Supporting Information

Solid-Phase Synthesis of Bis-heterocyclic Compounds with Skeletal Diversity from Resin-bound 3-propargylamino-2-seleno-ester

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General experiment procedures

Starting materials were obtained from commercial suppliers and used without further purification. CH_2Cl_2 and DMF were distilled from CaH_2 immediately prior to use. Polystyrene (H 1000, 100-200 mesh, cross-linked with 1% divinylbenzene) was purchased from commercial sources. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer, using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as internal standard; chemical shifts were quoted in parts per million and *J* values were given in hertz. Mass spectra (EI, 70 eV) were recorded on an Agilent 5975 inert mass selective detector. Infrared spectra were recorded on a Bruker Vector22 spectrometer. Elemental analysis was performed on a Flash EA1110 instrument. HPLC was performed on an Agilent 1100 high performance liquid chromatograph (HPLC). High resolution mass spectrometry (HRMS) was performed on a Waters Micromass GCT instrument. Purities of the products are determined by the crude products. Yields are calculated by mass recovery of the crude products based on the loading of the resin **5**. NMR, MS, FT-IR, EA, and the melting points are determined by the purified products. The chromatographic conditions (HPLC) were as follows: Column dp 5 μ 250 $\times$ 4.6 mm. Mobile phase MeOH. Flow rate 1.0 mL/min. Detector UV 254 nm. The chiral chromatographic conditions (HPLC) were as follows: Column OD 250 $\times$ 4.6 mm. Mobile phase isopropyl alcohol. Flow rate 1.0 mL/min. Detector UV 254 nm. The melting points were uncorrected.

Typical procedure for the preparation of dihydrouracils supported selenium resins 6:

To a suspension of the swollen polystyrene-supported selenenyl bromide resin **5** (1.0 g, 1.18 mmol Br/g) in CH_2Cl_2 (20 mL) was added $ZnCl_2$ (0.2 mmol) and methyl acrylate (3 mmol), and the mixture was stirred for 0.5 h at room temperature. Then, propargylamine (6 mmol) was added. After 24 h, the resin was collected by filtration and washed successively with H_2O (20 mL × 2), THF (10 mL × 2), DMF (10 mL × 2), THF (10 mL × 2), CH_2Cl_2 (10 mL × 2), and then dried under vacuum overnight to afford resin **4**. The reaction mixture of dried resin **4** (1.0 g), isocyanate (3.0 mmol) and K_2CO_3 (0.5 mmol) in DMF (15 mL) was stirred for 5 h at 65 ^oC. Then the resin was collected by filtration and washed successively with H_2O (20 mL × 2), THF (10 mL × 2), DMF (10 mL × 2), THF (10 mL × 2), CH_2Cl_2 (10 mL × 2) to afford resins **6**.

Typical procedure for the preparation of 1,4-diazepane-2,5-diones supported selenium resins 8:

To a suspension of the swollen resin **4** (1.0 g) in anhydrous THF (20 mL) was added Fmoc-α-amino-acid (3mmol) and DIC (3mmol), and the mixture was stirred for 24 h at room temperature. Then the resin was filtered and washed successively with THF (10 mL × 2), H_2O (20 mL × 2), DMF (10 mL × 2), THF (10 mL × 2), and CH_2Cl_2 (10 mL × 2) to afford resin **7**. To a suspension of the swollen resin **7** (1.0 g) in CH_2Cl_2 (10 mL) was added piperidine (2.5 mL), and the mixture was stirred for 12 h at room temperature. Then the resin was filtered and washed successively with THF

(10 mL × 2), H_2O (20 mL × 2), DMF (10 mL × 2), H_2O (20 mL × 2), THF (10 mL × 2), and CH_2Cl_2 (10 mL × 2) to afford resin **8**.

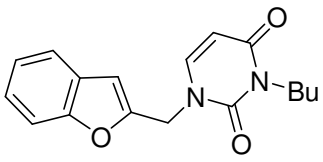
Typical procedure for the preparation of bis-heterocycles of uracil and benzofuran/indole 10a-n and bis-heterocycles of diazepinedione and benzofuran/indole 12a-j:

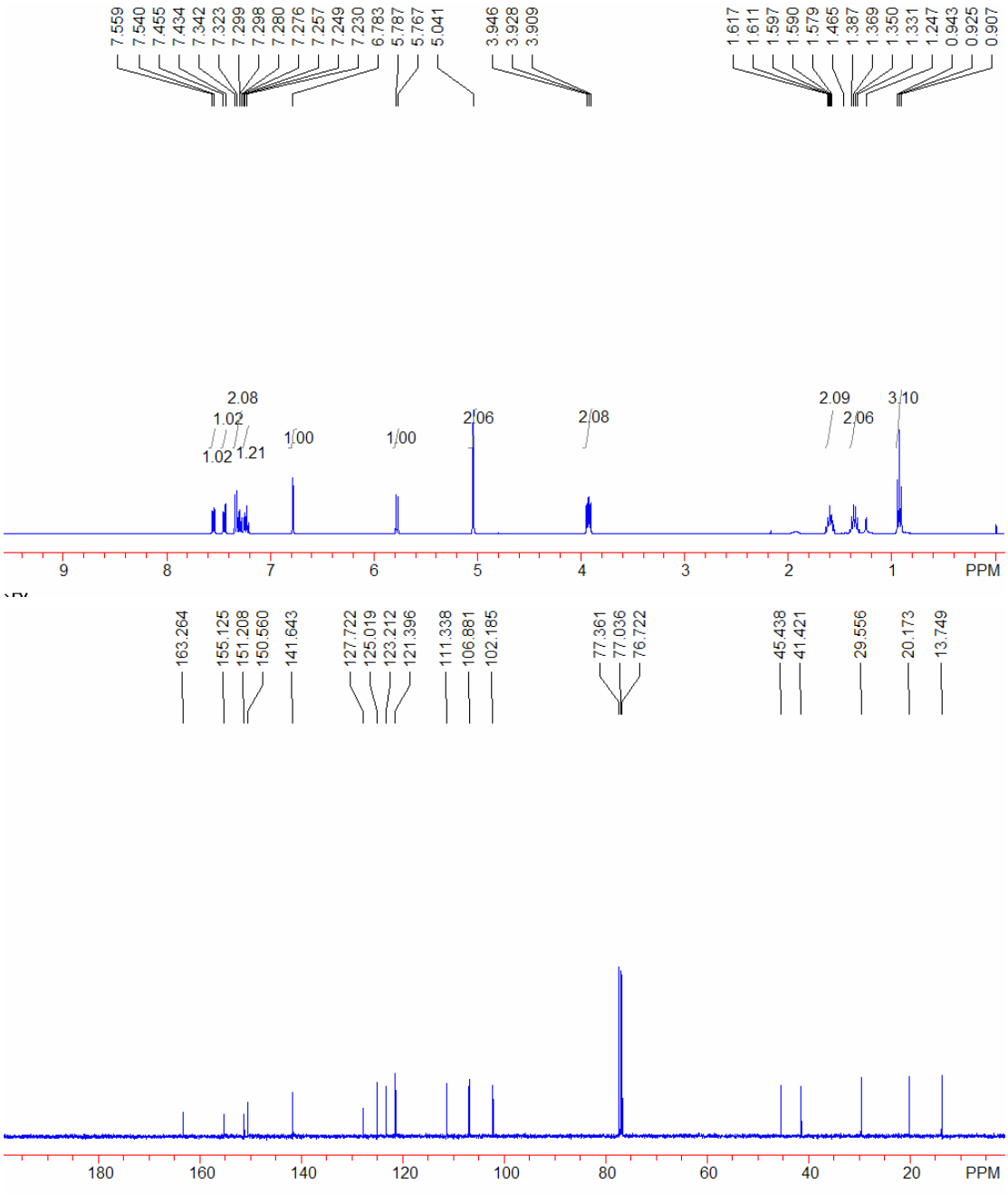
A suspension of resin **6** (0.5 g) in DMF (5 mL) was treated with 2-iodophenol or 2-iodobenzenamine (1.5 mmol), CuI (20 mol %, 0.12mmol), Et_3N (1 mL), and $Pd(PPh_3)_4$ (10 mol %, 0.06 mmol). After being stirred under N_2 atmosphere at 65 ^oC for 24 h, the black mixture was filtered, washed sequentially with THF (10 mL × 2), H_2O (20 mL × 2), DMF (10 mL × 2), H_2O (20 mL × 2), THF (10 mL × 2), and CH_2Cl_2 (10 mL × 2) to afford resin **9**.

To a suspension of the swollen resins **9** (0.5 g) in THF (10 mL) was added 30% H_2O_2 (0.5 mL), and the mixture was stirred for 1 h at room temperature. The mixture was filtered, and the resin was washed with CH_2Cl_2 (20 mL × 3). The filtrate was washed with H_2O (30 mL × 2), dried over $MgSO_4$, and evaporated to dryness under vacuum to obtain the crude products **10**. The crude products were subjected to thin-layer chromatography (TLC) on silica gel with ethyl acetate and light petroleum (1:1-1:4) as eluent to give the purified products for NMR and other microanalysis.

Bis-heterocycles of diazepinedione and benzofuran/indole **12a-j** were prepared with the same procedure form resin **8**.

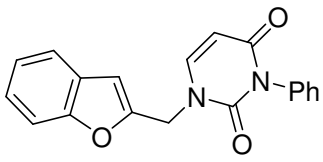
10a

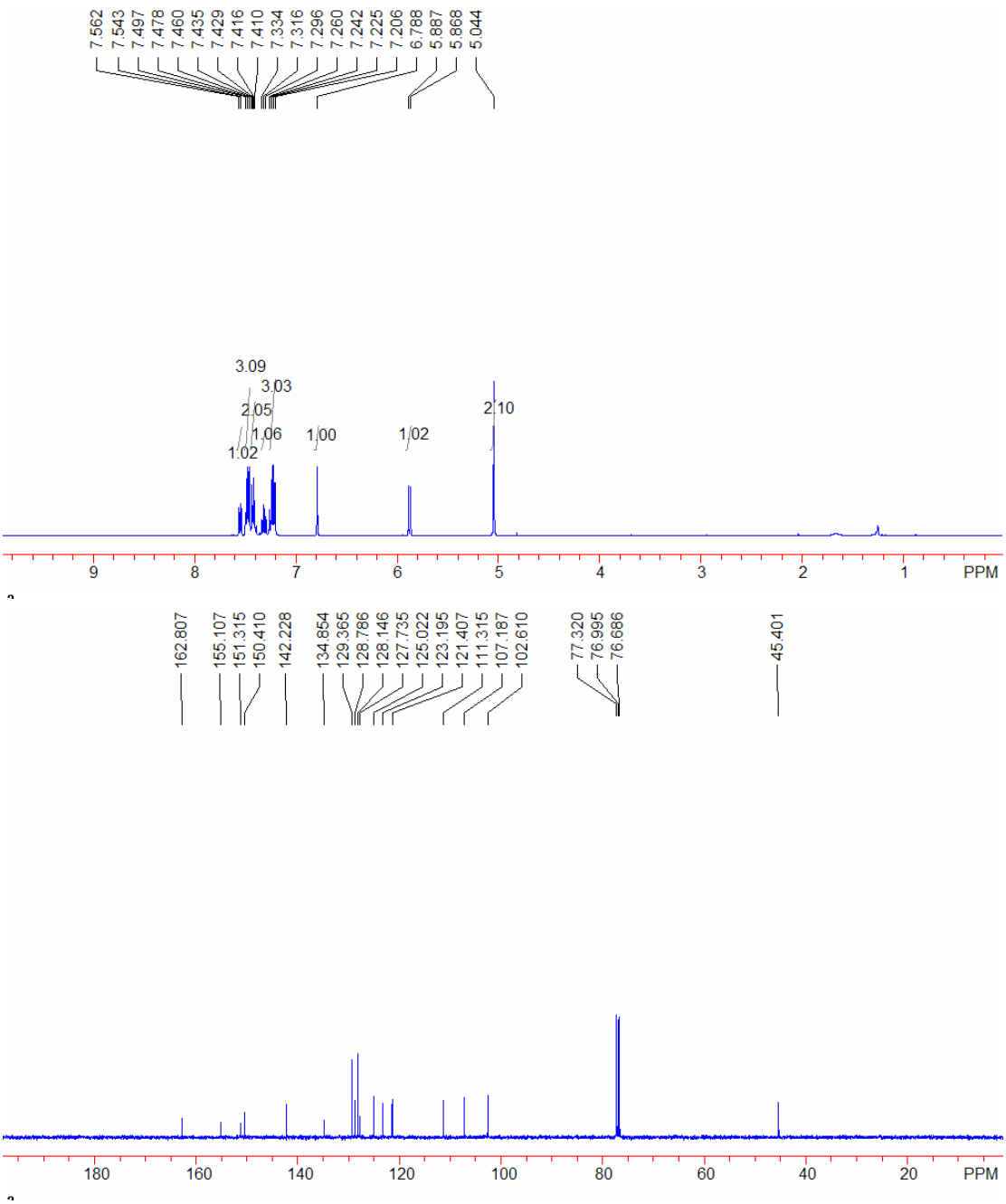




oil; ^{1}H NMR ($CDCl_3$) δ 0.93 (3H, t, *J* = 7.3 Hz), 1.33-1.38 (2H, m), 1.56-1.61 (2H, m), 3.93 (2H, t, *J* = 7.7 Hz), 5.04 (2H, s), 5.78 (1H, d, *J* = 7.9 Hz), 6.78 (1H, s), 7.21-7.34 (3H, m), 7.44 (1H, d, *J* = 8.2 Hz), 7.55 (1H, d, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 163.3, 155.1, 151.2, 150.6, 141.6, 127.7, 125.0, 123.2, 121.4, 111.4, 106.9, 102.2, 45.4, 41.4, 29.6, 20.2, 13.8; MS (EI) *m/z* 298 $(M)^+$; IR ν_{max} (cm^{-1}) 2958, 1705, 1650, 1453; HRMS: *m/z* calcd for $C_{17}H_{18}N_2O_3$: 298.1317; found: 298.1321.

