SUPPORTING INFORMATION FOR:

The Use of Sulfur Ylides in the Synthesis of Substituted Indoles.

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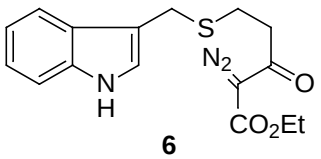
Experimental protocols and spectroscopic data for all new compounds.

General Information

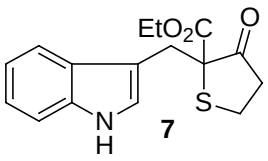
Purification with deactivated silica gel refers to silica gel that had been stirred with 5% NEt_3 and the eluting solvent for 15 min. Ether and THF were distilled from sodium/benzophenone. Benzene, toluene, CH_2Cl_2, $CHCl_3$, CH_3OH, *i*-Pr_2NEt, Et_3N, and Et_2NH were distilled from CaH_2. CH_3CN was distilled from K_2CO_3. All other reagents were used without purification. Unless otherwise stated, all reactions were run under an atmosphere of argon in flame-dried glassware.



6

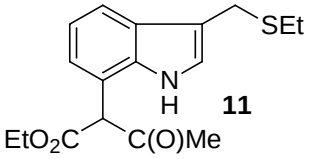
Preparation of Indole 6. To a solution of gramine methosulfate **4** (0.060 g, 0.21 mmol) and acetonitrile (1.0 mL) at 0°C was added K_2CO_3 (0.029g, 0.21 mmol) and Bu_4NBr (0.068 g, 0.21mmol.) followed by thiol **5** (0.046 g, 0.21 mmol) and acetonitrile (2.0 mL). The yellow mixture was allowed to warm to room temperature over 7 h and then poured into H_2O/Et_2O (1:1, 50 mL). The aqueous phase was extracted with Et_2O (2 x 25 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (neutralized silica gel, 3:1

hexanes: ethyl acetate) provided 0.070g (100%) of **6** as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.71 (dd, *J* = 7.7, 0.55 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.15 (m, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 2H), 3.13 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 191.1, 161.2, 136.4, 126.7, 123.0, 122.3, 119.2, 112.1, 111.2, 61.5, 40.0, 27.0, 25.7, 14.3; IR (CCl_4) 3412, 3048, 2979, 2148, 1733, 1664 cm^{-1}; HRMS calc'd for $C_{16}H_{17}N_3O_3S$ (M^+) 331.0991, found 331.0999.



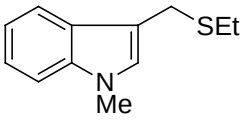
7

Indole 7. A solution of thioether **6** (0.035 g, 0.11 mmol), $Rh_2(OAc)_4$ (0.0023 g, 0.0052 mmol), and benzene (2.0 mL) was heated to reflux. After 5h the reaction mixture was concentrated. Flash chromatography (neutralized silica gel, 2:1 hexanes:ethyl acetate) gave 0.023 g (70% yield) of **7** as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.31 (dd, *J* = 6.9, 1.8 Hz, 1H), 7.14 (m, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 4.22 (m, 2H), 3.53 (q, *J* = 15.1 Hz, 2H), 3.00 (ddd, J = 10.9, 8.8, 7.0 Hz, 1H), 2.73 (ddd, J = 17.7, 7.0, 3.2 Hz, 1H), 2.56 (ddd, J = 17.7, 7.0, 3.2 Hz, 1H), 2.25 (ddd, *J* = 17.6, 8.7, 8.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) 210.6, 170.8, 135.6, 128.3, 124.5, 122.0, 119.5, 119.5, 110.9, 109.9, 64.0, 62.1, 40.2, 28.3, 23.9, ; 14.0 IR (CCl_4) 3481, 3420, 2979, 1759 cm^{-1}; HRMS calc'd for $C_{18}H_{18}NO_3S$ (M^+) 303.0929, found 303.0931.



11

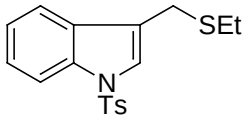
Indole 11. $Rh_2(OAc)_4$ (0.0046 g, 0.010 mmol) and **10** (0.039 g, 0.25 mmol) were added to a solution of 3-[(ethylthio)methyl]-1H-indole (0.040 g, 0.021 mmol) and benzene (5.0 mL). The mixture was heated to reflux over 3h and then concentrated. Flash chromatography (neutralized silica gel, 5:1 hexanes:ethyl acetate) provided 0.0080 g (12%) of C-7 insertion product **11** as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 12.70 (s, 1H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.17 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.08 (dt, *J* = 7.8, 1.3 Hz, 1H), 6.86 (s, 1H), 4.13 (m, 2H), 2.44 (q, *J* = 7.4 Hz, 2H), 1.74 (s, 3H), 1.22 (t, *J* = 7.4 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 176.3, 170.8, 138.1, 128.2, 127.2, 122.5, 119.8, 119.4, 112.7, 109.9, 103.7, 61.2, 26.2, 25.2, 17.7, 14.5, 14.1; IR (CCl_4) 2979, 2927, 1655, 1620 cm^{-1}; HRMS calc'd for $C_{17}H_{21}NO_3S$ (M^+) 319.1242, found 319.1239.



12

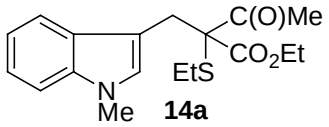
Ethylthiomethyl indole 12. To a cooled solution of EtSH (0.055 mL, 0.74 mmol) and CH_3OH (3.85 mL) was added Na(s) (0.017 g, 0.74 mmol) followed by a solution of 1-methylgramine (0.12 g, 0.64 mmol) and CH_3OH (1 mL). The resulting mixture was then heated to reflux for 12 h. The mixture then poured into H_2O, extracted with Et_2O (4 x 20 mL), dried ($MgSO_4$), and concentrated. Flash chromatography (neutralized silica gel, 10:1 hexanes:ethyl acetate) provided 0.017g (13%) of **12** as a colorless oil. ^{1}H NMR

(250 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.21 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.11 (dt, *J* = 7.3, 1.3 Hz, 1H), 6.97 (s, 1H), 3.93 (s, 2H), 3.74 (s, 3H), 2.48 (q, *J* = 7.4 Hz, 2H),1.24 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 137.2, 127.5, 127.4, 121.8, 119.3, 119.0, 111.1, 109.2, 32.7, 26.7, 25.6, 14.5; IR (CCl_4) 3048, 2970, 2936, cm^{-1}; HRMS calc'd for $C_{12}H_{15}NS$ (M^+) 205.0925, found 205.0928.



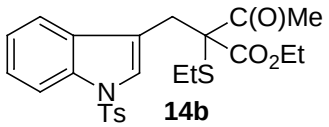
13

Ethylthiomethyl indole 13. To a mixture of 3-[(ethylthio)methyl]-1H-indole (0.13 g, 0.68 mmol), Bu_4NHSO_4 (0.023 g, 0.068 mmol), 0.7 mL of 50% KOH(aq.), and benzene (2.7 mL) was added TsCl (0.13 g, 0.68 mmol). The mixture was stirred vigorously for 1h and then poured into H_2O (15 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The organic extracts were dried (K_2CO_3) and concentrated. Flash chromatography (neutralized silica gel, 3:1 hexanes:ethyl acetate) provided 0.23 g (98%) of **13** as an off white solid. mp 72-73°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 7.8, 1H), 7.45 (s, 1H), 7.25 (m, 4H), 3.78 (s, 2H), 2.35 (q, *J* = 7.4 Hz, 2H), 2.30 (s, 3H),1.19 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 144.9, 135.5, 135.0, 130.0, 129.8, 126.7, 124.9, 124.1, 123.2, 120.0, 119.3, 113.8, 25.7, 25.3, 21.5, 14.2; IR (CCl_4) 2979, 2927, 1378, 1188 cm^{-1}; HRMS calc'd for $C_{18}H_{19}NO_2S_2$ (M^+) 345.0857, found 345.0853.



14a

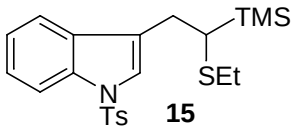
Preparation of 14a. A solution of **12** (0.017 g, 0.083 mmol), **10** (0.026 g, 0.17 mmol), and $Rh_2(OAc)_4$ (0.0037 g, 0.0084 mmol) and benzene (1.7 mL) was heated to reflux. An additional 0.026 g of **10** (0.17 mmol) was added after 1h and the mixture was heated to reflux for an additional 1h. Following concentration, flash chromatography (neutralized silica gel, 3:1 hexanes:ethyl acetate) provided 0.016 g (58%) of **14a** as an off white solid. mp 64-66°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.16 (dt, *J* = 7.3, 1.1 Hz, 1H), 7.06 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.06 (s, 1H), 3.98 (m, 2H), 3.72 (s, 3H), 3.61 (d, *J* = 15.6 Hz, 1H), 3.38 (d, *J* = 15.5 Hz, 1H), 2.43 (m, 2H), 2.30 (s, 3H), 1.21 (t, *J* = 7.5 Hz, 3H). 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.5, 169.3, 136.3, 128.5, 128.3, 121.4, 118.8, 118.7, 109.1, 107.4, 68.3, 62.1, 32.8, 27.7, 26.1, 23.2, 13.7, 13.5; IR (CCl_4) 2979, 2936, 1715 cm^{-1}; HRMS calc'd for $C_{18}H_{23}NO_3S$ (M^+) 333.1399, found 333.1402.



14b

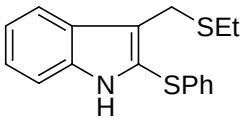
Preparation of 14b. To a solution of **13** (0.037 g, 0.11 mmol), $Rh_2(OAc)_4$ (0.0041, 0.0093 mmol), and benzene (2.2 mL) at reflux was slowly added a solution was **10** (0.044 g, 0.28 mmol) and benzene (1.0 mL) over 45 min. An additional 0.030 g (0.19 mmol) of **10** and benzene (1 mL) was added via syringe pump to the refluxing solution over 45

min. Concentration of the reaction mixture and flash chromatography (neutralized silica gel, 3:1 hexanes:ethyl acetate) yielded 0.026 g (50%) of **14b** as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.19 (m, 2H), 7.12 (d, *J* = 6.6 Hz, 1H), 7.02 (m, 3H), 5.49 (s, 1H), 5.27 (d, *J* = 1.5 Hz, 1H), 5.07 (d, *J* = 1.0 Hz, 1H), 3.47 (m, 2H), 2.84 (m, 1H), 2.32 (s, 3H), 2.28 (s, 3H), 2.17 (m, 1H), 1.24 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 197.7, 166.6, 143.9, 141.7, 133.8, 132.7, 129.3, 129.2, 127.6, 125.9, 120.6, 120.0, 110.3, 71.8, 66.1, 62.3, 27.7, 24.3, 21.5, 13.4, 12.8; IR (CCl_4) 2988, 2927, 1733, 1707 cm^{-1}; HRMS calc'd for $C_{24}H_{28}NO_5S_2$ (M^+) 474.1409, found 474.1393.



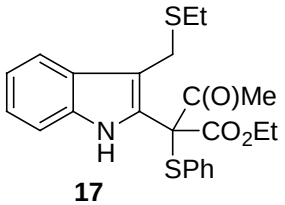
15

Preparation of 15. To a solution of indole **13** (0.051 g, 0.15 mmol), $Rh_2(OAc)_4$ (0.0033 g, 0.0074 mmol), and benzene (3 mL) at reflux was slowly added a solution of trimethylsilyl diazomethane (0.090 mL, 0.56 mmol) and benzene (2 mL) over 1.5 h. Concentration of the reaction mixture and flash chromatography (neutralized silica gel, 20:1 hexanes:ethyl acetate) provided 0.047 g (76%) of **15** as a pale yellow solid. Mp 99-101°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1 H), 7.48 (d, *J* = 8.3 Hz, 2 H), 7.26 (m, 2 H), 7.04 (m, 1 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 5.33 (d, *J* = 2.1 Hz, 1 H), 4.94 (d, J = 4.1, 2.0 Hz, 1 H), 4.86 (d, *J* = 1.5 Hz, 1 H), 2.88 (d, *J* = 2.4 Hz, 1 H), 2.72 (m, 1 H), 2.46 (m, 1 H), 2.31 (s, 3 H), 1.13 (t, *J* = 2.4 Hz, 1 H), 0.22 (s, 9 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 144.3, 144.0, 143.8, 134.3, 131.5, 129.7, 129.7, 129.6, 127.0, 124.6, 120.5, 116.3, 104.7, 69.5, 39.2, 29.5, 21.5, 14.8; IR (CCl_4) 2962, 2927, 1369, 1188 cm^{-1}; HRMS calc'd for $C_{22}H_{29}NO_2S_2Si$ (M^+) 431.1409, found 431.1416.



