Supporting information

Tandem [4 + 1 + 1] annulation and metal-free aerobic oxidative aromatization: straightforward synthesis of highly substituted phenols from one aldehyde and two ketones

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I. General

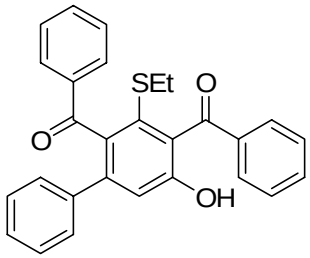
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel (300–400 mesh). All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F_{254}). Melting points were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were determined at ambient temperature on a Varian 500 MHz and 125 MHz, respectively, using TMS as internal standard. All shifts were given in ppm. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer in the range of 400-4000 cm^{-1}. Mass spectra were measured on an Agilient 1100 LCMsD spectrometer. Elemental analyses were obtained on a VarioEL analyzer. Starting materials **1** are known compounds and prepared according to the literatures.[1]

II. Synthesis of phenols 5 from ketene dithioacetals 1, aldehydes 2 and methyl ketones 3

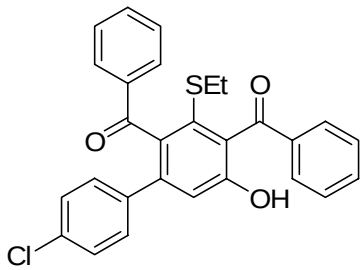
Typical procedure for one-pot synthesis of phenols 5 (5a as example): To a well-stirred mixture of benzaldehyde **2a** (0.11 mL, 1.1 mmol) with acetophenone **3a** (0.128 mL, 1.1 mmol) was added *t*-BuOK (56 mg, 0.5 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 0.5 h, a mixture of 2-(bis(ethylthio)methylene)-1-phenylbutane-1,3-dione **1a** (294 mg, 1.0 mmol) and *t*-BuOK (392 mg, 3.5 equiv) in dry DMF (10 mL) was added and the resulting reaction mixture was stirred at room temperature for additional 2.5 h. After completion of the reaction as indicated by TLC, the reaction was quenched by saturated sodium chloride aqueous (20 mL), neutralized with dilute HCl aq., and extracted with dichloromethane (3 × 20 mL). The combined organic phase was

washed with water (3 × 20 mL), dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether : diethyl ether = 3:1) to give (3-(ethylthio)-5-hydroxybiphenyl-2,4-diyl) bis(phenylmethanone) **5a** (293 mg, 67%) as a yellow oil.

III. Analytical data of phenols 5

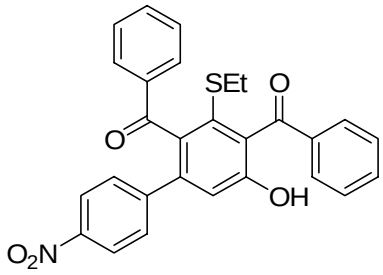


(3-(Ethylthio)-5-hydroxybiphenyl-2,4-diyl)bis(phenylmethanone) (5a): Yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.75 (t, J = 7.5 Hz, 3H), 2.44–2.49 (m, 2H), 7.06 (s, 1H), 7.16–7.18 (m, 3H), 7.24–7.26 (m, 2H), 7.28–7.32 (m, 2H), 7.41–7.45 (m, 3H), 7.56–7.59 (m, 1H), 7.61–7.63 (m, 2H), 7.83–7.85 (m, 2H), 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.9, 196.8, 156.2, 144.4, 138.5, 138.2, 137.9, 137.3, 133.4, 133.1, 132.4, 129.5 (2C), 129.3 (2C), 128.9 (3C), 128.5 (2C), 128.3 (2C), 128.2 (2C), 127.9, 118.5, 33.1, 13.9; IR (KBr) ν = 3294, 3060, 2971, 2870, 1666, 1586, 1397, 1230, 1176; ES–MS: calcd *m/z* 438.1, found 439.1 $[(M + 1)]^+$; Anal. Calcd for $C_{28}H_{22}O_3S$: C, 76.69; H, 5.06. Found: C, 76.60; H, 5.10.

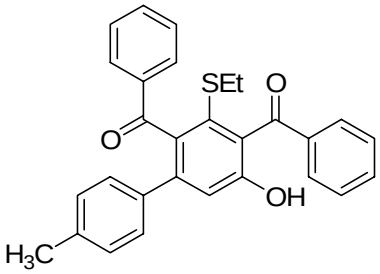


(4'-Chloro-3-(ethylthio)-5-hydroxybiphenyl-2,4-diyl)bis(phenylmethanone)

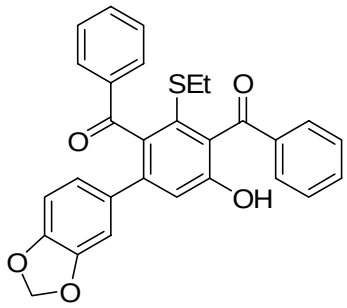
(5b): yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.77 (t, J = 7.5 Hz, 3H), 2.43–2.49 (m, 2H), 7.11 (s, 1H), 7.26–7.32 (m, 6H), 7.42–7.49 (m, 3H), 7.58–7.63 (m, 3H), 7.84 (d, J = 7.5 Hz, 2H), 7.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.8, 196.6, 156.1, 142.9, 138.1, 137.8, 137.2, 136.9, 134.2, 133.6, 133.4, 132.5, 130.3 (2C), 129.5 (2C), 129.3 (2C), 128.7 (2C), 128.5 (2C), 128.4 (3C), 118.4, 33.1, 14.0; IR (KBr) ν = 3377, 2967, 2869, 1665, 1585, 1448, 1314, 1229; ES–MS: calcd *m/z* 472.1, found 473.1 $[(M + 1)]^+$; Anal. Calcd for $C_{28}H_{21}ClO_3S$: C, 71.10; H, 4.48. Found: C, 71.19; H, 4.39.



(3-(Ethylthio)-5-hydroxy-4'-nitrobiphenyl-2,4-diyl)bis(phenylmethanone) (5c): yellow solid. Mp 218–220 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.75 (t, J = 7.5 Hz, 3H), 2.41 (q, J = 7.5 Hz 2H), 7.15–7.18 (m, 1H), 7.33 (s, 1H), 7.37–7.41 (m, 6H), 7.51–7.54 (m, 2H), 7.73–7.76 (m, 3H), 8.06–8.07 (m, 2H), 10.55 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 198.1, 195.8, 154.9, 154.1, 145.4, 138.0, 137.9, 137.2, 135.2, 133.8, 133.6, 132.8, 131.9, 129.9 (2C), 129.7, 129.4 (2C), 128.6 (2C), 128.5 (2C), 126.9, 125.2, 121.3, 120.4, 32.8, 14.1; IR (KBr) ν = 3459, 3250, 2960, 2862, 1670, 1584, 1442, 1219; ES–MS: calcd *m/z* 483.1, found 484.1 $[(M + 1)]^+$; Anal. Calcd for $C_{28}H_{21}NO_5S$: C, 69.55; H, 4.38; N, 2.90. Found: C, 69.46; H, 4.30; N, 2.79.

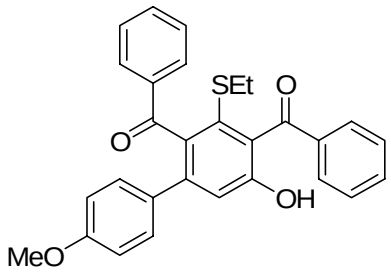


(3-(Ethylthio)-5-hydroxy-4'-methylbiphenyl-2,4-diyl)bis(phenylmethanone) (5d): yellow solid. Mp 95–97 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.75 (t, J = 7.5 Hz, 3H), 2.26 (s, 3H), 2.41–2.48 (m, 2H), 7.02 (d, J = 7.5 Hz, 2H), 7.09 (s, 1H), 7.18 (d, J = 7.5 Hz, 2H), 7.29–7.38 (m, 2H), 7.43–7.46 (m, 3H), 7.58 (t, J = 7.5 Hz, 1H), 7.64 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 7.5 Hz, 2H) 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 198.1, 196.7, 156.3, 144.6, 138.4, 138.0, 137.9, 137.4, 135.6, 133.4, 133.0, 132.5, 129.4 (2C), 129.3 (2C), 128.9 (2C), 128.8 (2C), 128.5 (2C), 128.3 (2C), 127.7, 118.5, 33.1, 21.1, 14.0; IR (KBr) ν = 3266, 3058, 2963, 2866, 1666, 1584, 1447, 1227; ES–MS: calcd *m/z* 452.1, found 453.2 $[(M + 1)]^+$; Anal. Calcd for $C_{29}H_{24}O_3S$: C, 76.96; H, 5.35. Found: C, 76.85; H, 5.46.



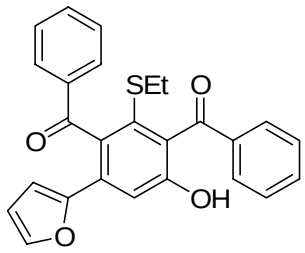
(4-(Benzo[*d*][1,3]dioxol-5-yl)-2-(ethylthio)-6-hydroxy-1,3-phenylene)bis(phenyl methanone) (5e): yellow solid. Mp 61–63 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.76 (t, J = 7.5 Hz, 3H), 2.44 (s, 2H), 5.90 (s, 2H), 6.65 (d, J = 8.0 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 7.06 (s, 1H), 7.20–7.26 (m, 2H), 7.31–7.34 (m, 2H), 7.37–7.47 (m, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.8, 196.8, 156.0, 147.4, 143.7, 138.1,

137.8, 137.1, 133.4, 133.1, 132.3, 129.4 (2C), 129.3 (2C), 128.4 (2C), 128.3 (2C), 128.0, 127.2, 125.3, 123.0, 118.3, 109.3, 108.0, 101.1, 33.0, 13.9; IR (KBr) ν = 3386, 3061, 2965, 2779, 1664, 1585, 1495, 1240; ES–MS: calcd *m/z* 482.1, found 483.1 [(M + 1)]$^+$; Anal. Calcd for $C_{29}H_{22}O_5S$: C, 72.18; H, 4.60. Found: C, 72.27; H, 4.49.



(3-(Ethylthio)-5-hydroxy-4'-methoxybiphenyl-2,4-diyl)bis(phenylmethanone)

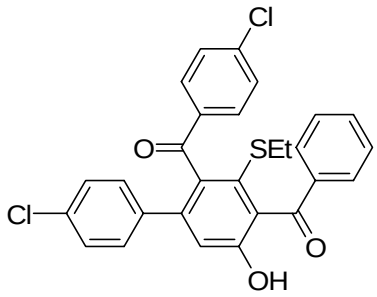
(5f): Yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.75 (t, J = 7.5 Hz, 3H), 2.41–2.47 (m, 2H), 3.74 (s, 3H), 6.76(d, J = 9.0 Hz, 2H), 7.08 (s, 1H), 7.24 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H), 7.43–7.49 (m, 3H), 7.58 -7.63 (m, 3H), 7.83 (d, J = 7.0 Hz, 2H), 8.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 198.2, 196.9, 159.4, 156.4, 144.2, 138.4, 137.9, 137.3, 133.4, 133.1, 132.6, 130.9 (2C), 130.2 (2C), 129.5 (2C), 129.3 (2C), 128.5 (2C), 128.3 (2C), 127.4, 118.4, 113.7, 55.1, 33.1, 14.0; IR (KBr) ν = 3383, 3060, 2963, 1664, 1583, 1514, 1393, 1297, 1249; ES–MS: calcd *m/z* 468.1, found 469.1 [(M + 1)]$^+$; Anal. Calcd for $C_{29}H_{24}O_4S$: C, 74.34; H, 5.16. Found: C, 74.45; H, 5.07.



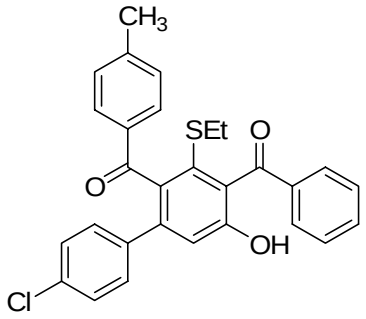
(2-(Ethylthio)-4-(furan-2-yl)-6-hydroxy-1,3-phenylene)bis(phenylmethanone)

(5g): yellow solid. Mp 99–101 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.74 (t, J = 7.5 Hz, 3H), 2.36–2.47 (m, 2H), 6.27–6.28 (m, 1H), 6.47 (d, J = 3.5 Hz, 1H), 7.34 (s, 1H),

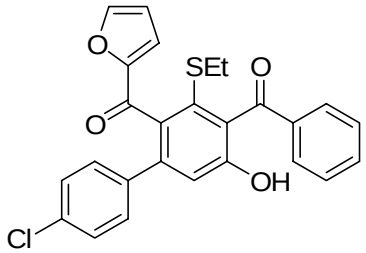
7.39–7.46 (m, 4H), 7.49 (s,1H), 7.52–7.58 (m, 2H), 7.77–7.80 (m, 4H), 8.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.8, 196.8, 156.5, 149.6, 143.3, 138.3, 137.6, 134.2, 133.3, 132.8, 132.0, 129.4 (2C), 129.2 (2C), 128.5 (2C), 128.4 (2C), 128.3, 128.0, 114.2, 112.0, 110.9, 33.1, 13.9; IR (KBr) ν = 3253, 3061, 2959, 2866, 1665, 1587,1448, 1312, 1231; ES–MS: calcd *m/z* 428.1, found 429.1 $[(M + 1)]^+$; Anal. Calcd for $C_{26}H_{20}O_4S$: C, 72.88; H, 4.70. Found: C, 72.80; H, 4.79.



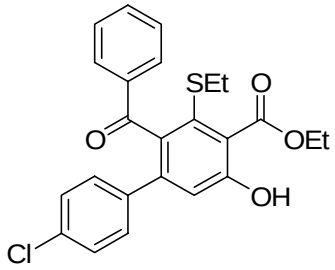
(4-Benzoyl-4'-chloro-3-(ethylthio)-5-hydroxybiphenyl-2-yl)(4-chlorophenyl)methanone (5h): yellow solid. Mp 96–98 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.78 (t, *J* = 7.5 Hz, 3H), 2.45 (s, 2H), 7.06 (s, 1H), 7.22 (s, 4H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.45–7.49 (m, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.7, 195.4, 156.0, 142.7, 139.8, 137.8, 136.7, 136.6, 136.0, 134.4, 133.7, 132.2, 130.5 (2C), 130.2 (2C), 129.4 (2C) , 128.9, 128.8 (2C), 128.6 (2C), 128.5 (2C), 118.4, 33.1, 14.0; IR (KBr) ν = 3303, 2928, 2870, 1666, 1585, 1229, 1092; ES–MS: calcd *m/z* 506.1, found 507.1 $[(M + 1)]^+$; Anal. Calcd for $C_{28}H_{20}Cl_2O_3S$: C, 66.28; H, 3.97. Found: C, 66.19; H, 4.08.