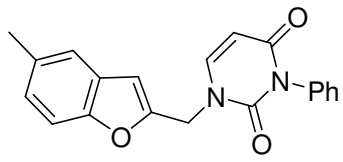
10b

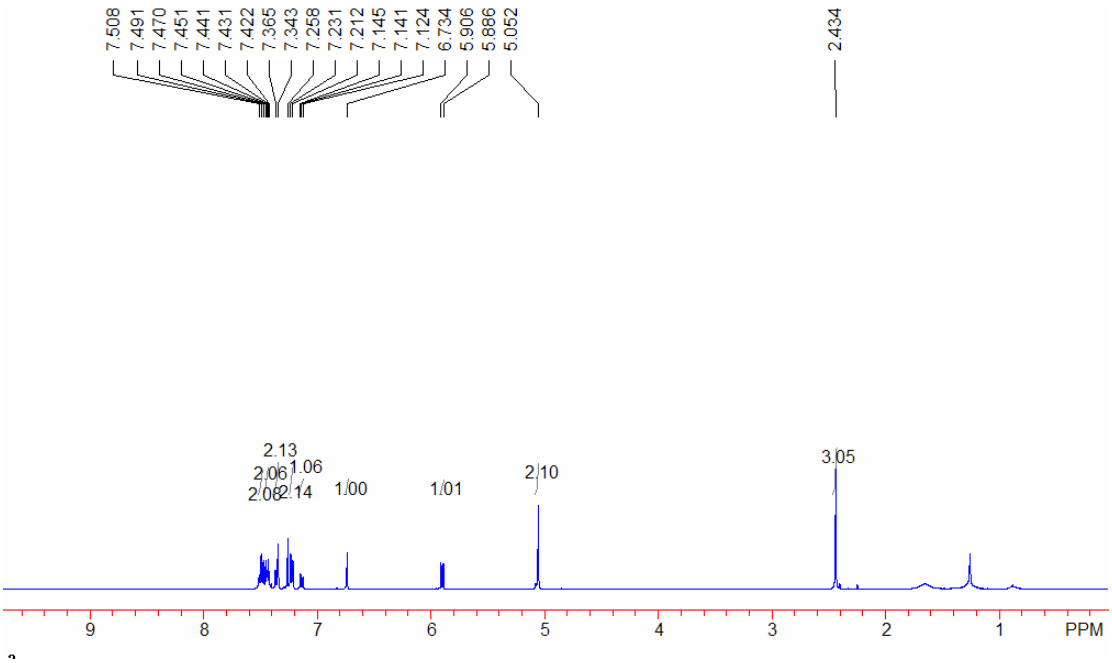


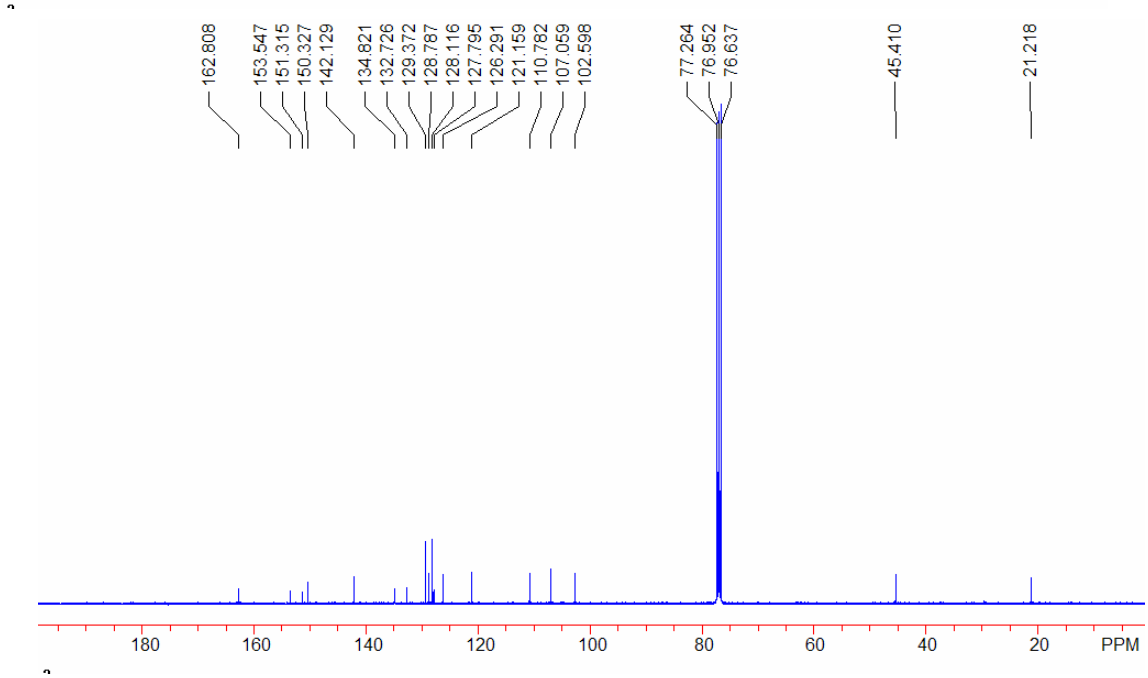


pale solid, mp 129-131 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 5.04 (2H, s), 5.88 (1H, d, *J* = 8.0 Hz), 6.79 (1H, s), 7.20-7.26 (3H, m), 7.32 (1H, t, *J* = 8.1 Hz), 7.41-7.50 (5H, m), 7.55 (1H, d, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 162.8, 155.1, 151.3, 150.3, 142.2, 134.9, 129.4, 128.8, 128.2, 127.7, 125.0, 123.2, 121.4, 111.3, 107.2, 102.6, 45.4; MS (EI) *m/z* 318 $(M)^+$; IR ν_{max} (cm^{-1}) 3102, 1706, 1659, 1490; Elemental analysis calcd. for $C_{19}H_{14}N_2O_3$, C 71.69 %; H 4.43 %; N 8.80 %. Found C 71.73 %; H 4.36 %; N 8.83 %.

10c

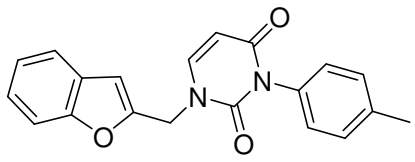


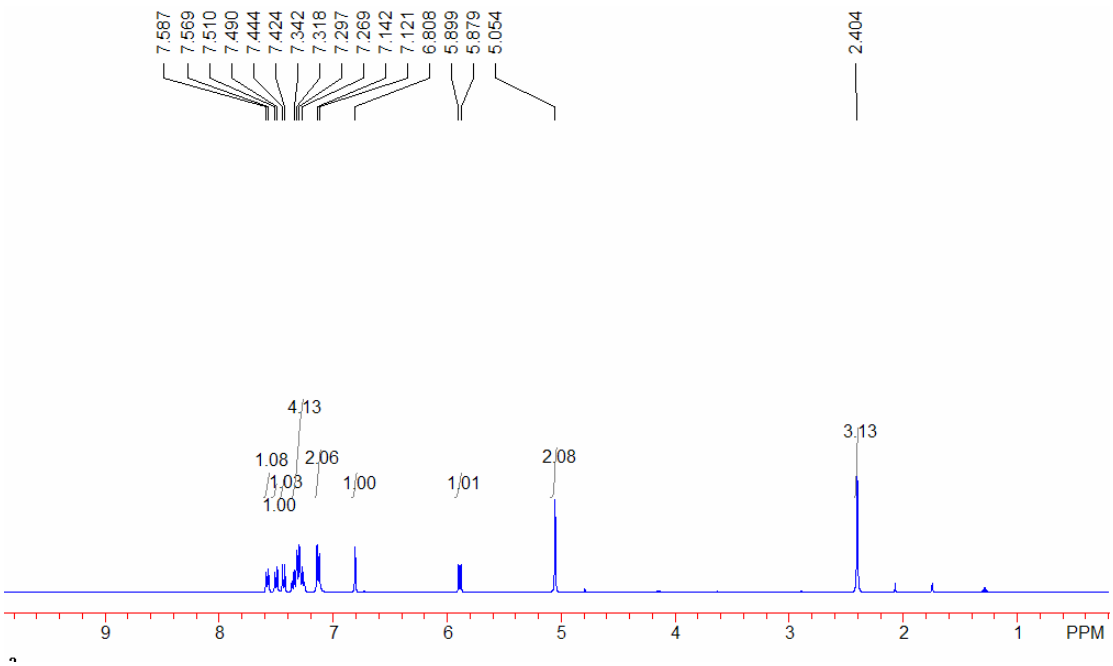


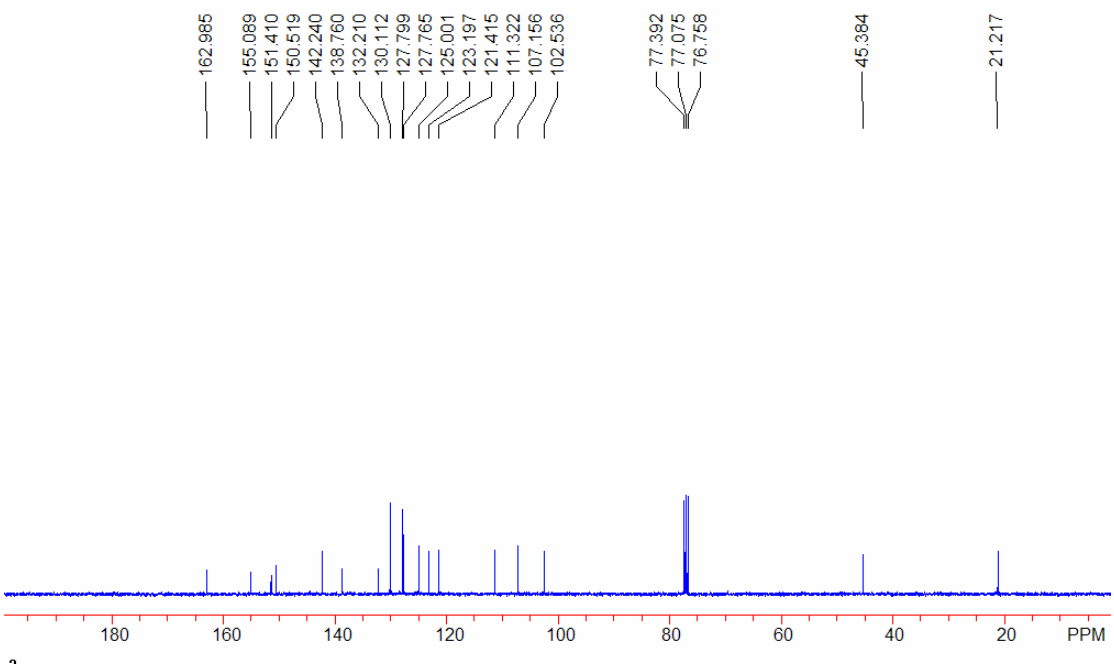


pale solid, mp 144-146 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.43 (3H, s), 5.05 (2H, s), 5.89 (1H, d, *J* = 8.0 Hz), 6.74 (1H, s), 7.14 (1H, d, *J* = 8.4 Hz), 7.22 (2H, d, *J* = 7.4 Hz), 7.34-7.37 (2H, m), 7.42-7.51 (4H, m),; ^{13}C NMR ($CDCl_3$) δ 162.8, 153.6, 151.3, 150.3, 142.1, 134.8, 132.7, 129.4, 128.8, 128.1, 127.8, 126.3, 121.2, 110.8, 107.1, 102.6, 45.4, 21.2; MS (EI) *m/z* 332 $(M)^{+}$; IR ν_{max} (cm^{-1}) 2922, 1714, 1666, 1444; Elemental analysis calcd. for $C_{20}H_{16}N_2O_3$, C 72.28 %; H 4.85 %; N 8.43 %. Found C 72.24 %; H 4.91 %; N 8.44 %.

10d

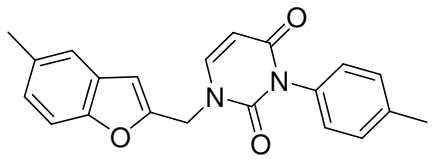


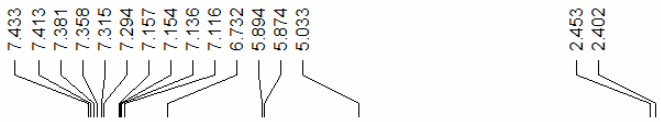


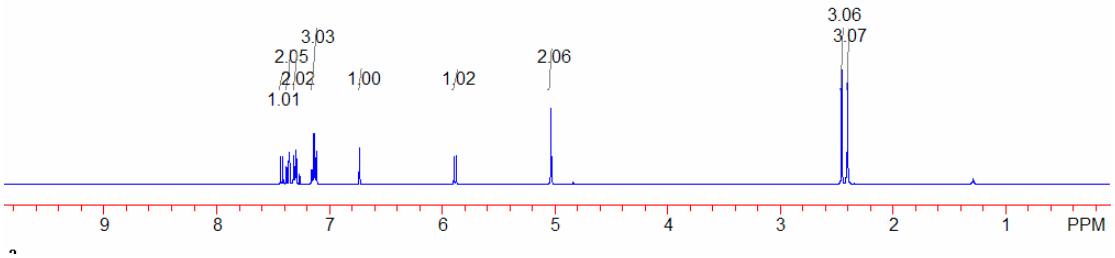


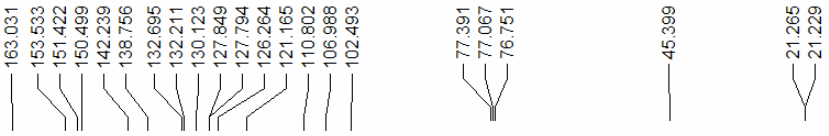
pale solid, mp 208-210 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.40 (3H, s), 5.06 (2H, s), 5.89 (1H, d, *J* = 8.0 Hz), 6.80 (1H, s), 7.13 (2H, d, *J* = 8.1 Hz), 7.25-7.36 (4H, m), 7.43 (1H, d, *J* = 8.0 Hz), 7.50 (1H, d, *J* = 8.2 Hz), 7.58 (1H, d, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 163.0, 155.1, 151.4, 150.5, 142.2, 138.8, 132.8, 130.1, 127.8, 127.7, 125.0, 123.2, 121.4, 111.3, 107.2, 102.5, 45.4, 21.2; MS (EI) *m/z* 332 $(M)^+$; IR ν_{max} (cm^{-1}) 3090, 1708, 1662, 1452; Elemental analysis calcd. for $C_{20}H_{16}N_2O_3$, C 72.28 %; H 4.85 %; N 8.43 %. Found C 72.25 %; H 4.80 %; N 8.47 %.

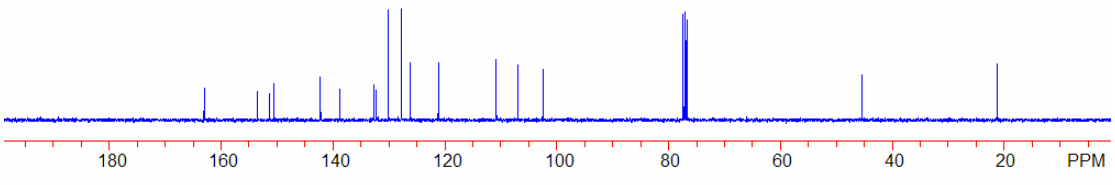
10e





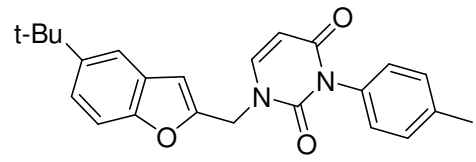


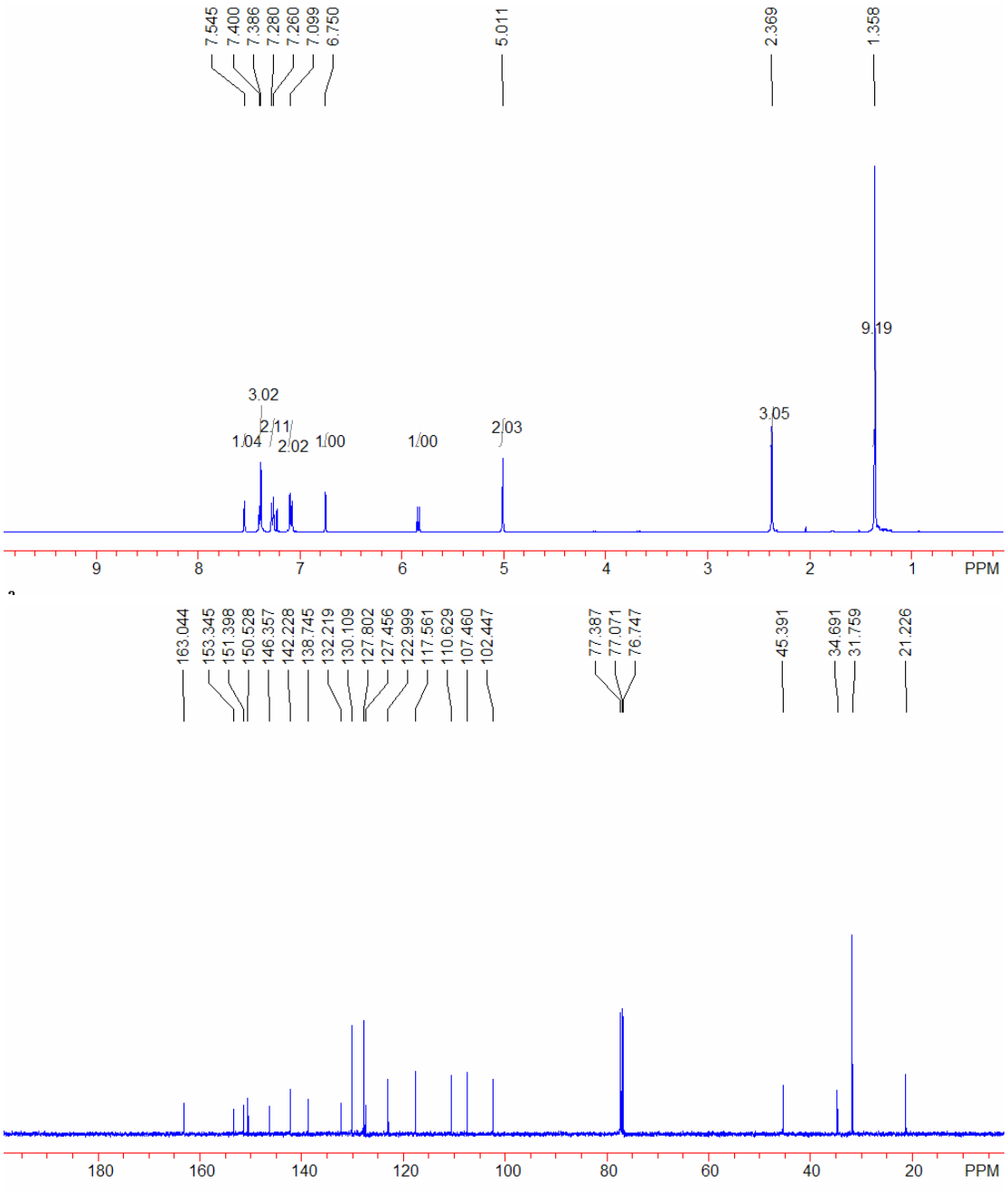




pale solid, mp 210-212 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.40 (3H, s), 2.45 (3H, s), 5.03 (2H, s), 5.88 (1H, d, *J* = 8.0 Hz), 6.73 (1H, s), 7.11-7.15 (3H, m), 7.30 (2H, d, *J* = 8.1 Hz), 7.35-7.38 (2H, m), 7.42 (1H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 163.0, 153.5, 151.4, 150.5, 142.2, 138.8, 132.7, 132.2, 130.1, 127.9, 127.8, 126.3, 121.2, 110.8, 107.0, 102.5, 45.4, 21.3, 21.2; MS (EI) *m/z* 346 $(M)^{+}$; IR ν_{max} (cm^{-1}) 1707, 1662, 1440; Elemental analysis calcd. for $C_{21}H_{18}N_2O_3$, C 72.82 %; H 5.24 %; N 8.09 %. Found C 72.79 %; H 5.29 %; N 8.13 %.