16

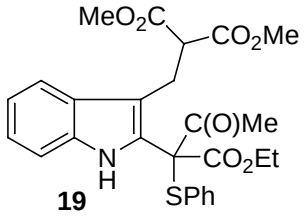
Preparation of 16. To a solution of 2-(phenylthio)-3[(phenylthio)(trimethylsilyl)-methyl]-1H-indole (0.58 g, 1.4 mmol) and acetonitrile (9.0 mL) was added EtSH (1.0 mL, 14 mmol), KF (0.12 g, 2.1 mmol), and 18-crown-6 (0.55 g, 2.1 mmol). After being heated to reflux for 7h the mixture was concentrated. Flash chromatography (neutralized silica gel, 20:1 hexanes:ethyl acetate) provided 0.37 g (88%) of **16** as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.84 (m, 1H), 7.13-7.34 (m, 8H), 4.10 (d, *J* = 4.5 Hz, 2H), 2.49 (m, 2H), 1.26 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 226.0, 137.1, 136.6, 129.2, 127.2, 127.1, 126.1, 123.8, 123.1, 120.1, 120.0, 111.0, 25.8, 25.7, 14.6; IR (CCl_4) 3481, 3420, 3039, 2979, 2927 cm^{-1}; HRMS calc'd for $C_{17}H_{17}NS_2$ (M^+) 299.0802, found 299.0800.



17

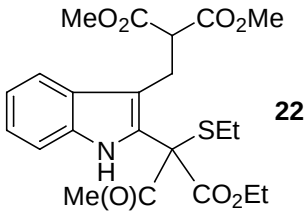
Preparation of 17. A solution of **16** (0.10 g, 0.33 mmol), $Rh_2(OAc)_4$ (0.0077 g, 0.017 mmol), **10** (0.072 mL, 0.52 mmol), and benzene (6.9 mL) was heated to reflux for 5h. Concentration of the reaction mixture and flash chromatography (neutralized silica gel, 5:1 hexanes:ethyl acetate) provided 0.067 g (47%) of **17** as a viscous yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 10.94 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.20 (m, 5H), 7.08 (m, 3H), 4.08 (m, 4H), 2.38 (m, 5H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 192.5, 166.7, 137.5, 131.0, 129.6, 126.1, 125.7, 125.5, 123.6, 120.8, 120.5, 118.7, 112.8, 59.9, 29.7, 26.3, 25.1, 14.7, 14.4; IR (CCl_4) 3238, 2988, 2936, 1741, 1689 cm^{-1}; HRMS calc'd for $C_{23}H_{26}NO_3S_2$ (M^+) 428.1354, found 428.1357.



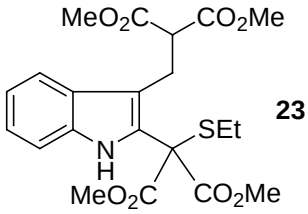
19

Preparation of 19. A solution of **17** (0.030 g, 0.070 mmol), dimethyl malonate (0.016 mL, 0.14 mmol), KF (0.0020 g, 0.034 mmol), 18-crown-6 (0.0092 g, 0.035 mmol), and acetonitrile (1.5 mL) was heated to reflux. After 2h, additional KF (0.0020 g, 0.034 mmol) and 18-crown-6 (0.0092 g, 0.035 mmol), were added. The reaction was allowed to proceed for 10 additional hours. Concentration of the reaction mixture and flash chromatography (neutralized silica gel, 3:1 hexanes:ethyl acetate) provided 0.012 g (34%) of **19** as a viscous yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 11.09 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.37 (m, 4H), 7.21 (m, 4H), 4.23 (m, 2H), 3.91 (dd, *J* = 9.2, 6.1 Hz, 1H), 3.76 (partially obscured m, 1 H), 3.69 (s, 3H), 3.68 (m, 1 H), 3.60 (dd, *J* = 14.5, 6.0 Hz, 1 H), 3.46 (s, 3H), 2.49 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 168.9, 168.8, 137.5, 131.1, 130.2, 129.6, 126.0, 125.7, 125.6, 122.3, 120.8, 120.1, 118.9, 112.9, 59.9, 52.8, 52.6, 29.6, 23.8, 14.6; IR (CCl_4) 3238, 3091, 3039, , 2953, 1751, 1750, 1689 cm^{-1}; HRMS calc'd for $C_{26}H_{28}NO_7S$ (M^+) 498.1586, found 498.1579.



22

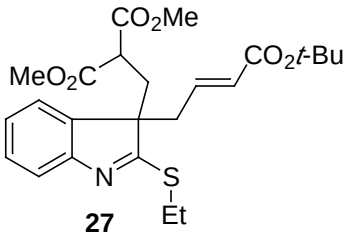
Representative Procedure for the Intermolecular Rhodium-Catalyzed Sulfur Ylide Reaction with 20. Preparation of 22. To a solution of **20** (0.032 g, 0.10 mmol), $Rh_2(OAc)_4$ (0.0041 g, 0.0093 mmol), and benzene (2.0 mL) was added a solution of **10** (0.051 g, 0.33 mmol) and benzene (1.0 mL) over 45 min. Concentration of the reaction mixture and flash chromatography (neutralized silica gel, 1:2 hexanes:ethyl acetate) yielded 0.028 g (61%) of **22** as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 11.22 (s, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.6, Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.17 (m, 4H), 3.89 (dd, *J* = 10.2, 5.2 Hz, 1H), 3.73 (s, 3H), 3.73-3.53 (m, 3H), 3.57 (s, 3H), 3.45 (dd, *J* = 14.5, 5.3 Hz), 2.50 (s, 3H), 1.28 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 193.9, 169.1, 169.0, 166.7, 137.2, 125.5, 125.4, 121.5, 120.6, 119.8, 119.1, 112.6, 59.7, 52.8, 52.5, 52.2, 37.0, 29.6, 23.8, 14.6, 10.0; IR (CCl_4) 3282, 3014, 2962, 1741, 1745, 1689 cm^{-1}; HRMS calc'd for $C_{22}H_{28}NO_7S$ (M^+) 450.1586, found 450.1589.



23

Preparation of 23. As described for the synthesis of **22**, indole **20** (0.074 g, 0.23 mmol), **21** (0.085 g, 0.54 mmol), $Rh_2(OAc)_4$ (0.0070 g, 0.016 mmol) and benzene (2.0 mL) were

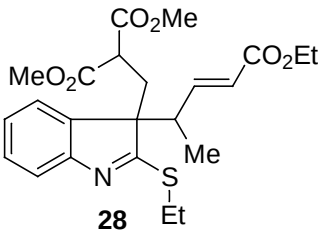
used. Flash chromatography (neutralized silica gel, 1:5 hexanes:ethyl acetate) provided 0.098 g (94%) of **23** as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 10.88 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.31 (t, *J* = 7.6, Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 4.08 (m, 1H), 3.90 (dd, *J* = 10.3, 5.0 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 6H), 3.75-3.41 (m, 4 H), 3.56 (s, 3H), 1.30 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 169.1, 169.0, 137.3, 125.7, 125.4, 121.9, 120.8, 120.0, 119.1, 112.5, 60.3, 52.9, 52.6, 52.1, 51.4, 38.0, 23.8, 9.8; IR (CCl_4) 3230, 2979, 2962, 1755, 1750, 1689 cm^{-1}; HRMS calc'd for $C_{21}H_{26}NO_8S$ (M^+) 452.1379, found 452.1379.



27

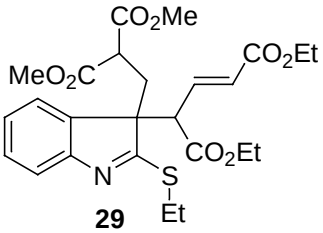
Representative Procedure for the Conjugate Addition of Indole 20 to Vinyl Diazo Compounds. Preparation of 27. To a solution of **20** (0.019 g, 0.059 mmol), $Rh_2(OAc)_4$ (0.0023 g, 0.0052 mmol) and benzene (1.2 mL) at reflux was added **24** (0.040 g, 0.24 mmol) and benzene (1.0 mL) over 45 min. Concentration and flash chromatography (neutralized silica gel, 2:1 hexanes:ethyl acetate) provided 0.024 g (88%) of **27** as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.43 (d, J = 7.7 Hz, 1H), 7.26 (m, 1H), 7.09 (m, 2H), 6.14 (ddd, 1H), 5.64 (dd, *J* = 15.4, 1.0 Hz, 1H), 3.63 (s, 3H), 3.16 (s, 3H), 3.11-3.88 (m, 2H), 2.73 (m, 3H), 2.48 (m, 2H), 1.40 (partially obscured t, *J* = 7.4 Hz, 3H), 1.36 (s, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 183.2, 169.3, 169.0, 165.0, 155.4, 140.0, 138.3, 128.7, 126.8, 124.0, 123.2, 118.9, 80.2, 61.4, 52.7, 52.3, 47.4, 41.2, 35.2, 28.0,

25.1, 14.3; IR (CCl_4) 3100, 3039, 2988, 2953, 1759, 1755.0, 1724.0 cm^{-1}; HRMS calc'd for $C_{24}H_{32}NO_6S$ (MH^+) 462.1950, found 462.1953.



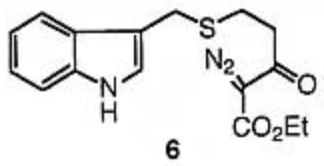
28

Preparation of 28. As described for the synthesis of **27**, indole **20** (0.042 g, 0.13 mmol), $Rh_2(OAc)_4$ (0.0039 g, 0.0088 mmol), **25** (0.080 g, 0.52 mmol) and benzene (2.6 mL) were used. Flash chromatography (neutralized silica gel, 2:1 hexanes:ethyl acetate) provided 0.054 g (93%) of thioimidate **28** as a 2:1 mixture of diastereomers as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.42 (t, *J* = 6.7 Hz, 3H), 7.27 (m, 3H), 7.06 (m, 7H), 6.41 (dd, *J* = 15.5, 9.3 Hz, 1H), 5.93 (d, *J* = 15.6 Hz, 2H), 5.80 (d, *J* = 15.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 4H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 12H), 3.26 (m, 6H), 3.14 (s, 4H), 3.10 (s, 6H), 2.74 (m, 10H), 2.36 (m, 2H), 1.42 (t, *J* = 7.4 Hz, 6H), 1.36 (t, *J* = 7.6 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 6H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.49 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 183.5, 183.2, 169.4, 169.2, 169.1, 166.0, 165.9, 156.1, 155.8, 147.4, 147.1, 137.5, 136.4, 128.8, 128.7, 124.5, 123.9, 123.8, 123.7, 123.1, 118.9, 118.8, 64.8, 60.5, 60.2, 52.7, 52.3, 52.2, 47.6, 47.5, 44.4, 44.3, 34.6, 33.9, 25.3, 25.1, 14.7, 14.2, 14.1, 13.9; IR (CCl_4) 3100, 3039, 2953, 2927, 1759, 1755, 1724 cm^{-1}; HRMS calc'd for $C_{23}H_{29}N\ O_6S$ (M^+) 447.1716, found 447.1713.