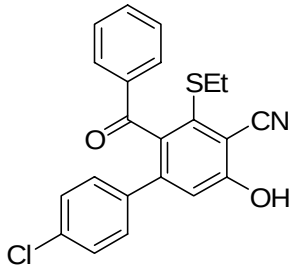
(4-Benzoyl-4'-chloro-3-(ethylthio)-5-hydroxybiphenyl-2-yl)(*p*-tolyl)methanone (5i): yellow solid. Mp 93–95 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.75 (t, J = 7.5 Hz, 3H), 2.32 (s, 3H), 2.42–2.52 (m, 2H), 7.00 (s, 1H), 7.10–7.18 (m, 6H), 7.24–7.26 (m, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.0 Hz, 1H), 7.83 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.0, 196.9, 155.0, 144.5, 141.8, 137.4, 137.0, 136.7, 135.2, 133.8, 133.6, 131.0, 130.5, 130.1 (2C), 129.5 (2C), 129.4 (2C), 129.1 (2C), 128.5 (2C), 128.2 (2C), 118.1, 33.0, 21.6, 13.8; IR (KBr) ν = 3388, 3059, 2964, 1662, 1578, 1445, 1312, 1228; ES–MS: calcd *m/z* 486.1, found 487.1 $[(M + 1)]^{+}$; Anal. Calcd for $C_{29}H_{23}ClO_3S$: C, 71.52; H, 4.76. Found: C, 71.63; H, 4.82.



(4-Benzoyl-4'-chloro-3-(ethylthio)-5-hydroxybiphenyl-2-yl)(furan-2-yl)methanone (5j): yellow solid. Mp 97–99 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.85 (t, J = 7.5 Hz, 3H), 2.48–2.55 (m, 2H), 6.38 (d, J = 3.0 Hz, 1H), 6.79 (s, 1H), 7.06 (s, 1H), 7.26–7.32 (m, 4H), 7.45–7.48 (m, 3H), 7.60 (t, J = 7.5 Hz, 1H), 7.83 (d, J = 7.5 Hz, 2H), 7.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.9, 183.7, 156.5, 153.4, 146.8, 144.6, 138.3, 138.2, 136.3, 133.3, 133.1, 129.3, 128.7 (2C), 128.5, 128.4 (2C), 128.2 (2C), 128.0, 127.7, 119.3, 118.4, 112.2, 33.0, 14.0; IR (KBr) ν = 3312, 3061, 2864, 1662, 1584, 1453, 1314, 1227; ES–MS: calcd *m/z* 462.1, found 463.1 $[(M + 1)]^{+}$; Anal. Calcd for $C_{26}H_{19}ClO_4S$: C, 67.45; H, 4.14. Found: C, 67.54; H, 4.06.

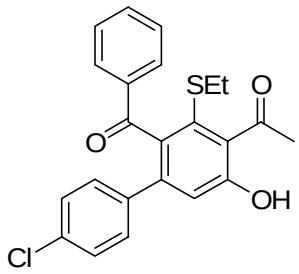


Ethyl 2-benzoyl-4'-chloro-3-(ethylthio)-5-hydroxybiphenyl-4-carboxylate (5k): yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.02 (t, J = 7.5 Hz, 3H), 1.15 (t, J = 7.0 Hz, 3H), 2.75 (s, 2H), 4.50 (q, J = 7.0 Hz, 2H), 7.01 (s, 1H), 7.16 (s, 4H), 7.31 (t, J = 7.0 Hz, 2H), 7.44 (t, J = 7.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 10.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ =195.5, 169.7, 160.7, 144.2, 138.4, 138.0, 136.6, 134.3, 133.7, 133.0, 130.2 (2C), 129.1 (2C), 128.4 (2C), 128.3 (2C), 119.5, 117.5, 62.4, 33.1, 14.0, 13.9; IR (KBr) ν = 3385, 3060, 2964, 2865, 1664, 1589, 1446, 1241; ES–MS: calcd *m/z* 440.1, found 441.1 $[(M + 1)]^+$; Anal. Calcd for $C_{24}H_{21}ClO_4S$: C, 65.37; H, 4.80. Found: C, 65.28; H, 4.89.

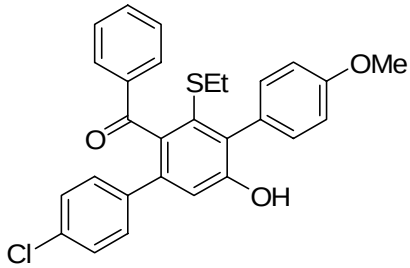


2-Benzoyl-4'-chloro-3-(ethylthio)-5-hydroxybiphenyl-4-carbonitrile (5l): yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.14 (t, J = 7.5 Hz, 3H), 2.91 (s, 2H), 7.00 (s, 1H), 7.13–7.19 (m, 4H), 7.34–7.39 (m, 3H), 7.47–7.52 (m, 1H), 7.59 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 195.3, 159.4, 145.1, 137.9, 137.3, 136.8, 136.2, 134.8, 133.7, 130.0 (2C), 129.5 (2C), 129.3 (2C), 128.6 (2C), 117.9, 114.6, 106.1, 32.0, 14.5; IR (KBr) ν = 3422, 2958, 2859, 1653, 1578, 1489, 1393, 1260; ES–MS: calcd *m/z* 393.1, found 394.1 $[(M + 1)]^+$; Anal. Calcd for

$C_{22}H_{16}ClNO_2S$: C, 67.08; H, 4.09; N, 3.56. Found: C, 67.20; H, 4.00; N, 3.61.

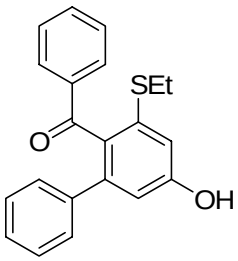


1-(2-Benzoyl-4'-chloro-3-(ethylthio)-5-hydroxybiphenyl-4-yl)ethanone (5m): Yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.99 (t, J = 7.5 Hz, 3H), 2.64–2.66 (m, 2H), 2.95 (s, 3H), 7.02 (s, 1H), 7.16–7.19 (m, 4H), 7.33 (t, J = 7.5 Hz, 2H), 7.44–7.49 (m, 2H), 7.61 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 206.5, 195.9, 160.0, 144.5, 137.7, 136.6, 134.5, 133.7, 133.3, 130.2 (2C), 129.1 (2C), 129.0 (2C), 128.5 (3C), 125.3, 119.7, 33.9, 32.7, 14.2; IR (KBr) ν = 3251, 3064, 2970, 2870, 1669, 1581, 1494, 1316, 1216; ES–MS: calcd *m/z* 410.1, found 411.1 $[(M + 1)]^+$; Anal. Calcd for $C_{23}H_{19}ClO_3S$: C, 67.23; H, 4.66. Found: C, 67.40; H, 4.55.

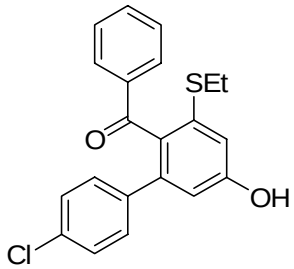


4-Methoxyl-2'-ethylthio-3'-benzoyl-6'-hydroxy-4''-chloro p-terphenyl (5n): yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.74 (t, J = 7.5 Hz, 3H), 2.20 (m, 2H), 3.87 (s, 3H), 5.31 (s, 1H), 7.01 (s, 1H), 7.06 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.30–7.33 (m, 2H) , 7.34–7.38 (m, 2H) , 7.39–7.46 (m, 1H) , 7.67 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 196.8, 159.6, 153.7, 139.7, 138.2, 137.6, 137.0, 133.6, 132.9, 132.0, 131.8, 131.7 (2C), 130.3 (2C), 129.3 (2C), 128.3 (2C), 128.2 (2C), 125.4, 117.0, 114.6 (2C), 55.2, 30.4, 14.0; IR (KBr) ν =

3415, 3060, 2835, 1651, 1591, 1444, 1245, 1173; ES–MS: calcd *m/z* 474.1, found 475.2 $[(M + 1)]^+$; Anal. Calcd for $C_{28}H_{23}ClO_3S$: C, 70.80; H, 4.88. Found: C, 70.91; H, 4.80.



(3-(Ethylthio)-5-hydroxybiphenyl-2-yl)(phenyl)methanone (5o): yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.56 (t, J = 7.5 Hz, 3H), 2.80 (q, J = 7.5 Hz, 2H), 6.72 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 2.0 Hz, 1H), 7.09–7.17 (m, 5H), 7.23–7.26 (m, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 199.5, 156.6, 142.6, 139.4, 137.8, 136.5, 133.1, 129.5 (2C), 128.9 (2C), 128.2 (2C), 128.0 (2C), 127.5 (2C), 115.2, 114.9, 28.5, 13.9; IR (KBr) ν = 3395，3055，2978，1627，1589，1267，1218，1068; ES–MS: calcd *m/z* 334.1, found 335.1 $[(M + 1)]^+$; Anal. Calcd for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.43. Found: C, 75.32; H, 5.40.



(4'-Chloro-3-(ethylthio)-5-hydroxybiphenyl-2-yl)(phenyl)methanone (5p): yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.22 (t, J = 7.5 Hz, 3H), 2.86 (q, J = 7.5 Hz, 2H), 5.99 (s, 1H), 6.69 (s, 1H), 6.98 (s, 1H), 7.14 (s, 4H), 7.14–7.33 (m, 2H), 7.45–7.48 (m, 1H), 7.62–7.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 198.1, 156.3, 141.3, 137.8, 137.7, 136.7, 133.7, 133.3, 132.6, 130.2 (2C), 129.5 (2C), 128.3

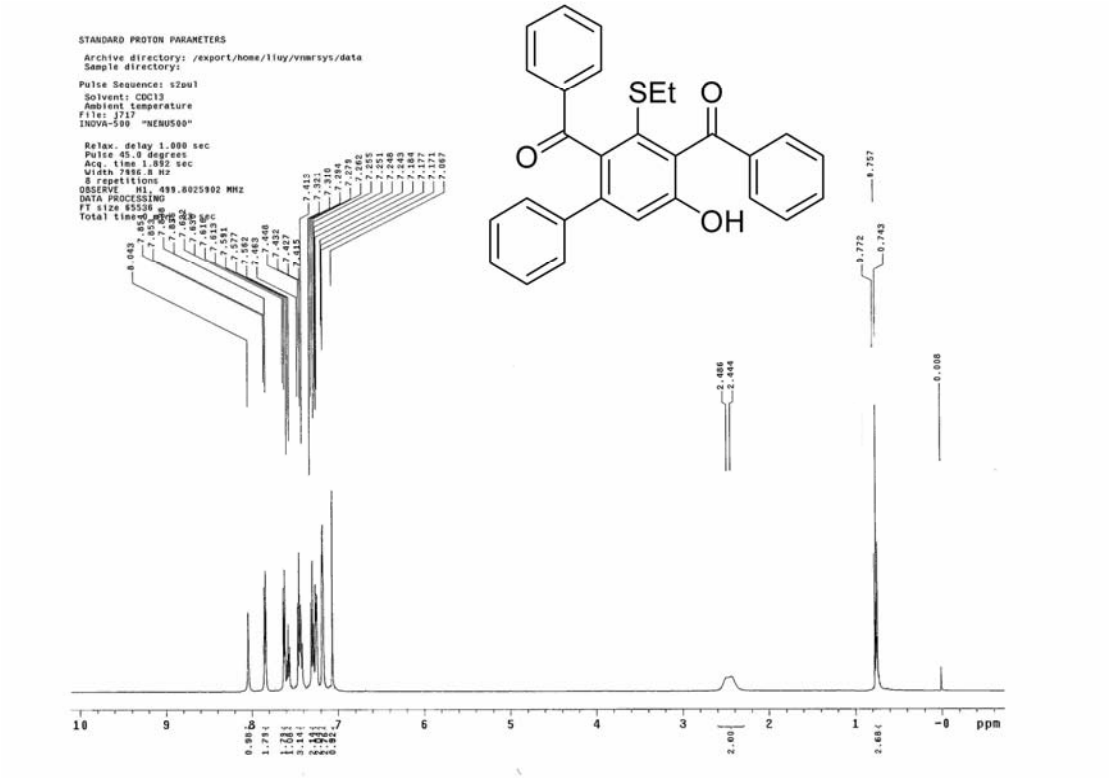
(2C), 128.2 (2C), 115.6, 114.8, 28.7, 13.9; IR (KBr) ν = 3386, 3060, 2869, 1645, 1588, 1309, 1169; ES–MS: calcd *m/z* 368.1, found 369.1 $[(M + 1)]^+$; Anal. Calcd for $C_{21}H_{17}ClO_2S$: C, 68.38; H, 4.65. Found: C, 68.26; H, 4.72.

