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Supplementary Information

Acid-Promoted Cycloisomerization of Phenylallenes Bearing Acetalic Functions at *ortho* Position: a Stereocontrolled Entry to Indeno-Fused Dioxepanes, Dioxocanes and Thioanalogues

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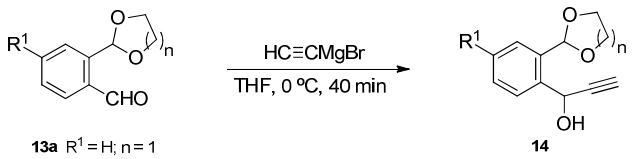
General Methods

All melting points are uncorrected. Infrared (IR) spectra were recorded as Nujol emulsions or neats.[1]H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at 300 or 400 MHz. ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at 75 or 100 MHz. The chemical shifts are expressed in ppm, relative to Me_4Si at δ = 0.00 ppm for ^1H, while the chemical shifts for ^{13}C are reported relative to the resonance of $CDCl_3$ δ = 77.1 ppm or CD_2Cl_2 δ = 54.0 ppm. Mass spectra were recorded on a HPLC/MS TOF 6220 Agilent Technologies apparatus.

Materials: 2-(1,3-Dioxolan-2-yl)benzaldehyde **13a**,[1] 2-(1,3-dioxolan-2-yl)-4-methoxybenzaldehyde **13b,**[2] 2-(1,3-dioxan-2-yl)benzaldehyde **13c**[3], 2-(2-bromophenyl)-1,3-oxathiolane **17**[4] and 2-(dimethoxymethyl)benzaldehyde **21**[5] were prepared following published experimental procedures.

General procedure for the preparation of the propargylic alcohols 14



13a R^1 = H; n = 1
13b R^1 = OCH_3; n = 1
13c R^1 = H; n = 2

14

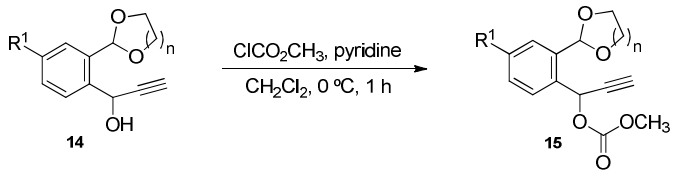
To a solution of the 2-(1,3-dioxolan-2-yl)benzaldehyde or 2-(1,3-dioxan-2-yl)benzaldehyde **13** (3 mmol) in anhydrous THF (30 mL) at 0 ºC was added 0.5 M solution of ethynylmagnesium bromide in THF (6 mL, 3 mmol). The reaction mixture was stirred at 0 °C for 40 min. Then, saturated aqueous solution of NH_4Cl (10 mL) was added. The mixture was extracted with dichloromethane (2 × 30 mL). The organic layers were combined, washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by silica gel column chromatography.

Propargylic alcohol 14a (R^1 = H, n = 1): (hexanes/diethyl ether 1:1); (0.66 g, 99%); yellow oil; δ_H (300 MHz; $CDCl_3$) 2.65 (d, *J*= 2.5 Hz, 1H), 3.79 (br s, 1H), 3.98-4.07 (m, 2H), 4.08-4.17 (m, 2H), 5.81 (s, 1H), 6.14 (br s, 1H), 7.32-7.44 (m, 2H), 7.56 (dd, *J*= 1.8, 7.3 Hz, 1H), 7.78 (dd, *J*= 1.8, 7.3 Hz, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 61.7, 65.0, 65.1, 74.8, 82.8 (s), 102.3, 127.2, 128.4, 128.5, 129.7, 134.2 (s), 138.7 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3417, 3288, 1456; HRMS (ESI): *m/z* calcd for $C_{12}H_{12}NaO_3$: 227.0679 $[M+Na]^+$; found: 227.0679.

Propargylic alcohol 14b (R^1 = OCH_3, n = 1): (hexanes/ethyl acetate 3:2); (0.61 g, 87%); yellow oil; δ_H (300 MHz; CD_2Cl_2) 2.65 (d, *J* = 2.4 Hz, 1H), 3.41 (d, *J* = 5.4 Hz, 1H), 3.80 (s, 3H), 4.03-4.13 (m, 4H), 5.70 (dd, *J* = 2,4, 5.4 Hz, 1H), 6.08 (s, 1H), 7.10 (d, *J* = 2.7 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 2.7, 8.4 Hz, 1H) ppm, δ_C (75 MHz; CD_2Cl_2) 55.9, 61.7, 65.6, 65.7, 74.7, 83.7 (s), 102.4, 113.3, 114.7, 130.4, 131.6 (s), 136.7 (s), 160.2 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3439, 3285, 1611, 1582; HRMS (ESI): *m/z* calcd for $C_{13}H_{14}NaO_4$: 257.0784 $[M+Na]^+$; found: 257.0787.

Propargylic alcohol 14c (R^1 = H, n = 2): (hexanes/diethyl ether 2:3); (0.40 g, 62%); yellow oil; δ_H (400 MHz; CD_2Cl_2) 1.39-1.47 (m, 1H), 2.14-2.26 (m, 1H), 2.67 (d, *J* = 2.4 Hz, 1H), 3.78 (d, *J* = 4.8 Hz, 1H), 3.93-4.02 (m, 2H), 4.19-4.27 (m, 2H), 5.77 (s, 1H), 5.95-5.97 (m, 1H), 7.30-7.40 (m, 2H), 7.48 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.74 (dd, *J* = 1.6, 7.2 Hz, 1H) ppm; δ_C (100 MHz; CD_2Cl_2) 26.1, 62.2, 68.1, 68.2, 74.9, 83.6 (s), 102.2, 128.0, 128.9, 130.0, 136.2 (s), 139.0 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3418, 3288, 1458, 1401; HRMS (ESI): *m/z* calcd for $C_{13}H_{14}NaO_3$: 241.0835 $[M+Na]^+$; found 241.0835.

General procedure for the preparation of the propargyl carbonates 15



To a solution of the appropriate propargylic alcohol **14** (3 mmol) in anhydrous dichlorometane (20 mL), under nitrogen at 0 ºC, dry pyridine (0.72 mL, 9 mmol) and methyl chloroformate (0.69 mL, 9 mmol) were added. The resulting mixture was stirred at 0 ºC for 1 h. Then, saturated aqueous solution of NH_4Cl (20 mL) was added, and the resulting mixture was extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with water (2 × 50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the residue was purified by silica gel column chromatography.