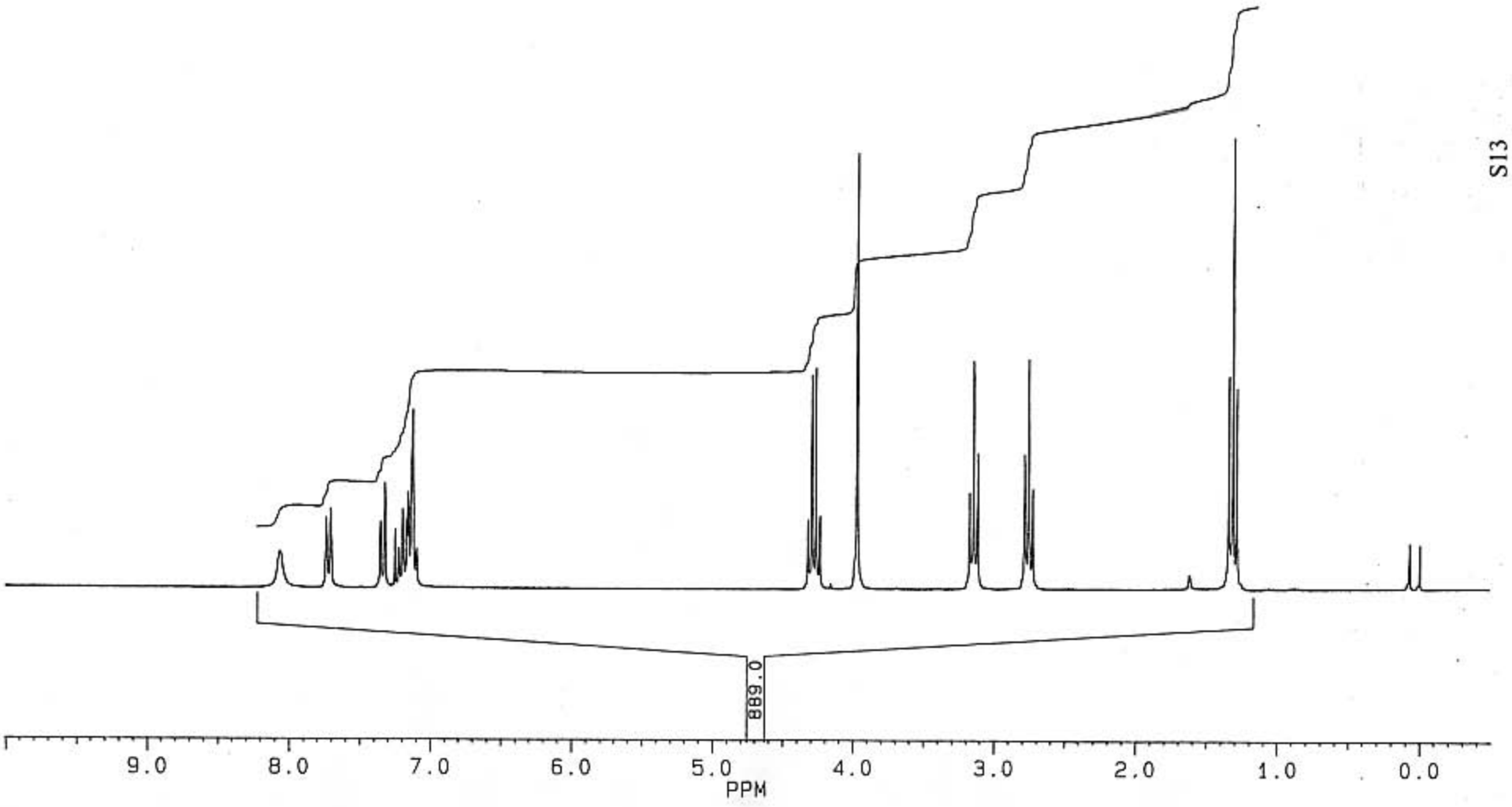
29

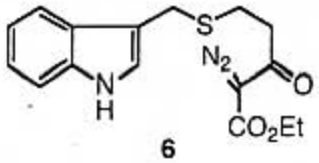
Preparation of 29. As described for the synthesis of **27**, indole **20** (0.041 g, 0.13 mmol), $Rh_2(OAc)_4$ (0.0046 g, 0.010 mmol), **26** (0.11 g, 0.52 mmol), and benzene (2.5 mL) were used. Flash chromatography (neutralized silica gel, 2:1 hexanes:ethyl acetate) provided 0.053 g (82%) of thioimidate **29** as a 2:1 mixture of diastereomers as a colorless oil. Thioimidate **29** proved to be somewhat unstable to chromatographic purification. ^{1}H NMR (250 MHz, $CDCl_3$) δ; 7.41 (t, *J* = 7.2 Hz, 3H), 7.31-7.01 (m, 7H), 6.33 (dd, *J* = 15.5, 9.9 Hz, 1H), 6.02 (d, *J* = 15.6 Hz, 2H), 5.86 (d, *J* = 15.7 Hz, 1H), 4.14 (m, 12H), 3.76 (m, 6H), 3.58 (m, 10H), 3.33 (m, 6H), 3.14 (s, 3H), 3.13 (s, 3H), 2.71 (m, 6H), 2.31 (dd, *J* = 13.8, 1.8 Hz, 2H), 1.29 (m, 18H), 0.86 (t, *J* = 7.1 Hz, 6H), 0.78 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 182.3, 181.4, 170.7, 169.1, 169.0, 168.8, 167.8, 165.2, 165.1, 155.8, 155.7, 139.6, 139.1, 136.3, 135.6, 134.7, 129.2, 129.1, 127.2, 126.0, 125.4, 124.5, 123.9, 123.4, 119.0, 118.9, 118.7, 63.9, 63.2, 62.6, 61.6, 61.1, 61.0, 60.8, 60.6, 60.4, 56.0, 55.1, 52.8, 52.7, 52.3, 47.3, 47.0, 46.8, 35.1, 34.1, 34.0, 33.4, 25.5, 25.3, 14.2, 14.1, 14.0, 13.5; IR (CCl_4) 3091, 3039, 2988, 2962, 1750, 1655 cm^{-1}; HRMS calc'd for $C_{25}H_{22}NO_8S$ (M^+) 506.1849, found 506.1857.