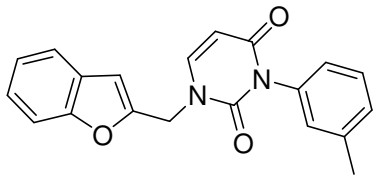
10f

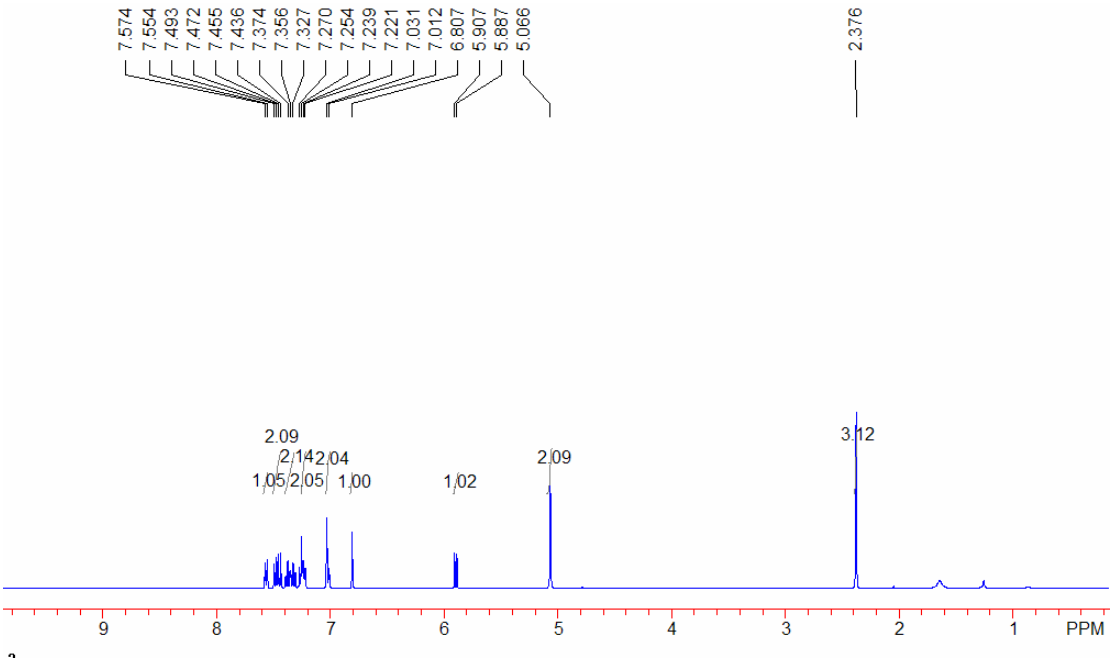


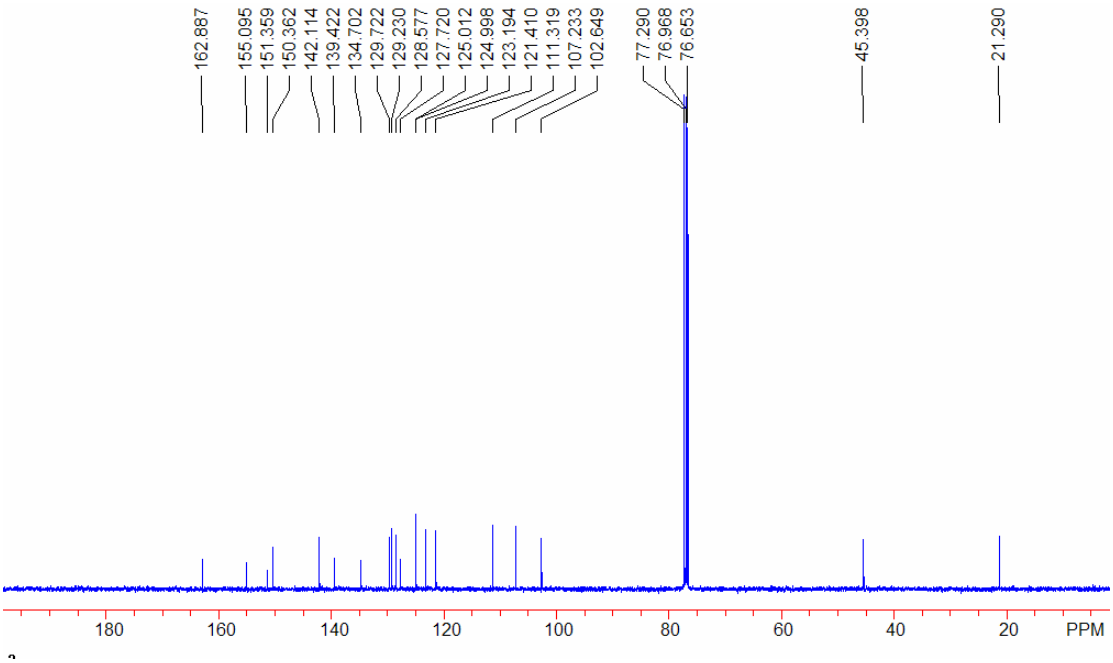


pale solid, mp 185-187 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 1.36 (9H, s), 2.37 (3H, s), 5.01 (2H, s), 5.84 (1H, d, *J* = 8.0 Hz), 6.75 (1H, s), 7.09 (2H, d, *J* = 8.1 Hz), 7.27 (2H, d, *J* = 8.1 Hz), 7.38-7.40 (3H, m), 7.55 (1H, s); ^{13}C NMR ($CDCl_3$) δ 163.1, 153.4, 151.4, 150.5, 146.4, 142.2, 138.8, 132.2, 130.1, 127.8, 127.5, 123.0, 117.6, 110.6, 107.5, 102.5, 45.4, 34.7, 31.8, 21.2; MS (EI) *m/z* 388 $(M)^+$; IR ν_{max} (cm^{-1}) 2961, 1708, 1662, 1441; Elemental analysis calcd. for $C_{24}H_{24}N_2O_3$, C 74.21 %; H 6.23 %; N 7.21 %. Found C 74.18 %; H 6.29 %; N 7.25 %.

10g

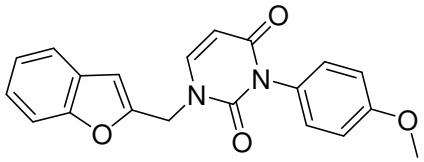


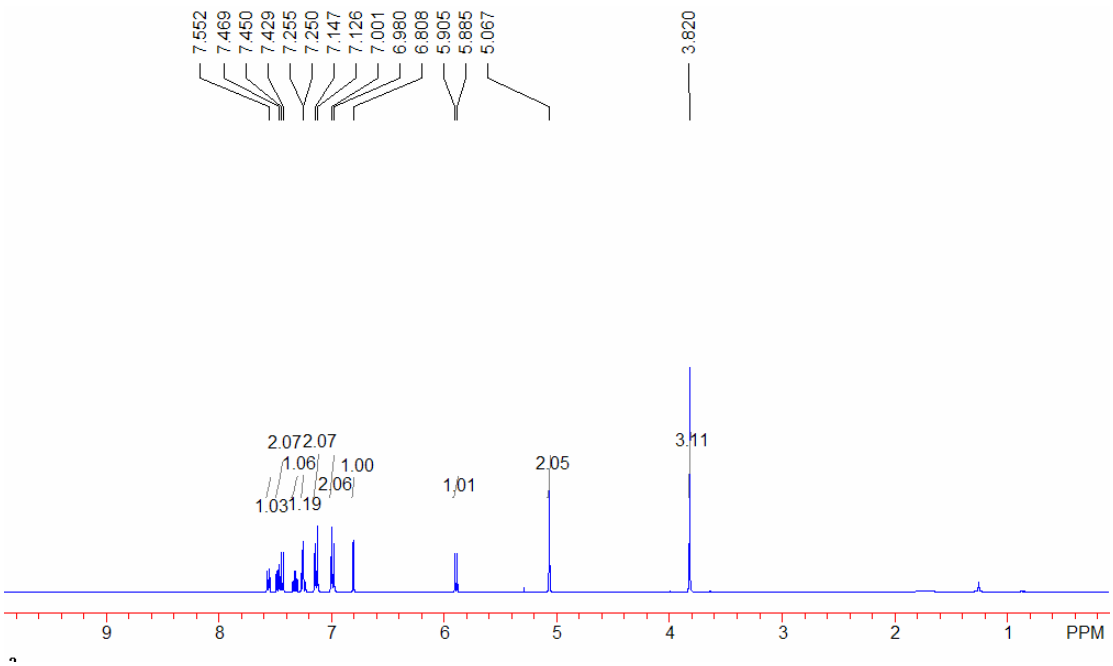


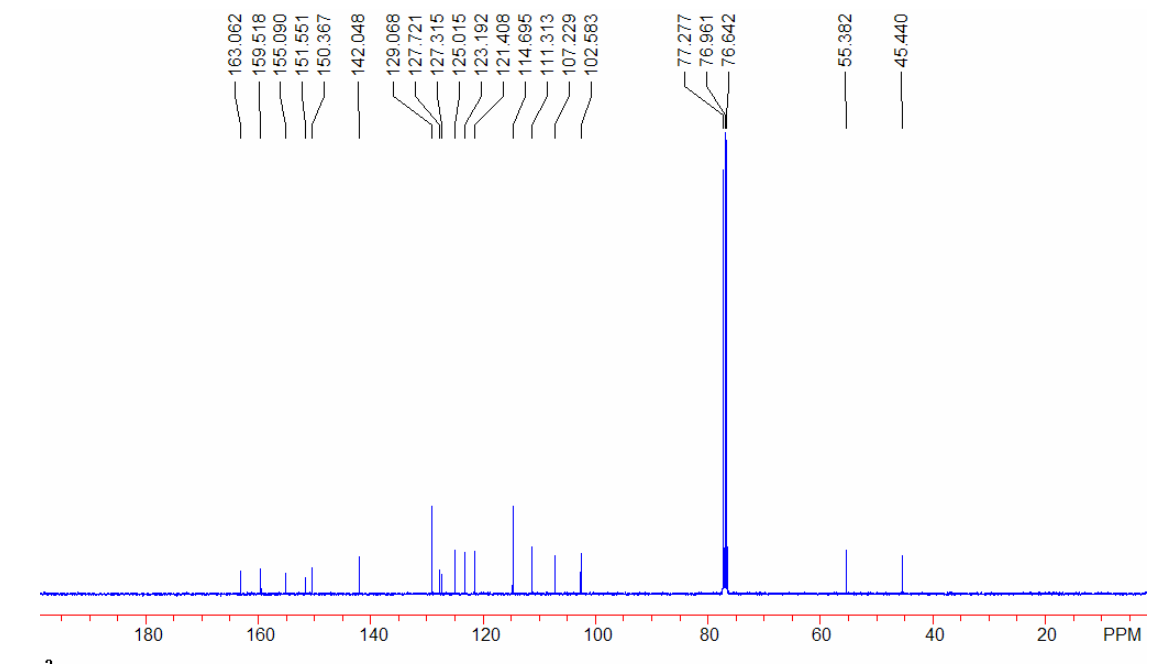


pale solid, mp 134-136 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.38 (3H, s), 5.07 (2H, s), 5.89 (1H, d, J = 8.0 Hz), 6.81 (1H, s), 7.01-7.03 (2H, m), 7.22-7.25 (2H, m), 7.30-7.39 (2H, m), 7.43-7.49 (2H, m), 7.56 (1H, d, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 162.9, 155.1, 151.4, 150.4, 142.1, 139.4, 134.7, 129.7, 129.2, 128.6, 127.7, 125.0, 125.0, 123.2, 121.4, 111.3, 107.2, 102.7, 45.4, 21.3; MS (EI) *m/z* 332 $(M)^{+}$; IR ν_{max} (cm^{-1}) 1708, 1662, 1446; Elemental analysis calcd. for $C_{20}H_{16}N_2O_3$, C 72.28 %; H 4.85 %; N 8.43 %. Found C 72.31 %; H 4.90 %; N 8.40 %.

10h

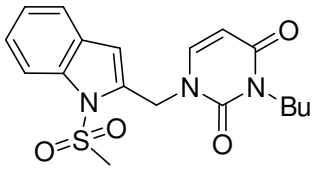


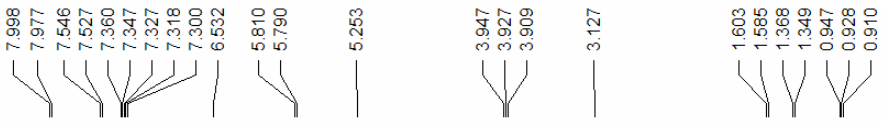


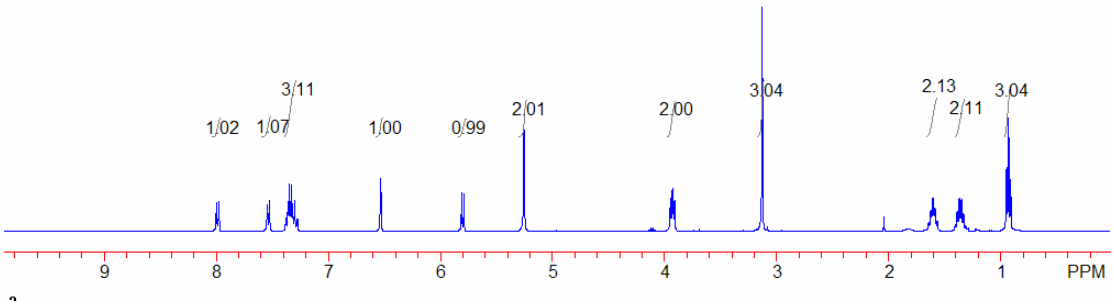


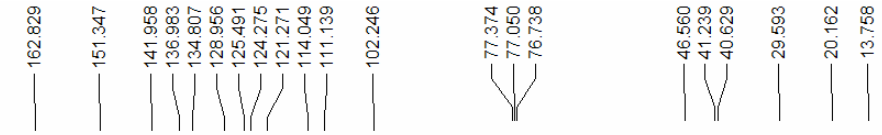
pale solid, mp 195-197 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 3.82 (3H, s), 5.07 (2H, s), 5.89 (1H, d, *J* = 8.0 Hz), 6.81 (1H, s), 6.99 (2H, d, *J* = 8.4 Hz), 7.13 (2H, d, *J* = 8.4 Hz), 7.23 (1H, t, *J* = 7.6 Hz), 7.32 (1H, t, *J* = 7.6 Hz), 7.42-7.49 (2H, m), 7.56 (1H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 163.1, 159.5, 155.1, 151.6, 150.4, 142.1, 129.1, 127.7, 127.3, 125.0, 123.2, 121.4, 114.7, 111.3, 107.3, 102.6, 55.4, 45.4; MS (EI) *m/z* 348 $(M)^+$; IR ν_{max} (cm^{-1}) 2928, 1706, 1661, 1447, 1252; Elemental analysis calcd. for $C_{20}H_{16}N_2O_4$, C 68.96 %; H 4.63 %; N 8.04 %. Found C 68.93 %; H 4.70 %; N 8.09 %.