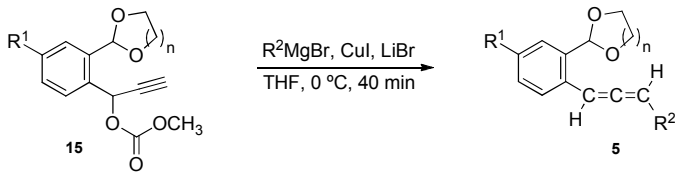
Propargyl carbonate 15a (R^1 = H, n = 1): (hexanes/diethyl ether 1:4); (0.69 g, 88%); yellow oil; δ_H (300 MHz; $CDCl_3$) 2.69 (d, *J* = 2.4 Hz, 1H), 3.81 (s, 3H), 4.00-4.19 (m, 4H), 6.04 (s, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 7.36-7.47 (m, 2H), 7.57 (dd, *J* = 1.8, 7.2 Hz, 1H), 7.79 (dd, *J* =

1.8, 7.2 Hz, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 55.2, 65.2, 65.3, 65.8, 76.2, 80.0 (s), 102.0, 127.2, 128.8, 129.3, 129.7, 134.6 (s), 135.0 (s), 154.8 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1747, 1441, 1315; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}NaO_5$: 285.0733 $[M+Na]^+$; found: 285.0727.

Propargyl carbonate 15b ($R^1 = OCH_3$, n = 1): (hexanes/diethyl ether 1:4); (0.79 g, 90%); yellow oil; δ_H (300 MHz; $CDCl_3$) 2.68 (d, *J* = 2.1 Hz, 1H), 3.79 (s, 3H), 3.82 (s, 3H), 4.06-4.18 (m, 4H), 6.02 (s, 1H), 6.69 (d, *J* = 2.1 Hz, 1H), 6.93 (dd, *J* = 2.7, 8.4 Hz, 1H), 7.11 (d, *J* = 2.7 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 55.1, 55.4, 65.3, 65.6, 76.0, 80.2 (s), 101.6, 112.5, 114.9, 126.5 (s), 130.7, 136.8 (s), 154.8 (s), 160.3 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3303, 1750, 1611, 1052; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}NaO_6$: 315.0839 $[M+Na]^+$; found 315.0841.

Propargyl carbonate 15c (R^1 = H, n = 2): (hexanes/diethyl ether 3:2); (0.61 g, 74%); yellow oil; δ_H (400 MHz; $CDCl_3$) 1.40-1.45 (m, 1H), 2.24-2.34 (m, 1H), 2.69 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 3H), 3.95-4.01 (m, 2H), 4.19-4.28 (m, 2H), 5.68 (s, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 7.37-7.41 (m, 2H), 7.53-7.55 (m, 1H), 7.78-7.80 (m, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 25.4, 55.0, 65.9, 67.5, 76.0, 80.2 (s), 100.7, 127.1, 129.0, 129.3, 129.4, 133.6 (s), 136.0 (s), 154.7 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3284, 1750, 1441; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}NaO_5$: 299.0895 $[M+Na]^+$; found 299.0890.

General procedure for the preparation of the allenes 5a-e



To a 0 ºC cooled solution of CuI (9.6 g, 50 mmol) and LiBr (4.34 g, 50 mmol) in anhydrous THF (40 mL), 1.0 M *tert*-butylmagnesium bromide in THF (50 mL, 50 mmol) or 1.0 M methylmagnesium bromide in THF (50 mL, 50 mmol) or 1.0 M phenylmagnesium bromide in THF (50 mL, 50 mmol) was added, and the stirring was continued at 0 ºC for 30 min. Then a solution of the corresponding propargyl carbonate **15** (5 mmol) in anhydrous THF (10 mL) was dropwise added. The resulting reaction mixture was stirred at 0 ºC for 40 min. Next, saturated solution of NH_4Cl (20 mL) was added, and the suspension extracted with diethyl

ether (2 x 40 mL). The organic layers were combined, washed with brine (30 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography.

Allene 5a (R^1 = H, R^2 = $C(CH_3)_3$, n = 1): (hexanes/ethyl acetate 9:1); (1.19 g, 88%); yellow oil; δ_H (400 MHz; CD_2Cl_2) 1.12 (s, 9H), 3.99-4.13 (m, 4H), 5.58 (d, *J* = 6.4 Hz, 1H), 5.97 (s, 1H), 6.58 (d, *J* = 6.4 Hz, 1H), 7.18 (td, *J* = 1.2, 7.6 Hz, 1H), 7.28 (td, *J* = 1.2,7.6 Hz, 1H), 7.47 (dd, *J*= 1.2, 7.6 Hz, 1H), 7.51 (dd, *J* = 1.2, 7.6 Hz, 1H) ppm; δ_C (100 MHz; CD_2Cl_2) 30.5, 33.1 (s), 65.8, 92.9, 102.2, 106.8, 126.8, 126.9, 127.5, 129.5, 134.2 (s), 134.3 (s), 203.7 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1946, 1602, 1454; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}$: 183.1168 $[M+H-C_2H_6O_2]^+$; found: 183.1172.

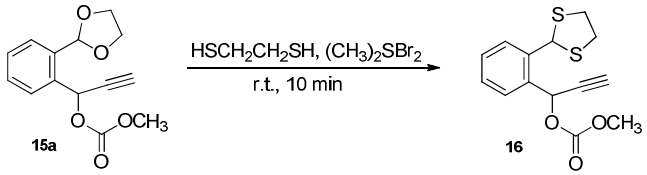
Allene 5b (R^1 = OCH_3, R^2 = CH_3, n = 1): (hexanes/diethyl ether 7:3); (0.69 g, 60%); white oil; δ_H (400 MHz; CD_2Cl_2) 1.75 (dd, *J* = 3.5, 6.9 Hz, 3H), 3.77 (s, 3H); 3.97-4.12 (m, 4H), 5.49 (q, *J* = 6.9 Hz, 1H), 5.93 (s, 1H), 6.38 (br s, 1H), 6.83 (dd, *J* = 3.5, 8.4 Hz, 1H), 7.07 (d, *J* = 2.7 Hz, 1H), 7.34 (dd, *J* = 8.4 Hz, 1H) ppm; δ_C (100 MHz; CD_2Cl_2) 14.4, 55.8, 65.8, 89.4, 90.3, 101.8, 111.5, 115.6, 126.1 (s), 129.4, 135.7 (s), 159.0 (s), 206.5 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1941, 1609, 1499; HRMS (ESI): *m/z* calcd for $C_{14}H_{17}O_3$: 233.1171 $[M+H]^+$, found 233.1172.