6

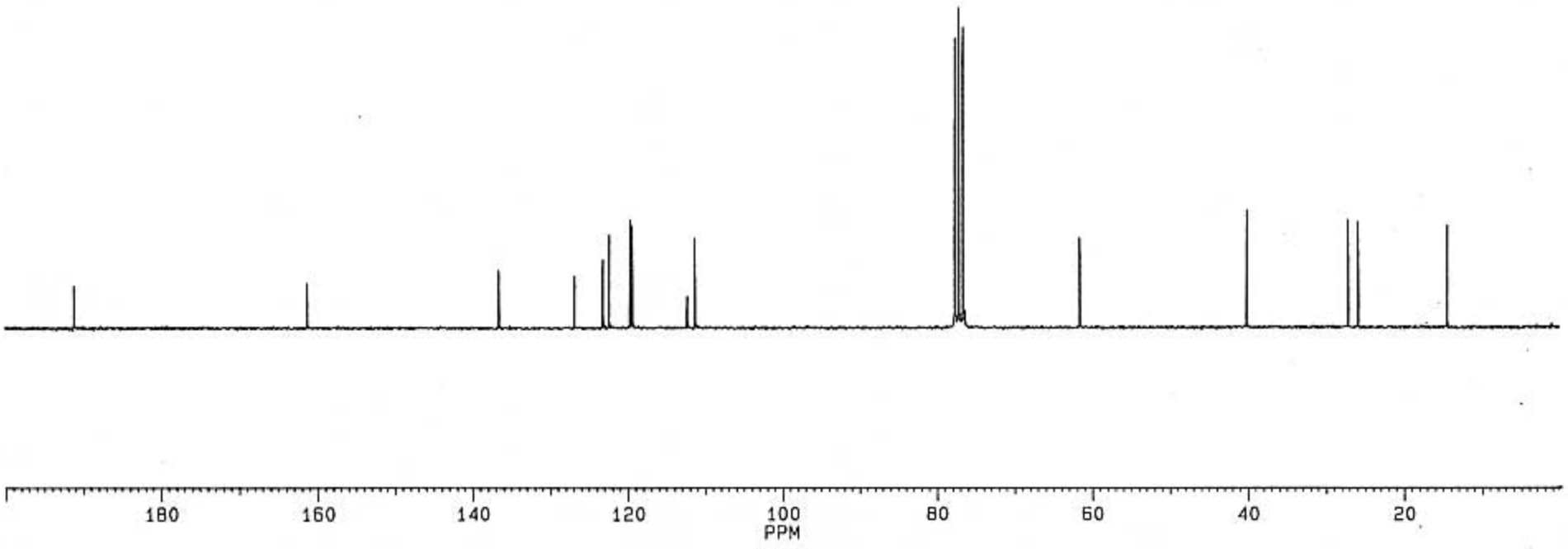
^{1}H NMR, 250 MHz
$CDCl_3$

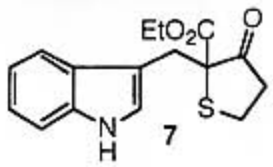




6

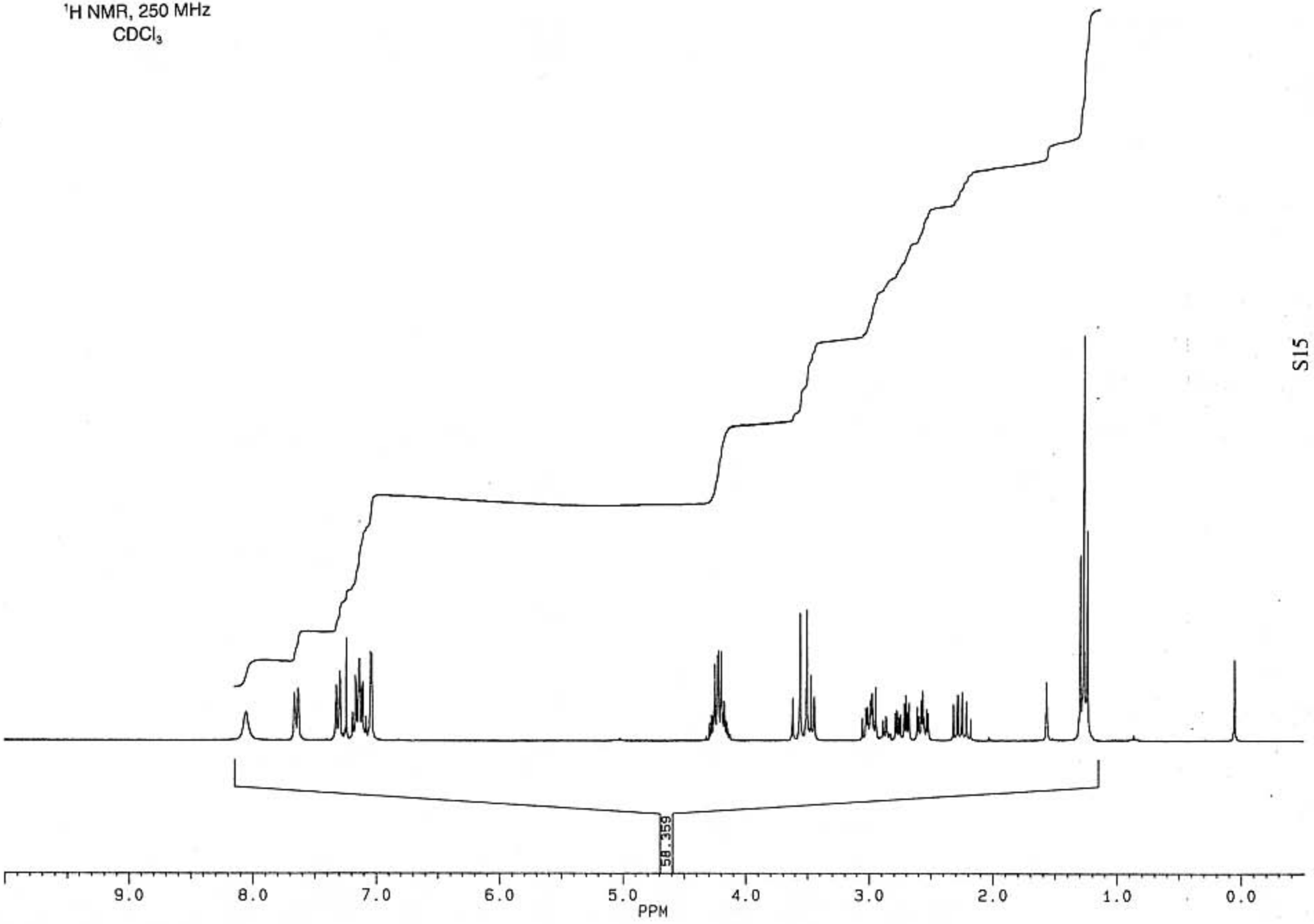
^{13}C NMR, 62.5 MHz
$CDCl_3$

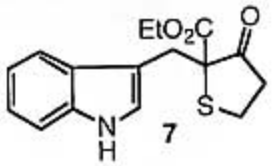




7

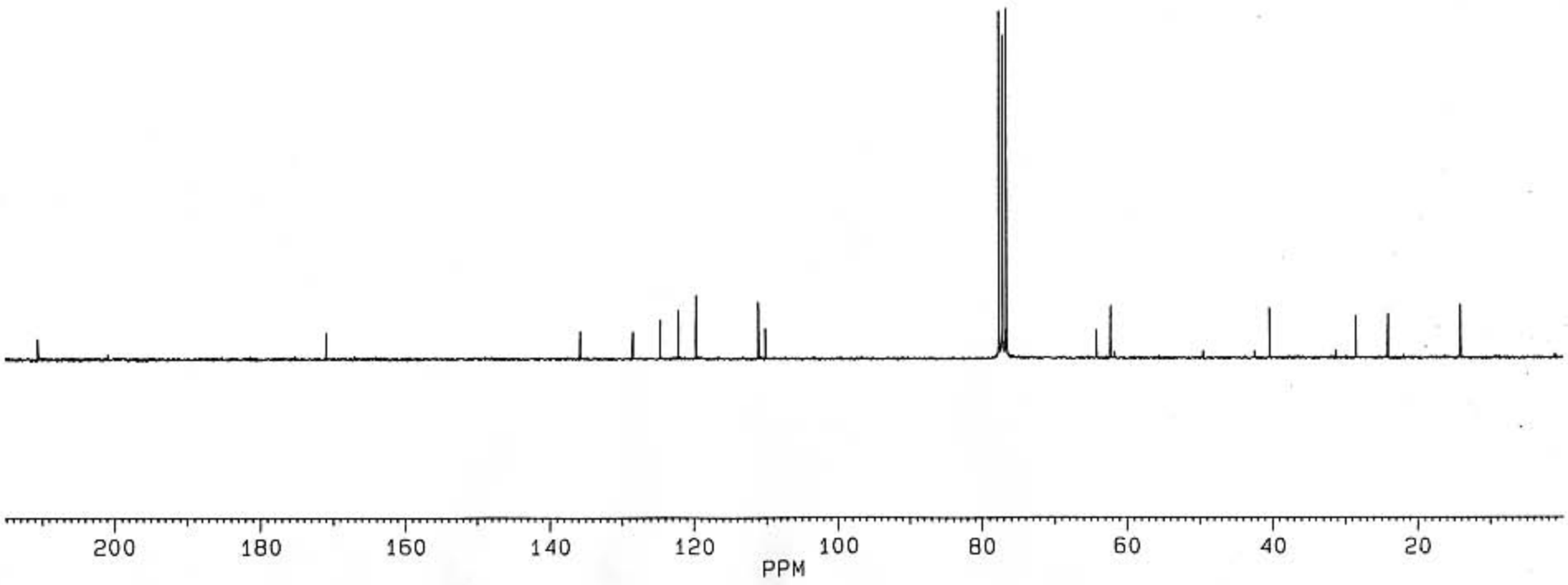
^{1}H NMR, 250 MHz
$CDCl_3$

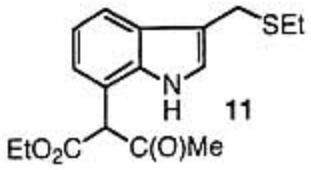




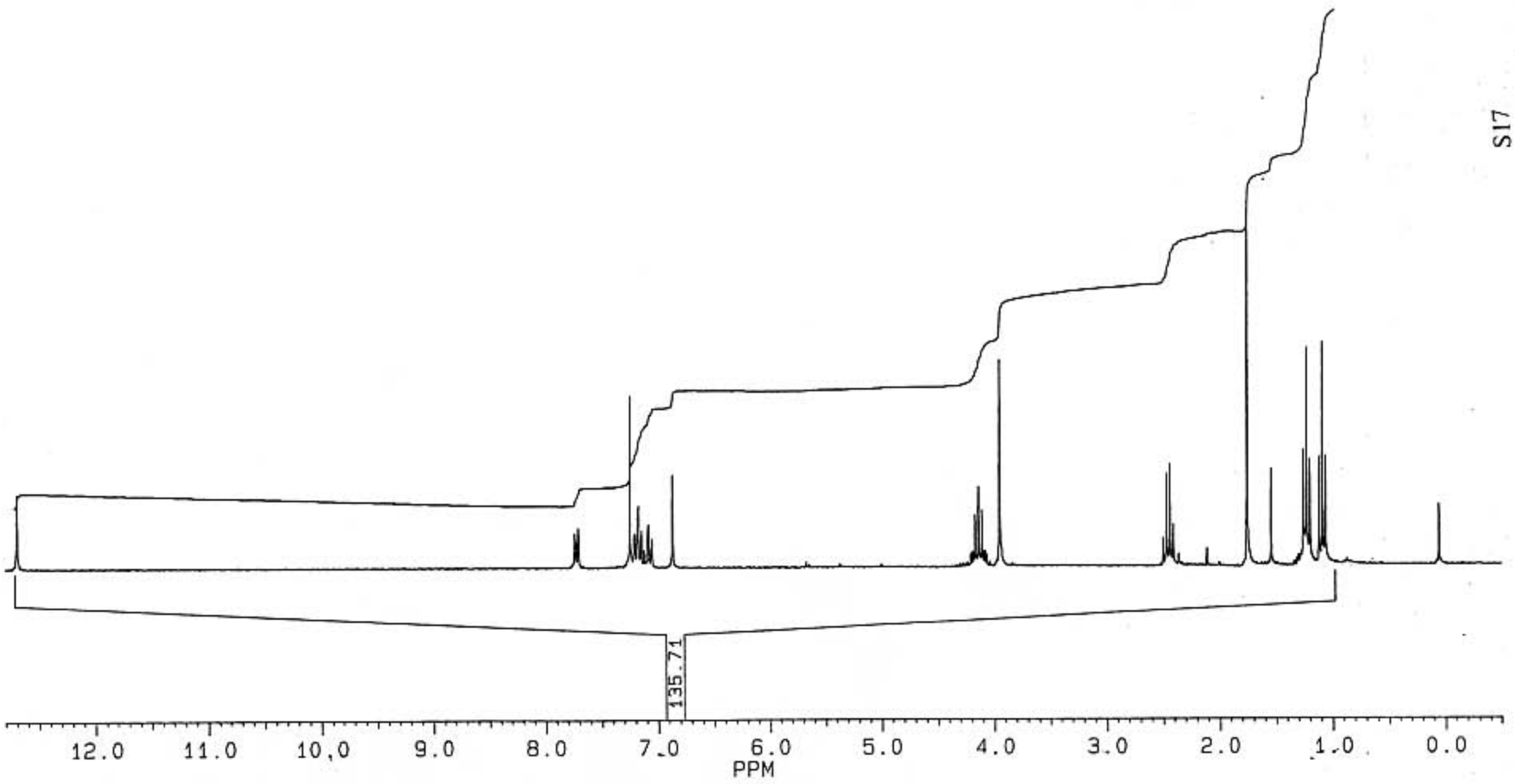
7

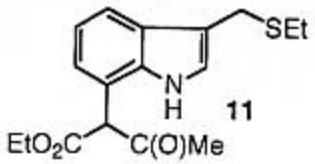
^{13}C NMR, 62.5 MHz
$CDCl_3$



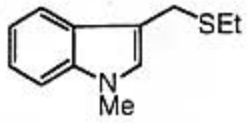


^{1}H NMR, 250 MHz
$CDCl_3$



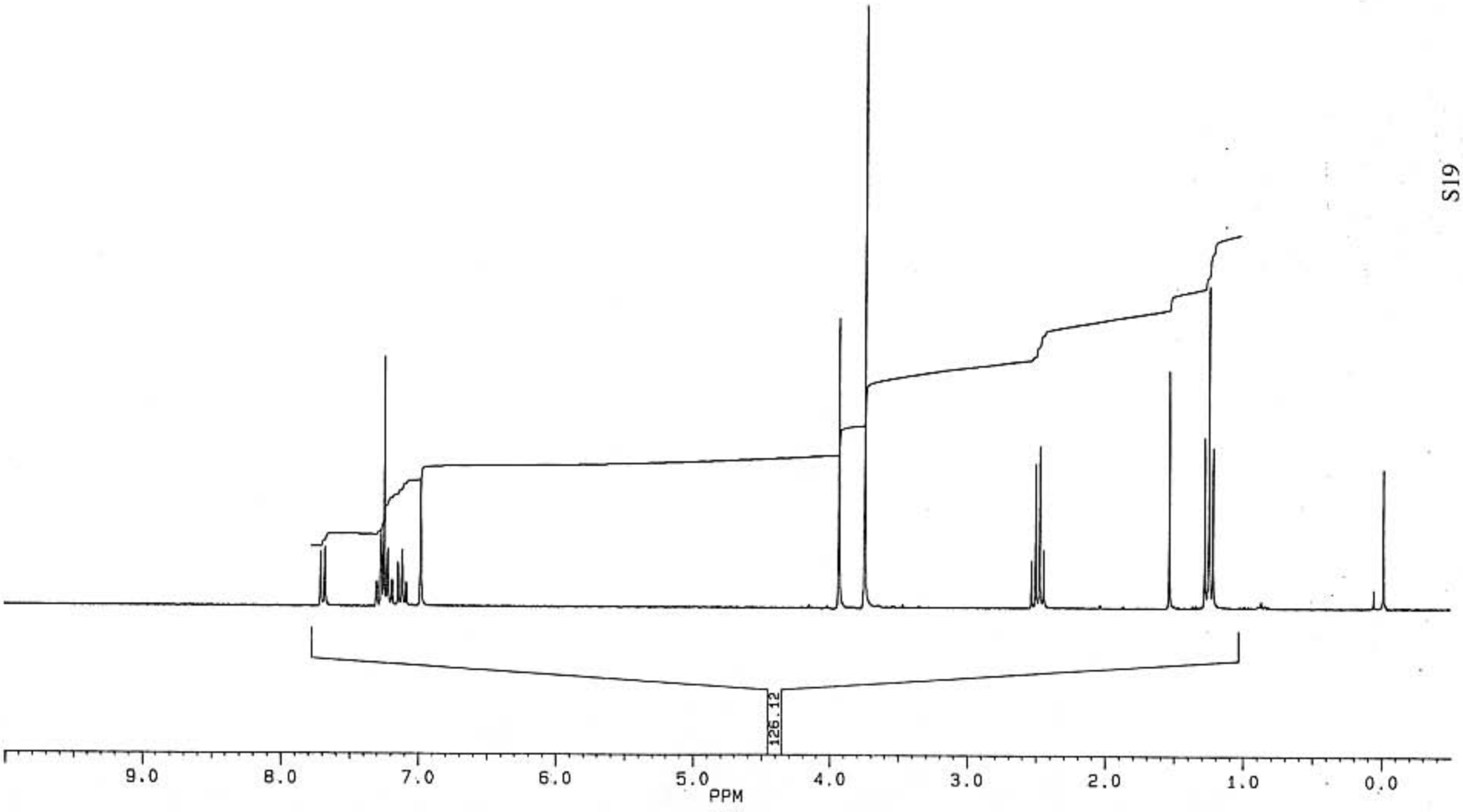