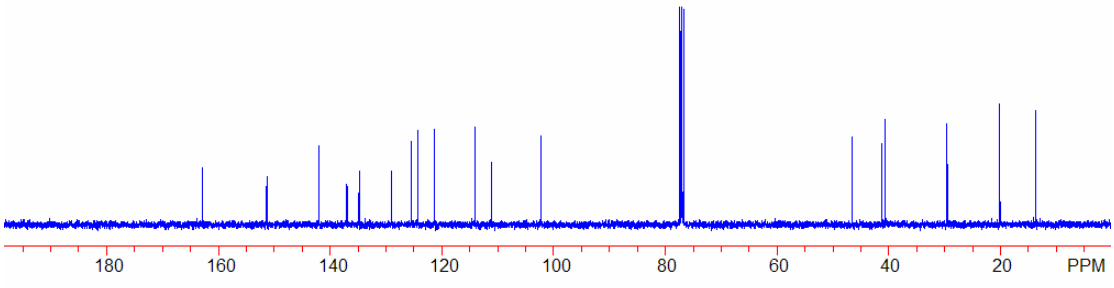
10i





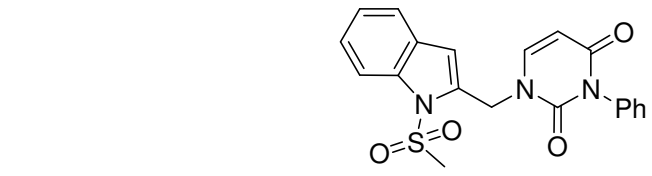


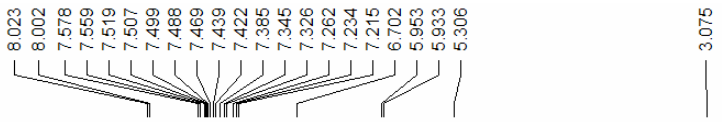


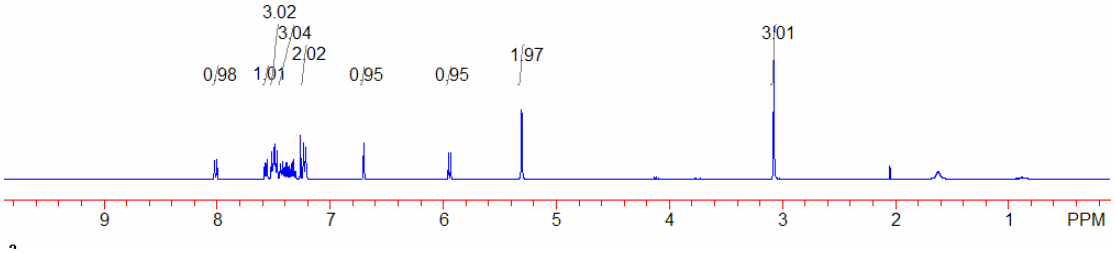


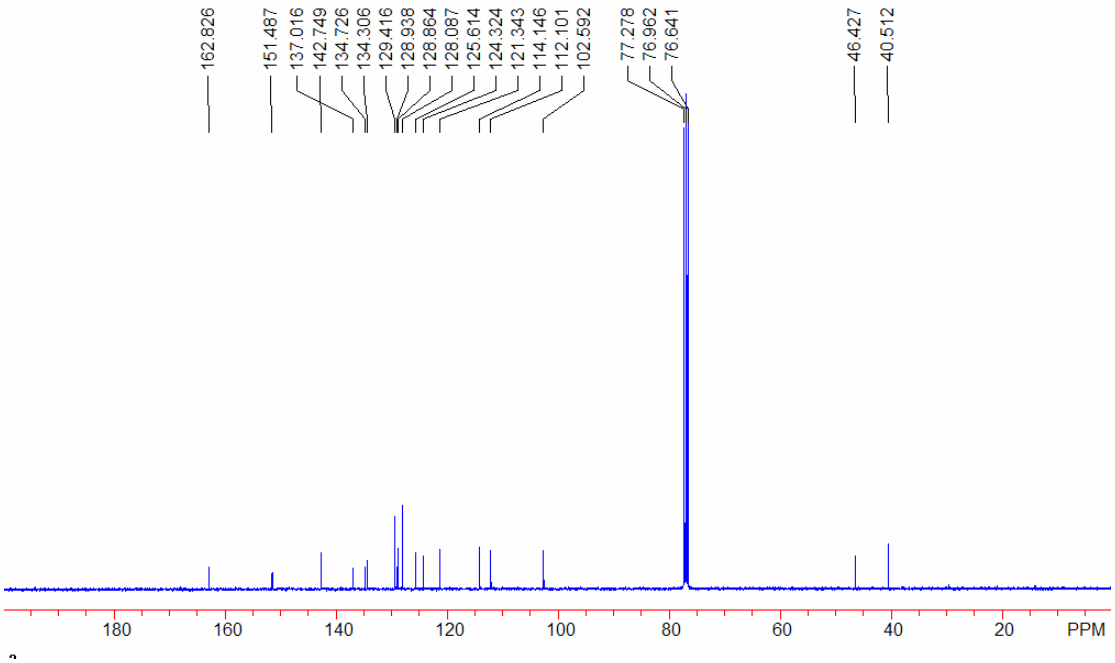
oil; ^{1}H NMR ($CDCl_3$) δ 0.93 (3H, t, *J* = 7.3 Hz), 1.33-1.38 (2H, m), 1.56-1.62 (2H, m), 3.13 (3H,s), 3.93 (2H, t, *J* = 7.5 Hz), 5.25 (2H, s), 5.80 (1H, d, *J* = 7.9 Hz), 6.53 (1H, s), 7.28-7.38 (3H, m), 7.53 (1H, d, *J* = 7.6 Hz), 7.99 (1H, d, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 162.8, 151.4, 142.0, 137.0, 134.8, 129.0, 125.5, 124.3, 121.3, 114.1, 111.1, 102.2, 46.6, 41.3, 40.6, 29.6, 20.2, 13.8; MS (EI) *m/z* 375 $(M)^+$; IR ν_{max} (cm^{-1}) 1708, 1663, 1453, 1365; HRMS: *m/z* calcd for $C_{18}H_{21}N_3O_4S$: 375.1253; found: 375.1250.

10j



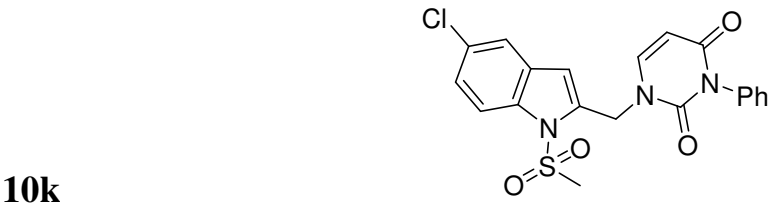


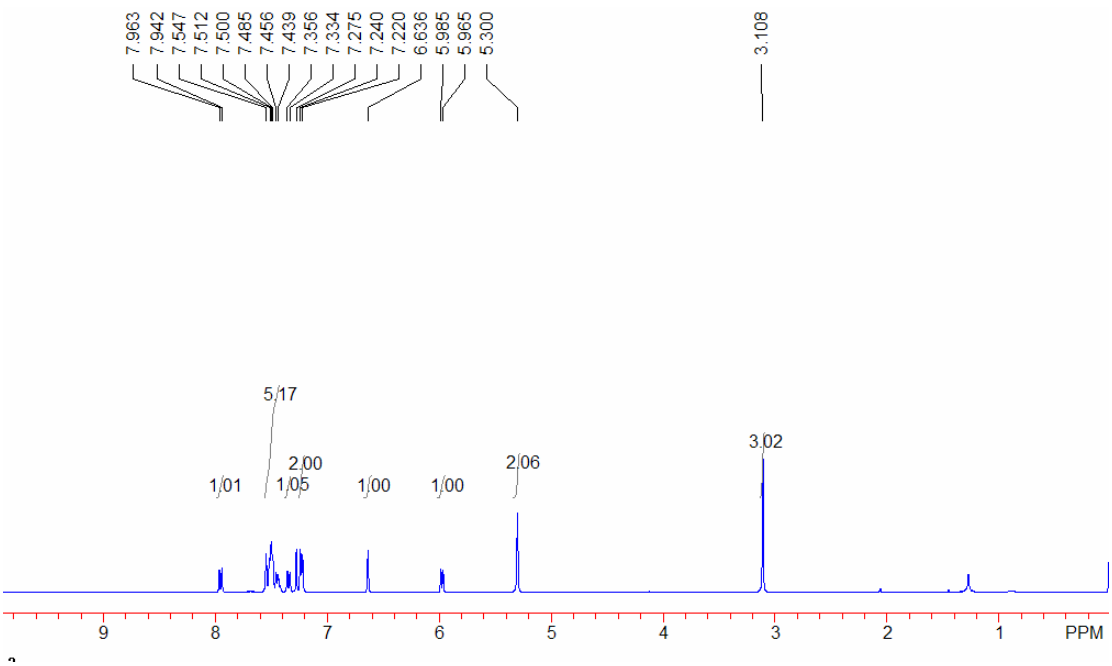


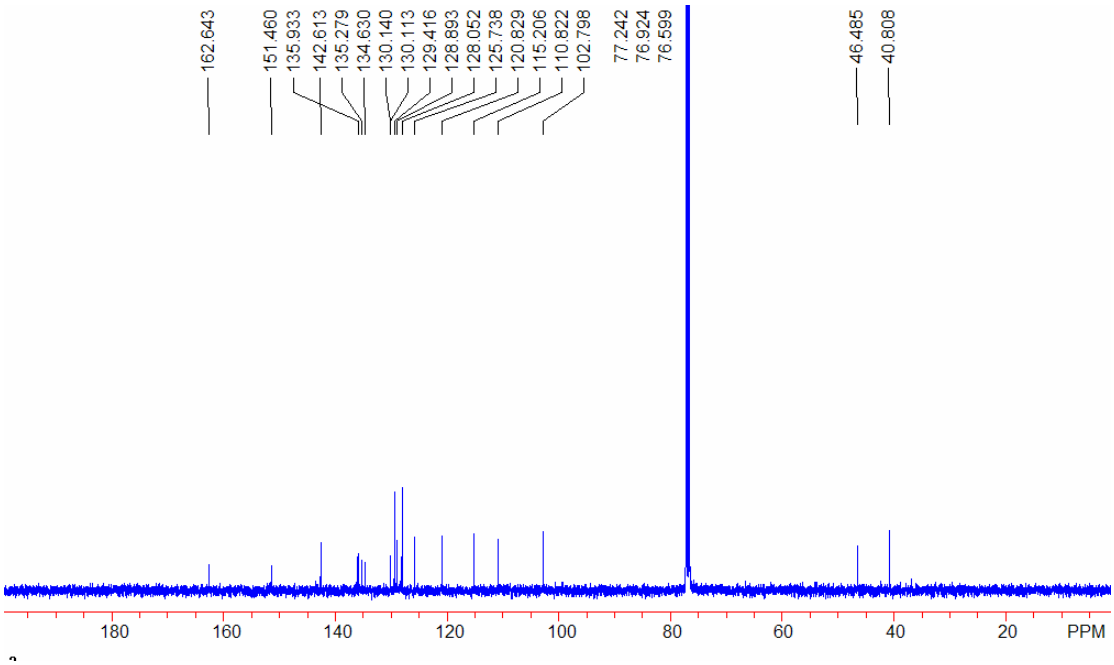


pale solid, mp 226-228 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 3.07 (3H, s), 5.31 (2H, s), 5.94 (1H, d, *J* = 8.0 Hz), 6.70 (1H, s), 7.22 (2H, d, *J* = 7.4 Hz), 7.32-7.44 (3H, m), 7.47-7.52 (3H, m), 7.57 (1H, d, *J* = 7.6 Hz), 8.01 (1H, d, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 162.8, 151.5, 142.8, 137.0, 134.7, 134.3, 129.4, 128.9, 128.8, 128.1, 125.6, 124.3, 121.3, 114.2, 112.1, 102.6, 46.4, 40.5; MS (EI) *m/z* 395 $(M)^{+}$; IR ν_{max} (cm^{-1}) 1715, 1655, 1450, 1362; Elemental analysis calcd. for $C_{20}H_{17}N_3O_4S$, C 60.75 %; H 4.33 %; N 10.63 %. Found C 60.71 %; H 4.39 %; N 10.60 %.

10k

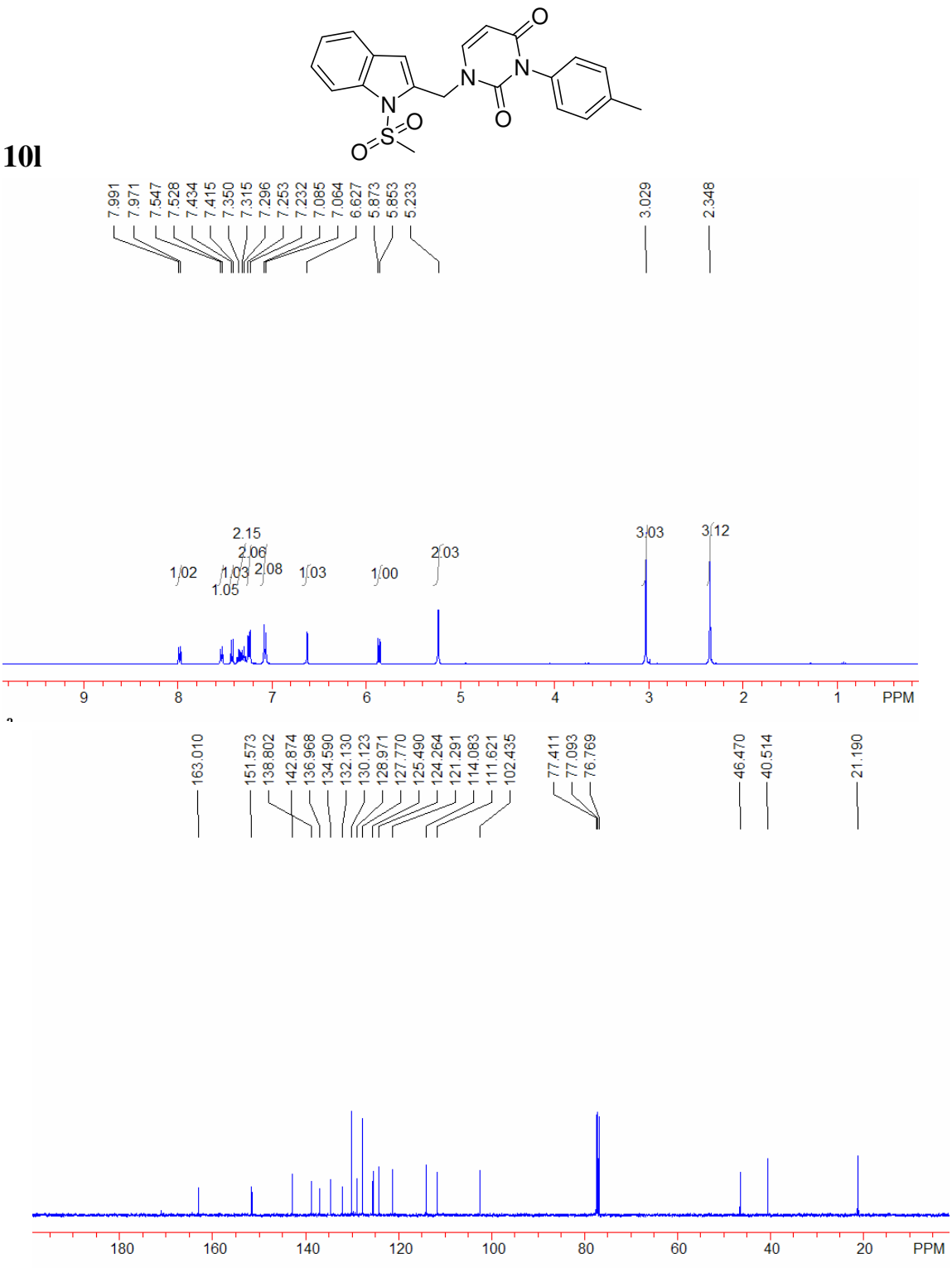






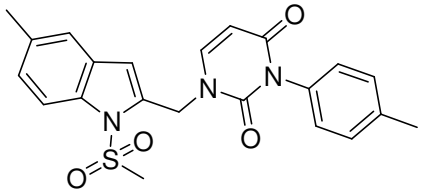
pale solid, mp 259-261 °C; ^{1}H NMR ($CDCl_3$) δ 3.11 (3H, s), 5.30 (2H, s), 5.97 (1H, d, *J* = 7.9 Hz), 6.64 (1H, s), 7.23 (2H, d, *J* = 7.5 Hz), 7.34 (1H, d, *J* = 8.9 Hz),7.43-7.54 (5H, m), 7.95 (1H, d, *J* = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 162.7, 151.5, 142.6, 135.9, 135.3, 134.6, 130.2, 130.1, 129.4, 128.9, 128.1, 125.7, 120.8, 115.2, 110.8, 102.8, 46.5, 40.8; MS (EI) *m/z* 429 $(M)^+$; IR ν_{max} (cm^{-1}) 1715, 1672, 1445, 1361; Elemental analysis calcd. for $C_{20}H_{16}ClN_3O_4S$, C 55.88 %; H 3.75 %; N 9.77 %. Found C 55.85 %; H 3.80 %; N 9.75 %.