Allene 5c (R^1 = H, R^2 = Ph, n =1): (hexanes/ethyl acetate 9:1); (0.63 g, 48%); yellow oil; δ_H (300 MHz; CD_2Cl_2) 3.96-4.16 (m, 4H), 6.01 (s, 1H), 6.59 (d, *J* = 6.6 Hz, 1H), 7.01 (d, *J* = 6.6 Hz, 1H), 7.18-7.36 (m, 7H), 7.46 (dd, *J* = 1.8, 7.5 Hz, 1H), 7.55 (dd, *J* = 1.8, 7.5 Hz, 1H) ppm; δ_C (75 MHz; CD_2Cl_2) 65.8, 95.4, 98.2, 102.3, 127.2, 127.4, 127.7, 127.8, 129.2, 129.7, 132.7 (s), 134.1 (s), 134.7 (s), 208.8 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1935, 1596, 1490; HRMS (ESI): *m/z* calcd for $C_{18}H_{17}O_2$: 265.1228 $[M+H]^+$; found: 265.1223.

Allene 5d (R^1 = H, R^2 = $C(CH_3)_3$, n = 2): (hexanes/ethyl acetate 9:1); (0.79 g, 62%); white oil; δ_H (400 MHz; CD_2Cl_2) 1.12 (s, 9H), 1.40-1.44 (m, 1H), 2.12-2.24 (m, 1H), 3.92-3.99 (m, 2H), 4.19-4.22 (m, 2H), 5.57 (d, *J* = 6.4 Hz, 1H), 5.62 (s, 1H), 6.62 (d, *J* = 6.4 Hz, 1H), 7.15 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.24 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.44-7.49 (m, 2H) ppm; δ_C (100 MHz; CD_2Cl_2) 26.3, 30.5, 33.1 (s), 68.0, 93.2, 100.9, 106.7, 126.9, 127.1, 129.1, 133.4 (s), 135.4 (s), 203.5 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1946, 1458, 1376; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}$: 183.1168 $[M+H-C_3H_8O_2]^+$; found 183.1171.

Allene 5e (R^1 = H, R^2 = CH_3, n = 2): (hexanes/ethyl acetate 9:1); (0.54 g, 50%); white oil; δ_H (300 MHz; CD_2Cl_2) 1.39-1.45 (m, 1H), 1.78 (dd, *J* = 3.3, 7.2 Hz, 3H), 2.10-2.27 (m, 1H), 3.91-4.00 (m, 2H), 4.19-4.24 (m, 2H), 5.53 (quint, *J* = 7.2 Hz, 1H), 5.62 (s, 1H), 6.51-6.56 (m, 1H), 7.14-7.31 (m, 2H), 7.43 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.49 (dd, *J* = 1.6, 7.6 Hz, 1H) ppm; δ_C (75 MHz; CD_2Cl_2) 14.0, 26.3, 68.0, 89.7, 91.2, 100.9, 127.0, 127.2, 128.0, 129.2, 133.2 (s), 135.6 (s), 207.0 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1943, 1456, 1375; HRMS (ESI): *m/z* calcd for $C_{11}H_9$: 141.0699 $[M+H-C_3H_8O_2]^+$; found 141.0703.

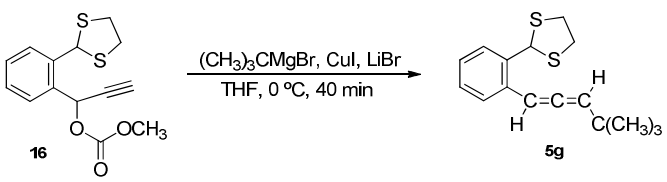
Procedure for the preparation of the propargyl carbonate 16



To a mixture of carbonate **15a** (1 mmol) and 1,2-ethanedithiol (1.1 mmol) a catalytic amount of (bromodimethyl)sulfonium bromide was added (0.023 g). After stirring at room temperature for 15 min the reaction mixture was neutralized by addition of two drops of saturated $NaHCO_3$ solution. Then, the resulting crude material was purified by silica gel column chromatography, using hexanes/diethyl ether (1:1 v/v) as eluyent.

Propargyl carbonate 16: (0.24 g, 83%); yellow oil; δ_H (400 MHz; $CDCl_3$) 2.77 (d, *J* = 2.4 Hz, 1H), 3.35-3.43 (m, 2H) 3.51-3.59 (m, 2H), 3.82 (s, 3H), 6.12 (s, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 7.30 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.39 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.56 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.88 (dd, *J* = 1.6, 7.6 Hz, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 40.5, 52.0, 55.3, 67.0, 77.2, 79.6 (s), 128.4, 128.9, 130.0, 133.9 (s), 138.7 (s), 154.6 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3284, 1750, 1440; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}NaO_3S_2$: 317.0277 $[M+Na]^+$; found 317.0274.

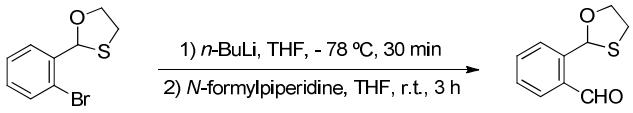
Procedure for preparation of the allene 5g



To a 0 ºC cooled solution of CuI (9.6 g, 50 mmol) and LiBr (4.34 g, 50 mmol) in anhydrous THF (40 mL), 1.0 M *tert*-butylmagnesium bromide in THF (50 mL, 50 mmol) was added, and the stirring was continued at 0 ºC for 30 min. Then a solution of propargyl carbonate **16** (5 mmol) in anhydrous THF (10 mL) was dropwise added. The resulting reaction mixture was stirred at 0 ºC for 40 min. Next, a saturated aqueous solution of NH_4Cl (20 mL) was added, and the suspension extracted with diethyl ether (2 x 40 mL). The organic layers were combined, washed with brine (30 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, using hexanes/ethyl acetate (9:1 v/v) as eluyent.

Allene 5g: (1.20 g, 87%); yellow oil; δ_H (400 MHz; $CDCl_3$) 1.12 (s, 9H), 3.50-3.51 (m, 4H), 5.58 (d, *J* = 6.4 Hz, 1H), 6.02 (s, 1H), 6.55 (d, *J* = 6.4 Hz, 1H), 7.15-7.21 (m, 2H), 7.34-7.38 (m, 1H), 7.77-7.80 (m, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 30.4, 33.1 (s), 40.4, 40.5, 53.1, 93.3, 106.6, 127.4, 127.9, 128.3, 128.6, 133.6 (s), 137.0 (s), 203.9 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1946, 1474, 1448; HRMS (ESI): *m/z* calcd for $C_{16}H_{21}S_2$: 277.1079 $[M+H]^+$; found 277.1080.