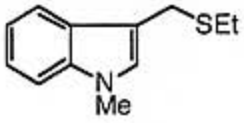
^{13}C NMR, 62.5 MHz
$CDCl_3$



12

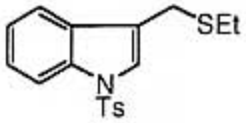
^{1}H NMR, 250 MHz
$CDCl_3$





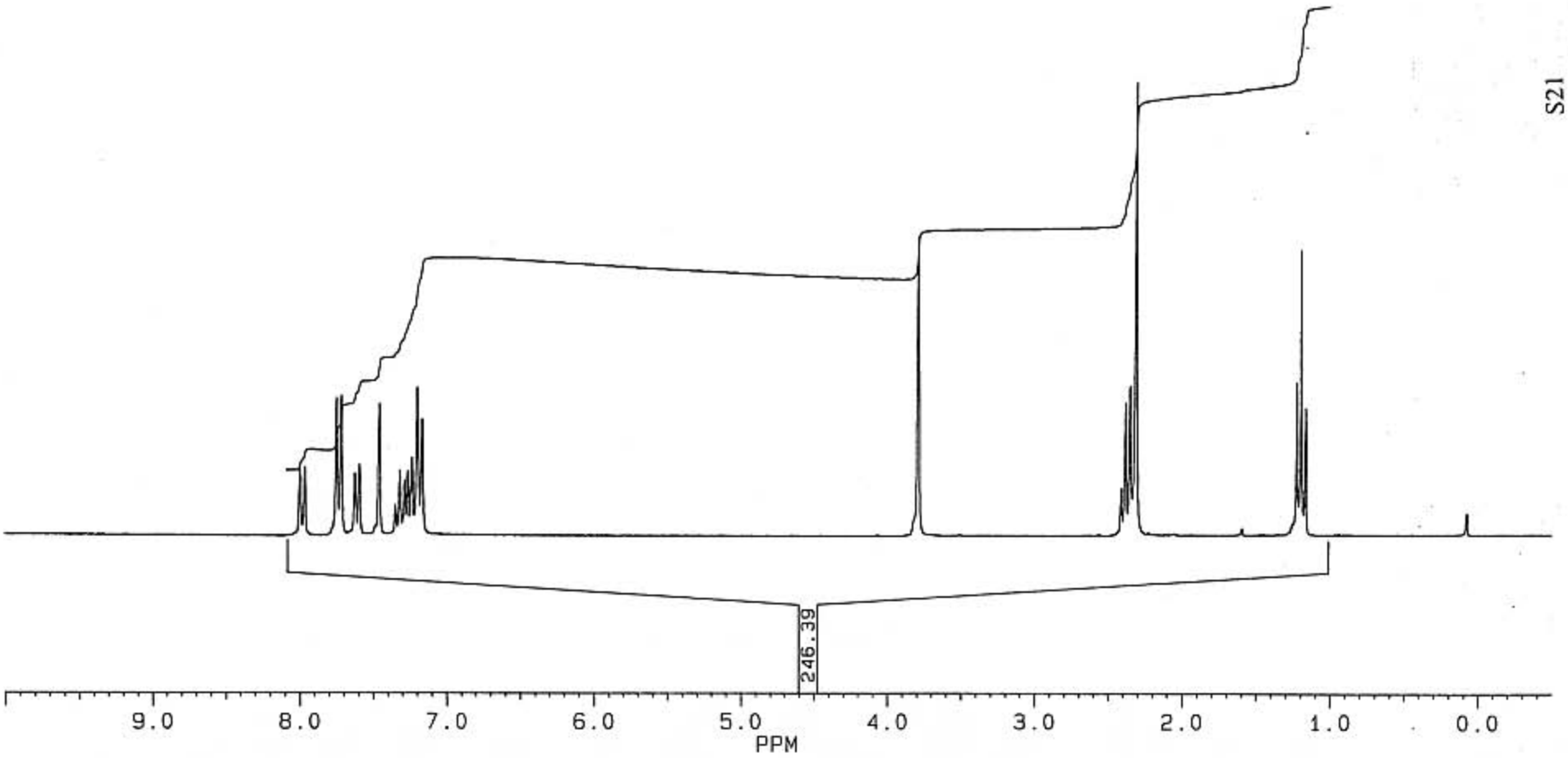
12

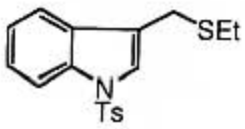
^{13}C NMR, 62.5 MHz
$CDCl_3$



13

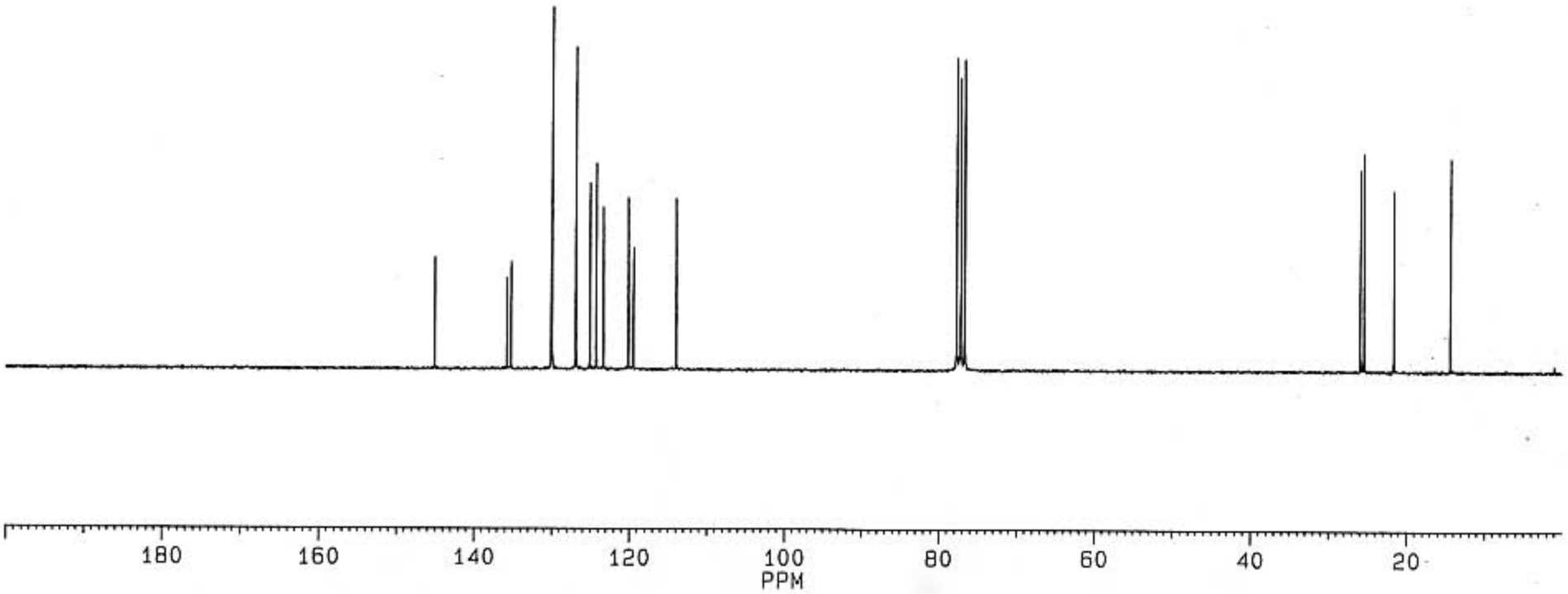
^{1}H NMR, 250 MHz
$CDCl_3$

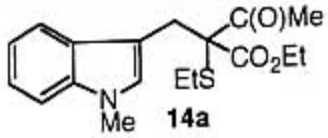




13

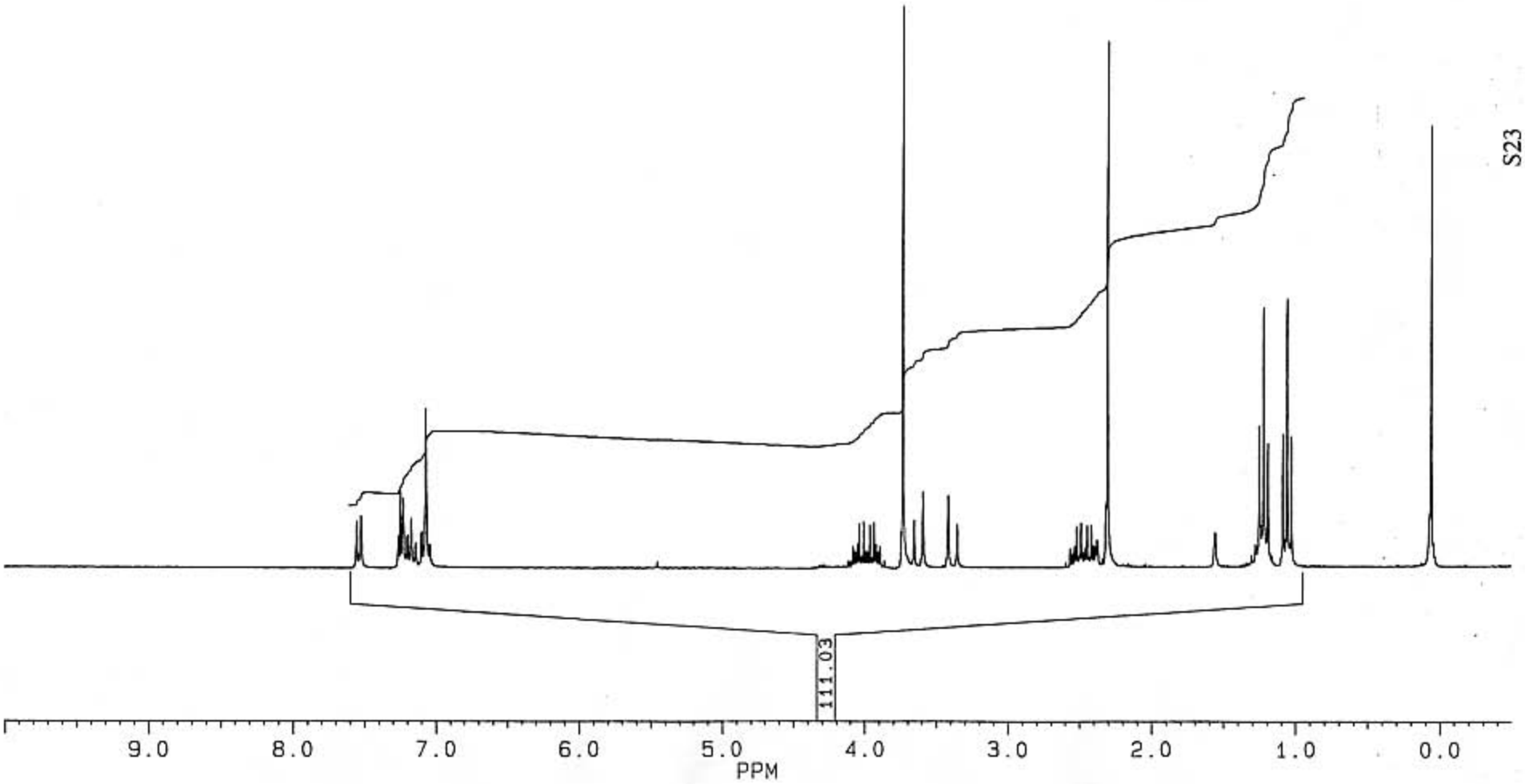
^{13}C NMR, 62.5 MHz
$CDCl_3$

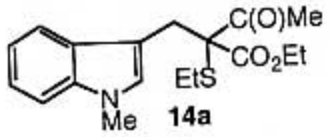




14a

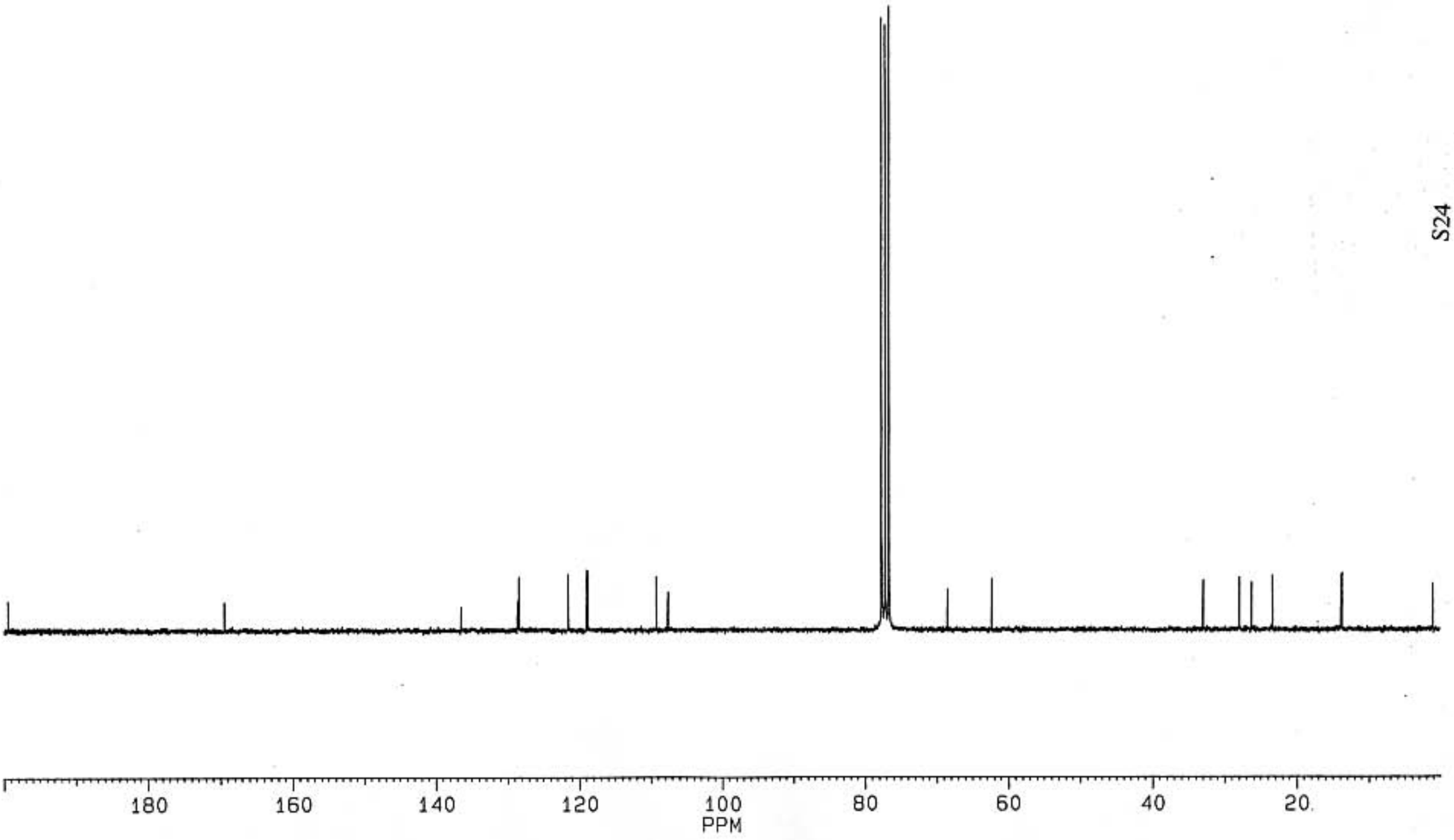
^{1}H NMR, 250 MHz
$CDCl_3$