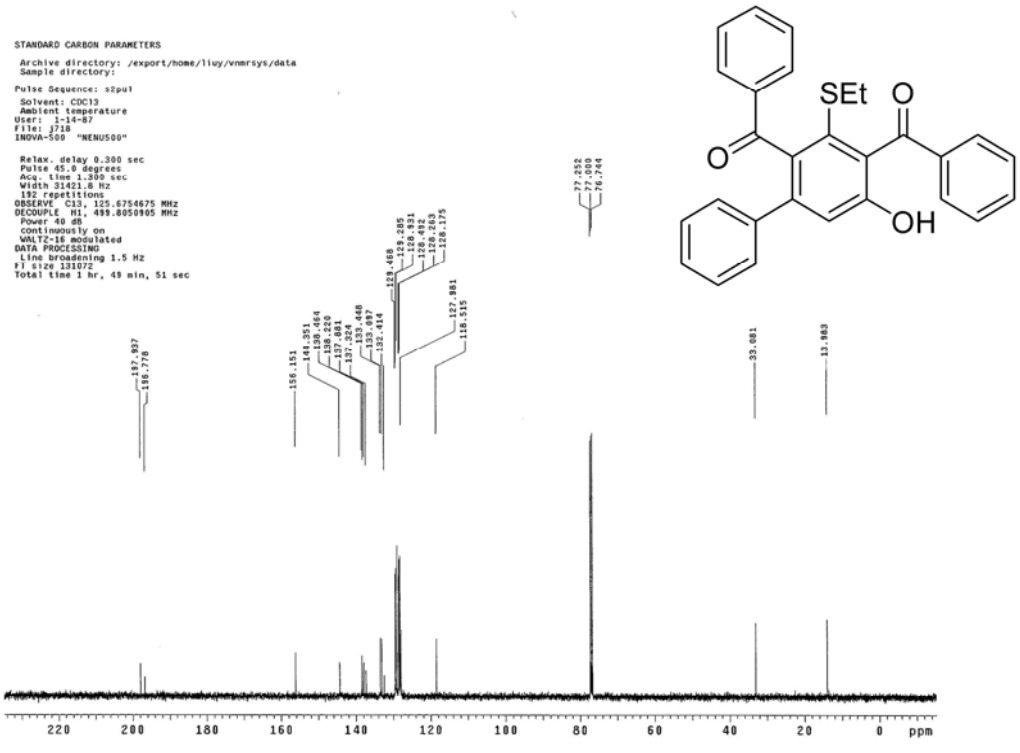
IV. References

1 (*a*) H. Yu, D. Dong, Y. Ouyang, Q. Liu, Y. Wang, *Lett. Org. Chem.,* 2005, **2**, 755–759; (*b*) Z. Fu, M. Wang, Y. Ma, Q. Liu, J. Liu, *J. Org. Chem.,* 2008, **73**, 7625−7630; (*c*) Z. Fu, M. Wang, Y. Dong, J. Liu, Q. Liu, *J. Org. Chem.,* 2009, **74**, 6105–6110.

V. Copies of NMR spectra for new compounds 5

5a





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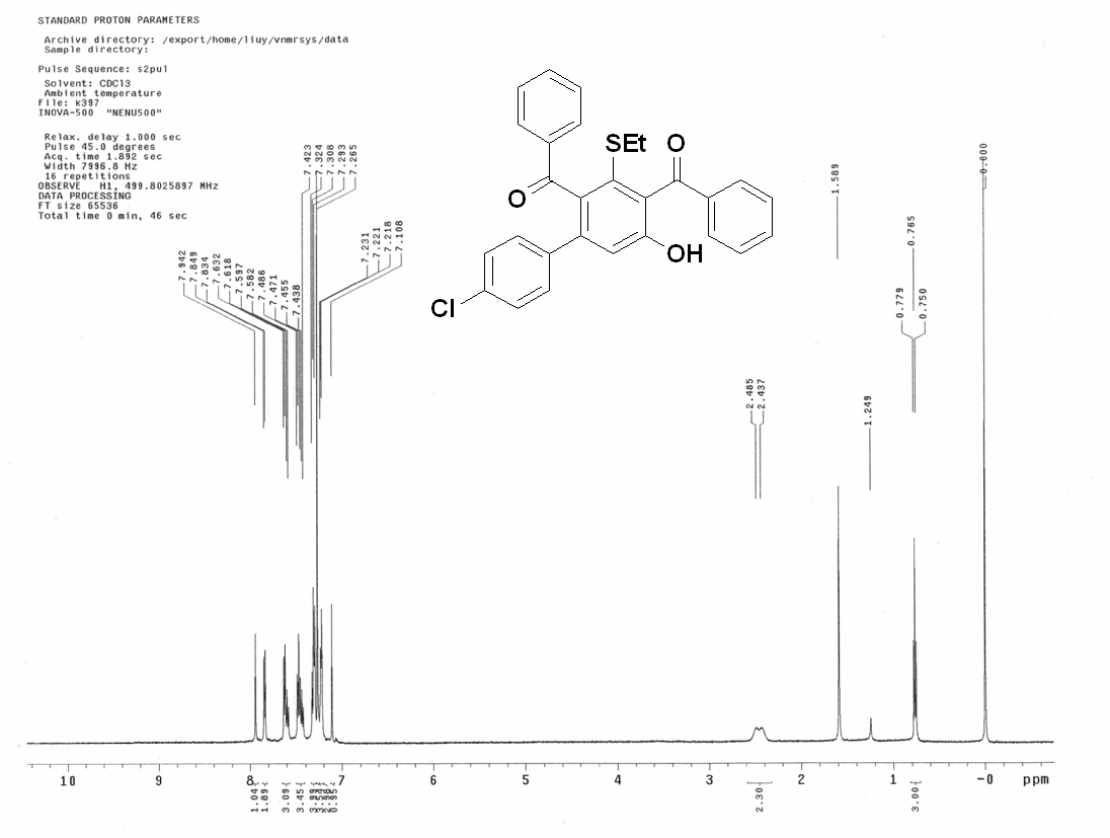
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Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.882 sec
Width 7986.8 Hz
16 repetitions
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DATA PROCESSING
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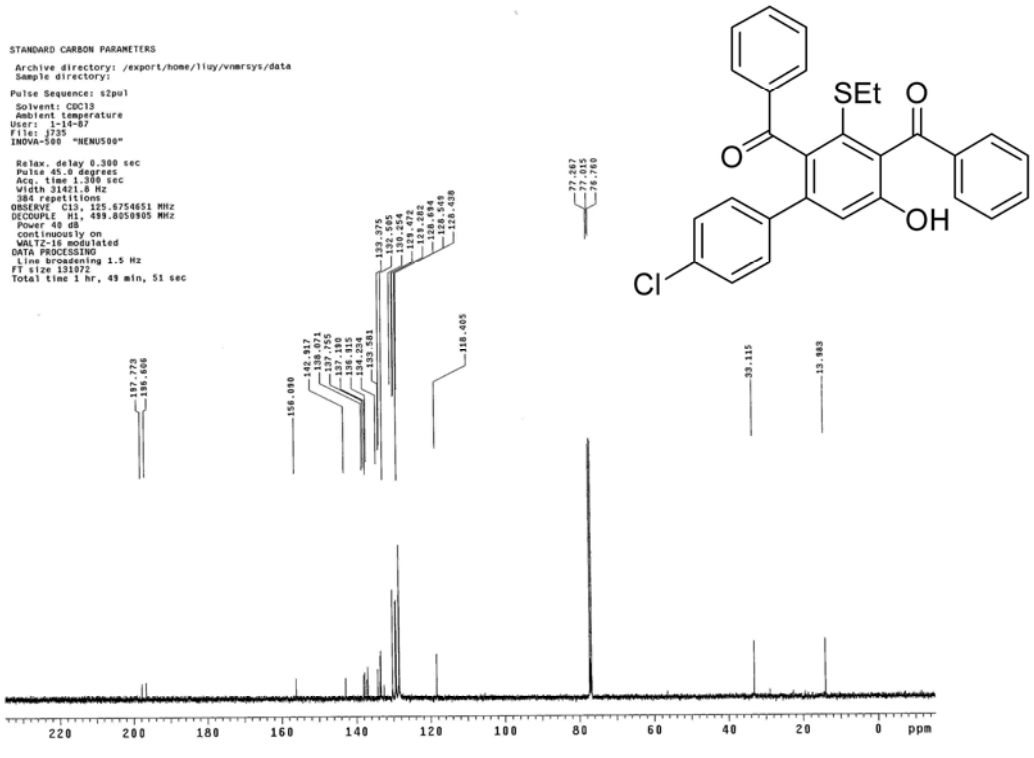
Total time 0 min, 46 sec
SEt
O
O
OH
Cl
ppm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Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
384 repetitions
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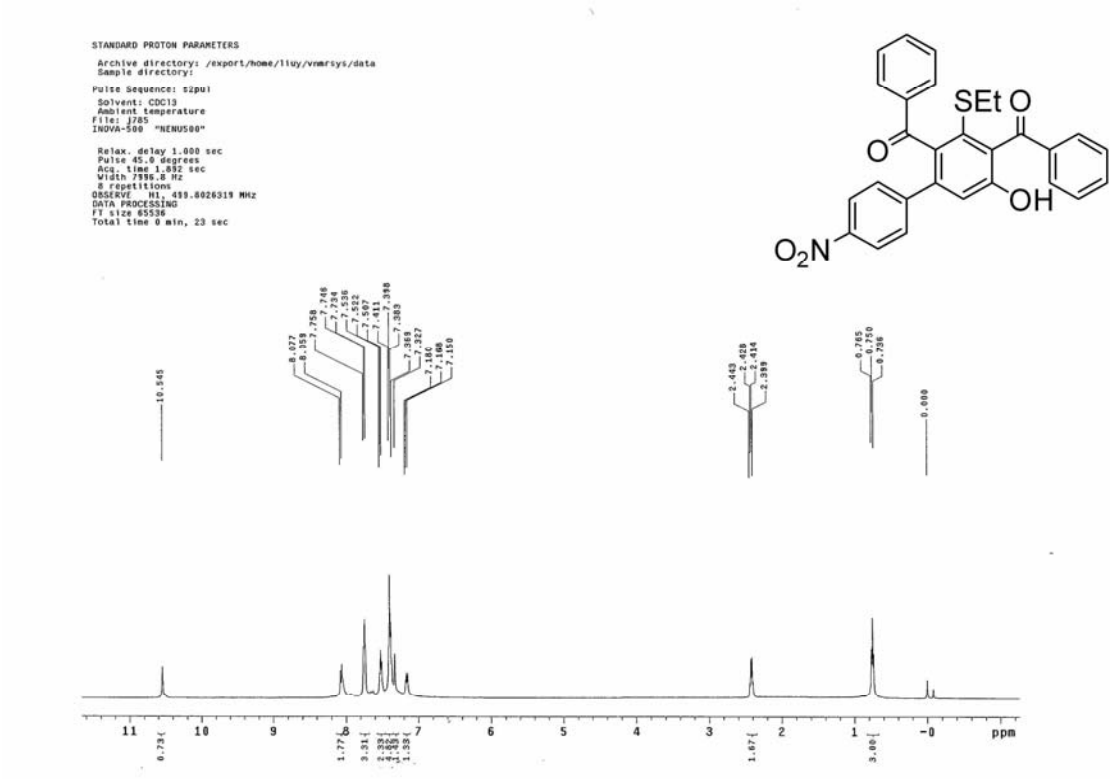
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
SEt
O
O
OH
Cl
ppm

5c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Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.8 Hz
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DATA PROCESSING
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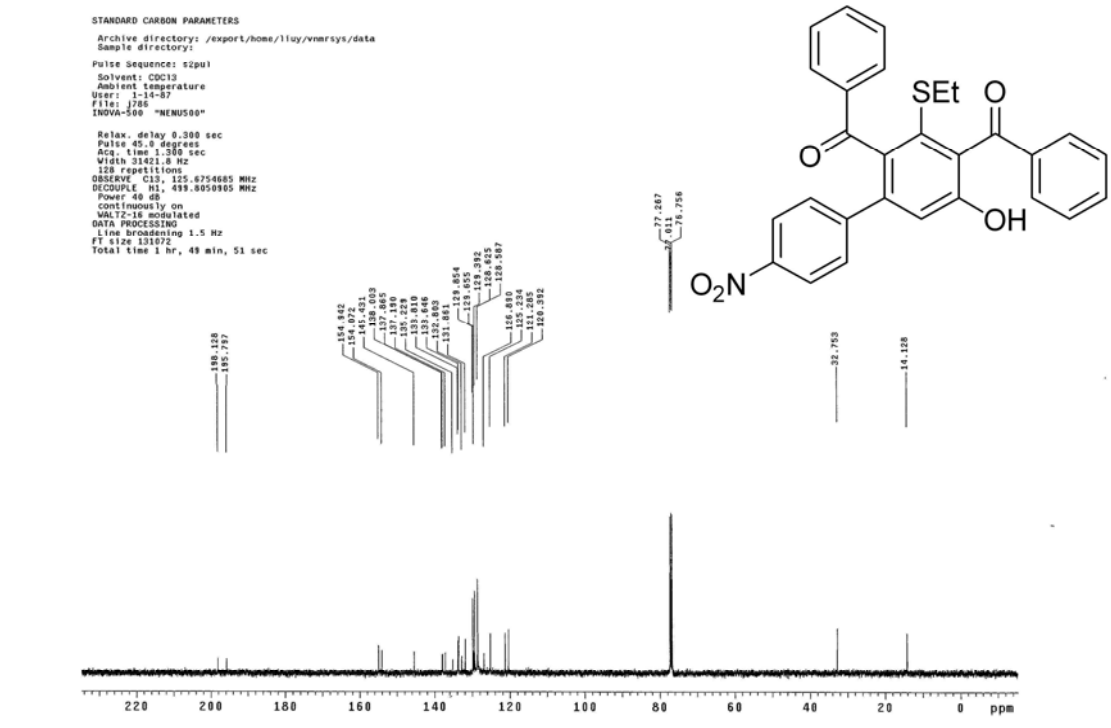
SEt
O
OH
O_2N
ppm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Sample directory:
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Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: j786
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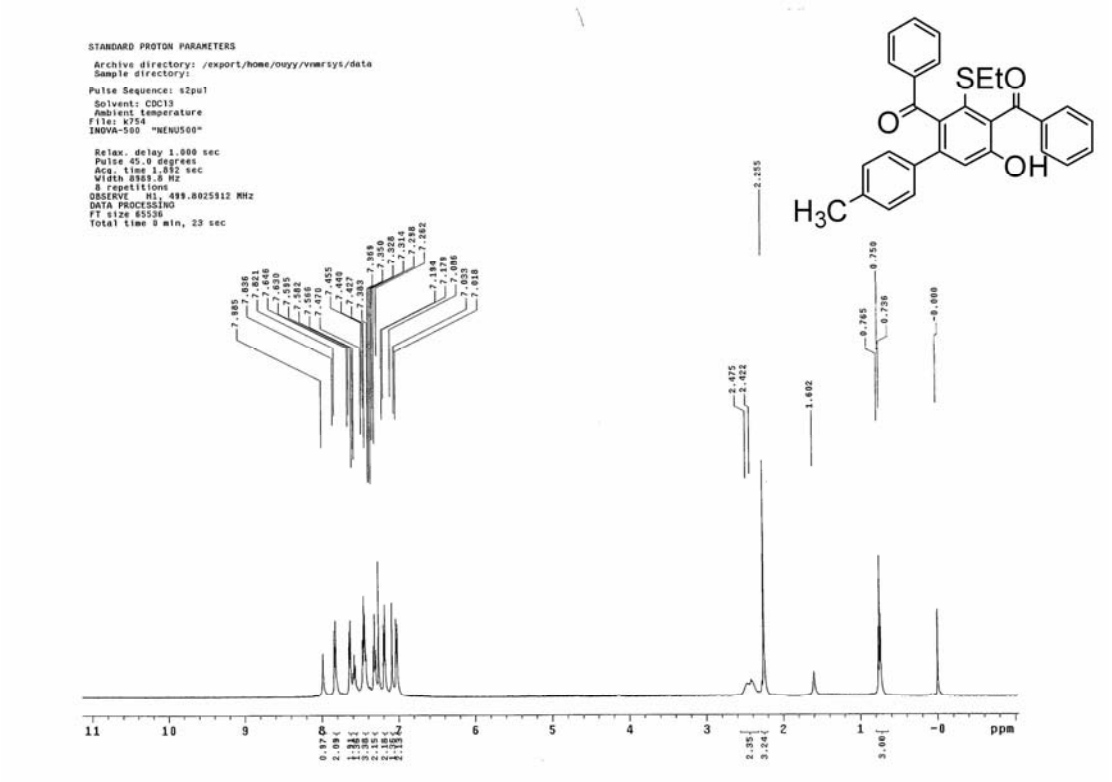
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
128 repetitions
OBSERVE C13, 125.6754685 MHz
DECOUPLE H1, 499.8050305 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
SEt
O
OH
O_2N
ppm