Preparation of 2-(1,3-oxathiolan-2-yl)benzaldehyde 18

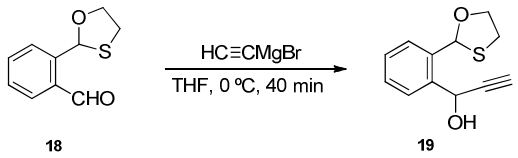


17 **18**

n-BuLi [5 mL, 2.5 M in hexane] was added dropwise to a solution of 2-(2-bromophenyl)-1,3-oxathiolane **17** (3 g, 12.2 mmol) in anhydrous THF (50 mL), at –78 ºC under an atmosphere of nitrogen. The mixture was stirred at –78 ºC for 30 min. Next, a solution of *N*-formylpiperidine (1.4 g, 12.3 mmol) in THF (10 mL) was added. The mixture was stirred at –78 ºC for 15 min, warmed to room temperature and the stirring continued for 3 h. Then, the reaction was quenched with the addition of water (25 mL). The mixture was extracted with ethyl acetate (2 × 30 mL). The combined organic layers were washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by silica gel column chromatography, using hexanes/diethyl ether (3:2, v/v) as eluent.

2-(1,3-Oxathiolan-2-yl)benzaldehyde 18: (2.1 g , 90%); yellow oil; δ_H (400 MHz; $CDCl_3$) 3.17-3.19 (m, 2H), 3.99-4.05 (m, 1H), 4.59-4.64 (m, 1H), 6.75 (s, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 10.21 (s, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 33.5, 72.4, 83.1, 126.2, 128.4, 132.6 (s), 133.2, 134.0, 142.0 (s), 192.6 ppm; IR (Neat): ν_{max}/cm^{-1} 1694, 1598, 1570, 1198; HRMS (ESI): *m/z* calcd for $C_{10}H_{11}O_2S$: 195.0474 $[M+H]^+$; found 195.0475.

Preparation of the propargylic alcohol 19

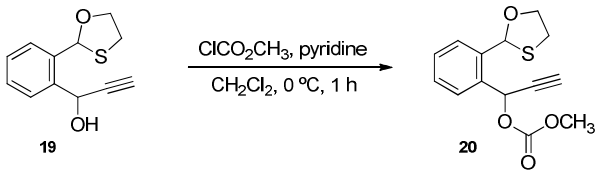


18 19

To a solution of 2-(1,3-oxathiolan-2-yl)benzaldehyde **18** (3 mmol) in anhydrous THF (30 mL) at 0 ºC was added 0.5 M solution of ethynylmagnesium bromide in THF (6 mL, 3 mmol). The reaction mixture was stirred at 0 °C for 40 min. Then a saturated aqueous solution of NH_4Cl (10 mL) was added. The mixture was extracted with dichloromethane (2 × 30 mL). The organic layers were combined, washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by silica gel column chromatography, using hexanes/diethyl ether (3:2 v/v) as eluyent.

Propargylic alcohol 19: mixture of diastereoisomers; (0.47 g, 72%); yellow oil; δ_H (400 MHz; CD_2Cl_2) 2.69 (d, *J* = 2.0 Hz, 1H), 2.72 (d, *J* = 2.0 Hz, 1H), 2.91-2.92 (m, 1H), 3.03-3.06 (m, 1H), 3.20-3.30 (m, 4H), 3.87-3.94 (m, 2H), 4.55-4.60 (m, 2H), 5.86 (dd, *J* = 2.4, 8.4 Hz, 1H), 5.89 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.32 (s, 1H), 6.37 (s, 1H), 7.35-7.38 (m, 4H), 7.54-7.58 (m, 2H), 7.74-7.76 (m, 2H) ppm; δ_C (100 MHz; CD_2Cl_2) 34.4, 34.5, 61.8, 61.9, 72.5, 72.6, 75.3, 75.7, 83.4 (s), 83.7 (s), 85.1, 85.6, 128.2, 128.3, 128.4, 128.8, 129.3, 129.4, 129.5, 129.7, 136.5 (s), 137.0 (s), 138.6 (s), 138.8 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3405, 3285, 2116, 1375; HRMS (ESI): *m/z* calcd for $C_{12}H_{12}NaO_2S$: 243.045 $[M+Na]^+$; found 243.0446.

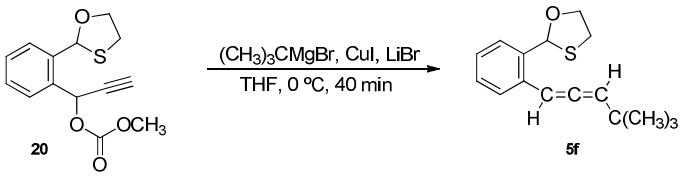
Preparation of the propargylic carbonate 20



To a solution of the propargylic alcohol **19** (3 mmol) in anhydrous dichlorometane (20 mL), under nitrogen at 0 ºC, dry pyridine (0.72 mL, 9 mmol) and methyl chloroformate (0.69 mL, 9 mmol) were added. The resulting mixture was stirred at 0 ºC for 1 h. Then, a saturated aqueous solution of NH_4Cl (20 mL) was added, and the resulting mixture was extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with water (2 × 50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was purified by silica gel column chromatography, using hexanes/diethyl ether (3:7 v/v) as eluent.

Propargyl carbonate 20: mixture of diastereoisomers; (0.71 g, 85%); yellow oil; δ_H (300 MHz; $CDCl_3$) 2.70 (d, *J* = 2.4 Hz, 1H), 2.75 (d, *J* = 2.4 Hz, 1H), 3.18-3.26 (m, 2H), 3.28-3.38 (m, 2H), 3.80 (s, 3H), 3.82 (s, 3H), 3.86-3.97 (m, 2H), 4.54-4.66 (m, 2H), 6.25 (s, 1H), 6.40 (s, 1H), 6.61 (d, *J* = 2.1 Hz, 1H), 6.70 (d, *J* = 2.1 Hz, 1H), 7.36-7.42 (m, 4H), 7.60-7.66 (m, 2H), 7.73-7.76 (m, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 34.0, 34.2, 55.1, 55.2, 66.0, 66.1, 72.1, 76.3, 76.9, 79.7 (s), 79.9 (s), 84.1, 84.7, 127.6, 128.2, 128.8, 129.0, 129.1, 129.2, 129.6, 129.7, 133.5 (s), 133.7 (s), 136.7 (s), 136.8 (s), 154.6 (s), 154.7 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1750, 1441, 1314; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}NaO_4S$: 301.0505 $[M+Na]^+$; found 301.0504.