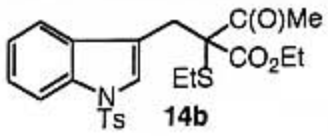




14a

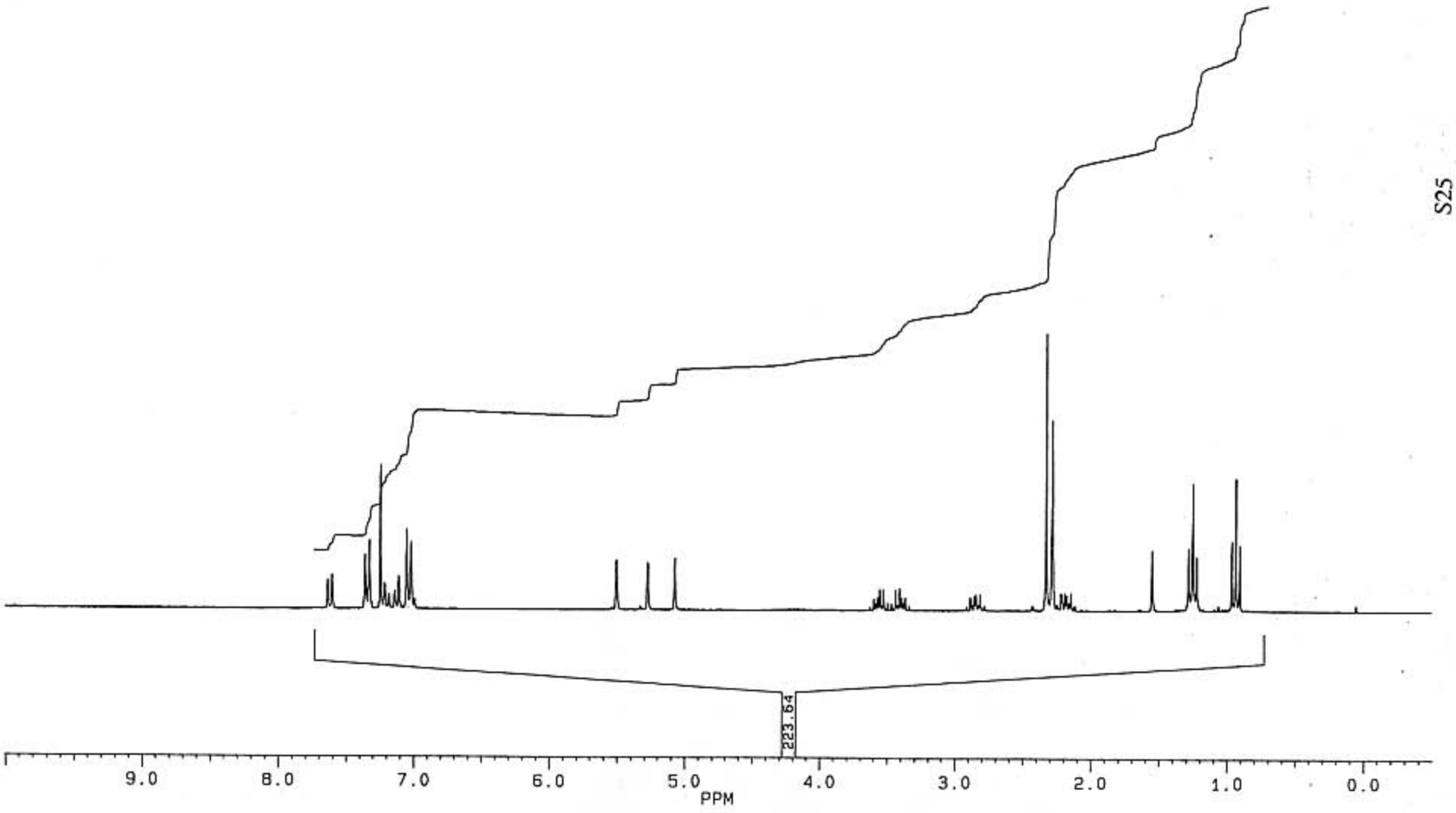
^{13}C NMR, 62.5 MHz
$CDCl_3$

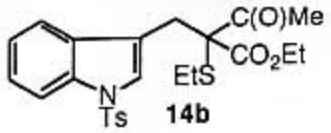




14b

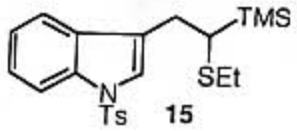
^{1}H NMR, 250 MHz
$CDCl_3$





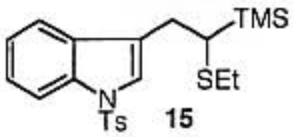
14b

^{13}C NMR, 62.5 MHz
$CDCl_3$



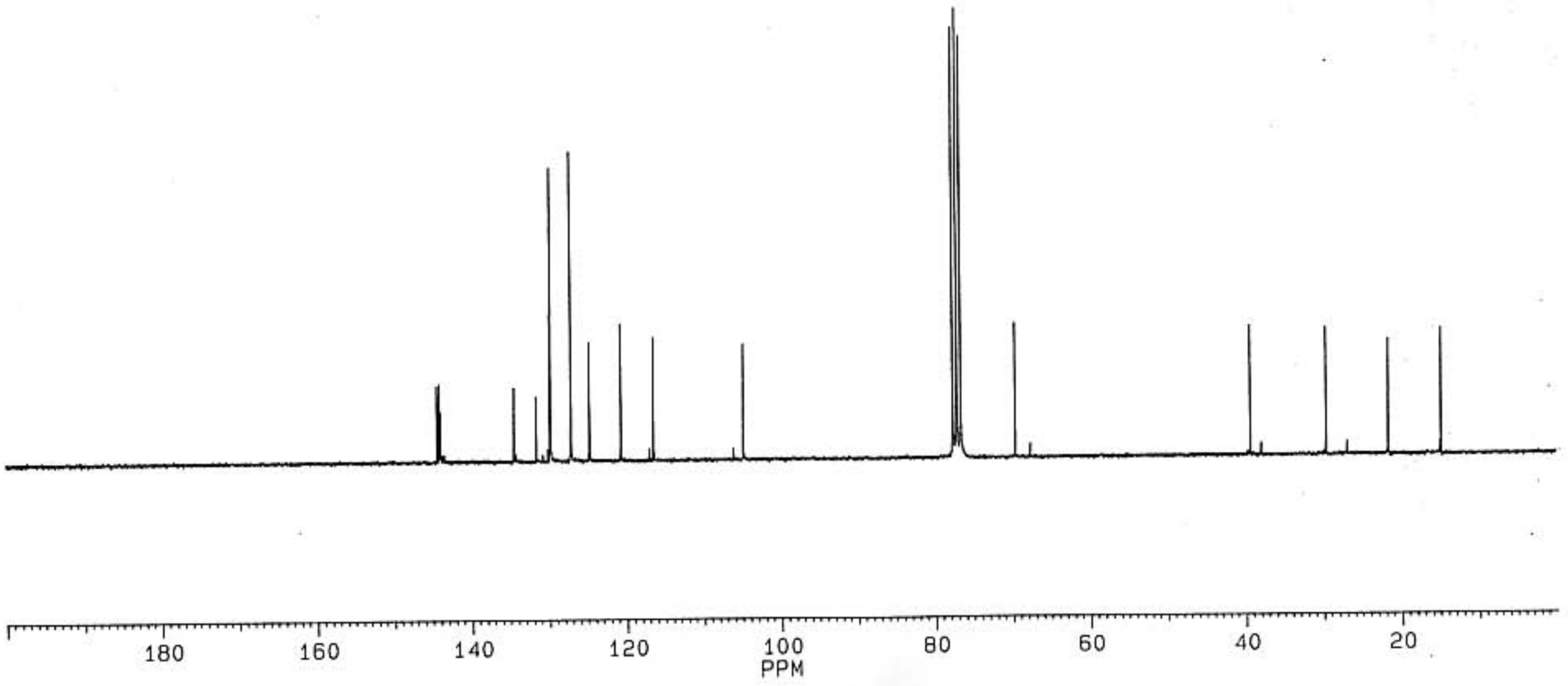
15

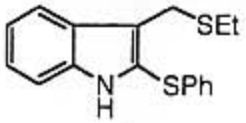
^{1}H NMR, 250 MHz
$CDCl_3$



15

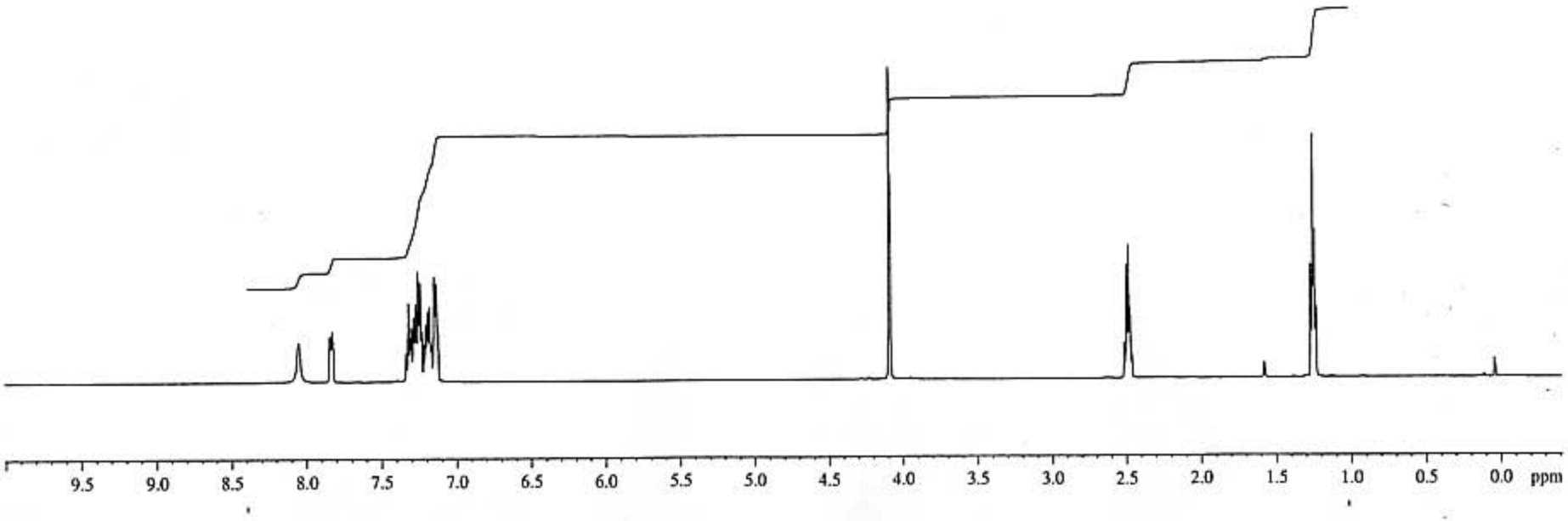
^{13}C NMR, 62.5 MHz
$CDCl_3$

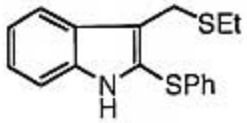




16

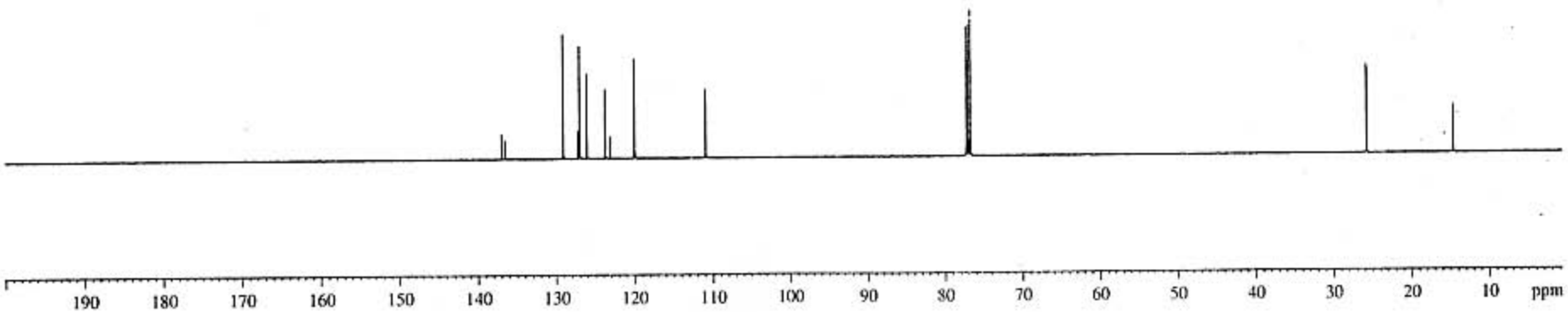
^{1}H NMR, 500 MHz
