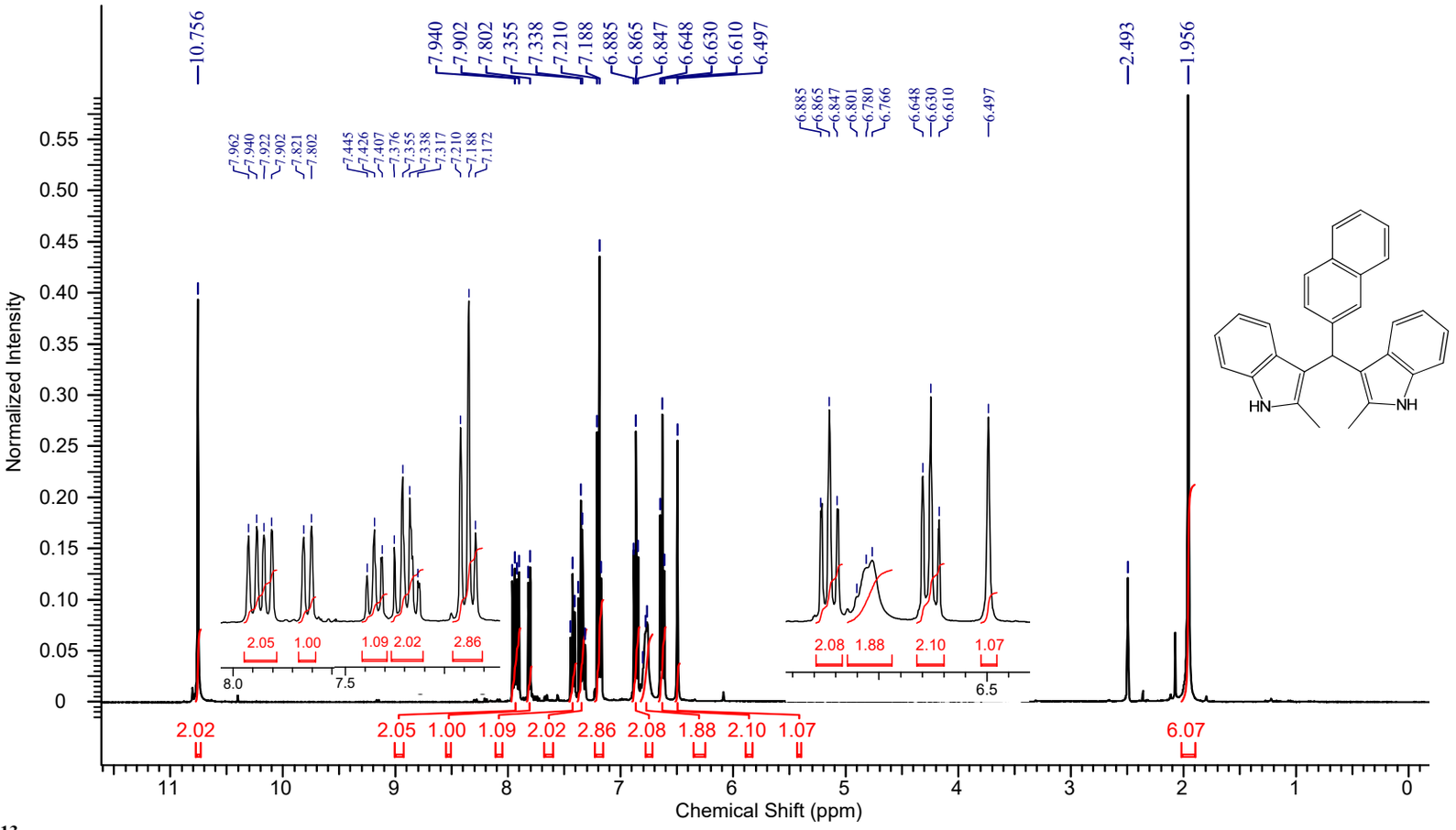
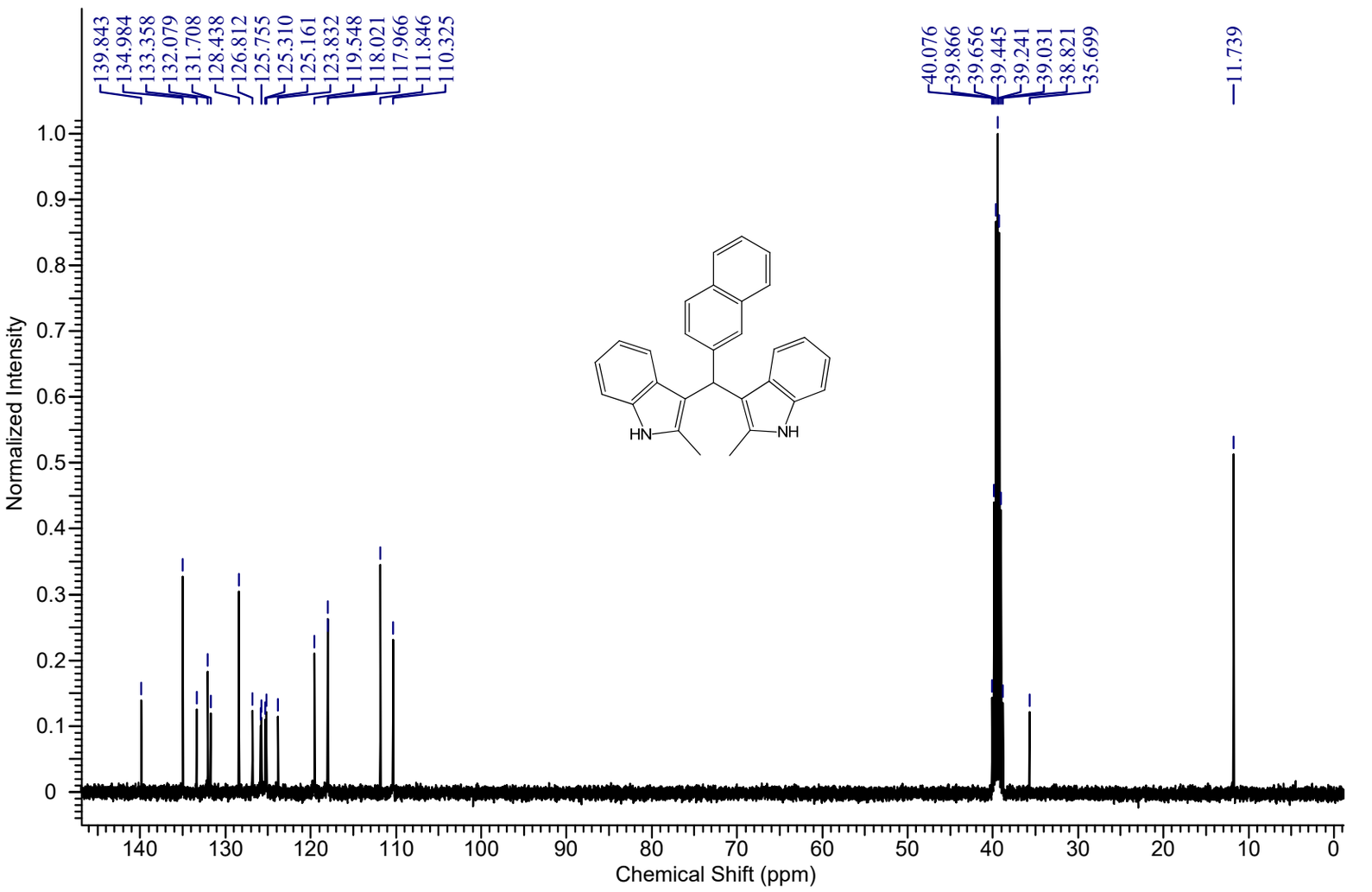