Preparation of the allene 5f

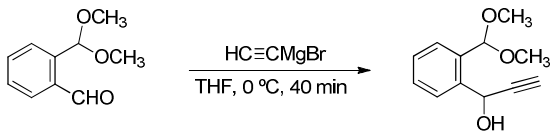


To a 0 ºC cooled solution of CuI (9.6 g, 50 mmol) and LiBr (4.34 g, 50 mmol) in anhydrous THF (40 mL), 1.0 M *tert*-butylmagnesium bromide in THF (50 mL, 50 mmol) was added, and the stirring was continued at 0 ºC for 30 min. Then a solution of the propargyl carbonate **20** (5 mmol) in anhydrous THF (10 mL) was dropwise added. The reaction mixture was stirred at 0 ºC for 40 min. Next, a saturated aqueous solution of NH_4Cl (20 mL) was added and the

suspension extracted with diethyl ether (2 x 40 mL). The organic layers were combined, washed with brine (30 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, using hexanes/ethyl acetate (9:1 v/v) as eluyent.

Allene 5f: (0.89 g, 68%); yellow oil; δ_H (300 MHz; CD_2Cl_2) 1.12 (s, 9H), 3.21-3.28 (m, 2H), 3.89-3.97 (m, 1H), 4.55-4.6 (m, 1H), 5.57-5.60 (m, 1H), 6.29 (s, 1H), 6.44 (d, J = 6.3 Hz, 1H), 7.17-7.26 (m, 2H), 7.39-7.44 (m, 1H), 7.55-7.58 (m, 1H) ppm; δ_C (75 MHz; CD_2Cl_2) 30.5, 33.2 (s), 34.5, 34.6, 72.5, 84.8, 84.9, 92.8, 93.0, 106.7, 106.9, 126.4, 126.5, 127.3, 127.5, 127.7, 128.7, 133.0 (s), 136.1 (s), 136.3 (s), 203.9 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1946, 1474, 1448; HRMS (ESI): *m/z* calcd for $C_{16}H_{21}OS$: 261.1308 $[M+H]^+$; found 261.1310.

Preparation of the propargylic alcohol 22

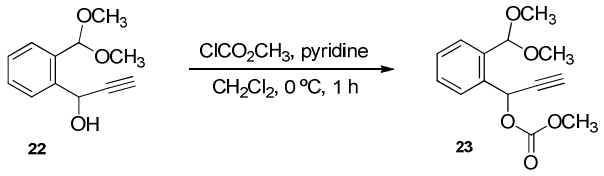


21 22

To a solution of 2-(dimethoxymethyl)benzaldehyde **21** (3 mmol) in anhydrous THF (30 mL) at 0 ºC was added 0.5 M solution of ethynylmagnesium bromide in THF (6 mL. 3 mmol). The reaction was stirred for 40 min at 0 °C. Then a saturated aqueous solution of NH_4Cl (10 mL) was added. The mixture was extracted with dichloromethane (2 × 30 mL). The organic layers were combined, washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by silica gel column chromatography, using hexanes/diethyl ether (3:2 v/v) as eluyent.

Propargylic alcohol 22: (0.34 g, 54%); yellow oil; δ_H (400 MHz; CD_2Cl_2) 2.70 (s, 1H), 3.38 (s, 3H), 3.39 (s, 3H), 3.68 (s, 1H), 5.66 (s, 1H), 5.89 (s, 1H), 7.38-7.44 (m, 2H), 7.53-7.55 (m, 1H), 7.77-7.79 (m, 1H) ppm; δ_C (100 MHz; CD_2Cl_2) 54.3, 54.4, 62.2, 74.8, 84.1 (s), 103.9, 128.3, 128.7, 128.8, 129.7, 135.8 (s), 139.1 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3403, 2937, 2115, 1454; HRMS (ESI): *m/z* calcd for $C_{12}H_{14}NaO_3$: 229.0835 $[M+Na]^+$; found 229.0830.

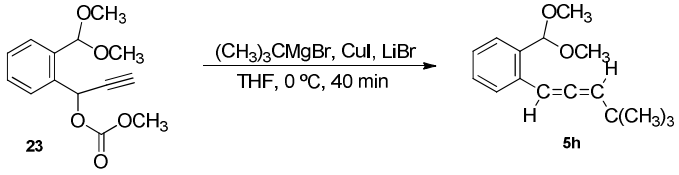
Preparation of the propargyl carbonate 23



To a solution of the propargylic alcohol **22** (3 mmol) in anhydrous dichlorometane (20 mL), under nitrogen at 0 ºC, dry pyridine (0.72 mL, 9 mmol) and methyl chloroformate (0.69 mL, 9 mmol) were added. The resulting mixture was stirred at 0 ºC for 1 h. Then, a saturated aqueous solution of NH_4Cl (20 mL) was added, and the resulting mixture was extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with water (2 × 50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the residue was purified by silica gel column chromatography, using hexanes/diethyl ether (1:1 v/v) as eluent.

Propargyl carbonate 23: (0.52 g, 66%); yellow oil; δ_H (300 MHz; $CDCl_3$) 2.67 (d, J = 2.1 Hz, 1H), 3.28 (s, 3H), 3.37 (s, 3H), 3.80 (s, 3H), 5.60 (s, 1H), 6.74 (d, J = 2.4 Hz, 1H), 7.35-7.43 (m, 2H), 7.56-7.59 (m, 1H), 7.73-7.76 (m, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 52.8, 53.9, 55.1, 65.8, 75.9, 80.1 (s), 101.6, 127.4, 128.5, 128.9, 129.2, 134.3 (s), 135.6 (s), 154.7 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3286, 1754, 1442; HRMS (ESI): *m/z* calcd for $C_{13}H_{13}O_4$: 233.0808 $[M+H-CH_4O]^+$; found 233.0812.

Preparation of the allene 5h

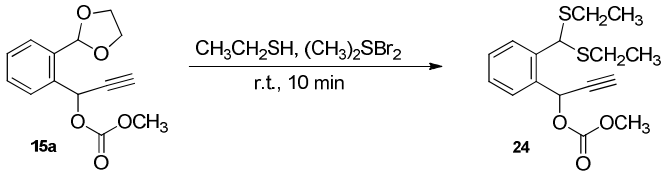


To a 0 ºC cooled solution of CuI (9.6 g, 50 mmol) and LiBr (4.34 g, 50 mmol) in anhydrous THF (40 mL), 1.0 M *tert*-butylmagnesium bromide in THF (50 mL, 50 mmol) was added, and the stirring was continued at 0 ºC for 30 min. Then a solution of the propargyl carbonate **23** (5 mmol) in anhydrous THF (10 mL) was dropwise added. The reaction mixture was stirred at 0 ºC for 40 min. Next, a saturated aqueous solution of NH_4Cl (20 mL) was added and the

suspension extracted with diethyl ether (2 x 40 mL). The organic layers were combined, washed with brine (30 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, using hexanes/ ethyl acetate (9:1 v/v) as eluyent.