$CDCl_3$

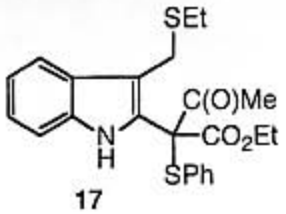




16

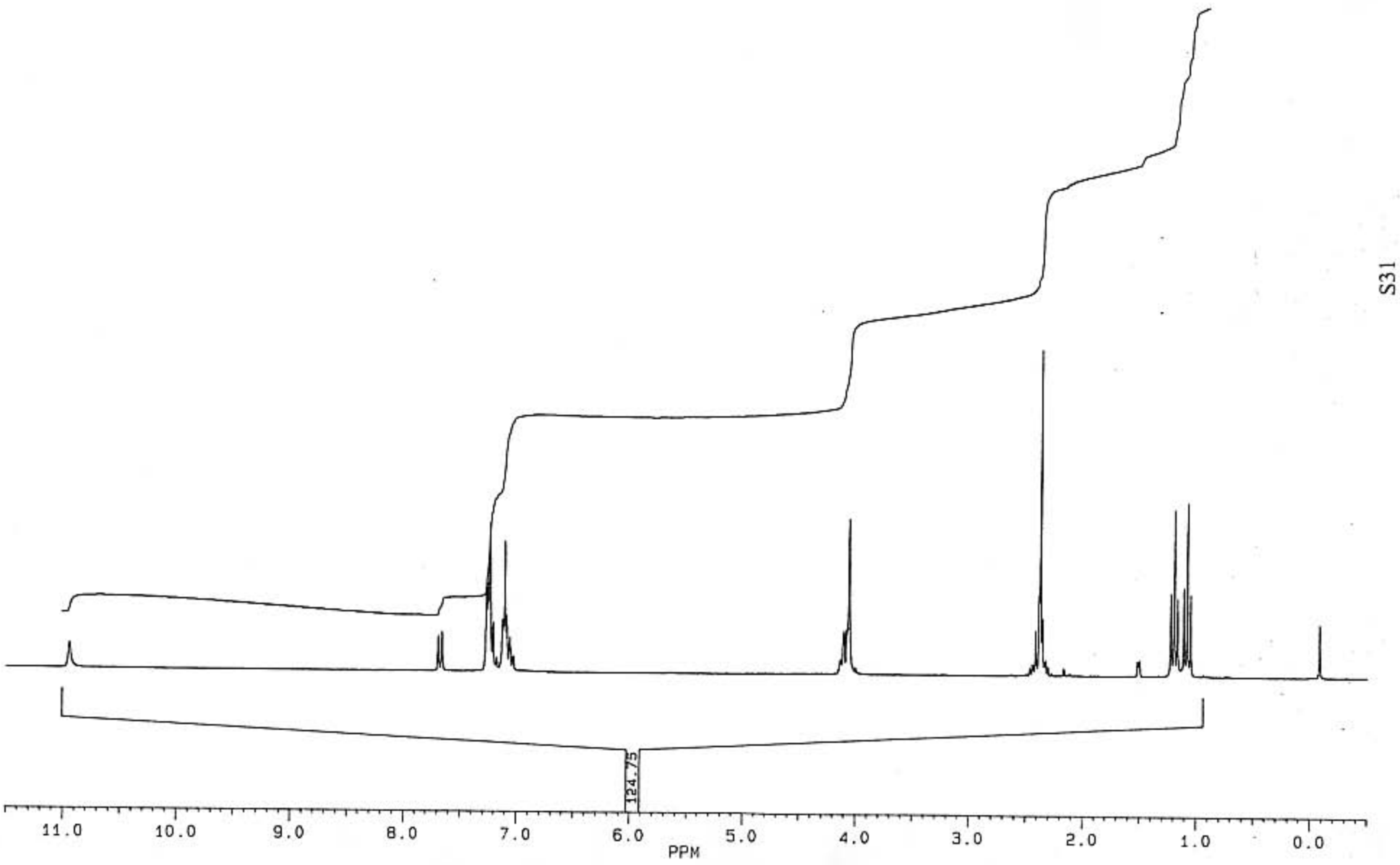
^{13}C NMR, 125 MHz
$CDCl_3$

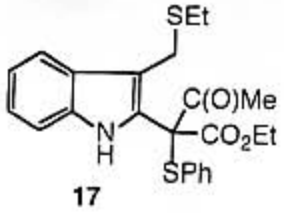




17

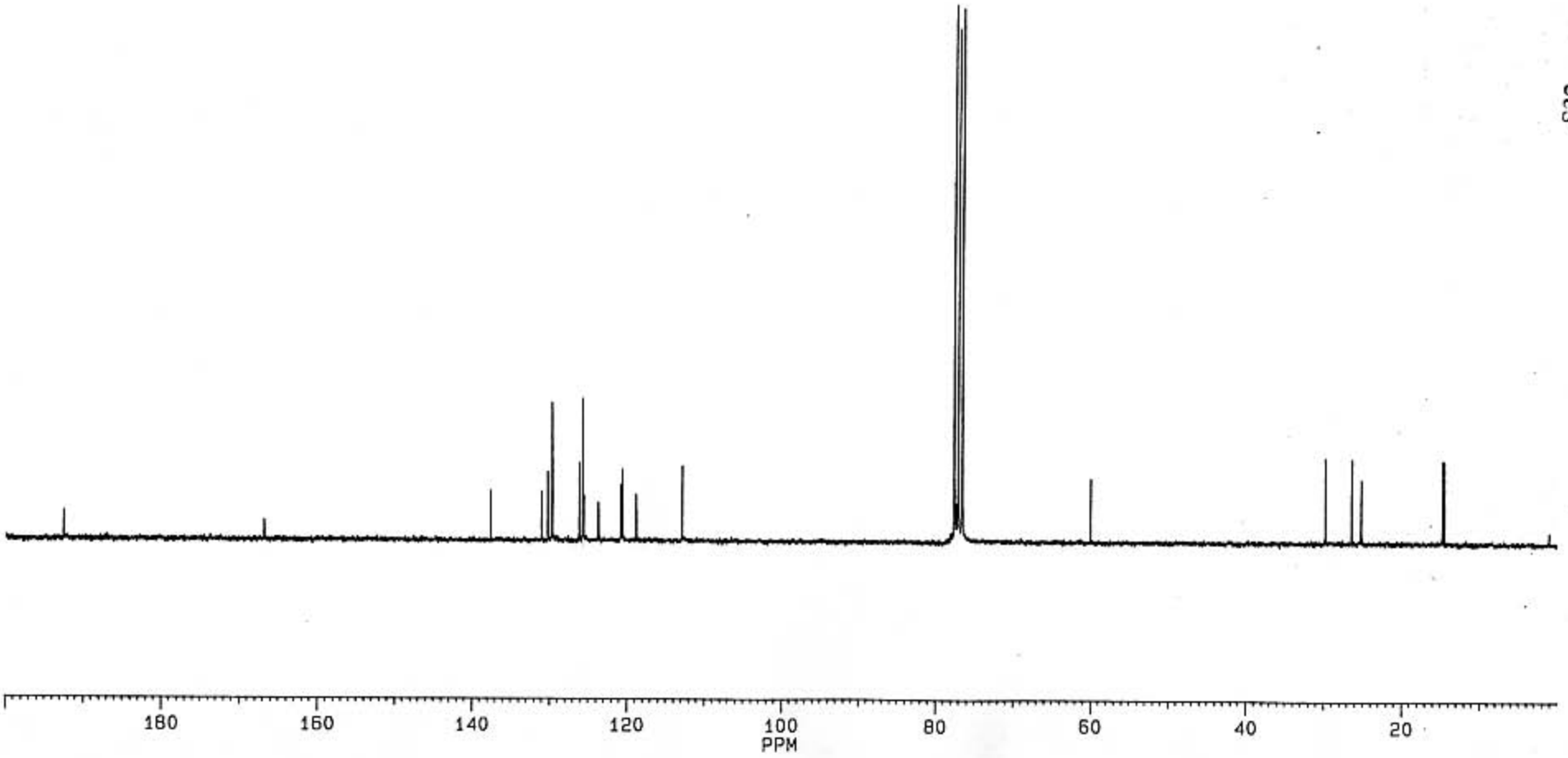
^{1}H NMR, 250 MHz
$CDCl_3$

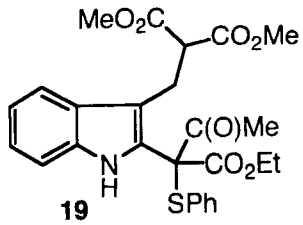




17

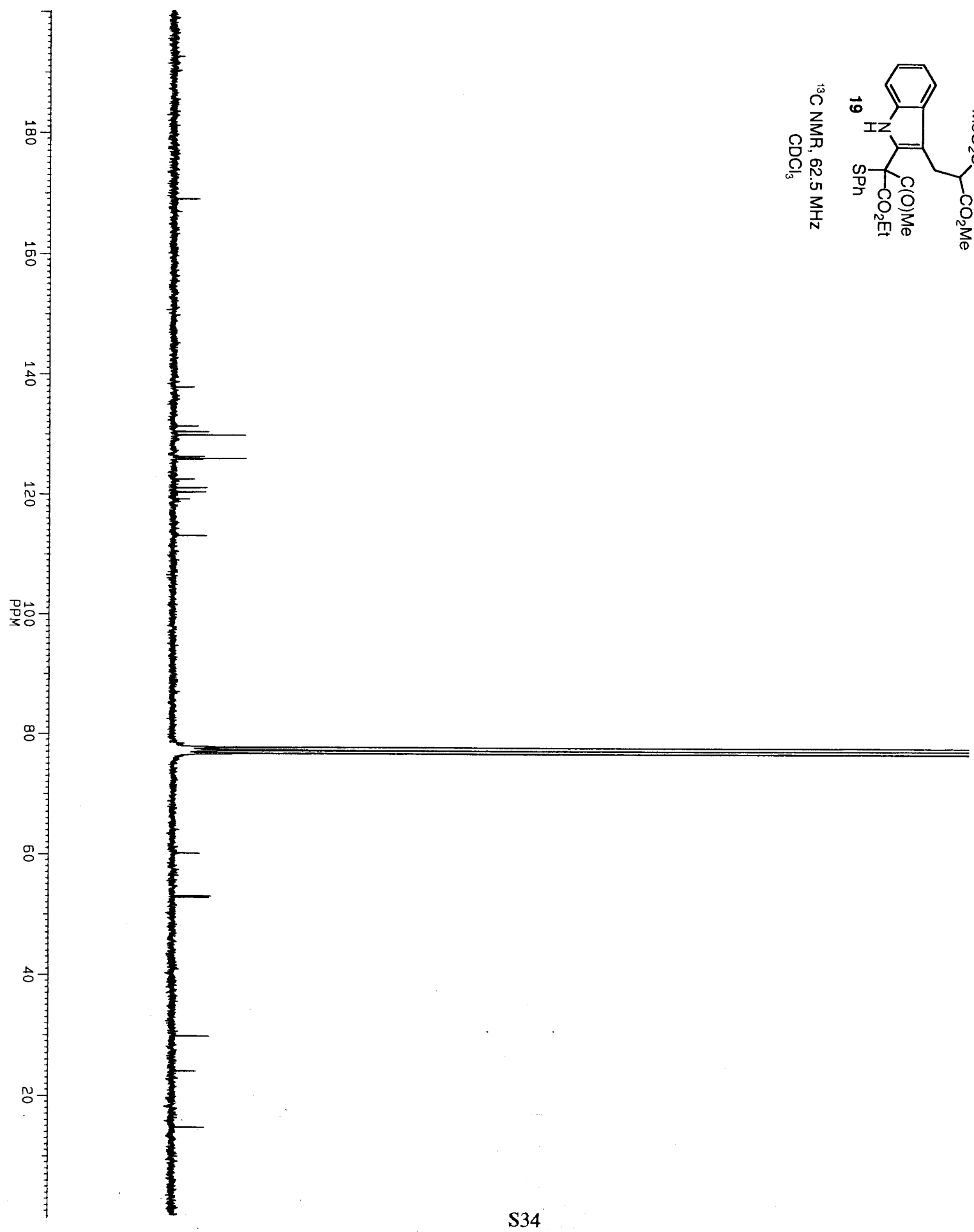
^{13}C NMR, 62.5 MHz
$CDCl_3$

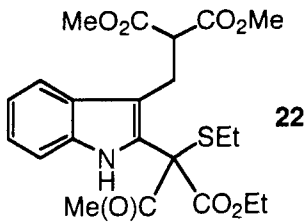




19

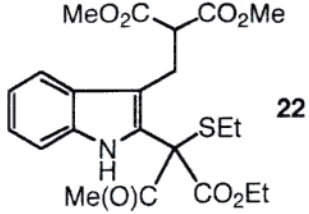
^{1}H NMR, 250 MHz
$CDCl_3$


MeO2C
CO2Me
19
N
H
C(O)Me
CO2Et
SPh
13C NMR, 62.5 MHz
CDCl3
180
160
140
120
100
80
60
40
20
PPM