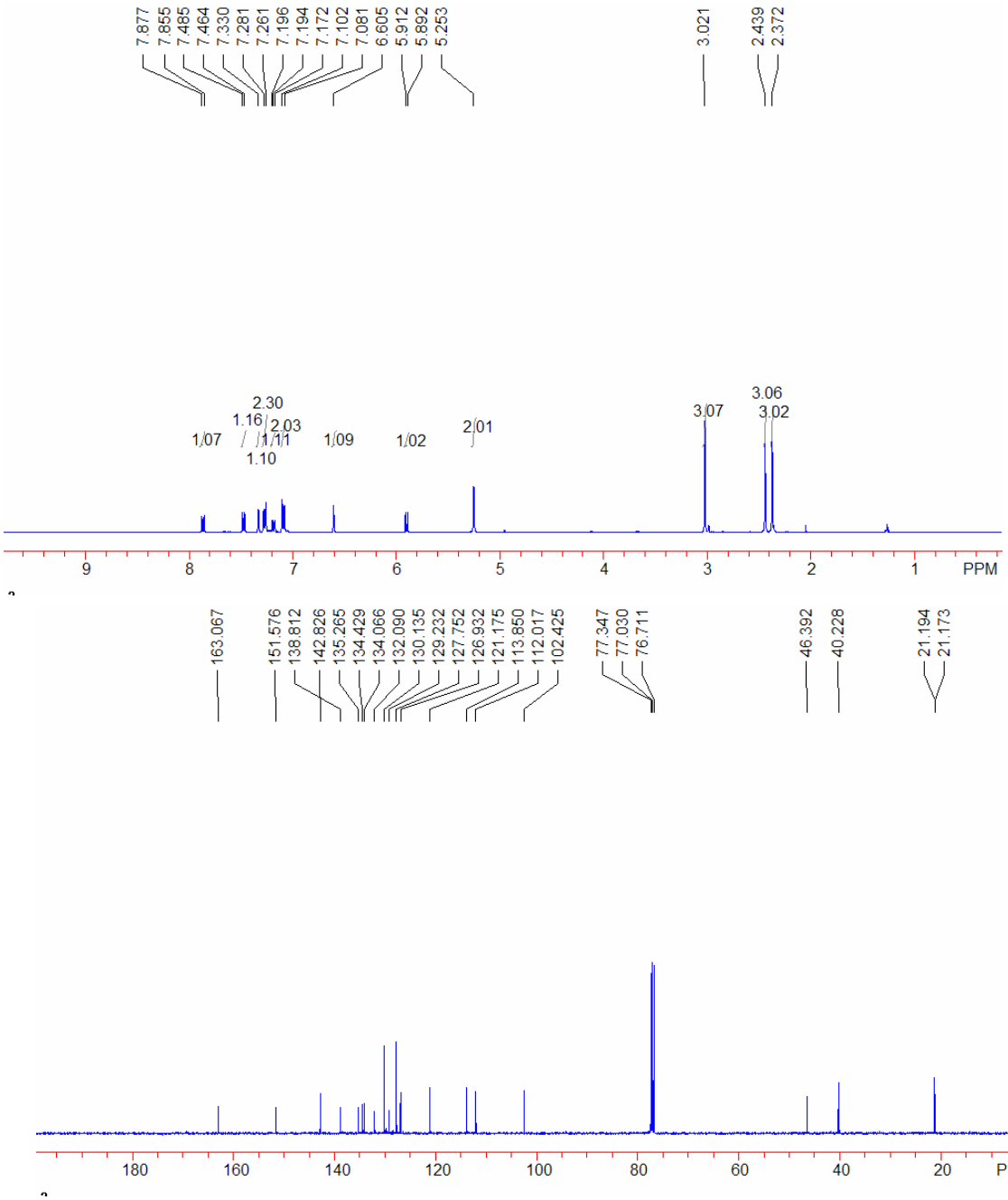
10l



pale solid, mp 190-192 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.35 (3H, s), 3.03 (3H, s), 5.23 (2H, s), 5.86 (1H, d, *J* = 8.0 Hz), 6.63 (1H, s), 7.07 (2H, d, *J* = 8.2 Hz), 7.24 (2H, d, *J* = 8.1 Hz), 7.29-7.35 (2H, m), 7.42 (1H, d, *J* = 8.0 Hz), 7.44 (1H, d, *J* = 7.5 Hz), 7.98 (1H, d, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 163.0, 151.6, 142.9, 138.8, 137.0, 134.6, 132.1, 130.1, 129.0, 127.8, 125.5, 124.3, 121.3, 114.1, 111.6, 102.4, 46.5, 40.5, 21.2; MS (EI) *m/z* 409 $(M)^+$; IR ν_{max} (cm^{-1}) 1714, 1661, 1446, 1373; Elemental analysis calcd. for $C_{21}H_{19}N_3O_4S$, C 61.60 %; H 4.68 %; N 10.26 %. Found C 61.57 %; H 4.74 %; N 10.30 %.

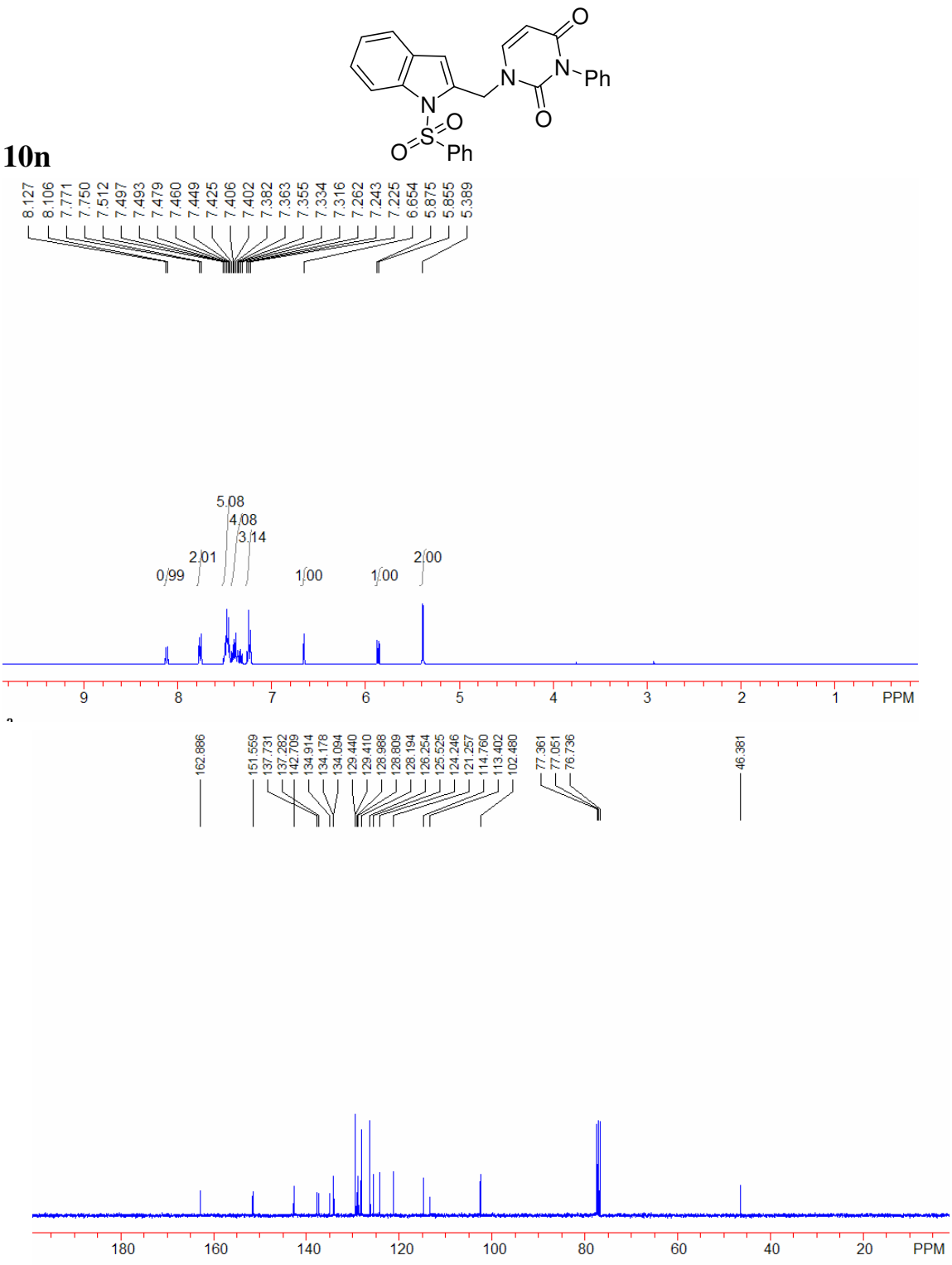
10m





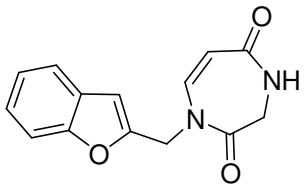
pale solid, mp 149-151 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.37 (3H, s), 2.44 (3H, s), 3.02 (3H, s), 5.25 (2H, s), 5.90 (1H, d, *J* = 8.0 Hz), 6.61 (1H, s), 7.09 (2H, d, *J* = 8.2 Hz), 7.18 (1H, d, *J* = 9.2 Hz), 7.27 (2H, d, *J* = 8.2 Hz), 7.31 (1H, s), 7.47 (1H, d, *J* = 8.0 Hz), 7.86 (1H, d, *J* = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 163.1, 151.6, 142.8, 138.8, 135.3, 134.4, 134.1, 132.1, 130.1, 129.2, 127.8, 126.9, 121.2, 113.9, 112.0, 102.4, 46.4, 40.2, 21.2, 21.1; MS (EI) *m/z* 423 $(M)^{+}$; IR ν_{max} (cm^{-1}) 1712, 1662, 1447, 1364; Elemental analysis calcd. for $C_{22}H_{21}N_3O_4S$, C 62.40 %; H 5.00 %; N 9.92 %. Found C 62.36 %; H 5.08 %; N 9.90 %.

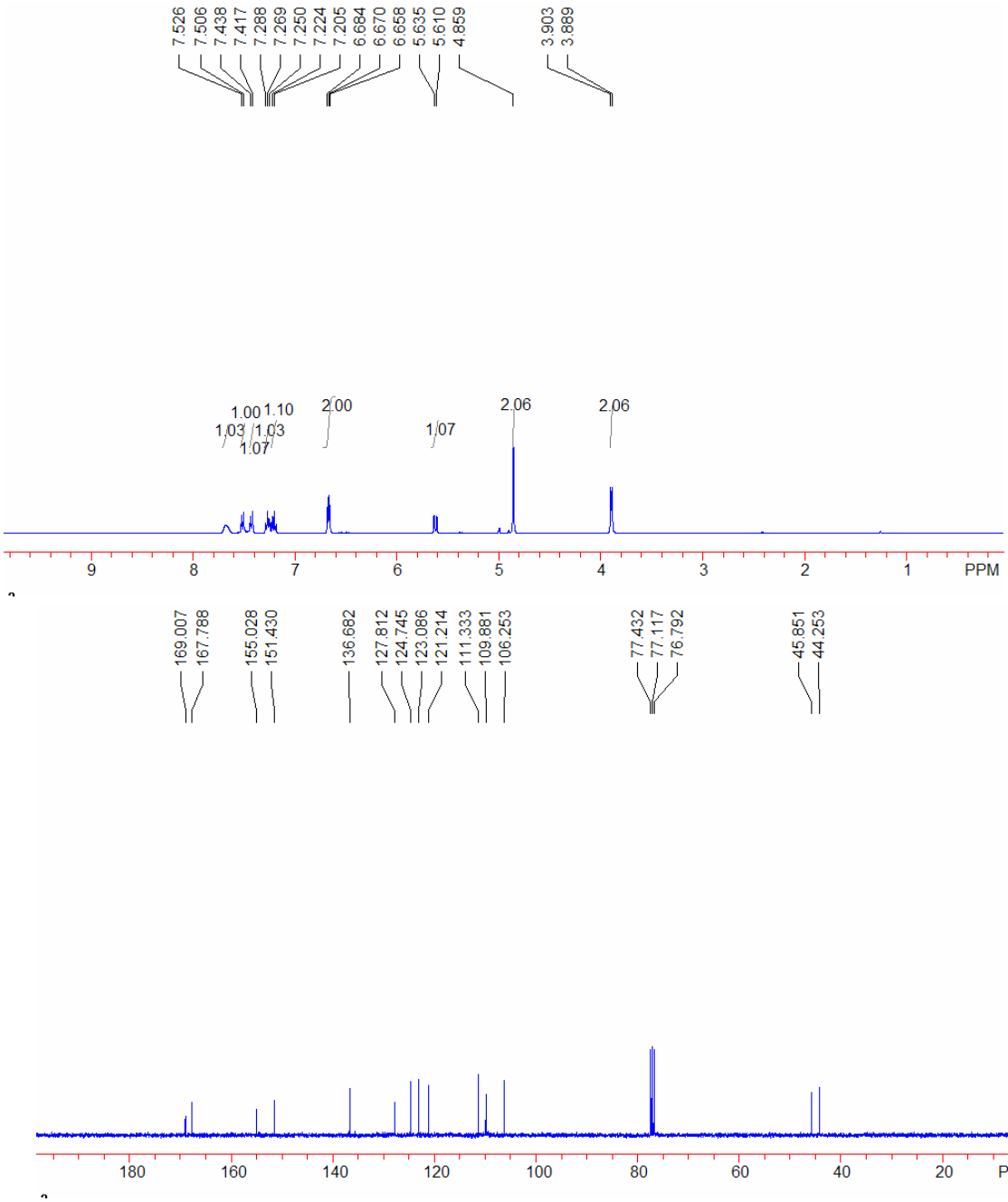
10n



oil; ^{1}H NMR ($CDCl_3$) δ 5.39 (2H, s), 5.86 (1H, d, *J* = 8.0 Hz), 6.66 (1H, s), 7.22-7.24 (3H, m), 7.32-7.50 (9H, m), 7.76 (2H, d, *J* = 8.0 Hz), 8.11 (1H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 162.9, 151.6, 142.7, 137.7, 137.3, 134.9, 134.2, 134.1, 129.5, 129.4, 129.0, 128.8, 128.2, 126.3, 125.5, 124.3, 121.3, 114.8, 113.4, 102.5, 46.4; MS (EI) *m/z* 457 $(M)^+$; IR ν_{max} (cm^{-1}) 1717, 1673, 1445, 1374; HRMS: *m/z* calcd for $C_{25}H_{19}N_3O_4S$: 457.1096; found: 457.1098.

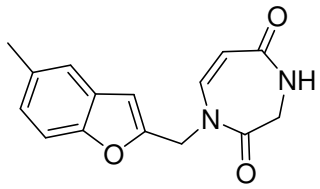
12a

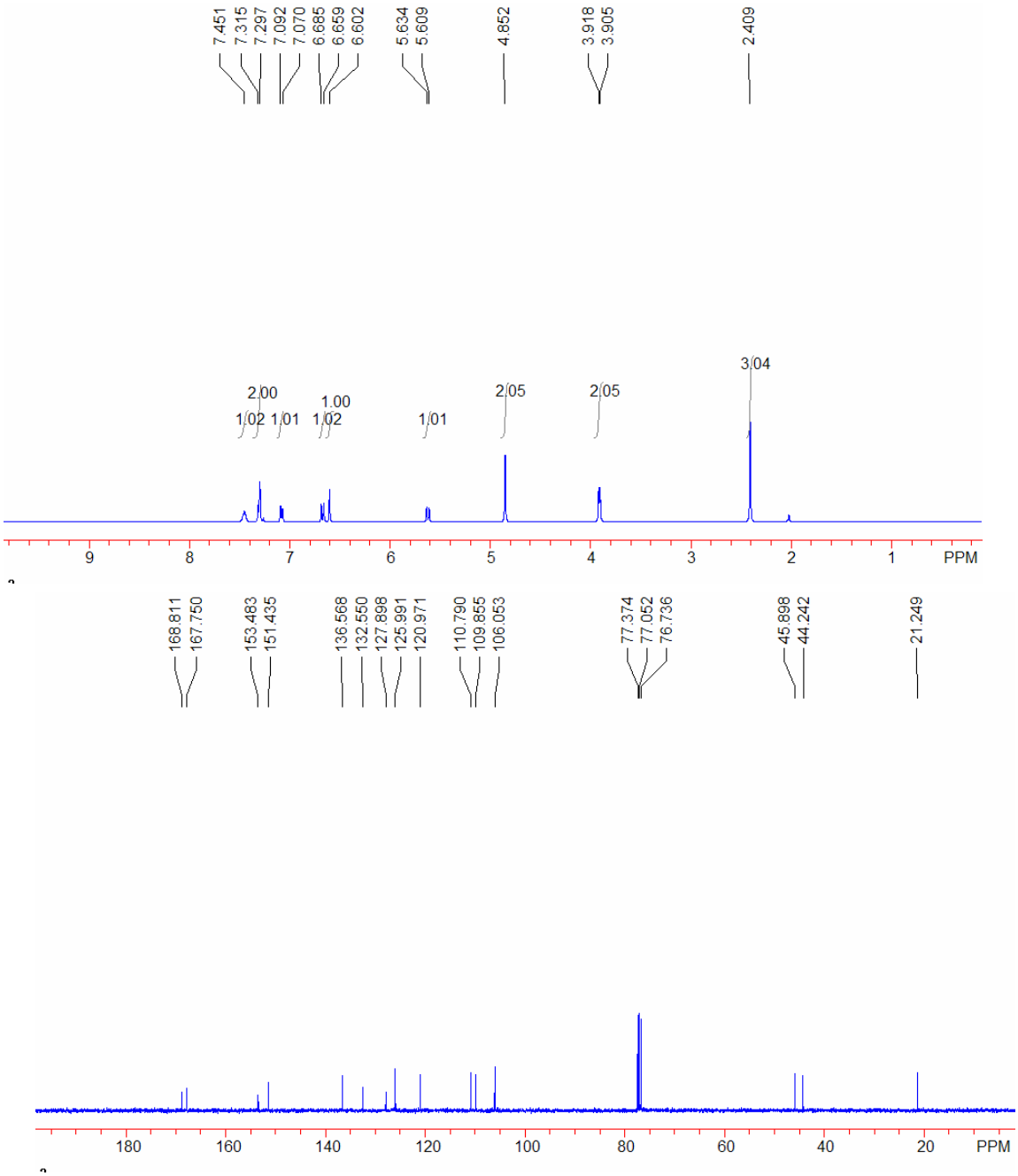




pale solid, mp 133-135 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 3.89 (2H, d, J = 5.4 Hz), 4.86 (2H, s), 5.62 (1H, d, J = 10.1 Hz), 6.65-6.68 (2H, m), 7.22 (1H, dd, $J_1 = J_2 =$ 8.2 Hz), 7.27 (1H, dd, $J_1 = J_2 =$ 8.2 Hz), 7.43 (1H, d, J = 8.2 Hz), 7.51 (1H, d, J = 8.2 Hz), 7.67 (1H, broad); ^{13}C NMR ($CDCl_3$) δ 169.0, 167.8, 155.0, 151.4, 136.7, 127.8, 124.8, 123.1, 121.2, 111.3, 109.9, 106.3, 45.9, 44.3; MS (EI) *m/z* 256 $(M)^+$; IR ν_{max} (cm^{-1}) 1679, 1652, 1399; Elemental analysis calcd. for $C_{14}H_{12}N_2O_3$, C 65.62 %; H 4.72 %; N 10.93 %. Found C 65.66 %; H 4.77 %; N 10.89 %.