Allene 5h: (0.89 g, 73%); white oil; δ_H (300 MHz; CD_2Cl_2) 1.10 (s, 9H), 3.29 (s, 3H), 3.30 (s, 3H), 5.47 (s, 1H), 5.56 (d, *J* = 6.6 Hz, 1H), 6.61 (d, *J* = 6.6 Hz, 1H), 7.16 (td, *J* = 1.2, 7.5 Hz, 1H), 7.25 (td, *J* = 1.2, 7.5 Hz, 1H), 7.46-7.48 (m, 2H) ppm; δ_C (75 MHz; CD_2Cl_2) 30.5, 33.1 (s), 53.6, 93.1, 102.6, 106.6, 126.6, 127.5, 127.7, 129.0, 133.9 (s), 134.6 (s), 203.6 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1947, 1453, 1361; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}$: 183.1168 $[M+H-C_2H_8O_2]^+$; found 183.1172.

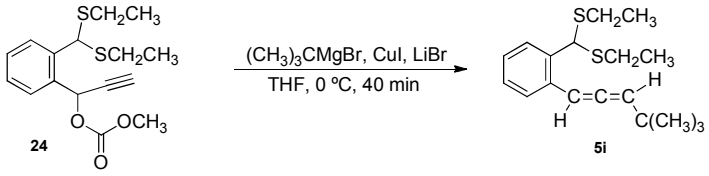
Preparation of the propargyl carbonate 24



To a mixture of the carbonate **15a** (1 mmol) and ethanethiol (2.2 mmol) a catalytic amount of (bromodimethyl)sulfonium bromide was added (0.023 g). After stirring at room temperature for 15 min the reaction mixture was neutralized by addition of two drops of saturated $NaHCO_3$ solution. Then, the resulting crude material was purified by silica gel column chromatography, using hexanes/diethyl ether (1:1 v/v) as eluyent.

Propargyl carbonate 24: (0.28 g, 87%); yellow oil; δ_H (400 MHz; $CDCl_3$) 1.21 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 2.51-2.71 (m, 4H), 2.72 (d, *J* = 2.4 Hz, 1H), 3.81 (s, 3H), 5.37 (s, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 7.31 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.39 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.64 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 14.3, 14.4, 26.5, 26.6, 48.3, 55.3, 66.4, 76.7, 79.6 (s), 128.2, 128.7, 129.0, 129.8, 133.0 (s), 138.3 (s), 154.7 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3285, 1751, 1441; HRMS (ESI): *m/z* calcd for $C_{16}H_{20}NaO_3S_2$: 347.0746 $[M+Na]^+$; found 347.0741.

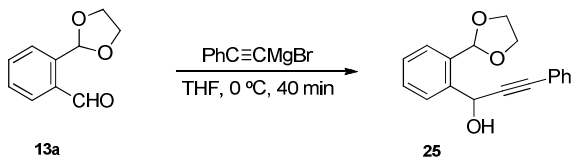
Preparation of the allene 5i



To a 0 ºC cooled solution of CuI (9.6 g, 50 mmol) and LiBr (4.34 g, 50 mmol) in anhydrous THF (40 mL), 1.0 M *tert*-butylmagnesium bromide in THF (50 mL, 50 mmol) was added, and the stirring was continued at 0 ºC for 30 min. Then a solution of the propargyl carbonate **24** (5 mmol) in anhydrous THF (10 mL) was dropwise added. The reaction mixture was stirred at 0 ºC for 40 min. Next, saturated solution of NH_4Cl (20 mL) was added and the suspension extracted with diethyl ether (2 x 40 mL). The organic layers were combined, washed with brine (30 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, using hexanes/ ethyl acetate (9:1 v/v) as eluyent.

Allene 5i: (0.78 g, 60%); yellow oil; δ_H (400 MHz; CD_2Cl_2) 1.11 (s, 9H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 2.24-2.64 (m, 4H), 5.29 (s, 1H), 5.57 (d, *J* = 6.4 Hz, 1H), 6.58 (d, *J* = 6.4 Hz, 1H), 7.15-7.21 (m, 2H), 7.38-7.40 (m, 1H), 7.59-7.61 (m, 1H) ppm; δ_C (100 MHz; CD_2Cl_2) 14.7, 14.8, 26.8, 26.9, 30.4, 33.1 (s), 49.3, 92.9, 106.6, 127.3, 128.1, 128.2, 129.0, 133.3 (s), 137.0 (s), 203.9 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1946, 1474, 1447; HRMS (ESI): *m/z* calcd for $C_{16}H_{21}S$: 245.1358 $[M+H-C_2H_6S]^+$; found 245.1360.

Preparation of the propargylic alcohol 25

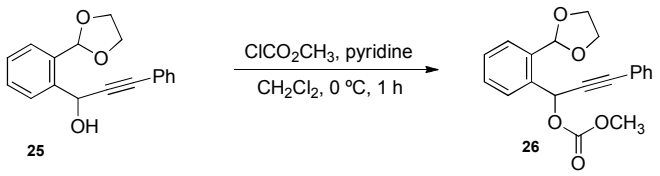


To a solution of 2-(1,3-dioxolan-2-yl)benzaldehyde **13a** (3 mmol) in anhydrous THF (30 mL) at 0 ºC was added 0.5 M solution of phenylethynylmagnesium bromide in THF (6 mL, 3 mmol). The reaction was stirred for 40 min at 0 °C. Then a saturated aqueous solution of NH_4Cl (10 mL) was added. The mixture was extracted with dichloromethane (2 × 30 mL).

The organic layers were combined, washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by silica gel column chromatography, using hexanes/diethyl ether (2:3 v/v) as eluyent.

Propargylic alcohol 25: (0.48 g, 57%); yellow oil; δ_H (300 MHz; CD_2Cl_2) 4.05-4.19 (m, 5H), 6.02 (s, 1H), 6.19 (s, 1H), 7.32-7.52 (m, 7H), 7.58-7.61 (m, 1H), 7.83-7.86 (m, 1H) ppm; δ_C (75 MHz; CD_2Cl_2) 62.8, 65.6, 65.7, 86.7 (s), 88.9 (s), 102.9, 123.1 (s), 127.8, 128.9, 129.0, 129.1, 130.2, 132.1, 135.1 (s), 140.1 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 3439, 1489, 1454, 1406; HRMS (ESI): *m/z* calcd for $C_{18}H_{17}O_3$: 281.1172 $[M+H]^+$; found: 281.1176.