5d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Ambient temperature
File: k754
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8869.8 Hz
8 repetitions
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DATA PROCESSING
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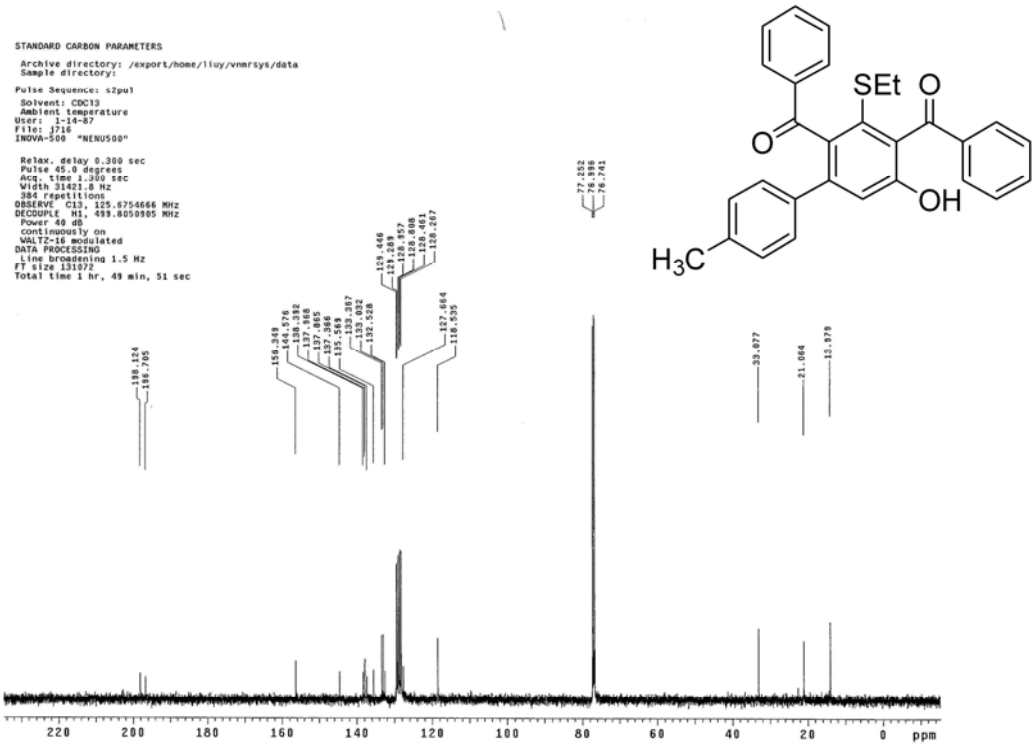
Total time 9 min, 23 sec
SEtO
O
OH
H3C
ppm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Ambient temperature
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File: j716
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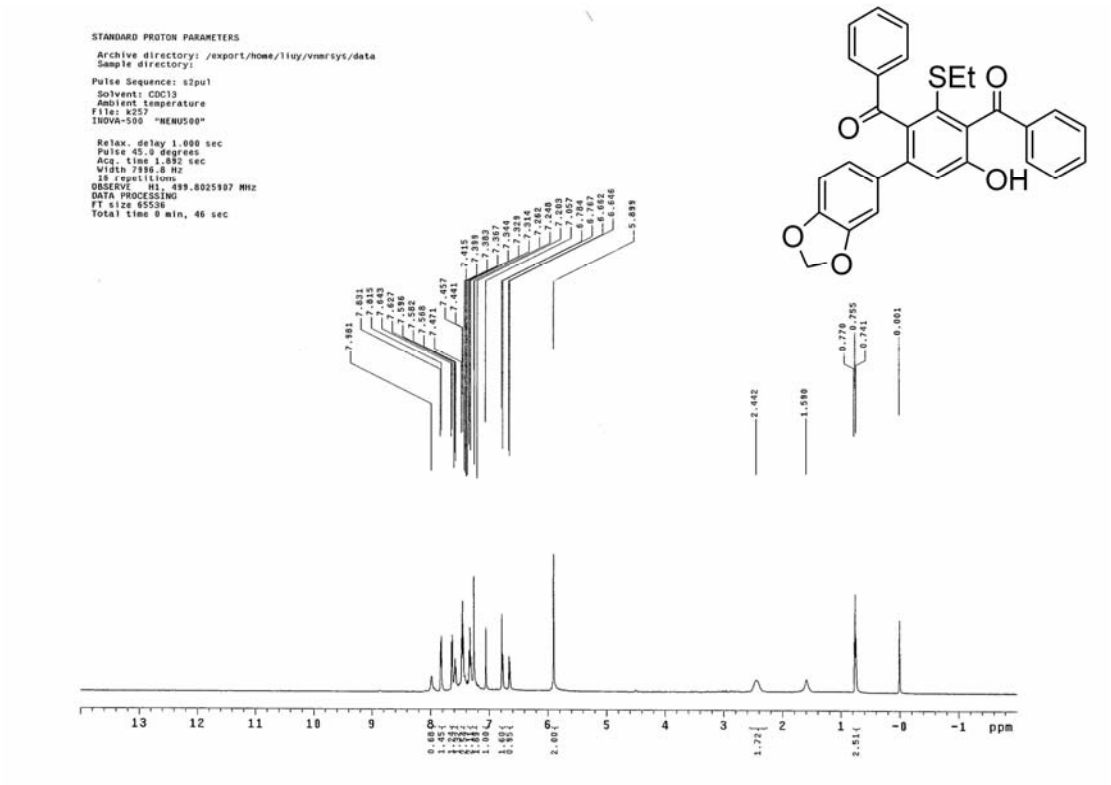
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31423.8 Hz
384 repetitions
OBSERVE C13, 125.6754666 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
SEt O
O
OH
H3C
ppm

5e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Sample directory:
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Ambient temperature
File: k257
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7886.8 Hz
16 repetitions
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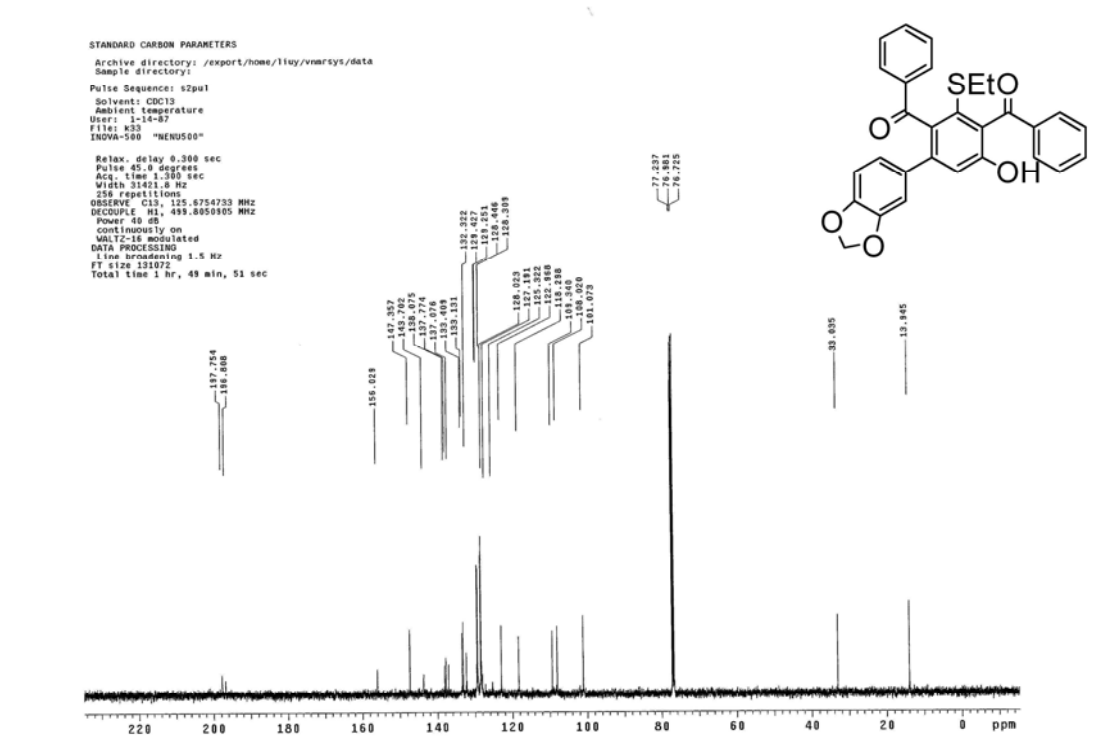
DATA PROCESSING
FT size 65536
Total time 0 min, 46 sec
SEt
O
O
OH
O
O
ppm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Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
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File: k33
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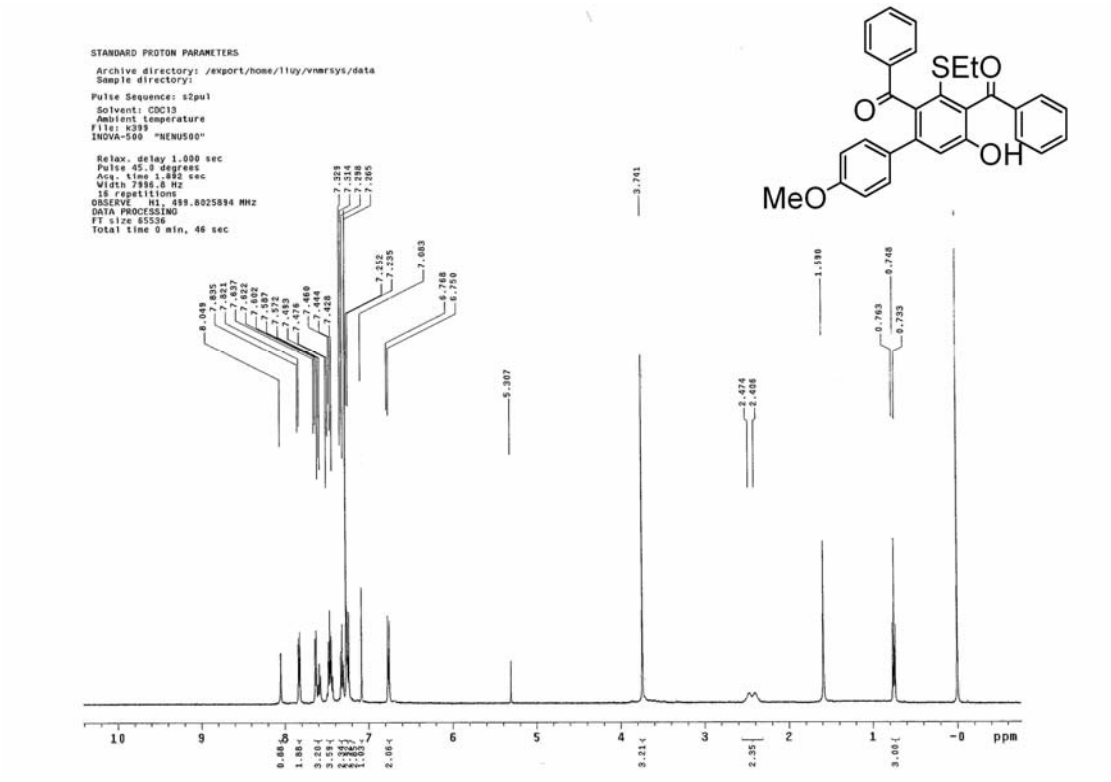
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
256 repetitions
OBSERVE C13, 125.6754733 MHz
DECOUPLE H1, 499.8050805 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
SEtO
O
OH
O
O
ppm