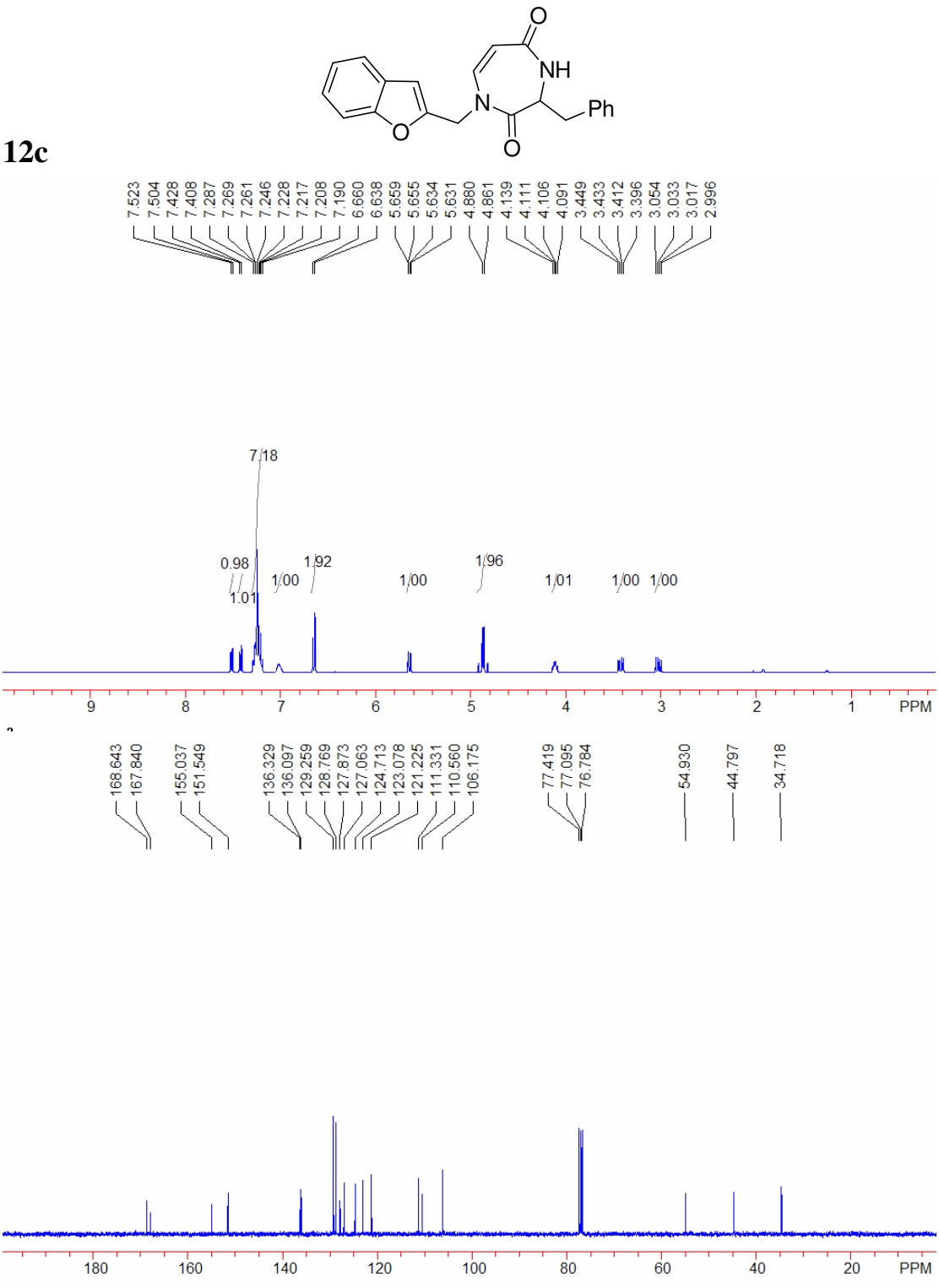
12b





pale solid, mp 175-177 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.41 (3H, s), 3.91 (2H, d, *J* = 5.3 Hz), 4.85 (2H, s), 5.62 (1H, d, *J* = 10.1 Hz), 6.60 (1H, s), 6.67 (1H, d, *J* = 10.1 Hz), 7.08 (1H, d, *J* = 8.5 Hz), 7.29-7.32 (2H, m), 7.45 (1H, broad); ^{13}C NMR ($CDCl_3$) δ 168.8, 167.8, 153.5, 151.4, 136.6, 132.6, 127.9, 126.0, 121.0, 110.8, 109.9, 106.1, 45.9, 44.3, 21.3; MS (EI) *m/z* 270 $(M)^{+}$; IR ν_{max} (cm^{-1}) 1697, 1668, 1372; Elemental analysis calcd. for $C_{15}H_{14}N_2O_3$, C 66.66 %; H 5.22 %; N 10.36 %. Found C 66.62 %; H 5.29 %; N 10.40 %.

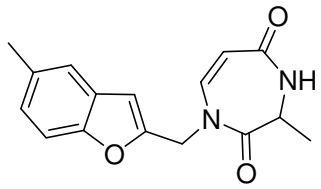
12c

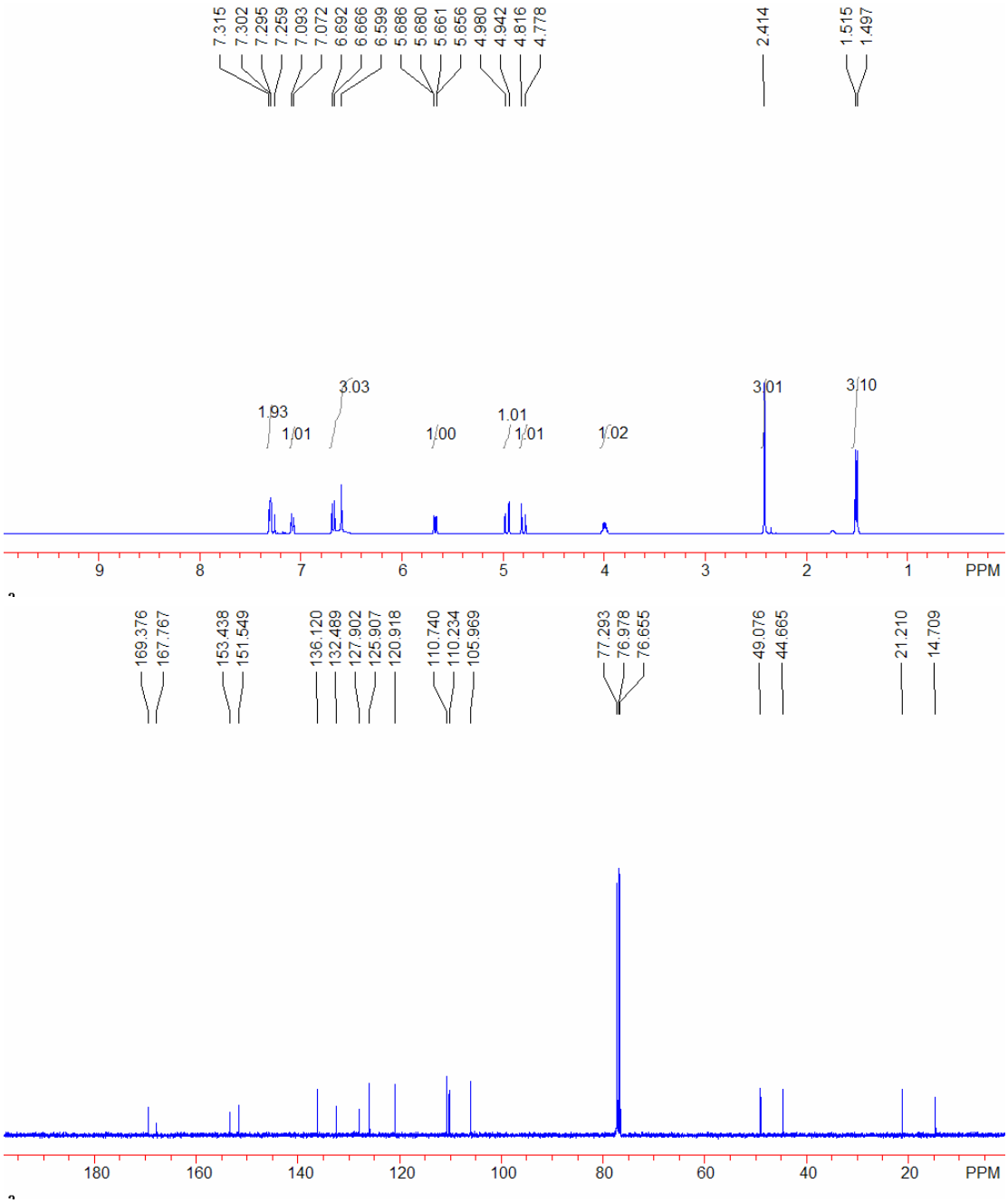


pale solid, mp 176-178 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 3.02 (1H, dd, J_1 = 8.4 Hz, J_2 = 14.6 Hz), 3.42 (1H, dd, J_1 = 6.2 Hz, J_2 = 14.6 Hz), 4.09-4.13 (1H, m), 4.84 (1H, d, J = 15.5 Hz), 4.90 (1H, d, J = 15.5 Hz), 5.64 (1H, d, J = 10.0 Hz), 6.63-6.66 (2H, m), 7.02 (1H, broad), 7.19-7.29 (7H, m), 7.42 (1H, d, J = 8.1 Hz), 7.51 (1H, d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 168.6, 167.8, 155.0, 151.6, 136.3, 136.1, 129.3, 128.8, 127.9, 127.1, 124.7, 123.1, 121.2, 111.3, 110.6, 106.2, 54.9, 44.8, 34.7; MS (EI) *m/z* 346 $(M)^+$; IR ν_{max} (cm^{-1}) 1702, 1663, 1429; Elemental analysis calcd. for $C_{21}H_{18}N_2O_3$, C 72.82 %; H 5.24 %; N 8.09 %. Found C 72.85 %; H 5.30 %; N 8.04 %. $[\alpha]_D^{20}$ =

-324.4 (*c* 1.0, CH_2Cl_2).