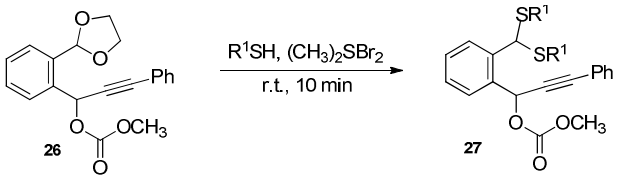
Preparation of the propargyl carbonate 26



To a solution of the propargylic alcohol **25** (3 mmol) in anhydrous dichlorometane (20 mL), under nitrogen at 0 ºC, dry pyridine (0.72 mL, 9 mmol) and methyl chloroformate (0.69 mL, 9 mmol) were added. The resulting mixture was stirred at 0 ºC for 1 h. Then, a saturated aqueous solution of NH_4Cl (20 mL) was added and the resulting mixture was extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with water (2 × 50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the residue was purified by silica gel column chromatography, using hexanes/diethyl ether (3:2 v/v) as eluent.

Propargyl carbonate 26: (0.61, 60%); yellow oil; δ_H (300 MHz; $CDCl_3$) 3.82 (s, 3H), 4.22-4.30 (m, 4H), 6.13 (s, 1H), 6.98 (s, 1H), 7.27-7.33 (m, 3H), 7.38-7.48 (m, 4H), 7.60 (dd, *J*= 1.8, 7.2 Hz, 1H), 7.85 (dd, *J*= 1.8, 7.2 Hz, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 54.9, 65.2, 66.6, 85.1 (s), 87.8 (s), 101.7, 122.0, 126.9, 128.1, 128.7, 128.9, 129.1, 129.5, 131.8, 134.9 (s), 135.0 (s), 154.7 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1750, 1441, 1263; HRMS (ESI): *m/z* calcd for $C_{20}H_{18}NaO_5$: 361.1046 $[M+Na]^+$; found: 361.1043.

General procedure for the preparation of the propargyl carbonates 27



To a mixture of propargyl carbonate **26** (1 mmol) and ethanethiol (2.2 mmol) or 2-phenylethanethiol (2.2 mmol) or (4-chlorophenyl)methanethiol (2.2 mmol) or (4-bromophenyl)methanethiol (2.2 mmol) a catalytic amount of (bromodimethyl)sulfonium bromide was added (0.023 g). After stirring at room temperature for 15 min the reaction mixture was neutralized by addition of two drops of saturated $NaHCO_3$ solution. Then, the resulting crude material was purified by silica gel column chromatography.

Propargyl carbonate 27a (R^1 = CH_3CH_2): (hexanes/diethyl ether 2:3); (0.30 g, 76%); yellow oil; δ_H (300 MHz; $CDCl_3$) 1.18 (t, *J* = 7.5 Hz, 3H), 1.21 (t, *J* = 7.5 Hz, 3H); 2.54-2.73 (m, 4H), 3.83 (s, 3H), 5.50 (s, 1H), 6.86 (s, 1H), 7.30-7.35 (m, 4H), 7.40 (td, *J* = 1.8, 7.5 Hz, 1H), 7.45-7.48 (m, 2H), 7.67 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.84 (dd, *J* = 1.5, 7.8 Hz, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 14.2, 14.4, 26.6, 26.7, 48.5, 55.2, 67.6, 84.9 (s), 88.4 (s), 121.9 (s), 128.1, 128.3, 128.7, 129.0, 129.2, 129.6, 131.9, 133.6 (s), 138.7 (s), 154.8 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1752, 1490, 1441; HRMS (ESI): *m/z* calcd for $C_{22}H_{24}KO_3S_2$: 439.0798 $[M+K]^+$; found 439.0793.

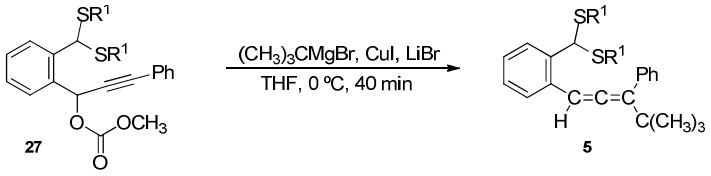
Propargyl carbonate 27b (R^1 = $PhCH_2CH_2$): (hexanes/diethyl ether 3:2); (0.35 g, 63%); yellow oil; δ_H (400 MHz; $CDCl_3$) 2.77-2.87 (m, 8H), 3.73 (s, 3H), 5.85 (s, 1H), 6.82 (s, 1H), 7.05-7.46 (m, 17H), 7.66 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 34.7, 34.9, 36.5, 36.6, 50.4, 56.0, 68.6, 85.7 (s), 89.4 (s), 122.7 (s), 127.1, 129.1, 129.2, 129.3, 129.4, 129.8, 130.1, 130.6, 132.8 (s), 139.3 (s), 141.2 (s), 141.3 (s), 155.6 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1751, 1491, 1453; HRMS (ESI): *m/z* calcd for $C_{34}H_{32}NaO_3S_2$; 575.1685 $[M+Na]^+$; found 575.1680.

Propargyl carbonate 27c (R^1 = 4-Cl-C_6H_4-CH_2): (hexanes/diethyl ether 3:2); (0.41 g, 70%); yellow oil; δ_H (300 MHz; $CDCl_3$) 3.61-3.79 (m, 4H), 3.80 (s, 3H), 5.15 (s, 1H), 6.49 (s, 1H), 7.06-7.24 (m, 8H), 7.29-7.43 (m, 7H), 7.64-7.67 (m, 1H), 7.78-7.79 (m, 1H) ppm; δ_C (75

MHz; $CDCl_3$) 36.2, 36.3, 48.4, 55.3, 66.9, 84.9 (s), 88.1 (s), 121.8 (s), 128.4, 128.6, 128.7, 128.8, 129.1, 129.2, 129.6, 130.3, 130.4, 132.0, 132.9 (s), 133.0 (s), 134.5 (s), 135.7 (s), 135.8 (s), 136.5 (s), 154.4 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1754, 1489, 1440; HRMS (ESI): *m/z* calcd for $C_{32}H_{26}Cl_2KO_3S_2$: 631.0332 $[M+K]^+$; found 631.0342.