5f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Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: k399
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Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7986.8 Hz
16 repetitions
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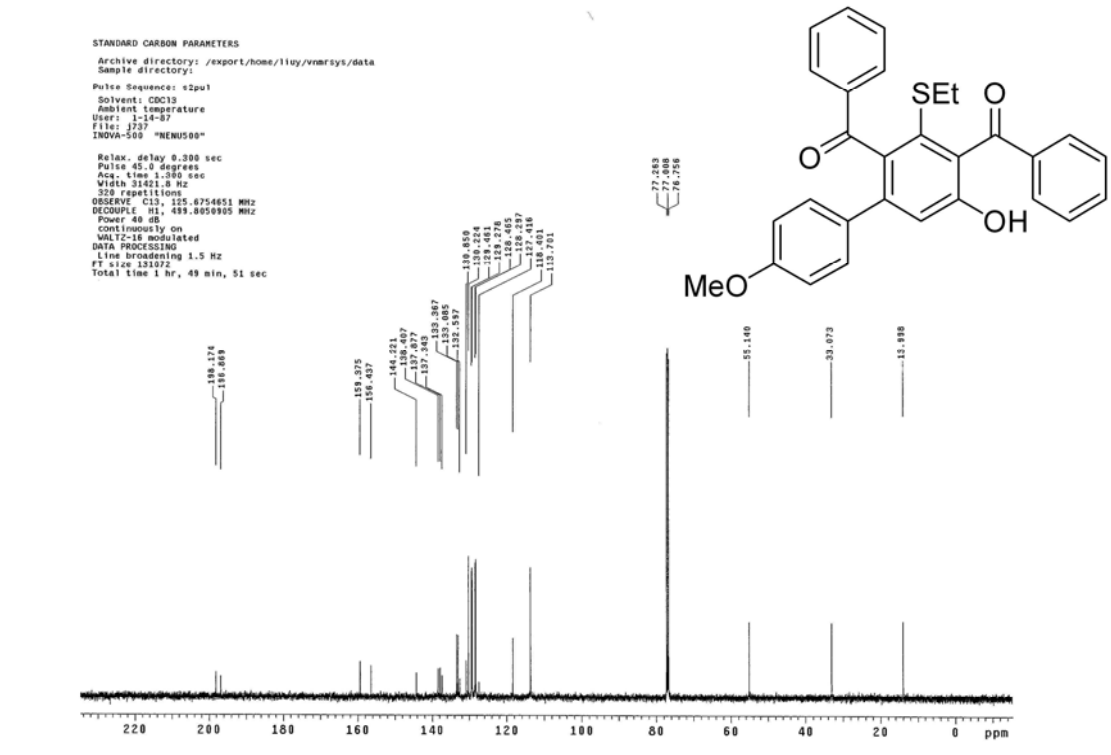
DATA PROCESSING
FT size 65536
Total time 0 min, 46 sec
SEtO
O
OH
MeO
ppm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Ambient temperature
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File: j737
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Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
320 repetitions
OBSERVE C13, 125.6754651 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
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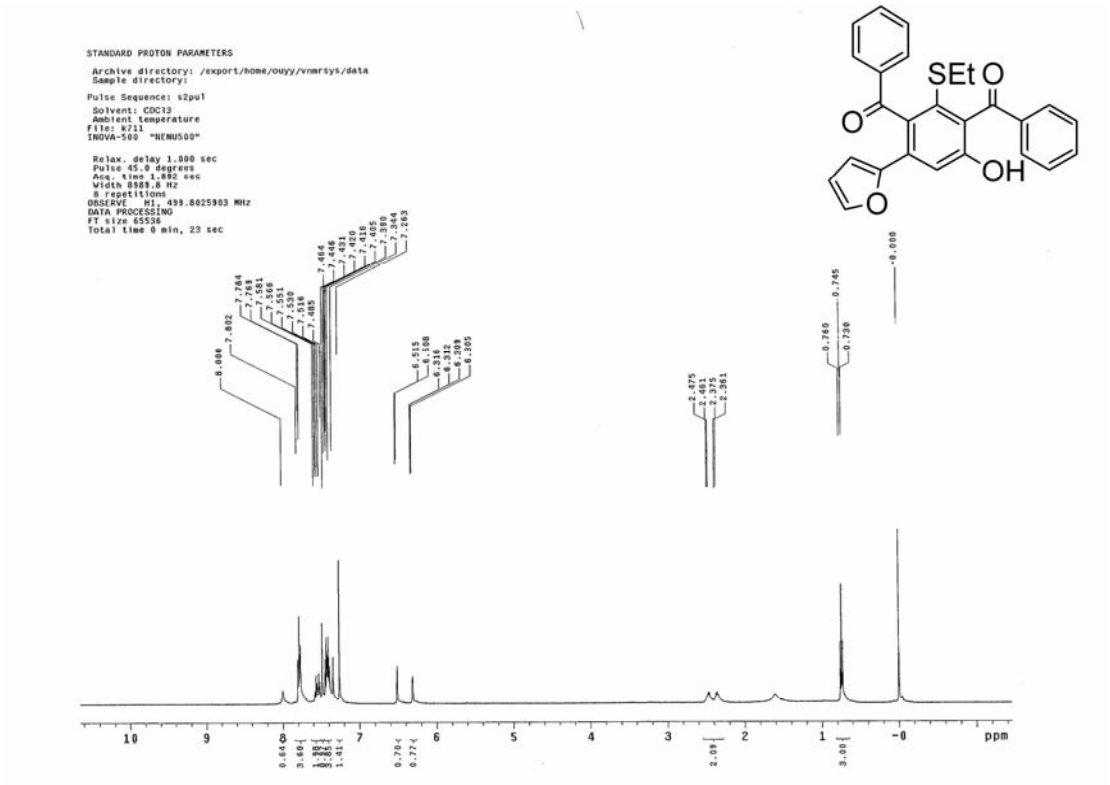
Total time 1 hr, 49 min, 51 sec
SEt O
O
OH
MeO
ppm

5g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Sample directory:
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Ambient temperature
File: k211
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Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8985.8 Hz
8 repetitions
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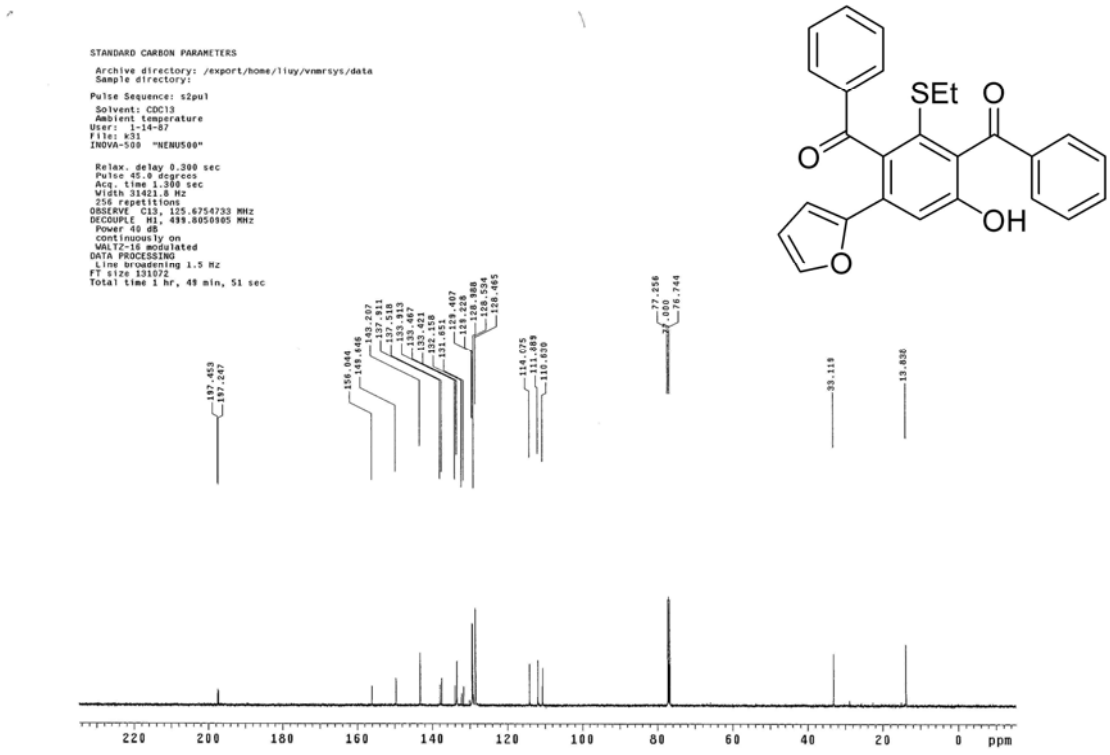
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
SEt
O
OH
ppm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Sample directory:
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Ambient temperature
User: 1-14-87
File: k31
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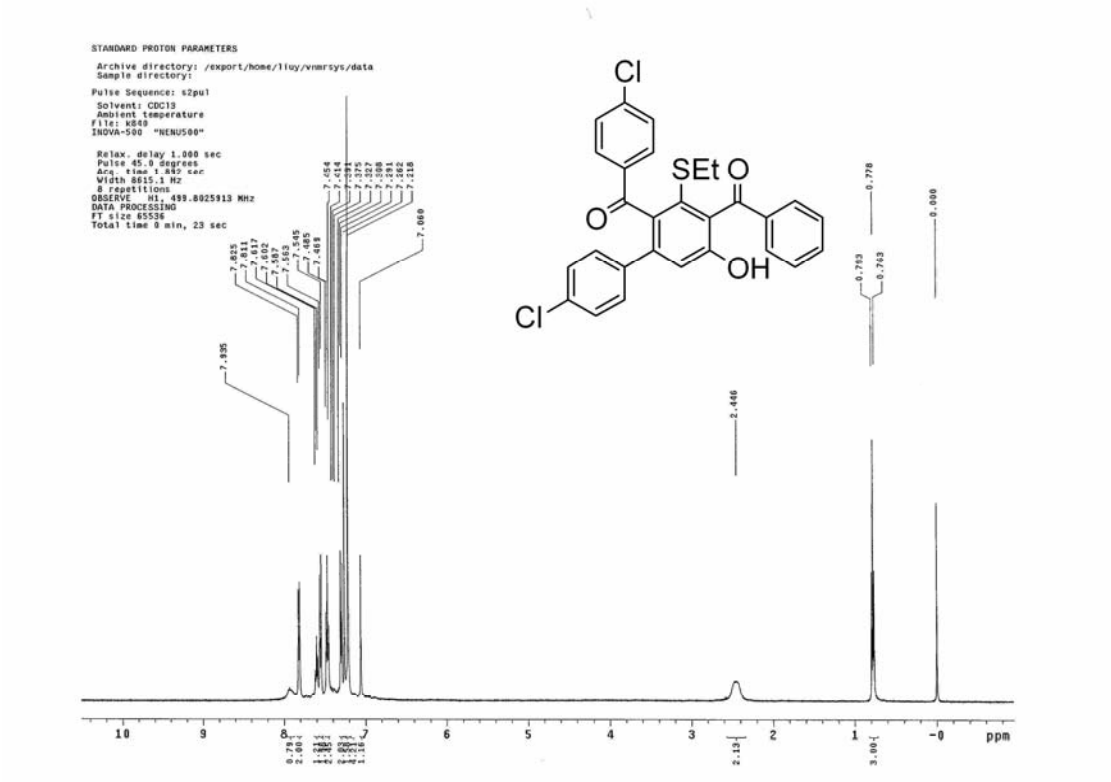
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
256 repetitions
OBSERVE C13, 125.6754733 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
SEt
O
OH
ppm

5h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Solvent: CDCl3
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Pulse 45.0 degrees
Acq. time 1.882 sec
Width 8615.1 Hz
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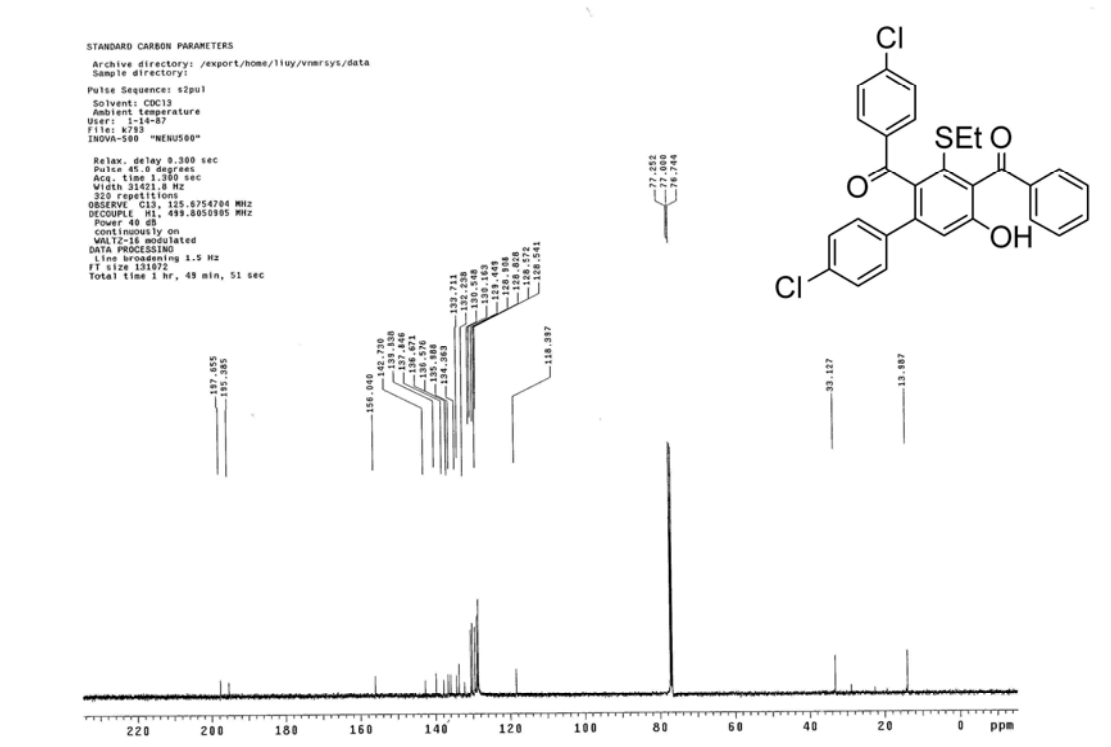
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
Cl
SEt O
O
OH
Cl
ppm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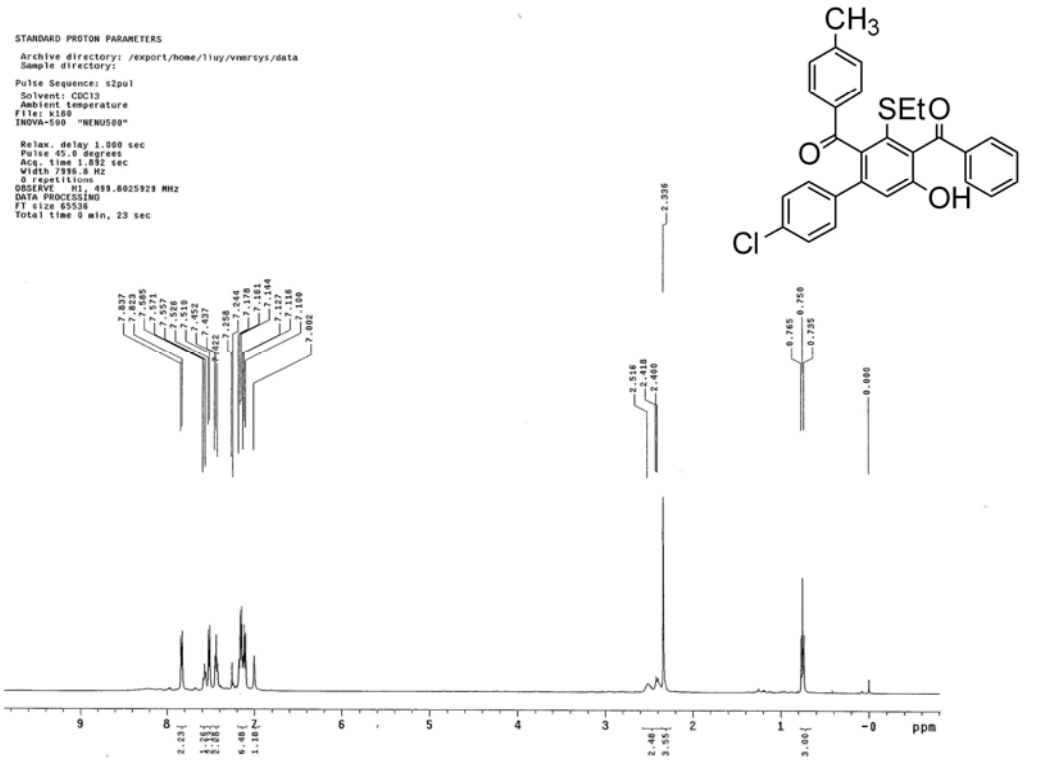
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: k793
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
320 repetitions
OBSERVE C13, 125.6754704 MHz
DECOUPLE H1, 499.8050305 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
Cl
SEt O
O
OH
Cl
ppm