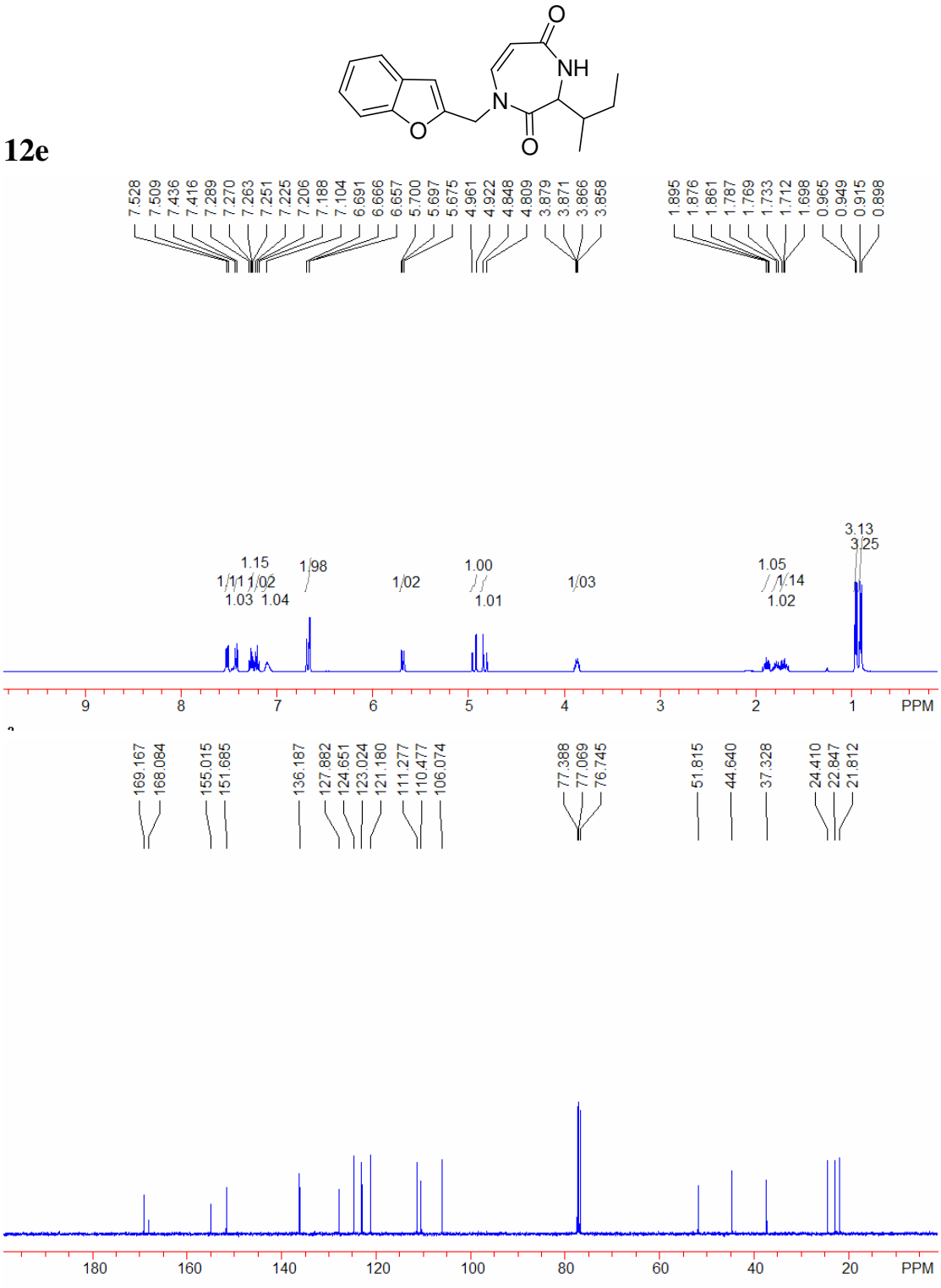
12d





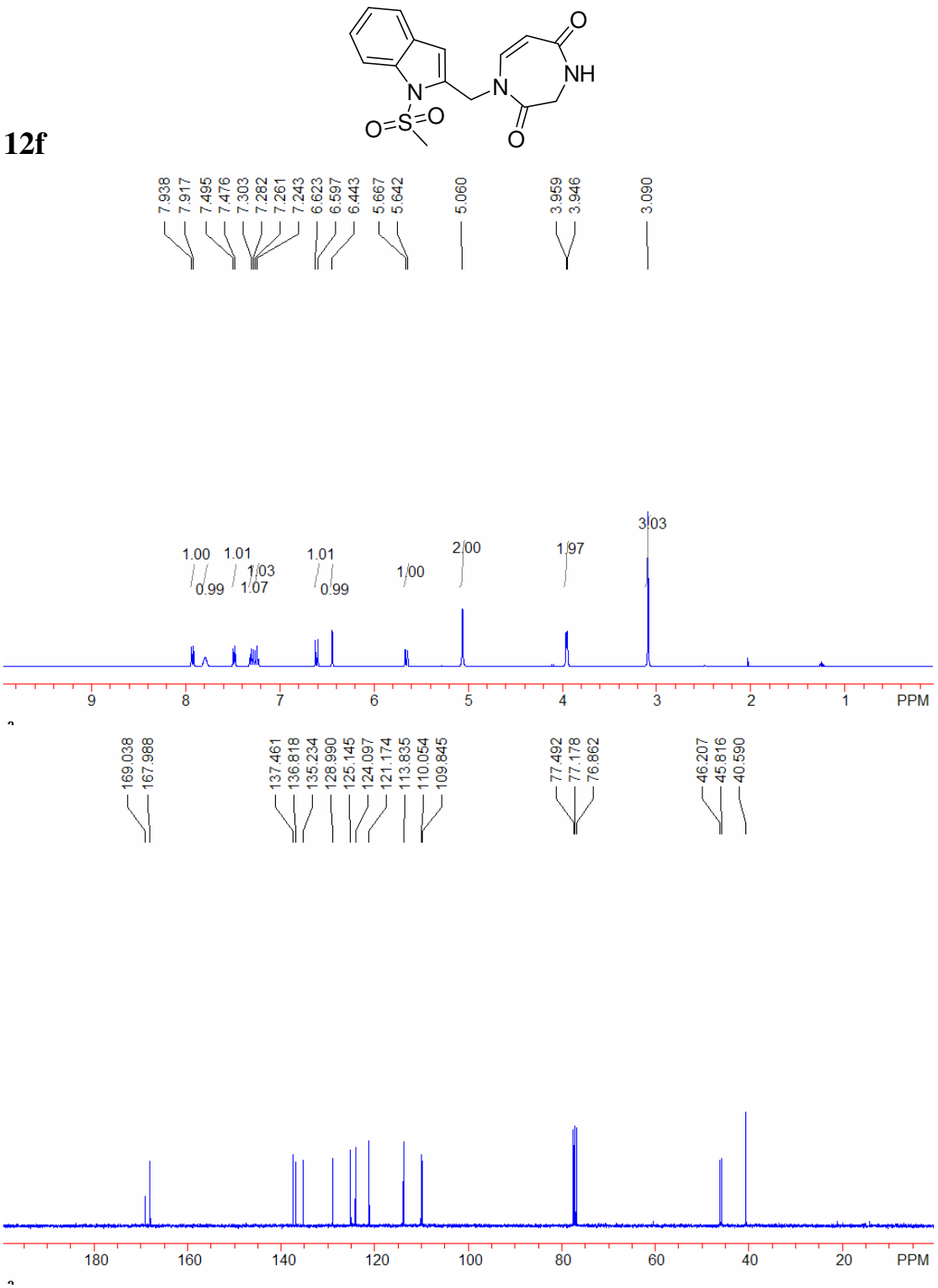
pale solid, mp 195-197 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 1.50 (3H, d, J = 6.8 Hz), 2.41 (3H, s), 3.98-4.00 (1H, m), 4.80 (1H, d, J = 15.5 Hz), 4.96 (1H, d, J = 15.5 Hz), 5.67 (1H, d, J = 10.0 Hz), 6.60-6.70 (3H, m), 7.08 (1H, d, J = 8.7 Hz), 7.29-7.32 (2H, m); ^{13}C NMR ($CDCl_3$) δ 169.4, 167.8, 153.4, 151.6, 136.5, 132.5, 127.9, 125.9, 120.9, 110.7, 110.2, 106.0, 49.1, 44.7, 21.2, 14.7; MS (EI) *m/z* 284 $(M)^+$; IR ν_{max} (cm^{-1}) 1692, 1670, 1432; Elemental analysis calcd. for $C_{16}H_{16}N_2O_3$, C 67.59 %; H 5.67 %; N 9.85 %. Found C 67.55 %; H 5.72 %; N 9.83 %. $[\alpha]_D^{20}$ = +493.7 (*c* 1.0, CH_2Cl_2).

12e



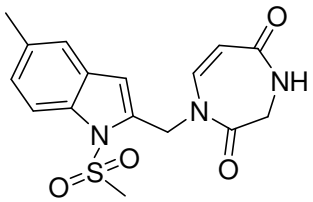
pale solid, mp 140-142 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 0.90-0.97 (6H, m), 1.67-1.91 (3H, m), 3.84-3.89 (1H, m), 4.83 (1H, d, J = 15.5 Hz), 4.94 (1H, d, J = 15.5 Hz), 5.69 (1H, d, J = 9.9 Hz), 6.65-6.69 (2H, m), 7.10 (1H, broad), 7.18-7.29 (2H, m), 7.42 (1H, d, J = 8.2 Hz), 7.52 (1H, d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 169.2, 168.1, 155.0, 151.7, 136.2, 127.9, 124.7, 123.0, 121.2, 111.3, 110.5, 106.1, 51.8, 44.6, 37.3, 24.4, 22.9, 21.8; MS (EI) *m/z* 312 $(M)^{+}$; IR ν_{max} (cm^{-1}) 1689, 1658, 1384; Elemental analysis calcd. for $C_{18}H_{20}N_2O_3$, C 69.21 %; H 6.45 %; N 8.97 %. Found C 69.17 %; H 6.40 %; N 8.99 %. $[\alpha]_D^{20}$ = +356.1 (*c* 1.0, CH_2Cl_2).

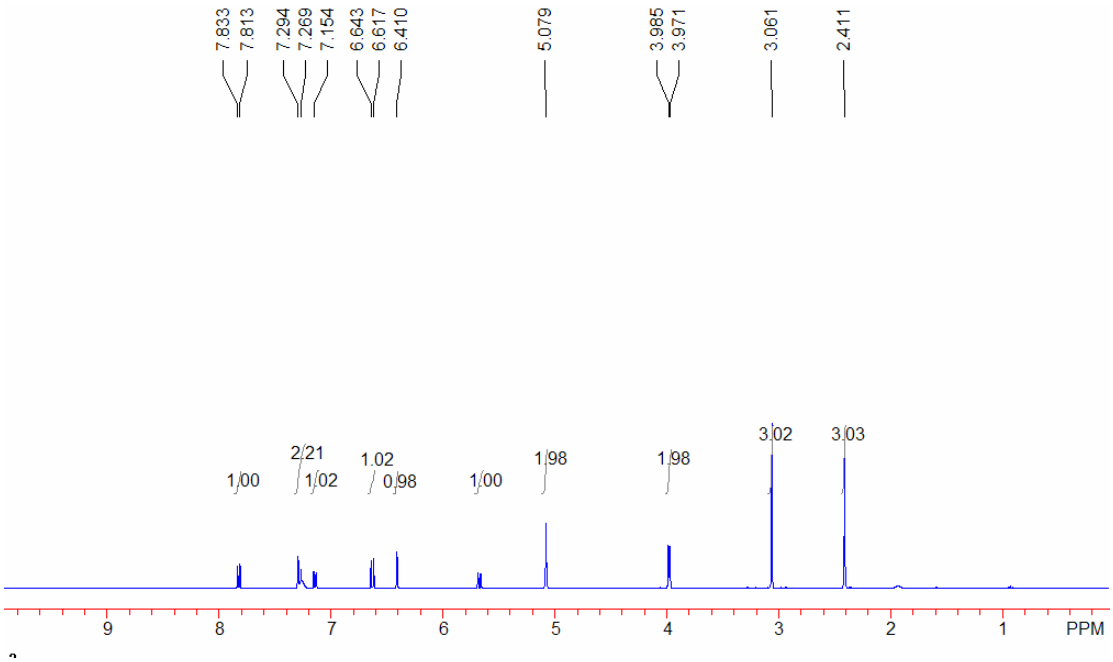
12f

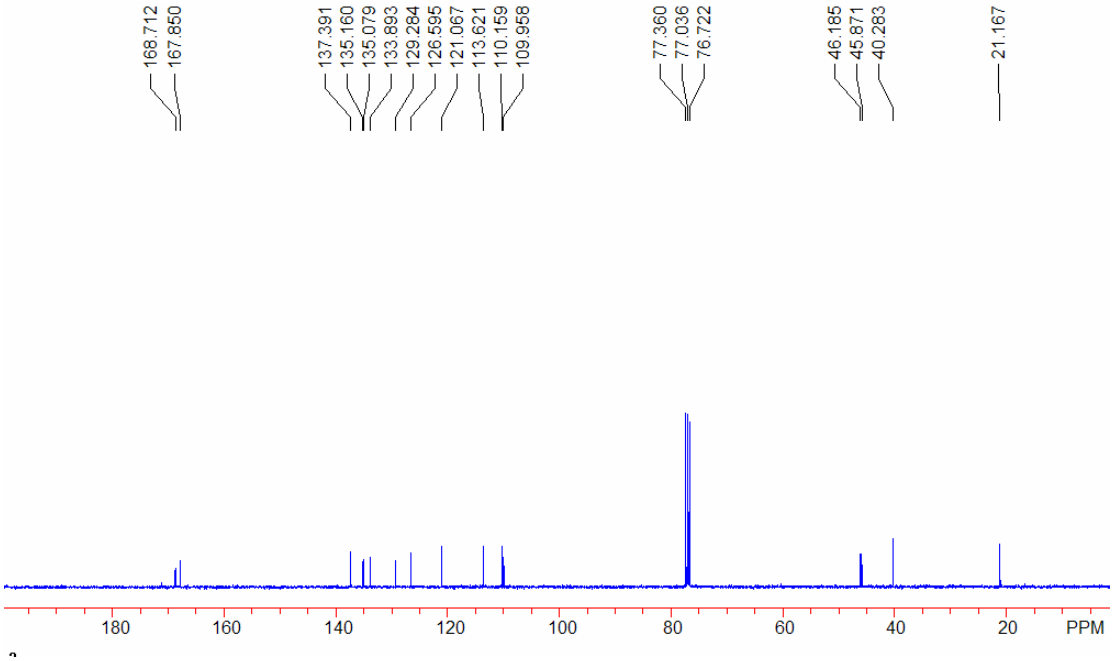


pale solid, mp 138-140 °C; ^{1}H NMR ($CDCl_3$) δ 3.09 (3H, s), 3.95 (2H, d, *J* = 5.4 Hz), 5.09 (2H, s), 5.65 (1H, d, *J* = 10.1 Hz), 6.44 (1H, s), 6.61 (1H, d, *J* = 10.1 Hz), 7.22-7.32 (2H, m), 7.48 (1H, d, *J* = 7.8 Hz), 7.79 (1H, broad), 7.92 (1H, d, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 169.0, 168.0, 137.5, 136.8, 135.2, 129.0, 125.1, 124.1, 121.2, 113.8, 110.1, 109.9, 46.2, 45.8, 40.6; MS (EI) *m/z* 333 $(M)^+$; IR ν_{max} (cm^{-1}) 1699, 1643, 1369; Elemental analysis calcd. for $C_{15}H_{15}N_3O_4S$, C 54.04 %; H 4.54 %; N 12.60 %. Found C 54.01 %; H 4.58 %; N 12.63 %.

12g

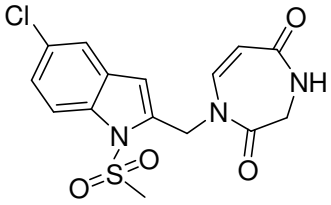


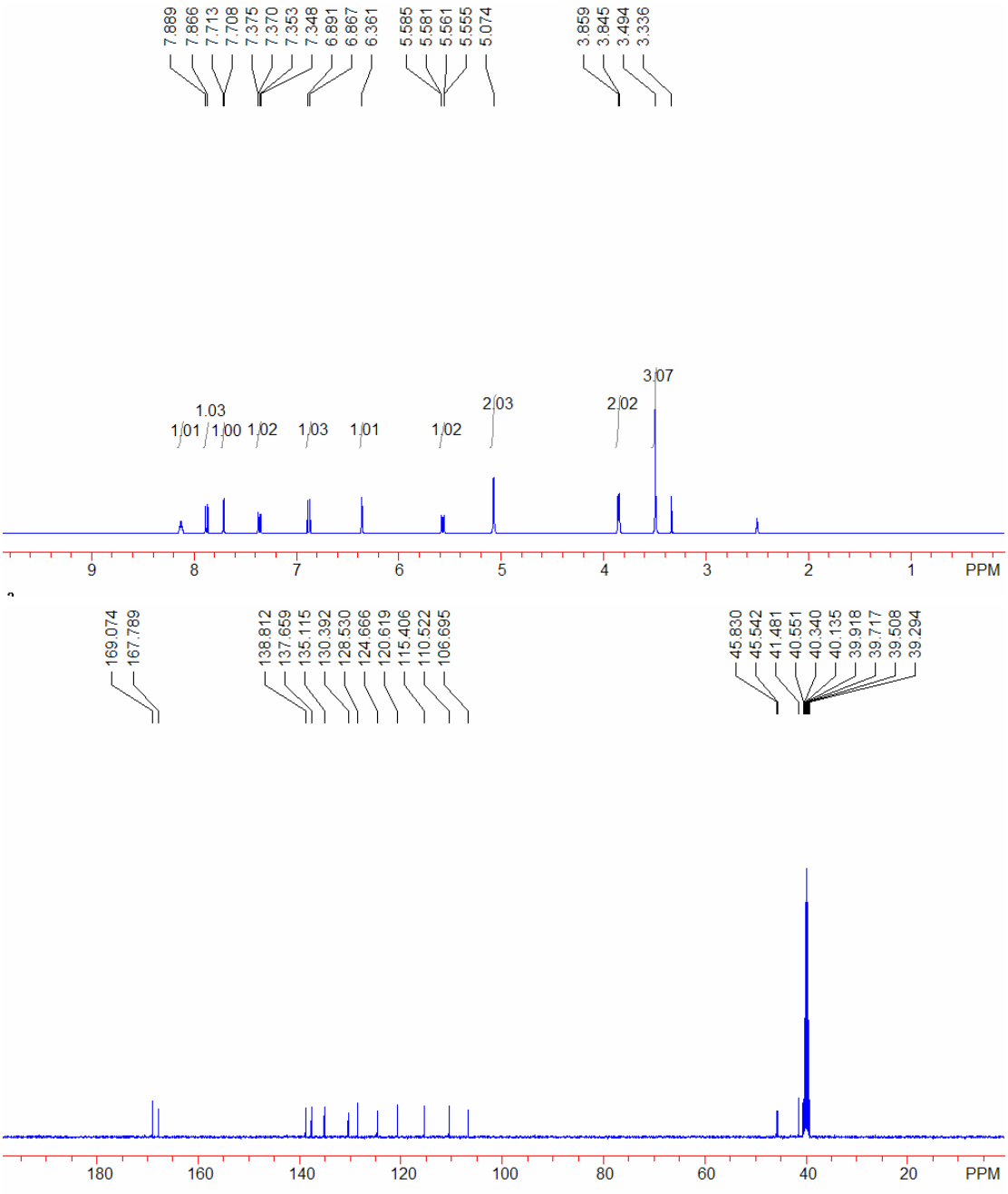




pale solid, mp 135-137 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.41 (3H, s), 3.06 (3H, s), 3.98 (2H, d, *J* = 5.5 Hz), 5.08 (2H, s), 5.67 (1H, d, *J* = 10.1 Hz), 6.41 (1H, s), 6.62 (1H, d, *J* = 10.1 Hz), 7.14 (1H, d, *J* = 8.5 Hz), 7.25-7.30 (2H, m), 7.82 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 168.7, 167.9, 137.4, 135.2, 135.1, 133.9, 129.3, 126.6, 121.1, 113.6, 110.2, 110.0, 46.2, 45.9, 40.3, 21.2; MS (EI) *m/z* 347 $(M)^+$; IR ν_{max} (cm^{-1}) 1700, 1664, 1363; Elemental analysis calcd. for $C_{16}H_{17}N_3O_4S$, C 55.32 %; H 4.93 %; N 12.10 %. Found C 55.35 %; H 4.99 %; N 12.07 %.