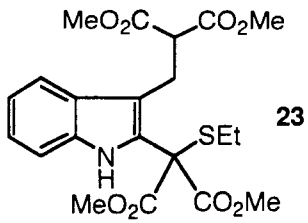
22

^{1}H NMR, 250 MHz
$CDCl_3$



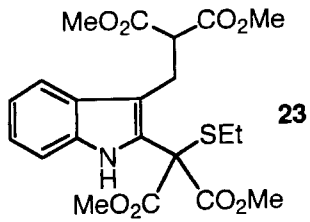
22

^{13}C NMR, 62.5 MHz
$CDCl_3$



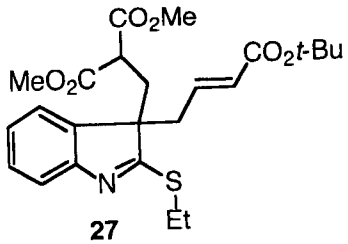
23

^{1}H NMR, 250 MHz
$CDCl_3$



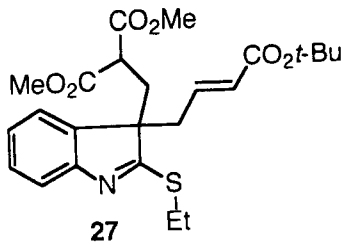
23

^{13}C NMR, 62.5 MHz
$CDCl_3$



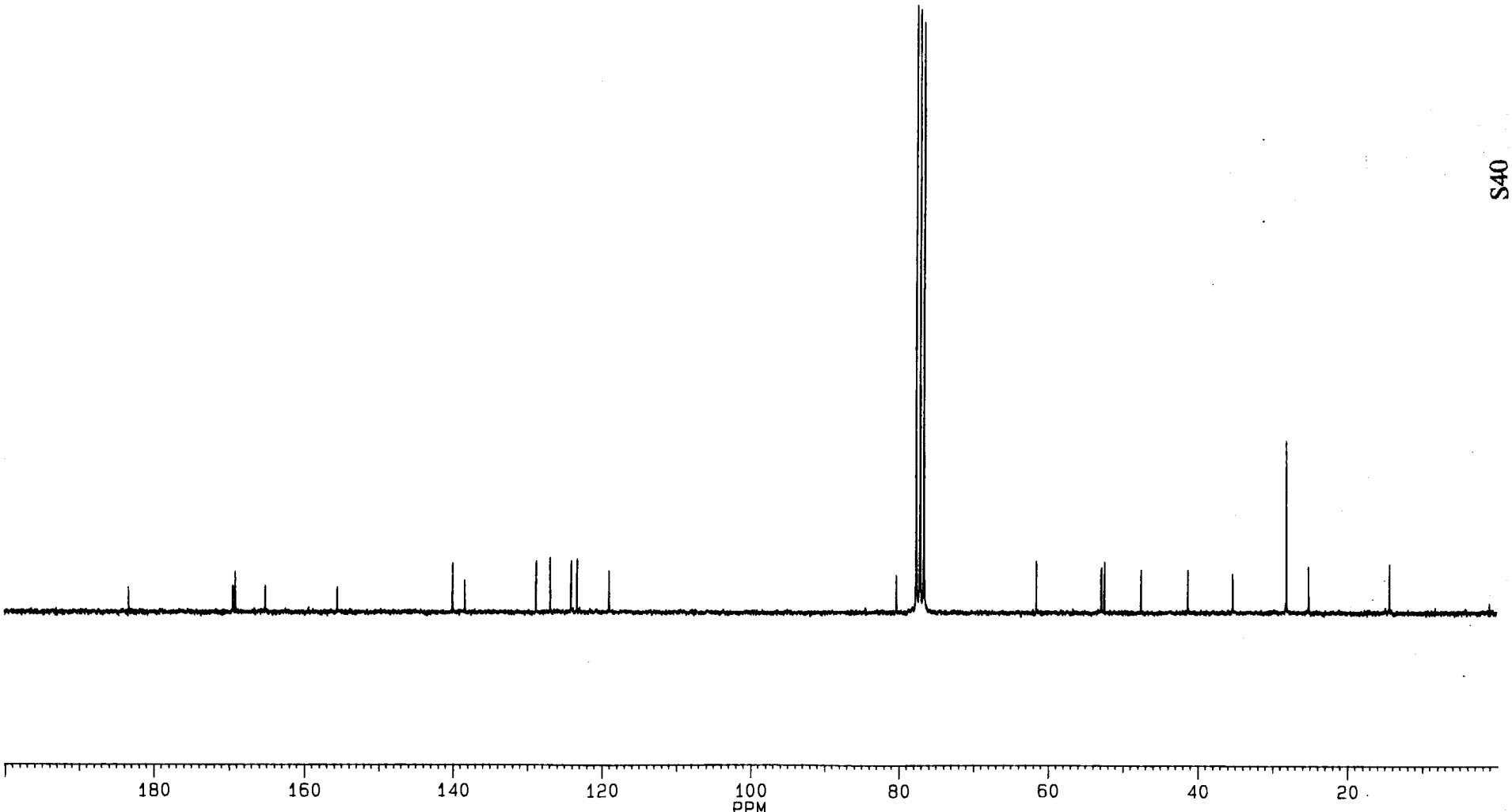
27

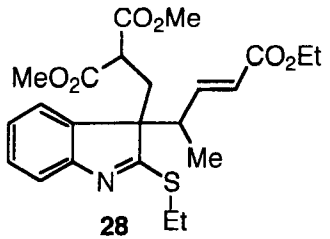
^{1}H NMR, 250 MHz
$CDCl_3$



27

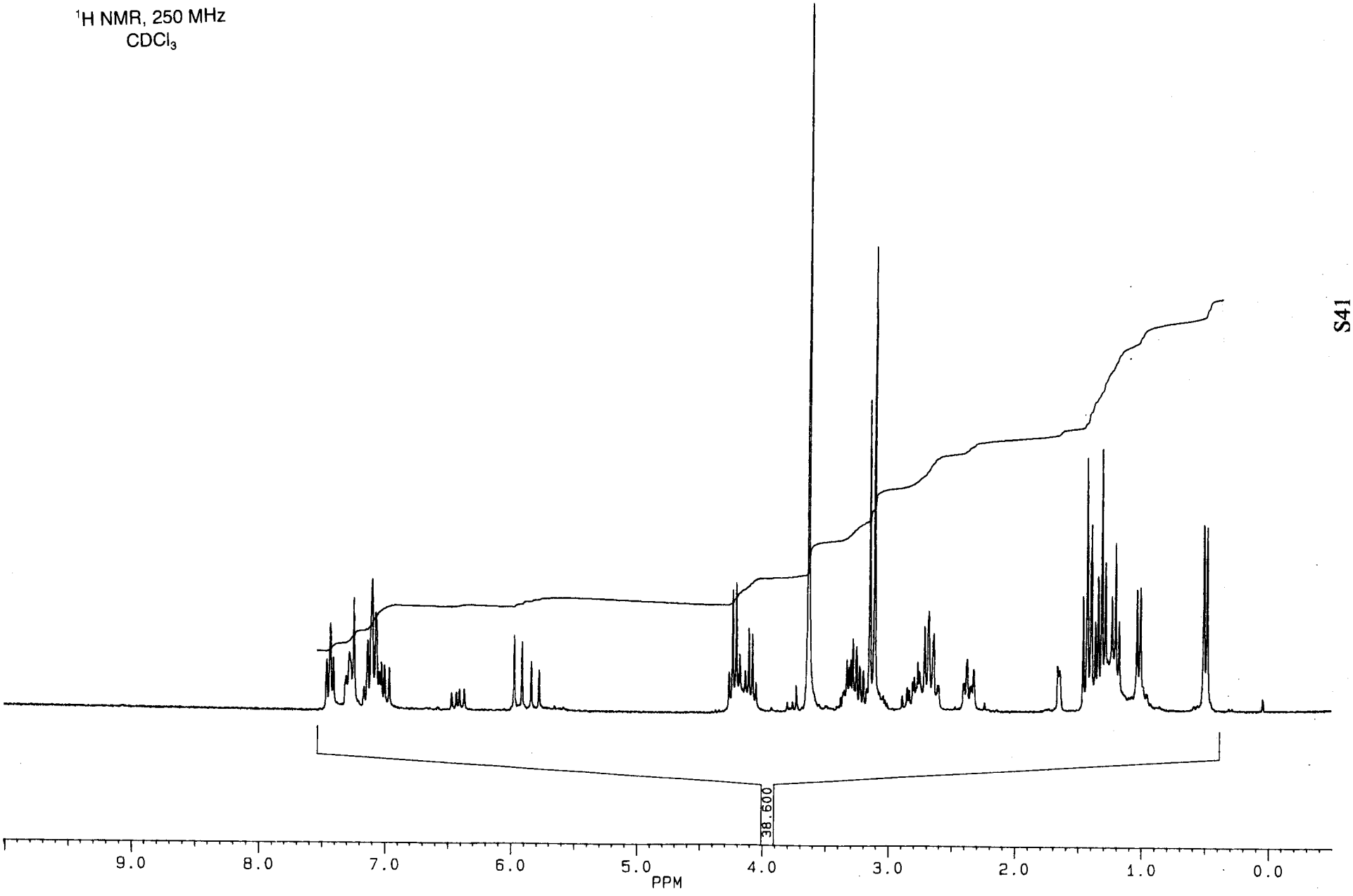
^{13}C NMR, 62.5 MHz
$CDCl_3$

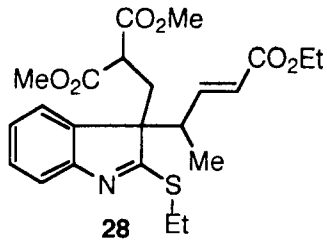




28

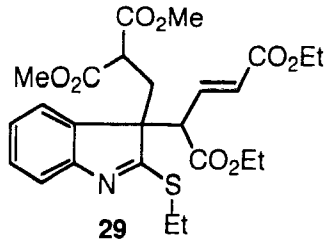
^{1}H NMR, 250 MHz
$CDCl_3$





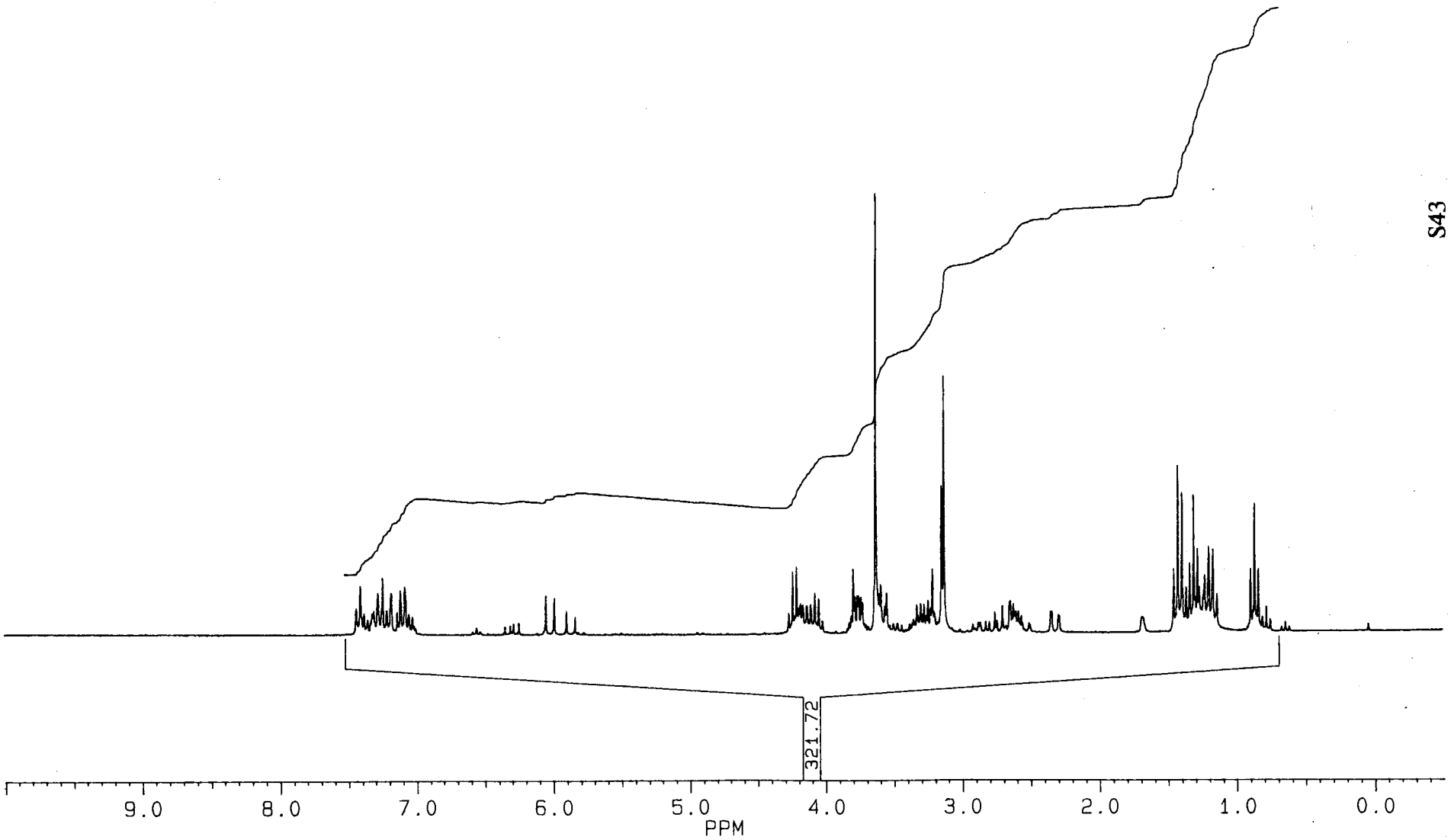
28

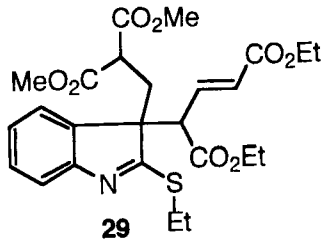
^{13}C NMR, 62.5 MHz
$CDCl_3$



29

^{1}H NMR, 250 MHz
$CDCl_3$





29

^{13}C NMR, 62.5 MHz
$CDCl_3$