5i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Ambient temperature
File: k180
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7986.8 Hz
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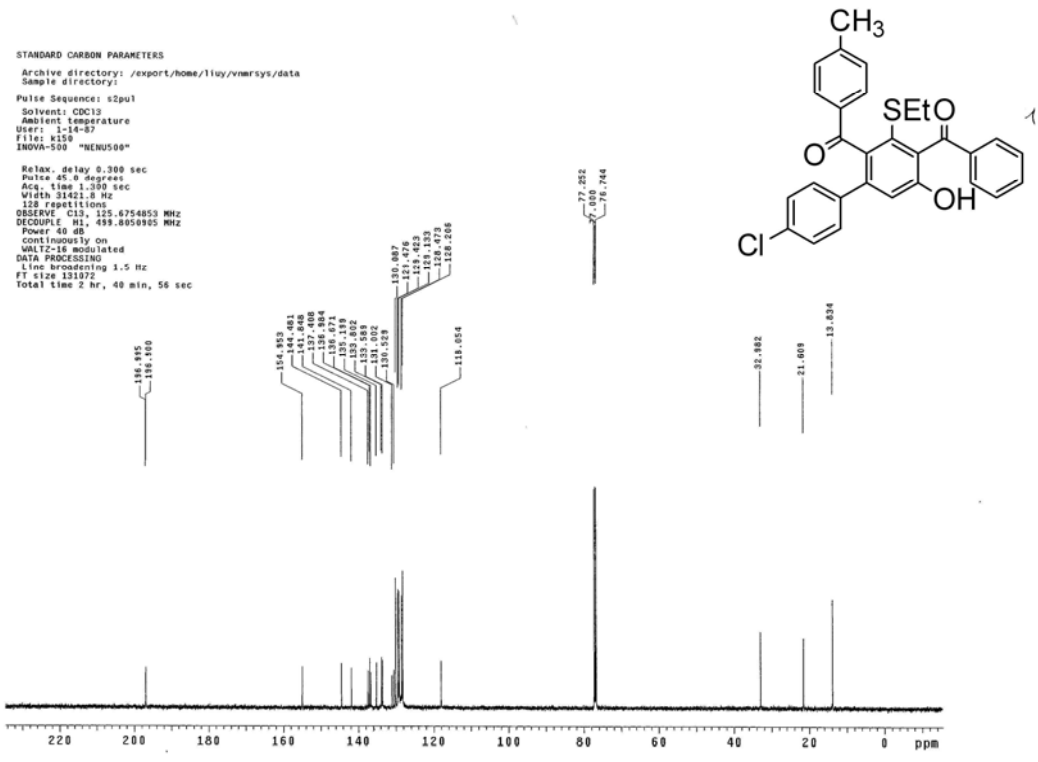
CH3
SEtO
O
OH
Cl
ppm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Ambient temperature
User: 1-14-87
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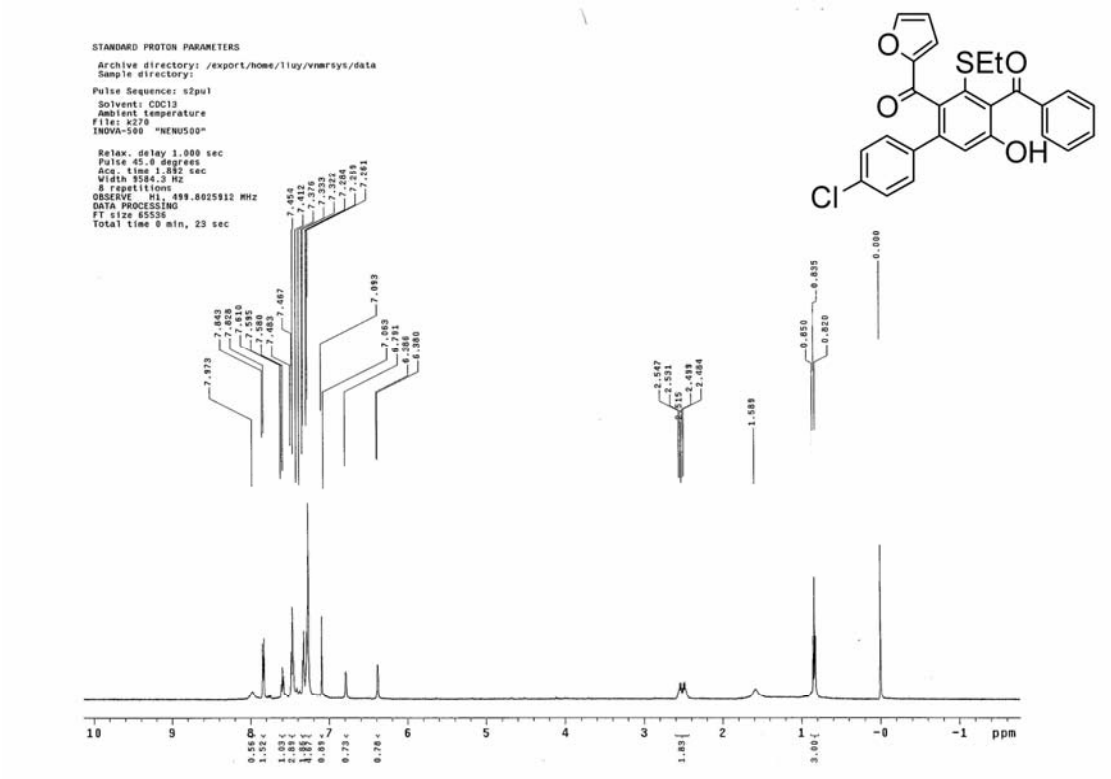
Acq. time 1.300 sec
Width 31421.8 Hz
128 repetitions
OBSERVE C13, 125.6754853 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 40 min, 56 sec
CH3
SEtO
O
OH
Cl
ppm

5j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Ambient temperature
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Acq. time 1.882 sec
Width 5584.3 Hz
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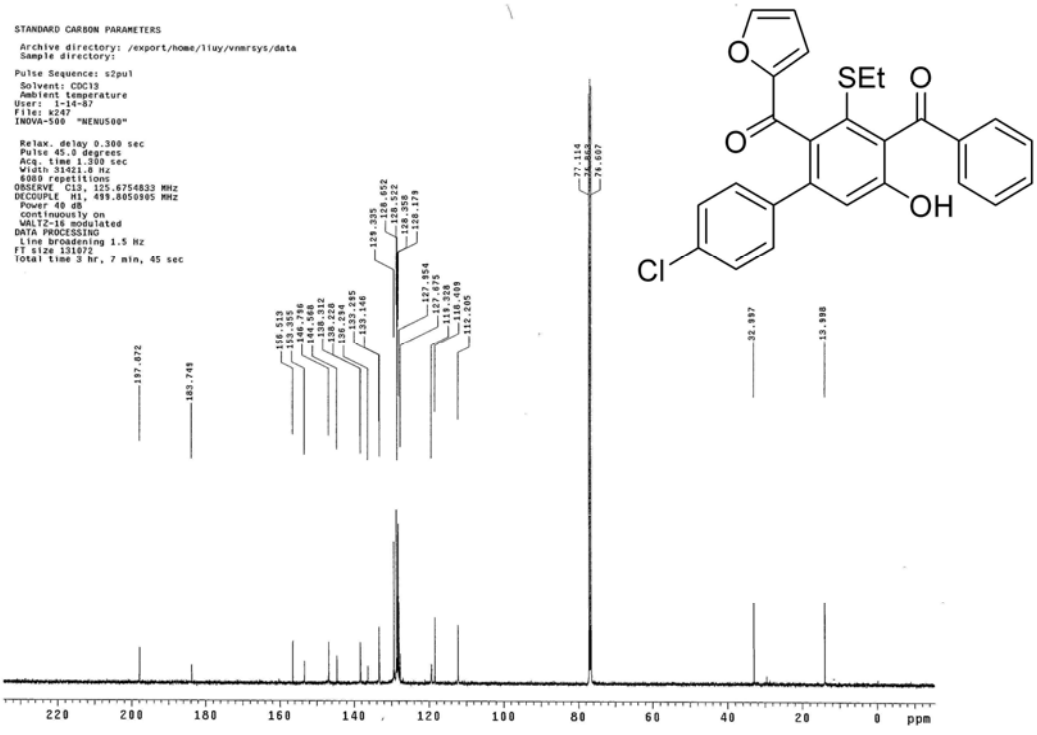
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
SEtO
O
OH
Cl
ppm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Sample directory:
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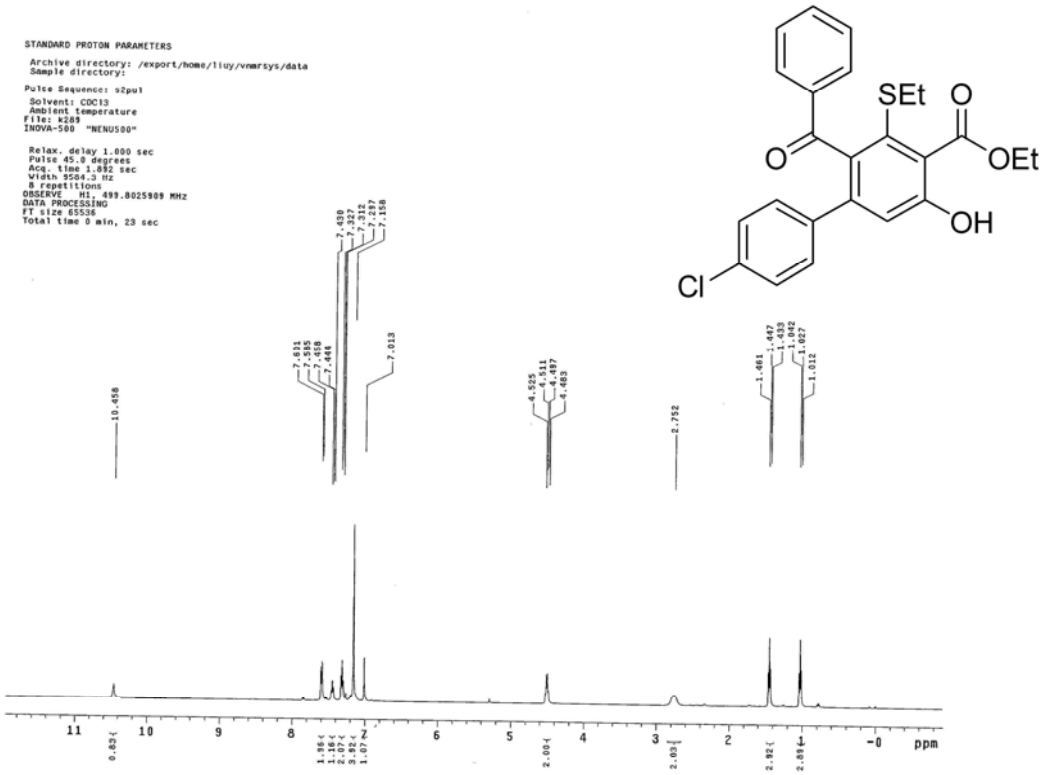
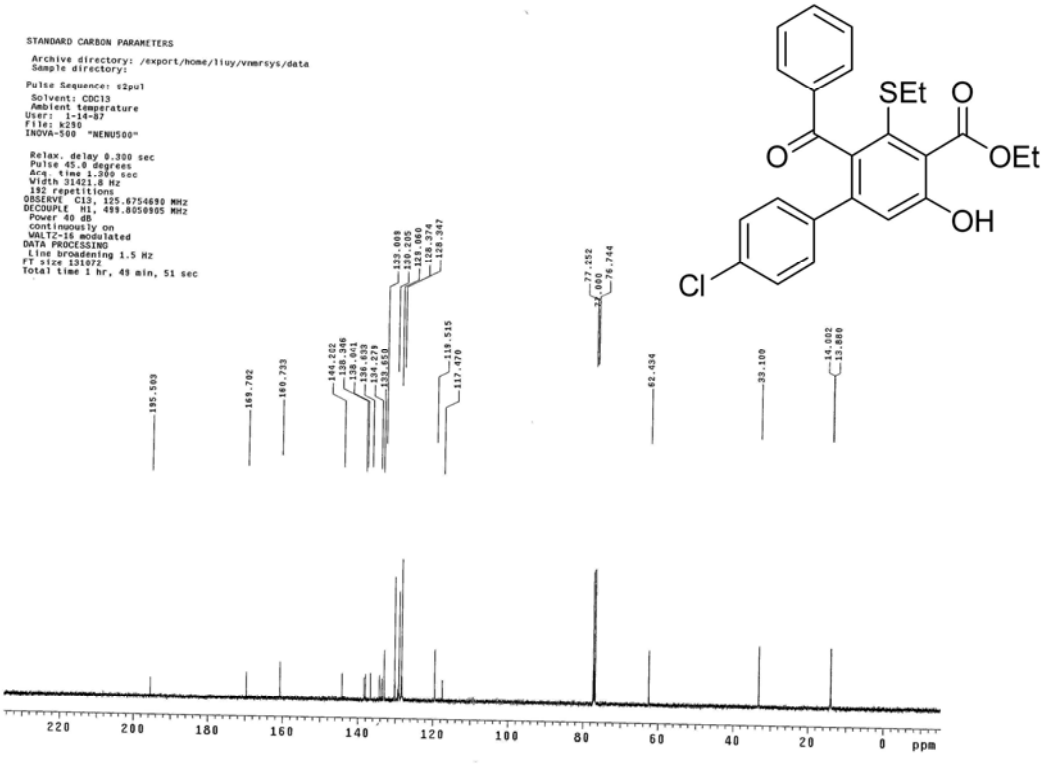
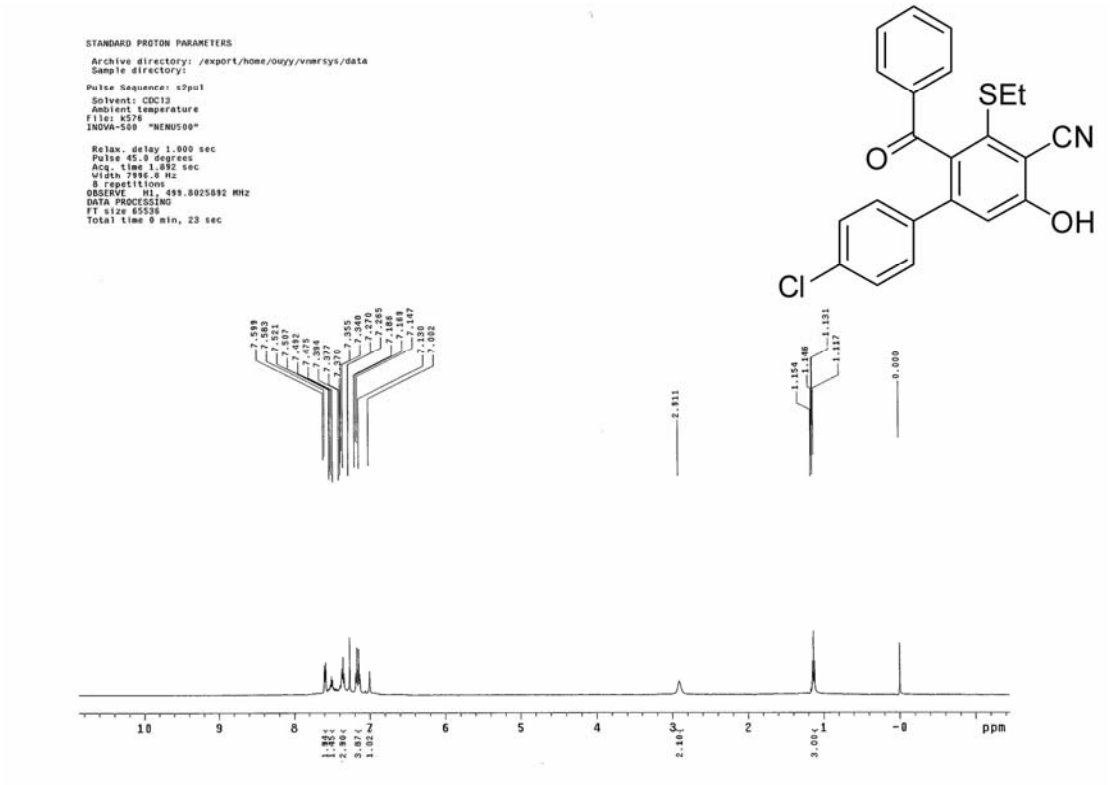
Ambient temperature
User: 1-14-87
File: k247
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
6080 repetitions
OBSERVE C13, 125.6754833 MHz
DECOUPLE H1, 499.8050305 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 7 min, 45 sec
SEt
O
OH
Cl
ppm