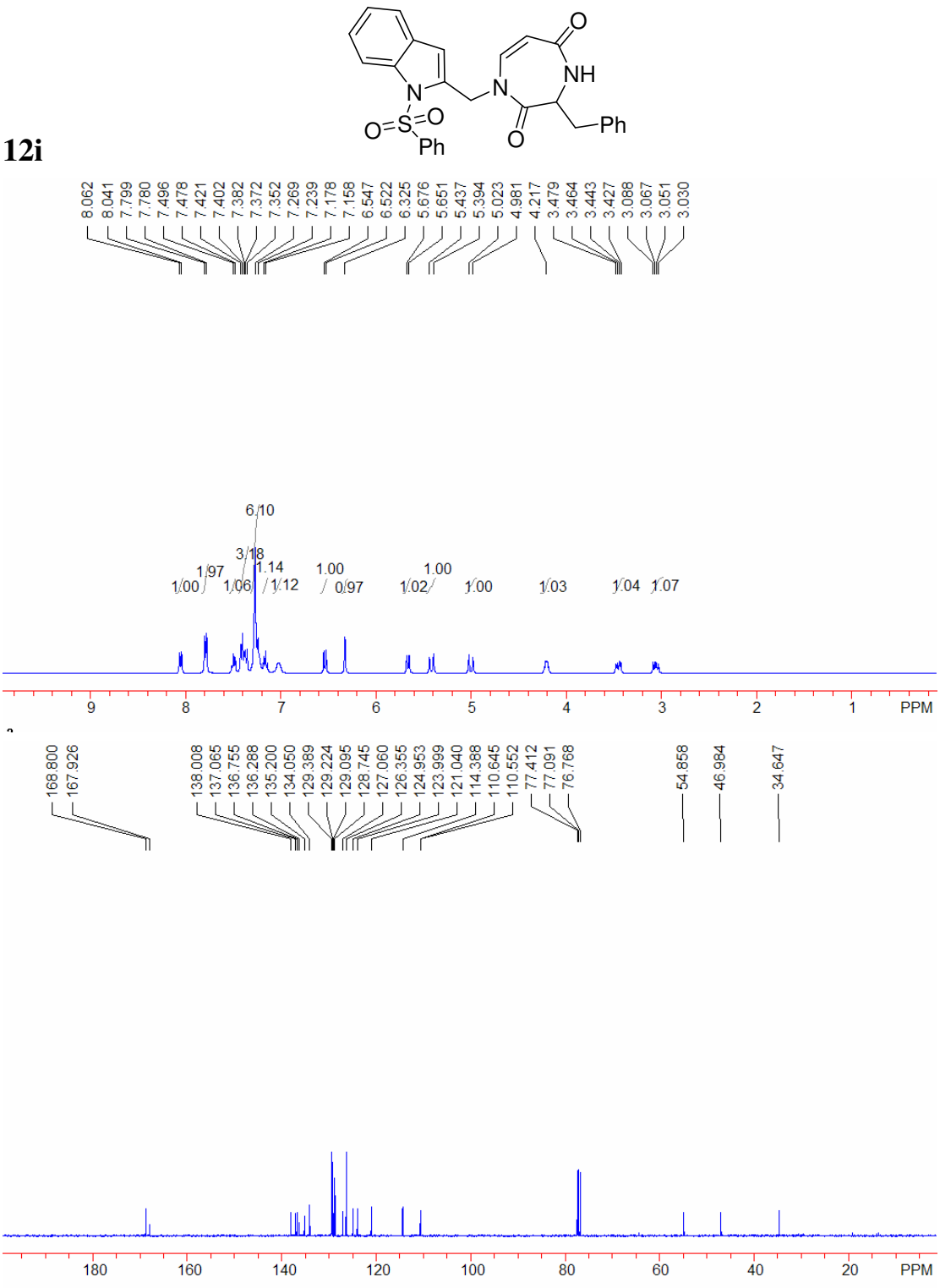
12h





pale solid, mp 160-162 °C; ^{1}H NMR (DMSO-d_6) δ 3.49 (3H, s), 3.85 (2H, d, J = 5.4 Hz), 5.07 (2H, s), 5.57 (1H, d, J = 10.1 Hz), 6.36 (1H, s), 6.88 (1H, d, J = 10.1 Hz), 7.36 (1H, d, J = 8.9 Hz), 7.71 (1H, s), 7.88 (1H, d, J = 9.0 Hz), 8.12 (1H, broad); ^{13}C NMR (DMSO-d_6) δ 169.1, 167.8, 138.8, 137.7, 135.1, 130.4, 128.5, 124.7, 120.6, 115.4, 110.5, 106.7, 55.3, 45.8, 45.5; MS (EI) *m/z* 367 $(M)^+$; IR ν_{max} (cm^{-1}) 1696, 1664, 1363; Elemental analysis calcd. for $C_{15}H_{14}ClN_3O_4S$, C 48.98 %; H 3.84 %; N 11.42 %. Found C 48.95 %; H 3.90 %; N 11.45 %.

12i

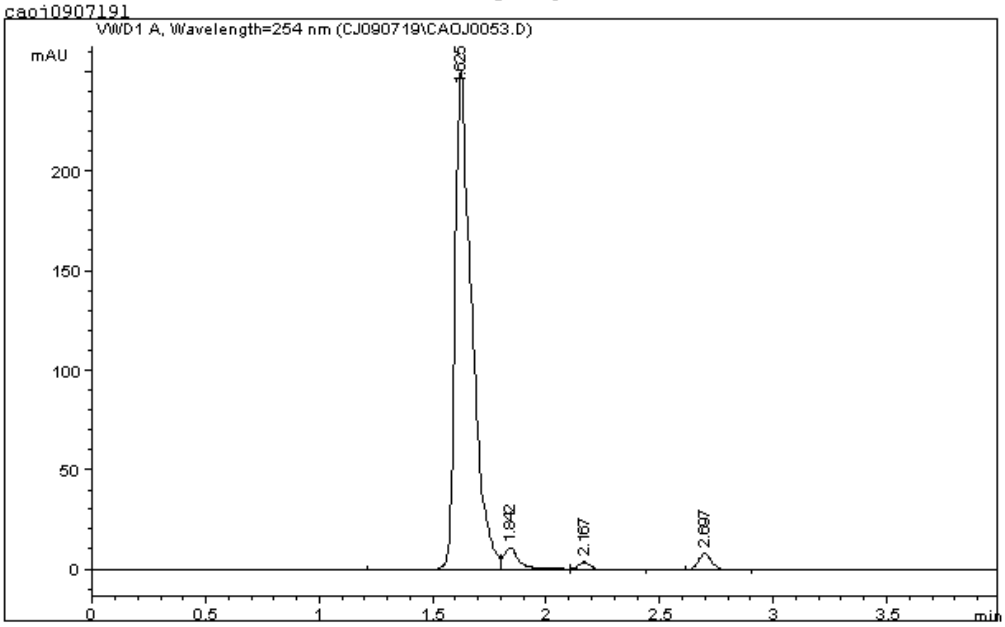


oil; ^{1}H NMR ($CDCl_3$) δ 3.06 (1H, dd, J_1 = 8.4 Hz, J_2 = 14.6 Hz), 3.45 (1H, dd, J_1 = 6.1 Hz, J_2 = 14.6 Hz), 4.20-4.22 (1H, m), 4.99 (1H, d, J = 17.1 Hz), 5.42 (1H, d, J = 17.1 Hz), 5.66 (1H, d, J = 10.0 Hz), 6.33 (1H, s), 6.53 (1H, d, J = 9.9 Hz), 7.02 (1H, broad), 7.14-7.51 (11H, m), 7.79 (2H, d, J = 7.7 Hz), 8.05 (1H, d, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 168.8, 167.9, 138.1, 137.8, 136.8, 136.3, 135.2, 134.1, 129.4, 129.2, 129.1, 128.8, 127.1, 126.4, 125.0, 124.0, 121.0, 114.4, 110.7, 110.6, 54.9, 47.0, 34.7; MS (EI) *m/z* 485 $(M)^+$; IR ν_{max} (cm^{-1}) 1697, 1660, 1449, 1369; HRMS: *m/z* calcd for $C_{27}H_{23}N_3O_4S$: 485.1409; found: 485.1412. $[\alpha]_D^{20}$ = -149.3 (*c* 1.0, CH_2Cl_2).

10d

Data File D:\HPCHEM\1\DATA\CJ090719\CAOJ0053.D

```
=====================================================================
Injection Date  : 2009-7-19 15:34:24 下午
Sample Name     :                                  Location : Vial 1
Acq. Operator   : caoj
Acq. Instrument : Instrument 1
Acq. Method     : D:\HPCHEM\1\METHODS\CJ090719.M
Last changed    : 2009-7-19 10:24:07 下午 by caoj
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\CJ090720.M
Last changed    : 2009-7-19 17:12:19 下午 by caoj
caoj0907191
```

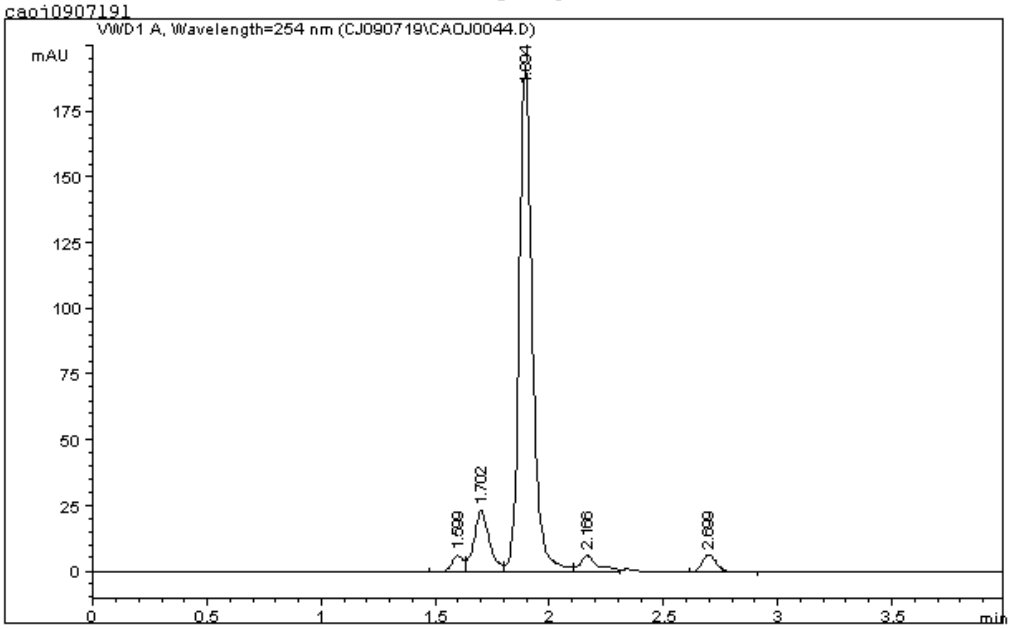



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   1.625 BV    0.0734 1298.65833  251.42966  91.4627
   2   1.842 VV    0.0793   62.43217   11.00124   4.3970
   3   2.167 VB    0.0740   21.76415    4.27432   1.5328
   4   2.697 VB    0.0682   37.02264    8.27569   2.6075

Totals :                  1419.87728  274.98090

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```

10n

Data File D:\HPCHEM\1\DATA\CJ090719\CAOJ0044.D

```
Injection Date  : 2009-7-19 14:45:49 下午
Sample Name     :                                  Location : Vial 1
Acq. Operator   : caoj
Acq. Instrument : Instrument 1
Acq. Method     : D:\HPCHEM\1\METHODS\CJ090719.M
Last changed    : 2009-7-19 10:24:07 下午 by caoj
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\CJ090720.M
Last changed    : 2009-7-19 17:12:19 下午 by caoj
caoj0907191
```

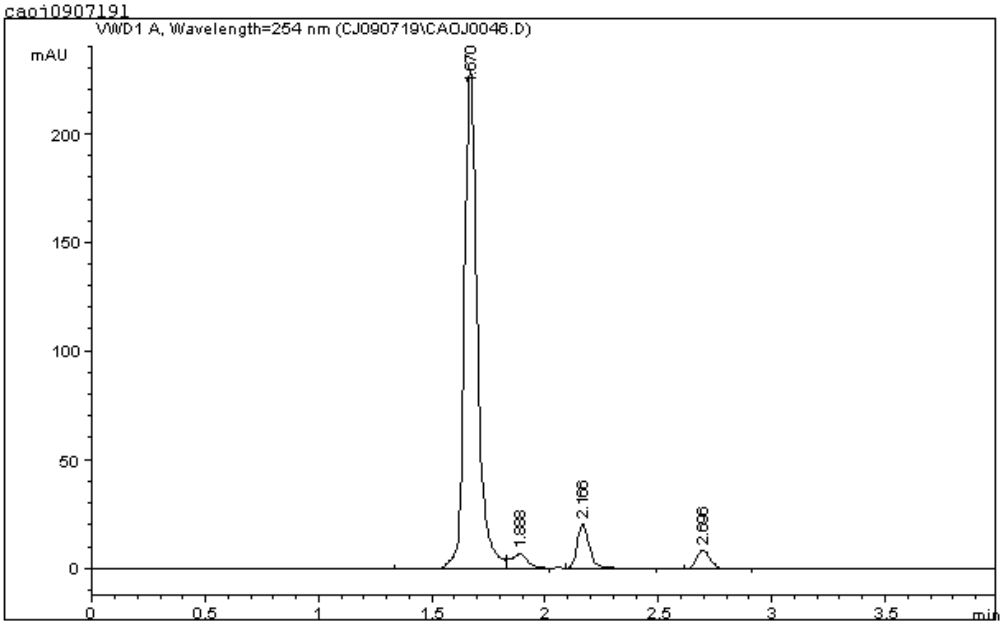



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   1.599 BV    0.0569   24.33481    6.27081   2.4487
   2   1.702 VV    0.0704  113.65505   23.75422  11.4367
   3   1.894 VV    0.0625  787.37238  191.48233  79.2303
   4   2.166 VV    0.0817   37.11187    6.31213   3.7344
   5   2.699 BB    0.0691   31.30235    6.87373   3.1498

Totals :                   993.77646  234.69323

 Results obtained with enhanced integrator!
                          *** End of Report ***
```

12d

Data File D:\HPCHEM\1\DATA\CJ090719\CAOJ0046.D

```
=====================================================================
Injection Date  : 2009-7-19 14:55:22 下午
Sample Name     :                                  Location : Vial 1
Acq. Operator   : caoj
Acq. Instrument : Instrument 1
Acq. Method     : D:\HPCHEM\1\METHODS\CJ090719.M
Last changed    : 2009-7-19 10:24:07 下午 by caoj
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\CJ090720.M
Last changed    : 2009-7-19 17:12:19 下午 by caoj
caoj0907191
```

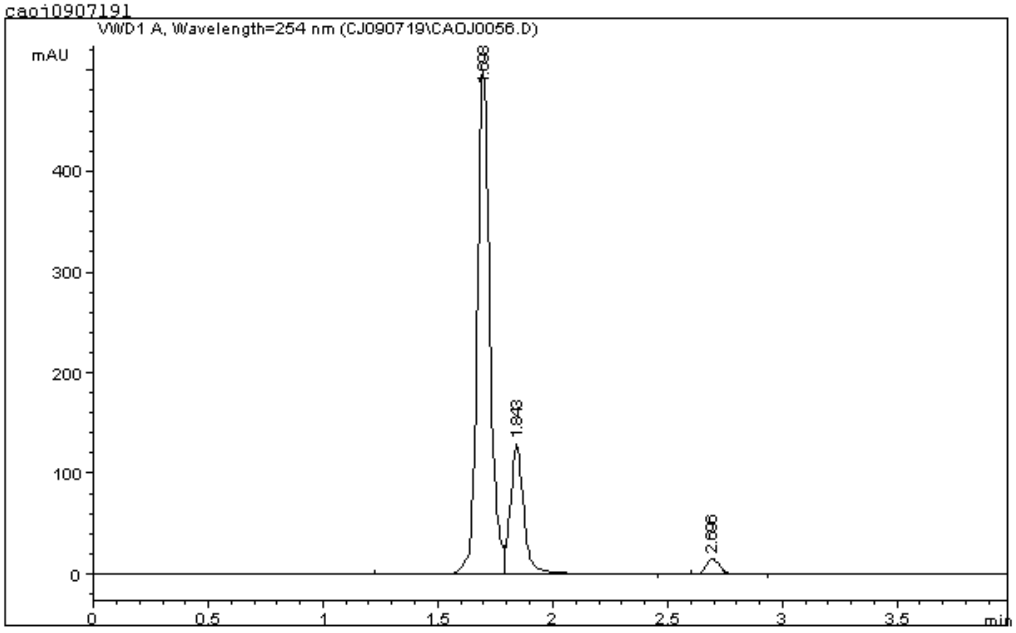



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   1.670 VV    0.0599  922.27057  230.15698  84.5255
   2   1.888 VV    0.0825   41.48692    6.97956   3.8023
   3   2.166 VB    0.0616   87.35103   21.00791   8.0057
   4   2.696 BB    0.0691   40.00616    9.03593   3.6665

Totals :                  1091.11468  267.18038

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```

12i

Data File D:\HPCHEM\1\DATA\CJ090719\CAOJ0056.D

```
================================================================================
Injection Date  : 2009-7-19 15:48:40 下午
Sample Name     :                                   Location : Vial 1
Acq. Operator   : caoj
Acq. Instrument : Instrument 1
Acq. Method     : D:\HPCHEM\1\METHODS\CJ090719.M
Last changed    : 2009-7-19 10:24:07 下午 by caoj
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\CJ090720.M
Last changed    : 2009-7-19 17:12:19 下午 by caoj
caoj0907191
```




```
================================================================================
                            Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1   1.698 BV    0.0584 1943.40161  500.96759  75.9319
   2   1.843 VB    0.0626  546.55157  128.81966  21.3547
   3   2.696 VB    0.0685   69.44610   15.43425   2.7134

Totals :                  2559.39928  645.22149

 Results obtained with enhanced integrator!
================================================================================
                            *** End of Report ***
```