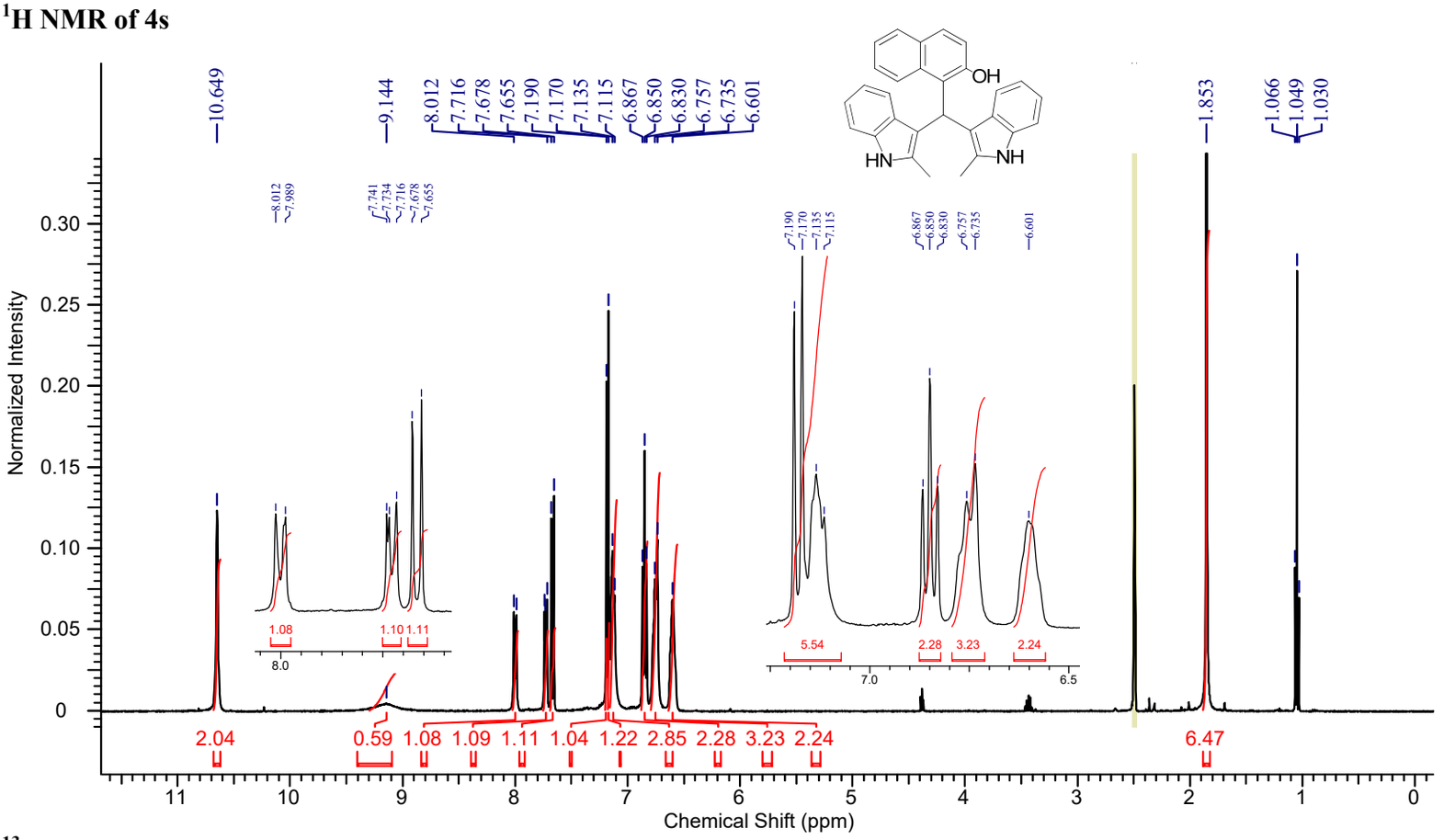
^{1}H NMR of 4r



^{13}C NMR of 4r



^{1}H NMR of 4s



^{13}CNMR of 4s