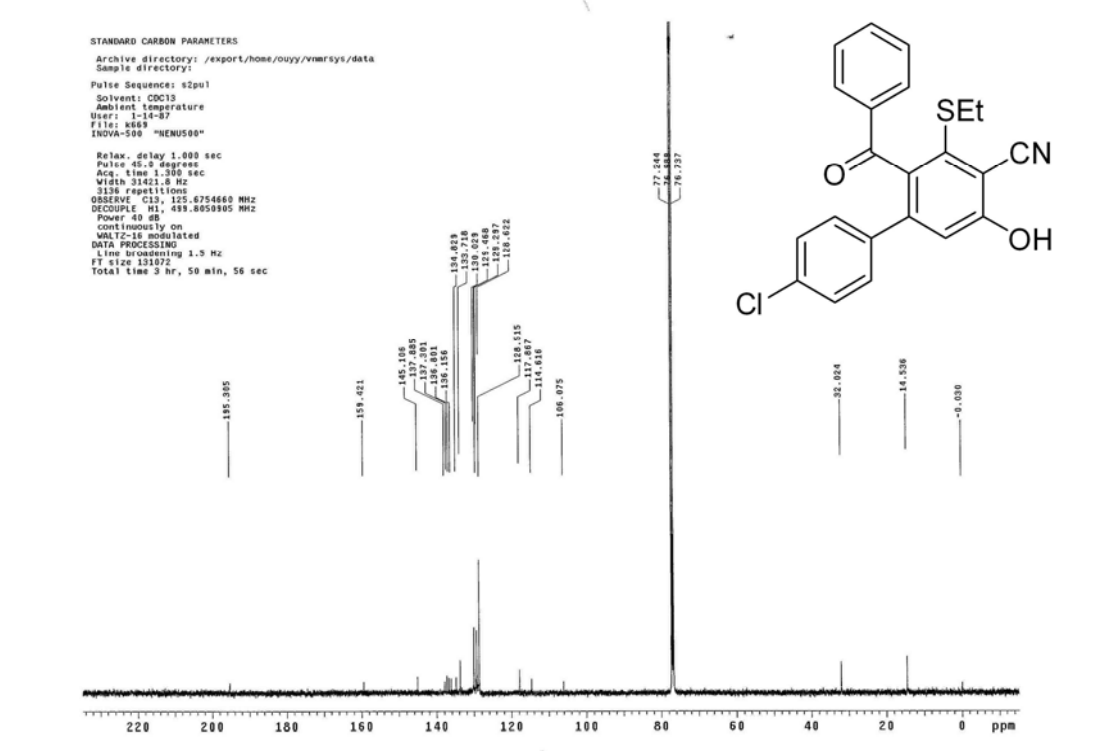
5k


STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: k289
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 9504.3 Hz
8 repetitions
OBSERVE H1, 499.8025909 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
SEt
O
O
OEt
OH
Cl
ppm

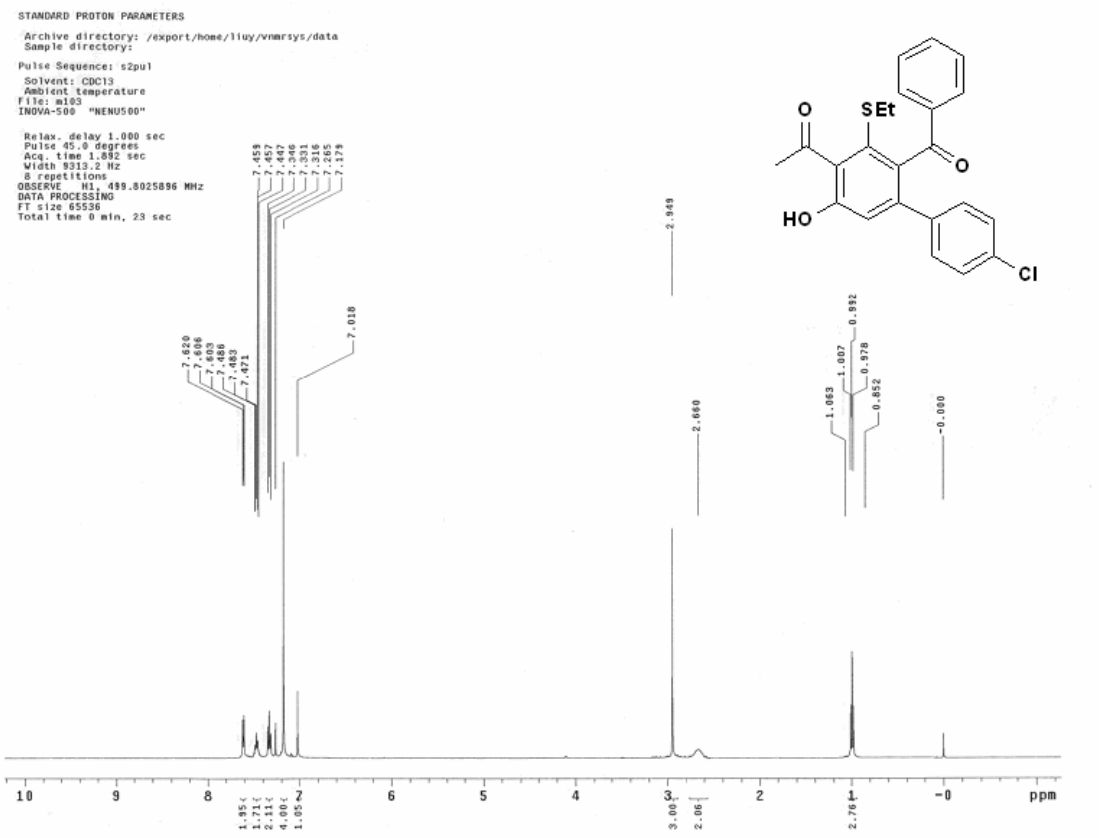

STANDARD CARBON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: k290
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.309 sec
Width 31421.8 Hz
192 repetitions
OBSERVE C13, 125.6754690 MHz
DECOUPLE H1, 499.8050805 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
SEt
O
O
OEt
OH
Cl
ppm

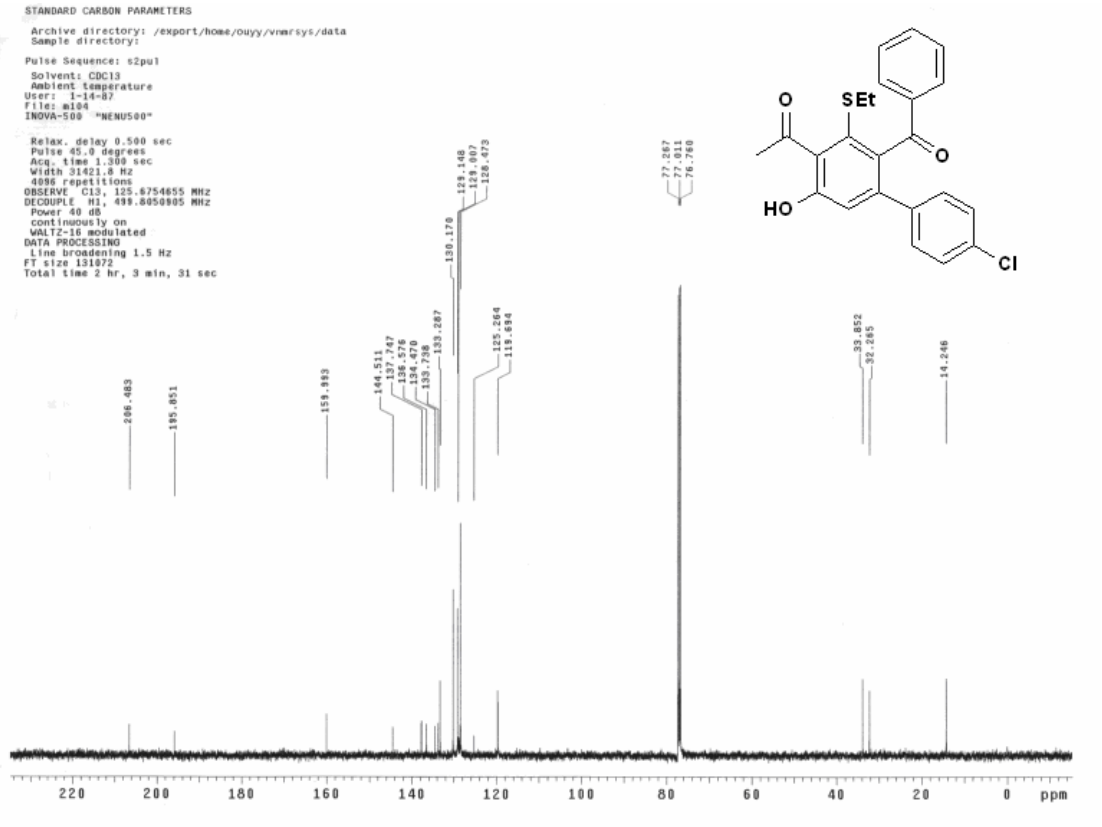
5l


STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: k576
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.8 Hz
8 repetitions
OBSERVE H1, 499.8025892 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
SEt
CN
O
OH
Cl
ppm

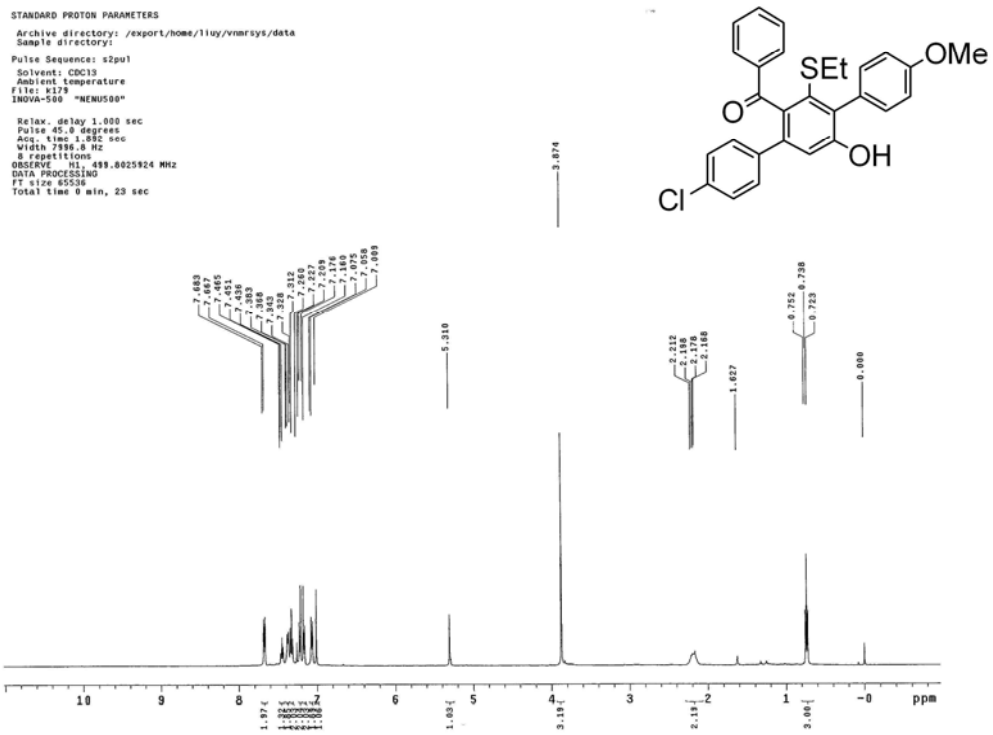

STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: k669
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
3136 repetitions
OBSERVE C13, 125.6754660 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 50 min, 56 sec
SEt
CN
O
OH
Cl
ppm

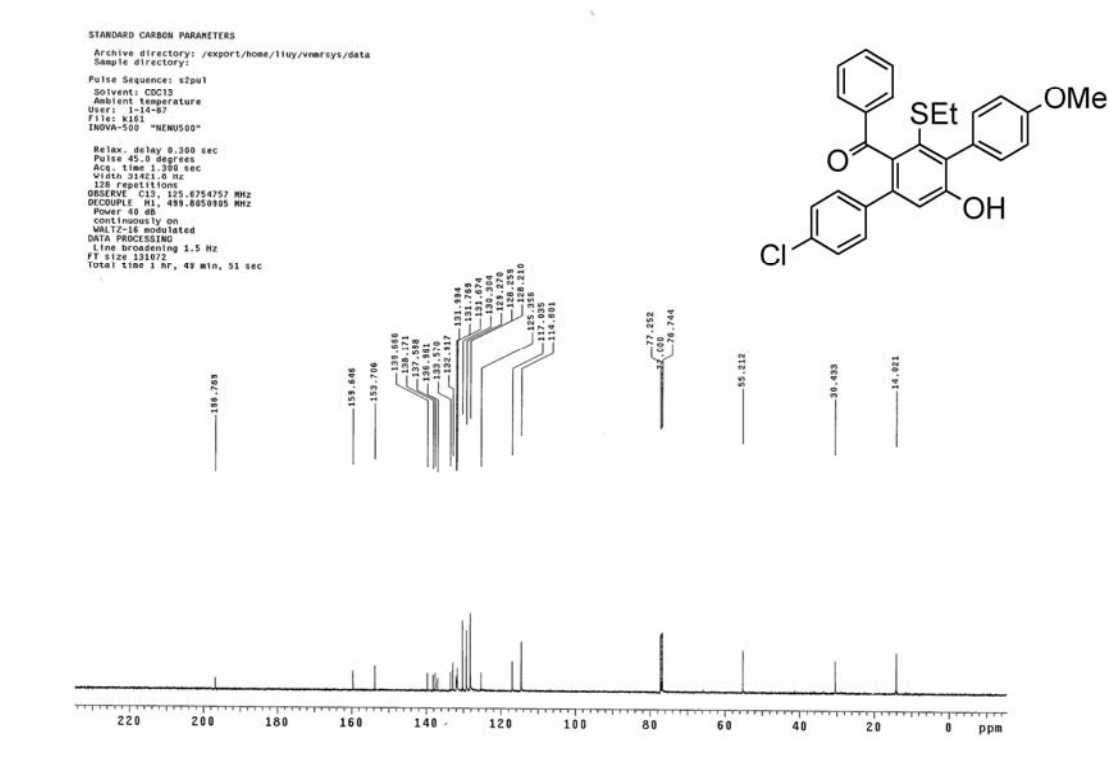
5m


STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: m103
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 9313.2 Hz
8 repetitions
OBSERVE H1, 499.8025896 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
O
SEt
O
HO
Cl
ppm

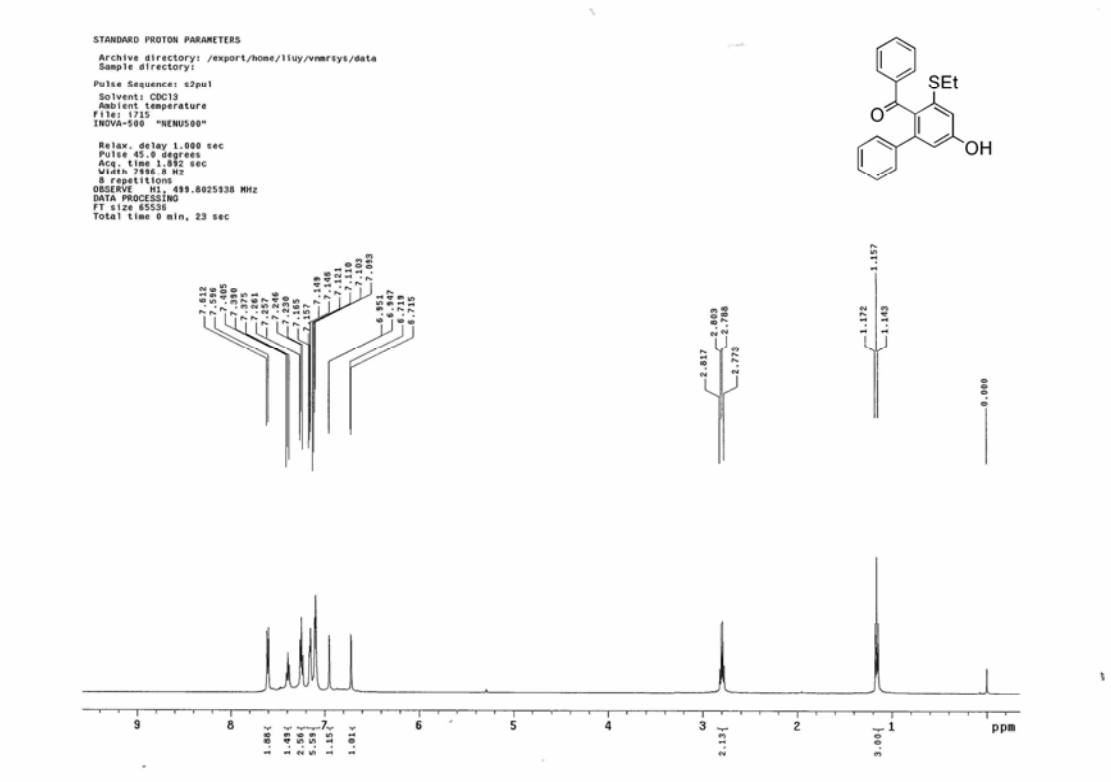

STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: m104
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
4096 repetitions
OBSERVE C13, 125.6754655 MHz
DECOUPLE H1, 499.8050805 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec
O
SEt
O
HO
Cl
ppm

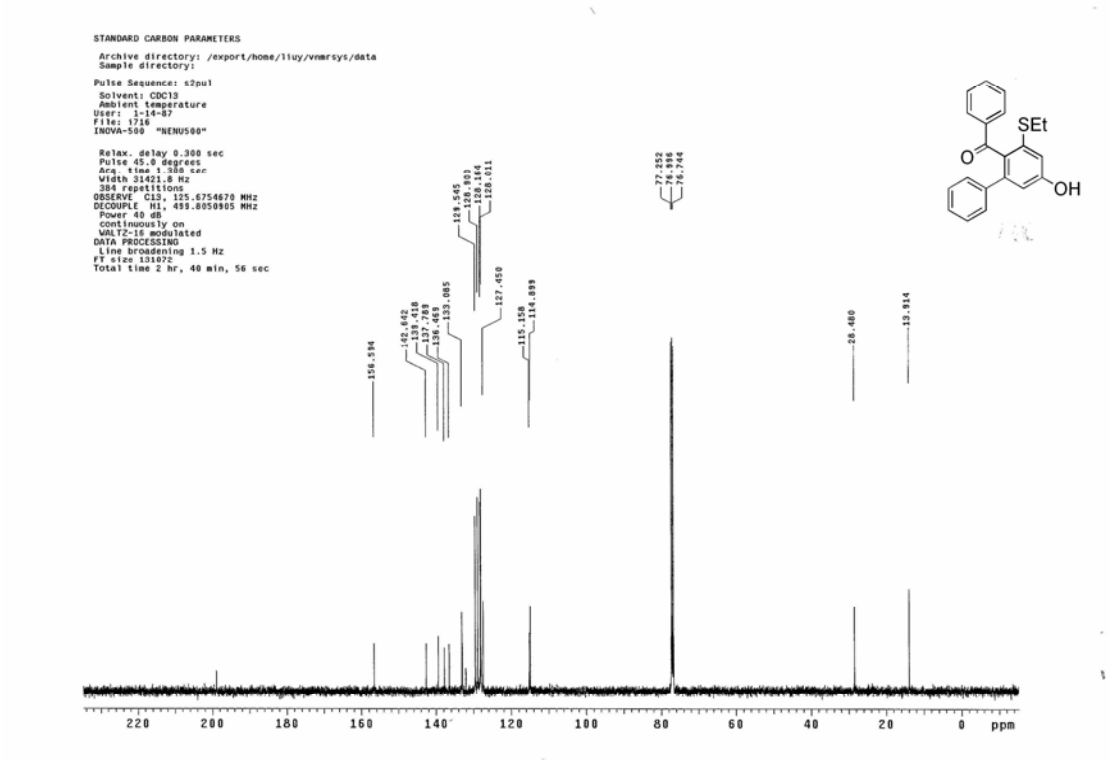
5n


STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: k179
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.802 sec
Width 7896.8 Hz
8 repetitions
OBSERVE H1, 499.8025924 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
SEt
OMe
O
OH
Cl
ppm

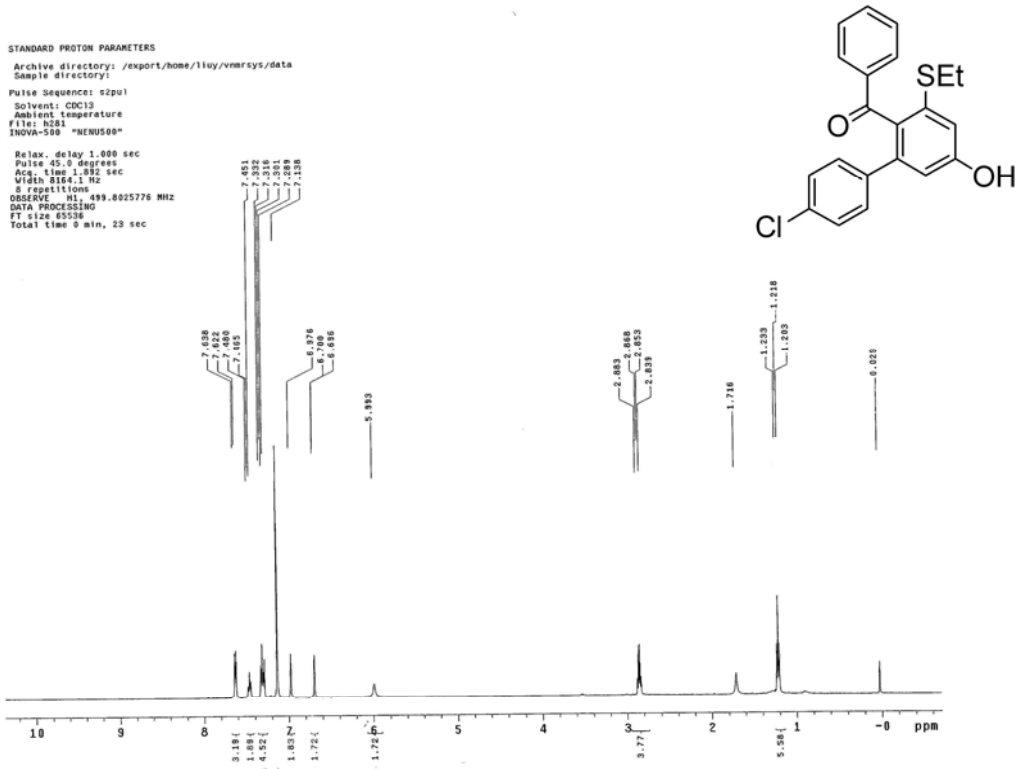

STANDARD CARBON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-07
File: k161
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
128 repetitions
OBSERVE C13, 125.6754757 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
SEt
OMe
O
OH
Cl
ppm

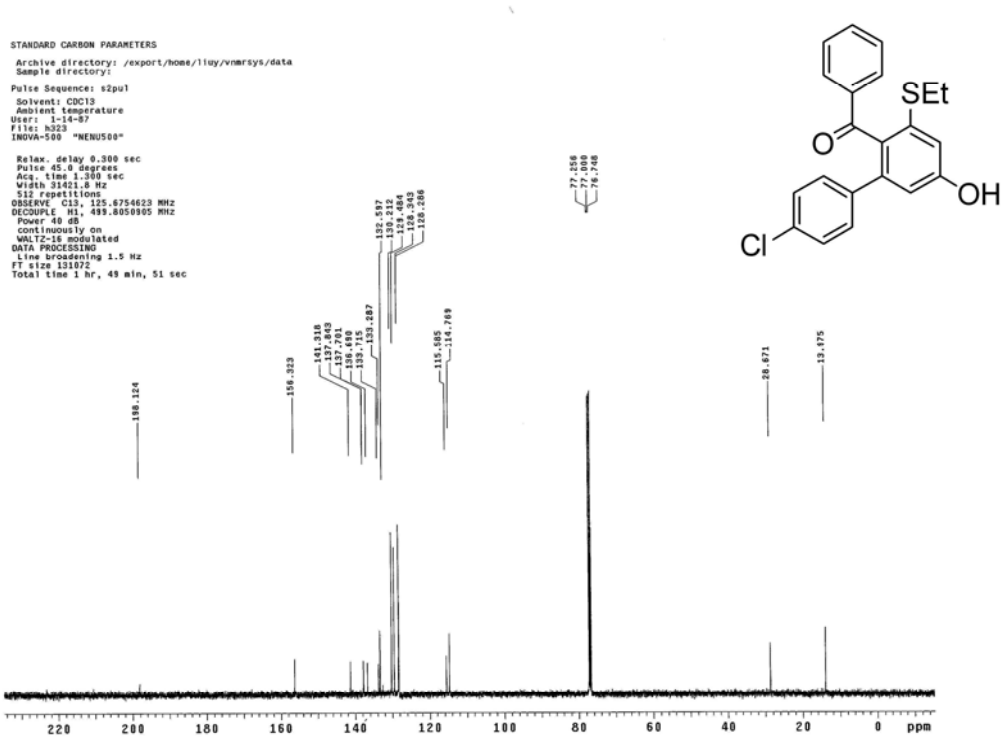
5o


STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 1715
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7986.8 Hz
8 repetitions
OBSERVE H1, 499.8025938 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
SEt
O
OH
ppm


STANDARD CARBON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: 1716
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.988 sec
Width 31421.8 Hz
384 repetitions
OBSERVE C13, 125.6754670 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 40 min, 56 sec
SEt
O
OH
ppm

5p


STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: h281
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8164.1 Hz
8 repetitions
OBSERVE H1, 499.8025776 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
SEt
O
OH
Cl
ppm


STANDARD CARBON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: h323
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
512 repetitions
OBSERVE C13, 125.6754623 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
SEt
O
OH
Cl
ppm