Propargyl carbonate 27d (R^1 = 4-Br-C_6H_4-CH_2): (hexanes/diethyl ether 3:2); (0.41 g, 60%); yellow oil; δ_H (300 MHz; $CDCl_3$) 3.55-3.77 (m, 4H), 3.81 (s, 3H), 5.17 (s, 1H), 6.49 (s, 1H), 7.00-7.77 (m, 17H) ppm; δ_C (75 MHz; $CDCl_3$) 36.3, 36.4, 48.5, 55.3, 67.0, 85.0 (s), 88.2 (s), 121.0 (s), 121.8 (s), 128.4, 128.5, 128.6, 128.8, 129.1, 129.6, 130.6, 130.7, 130.8, 131.1, 131.6, 132.0, 134.5 (s), 136.2 (s), 136.3 (s), 136.5 (s), 154.4 (s) pm; IR (Neat): ν_{max}/cm^{-1} 1753, 1486, 1440; HRMS (ESI): *m/z* calcd for $C_{30}H_{23}Br_2S_2$: 606.9764 $[M+H-C_2H_4O_3]^+$; found 606.9524.

General procedure for the preparation of the allenes 5j-m



To a 0 ºC cooled solution of CuI (9.6 g, 50 mmol) and LiBr (4.34 g, 50 mmol) in anhydrous THF (40 mL), 1.0 M *tert*-butylmagnesium bromide in THF (50 mL, 50 mmol) was added, and the stirring was continued at 0 ºC for 30 min. Then a solution of the propargyl carbonate **27** (5 mmol) in anhydrous THF (10 mL) was dropwise added. The reaction mixture was stirred at 0 ºC for 40 min. Next, a saturated aqueous solution of NH_4Cl (20 mL) was added and the suspension extracted with diethyl ether (2 x 40 mL). The organic layers were combined, washed with brine (30 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography.

Allene 5j (R^1 = CH_3CH_2): (hexanes/ ethyl acetate 9:1); (0.68 g, 36%); yellow oil; δ_H (400 MHz; CD_2Cl_2) 1.13 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 9H), 2.41-2.57 (m, 4H), 6.64 (s, 1H), 7.17-7.28 (m, 4H), 7.29-7.34 (m, 4H), 7.47 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H) ppm; δ_C (100 MHz; CD_2Cl_2) 14.7, 14.8, 26.8, 26.9, 30.1, 35.6 (s), 91.8, 119.6 (s), 127.4, 127.5, 128.0, 128.3, 128.4, 129.1, 129.9, 133.5 (s), 137.1 (s), 137.5 (s), 204.3

(s) ppm; IR (Neat): ν_{max}/cm^{-1} 1944, 1596, 1476; HRMS (ESI): *m/z* calcd for $C_{24}H_{30}KS_2$: 421.1421 $[M+K]^+$; found 421.1419.

Allene 5k (R^1 = $PhCH_2CH_2$): (hexanes/ethyl acetate 95:5); (1.76 g, 66%); colorless oil; δ_H (400 MHz; CD_2Cl_2) 1.24 (s, 9H), 2.73-2.85 (m, 8H), 5.21 (s, 1H), 6.54 (s, 1H), 7.09-7.39 (m, 17H), 7.55 (dd, *J* = 1.4, 7.6 Hz, 1H), 7.60 (dd, *J* = 7.4 Hz, 1H) ppm; δ_C (100 MHz; CD_2Cl_2) 30.1, 34.2, 34.3, 35.7 (s), 36.4, 91.8, 119.7 (s), 126.7, 126.8, 127.4, 127.5, 127.9, 128.5, 128.8, 128.9, 129.0, 129.1, 129.2, 129.9, 133.5 (s), 136.7 (s), 137.5 (s), 140.9 (s), 141.0 (s), 204.3 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1944, 1597, 1494; HRMS (ESI): *m/z* calcd for $C_{36}H_{38}KS_2$: 573.2047 $[M+K]^+$; found 573.2047.

Allene 5l (R^1 = 4-Cl-C_6H_4-CH_2): (hexanes/ ethyl acetate 9:1); (1.20 g, 42%); yellow oil; δ_H (300 MHz; CD_2Cl_2) 1.17 (s, 9H), 3.26 (d, *J* = 13.8 Hz, 1H), 3.46 (d, *J* = 13.8 Hz, 1H), 3.53 (d, *J* = 13.8 Hz, 1H), 3.69 (d, *J* = 13.8 Hz, 1H), 4.43 (s, 1H), 5.17 (s, 1H), 6.76-6.79 (m, 2H), 6.84-6.90 (m, 4H), 7.16-7.38 (m, 10H), 7.45 (dd, *J* = 2.4, 6.9 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 1H) ppm; δ_C (75 MHz; CD_2Cl_2) 30.1, 35.6 (s), 36.5, 36.7, 45.9, 90.2, 119.6 (s), 127.6, 127.8, 128.6, 128.7, 128.8, 129.1, 129.2, 130.0, 130.5, 130.9, 133.1 (s), 133.3 (s), 134.4 (s), 137.5 (s), 137.4 (s), 137.7 (s), 203.8 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1945, 1595, 1489; HRMS (ESI): *m/z* calcd for $C_{34}H_{33}Cl_2S_2$: 575.1395 $[M+H]^+$; found 575.1396.

Allene 5m (R^1 = 4-Br-C_6H_4-CH_2): (hexanes/ ethyl acetate 9:1); (1.39 g, 42%); yellow oil; δ_H (300 MHz; CD_2Cl_2) 1.20 (s, 9H), 3.21 (d, *J* = 12.0 Hz, 1H), 3.44 (d, *J* = 12.0 Hz, 1H), 3.48 (d, *J* = 12.0 Hz, 1H), 3.64 (d, *J* = 12.0 Hz, 1H), 4.43 (s, 1H), 5.14 (s, 1H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 3H), 7.19-7.47 (m, 8H), 7.83 (m, 2H) ppm; δ_C (75 MHz; CD_2Cl_2) 29.9, 35.2 (s), 36.0, 36.3, 45.1, 89.7, 119.0 (s), 120.9 (s), 121.0 (s), 127.1, 127.3, 128.1, 128.2, 128.3, 129.5, 130.7, 131.6, 131.7, 133.7, 136.9 (s), 137.1 (s), 137.2 (s), 203.3 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1946, 1596, 1485; HRMS (ESI): *m/z* calcd for $C_{34}H_{33}Br_2S_2$: $C_{34}H_{33}Br_2S_2$; 663.0385 $[M+H]^+$, found 663.0386.

Acid-triggered cyclization of acetallic allenes 5

Conditions A: To a solution of the appropriate allene **5** (1 mmol) in dichloromethane (10 mL) at room temperature silver hexafluoroantimoniate(V) (0.1 equivalent) was added. The reaction mixture was stirred at room temperature for 20 min. Then, the solution was filtrated

through Celite® and the solvent was removed under reduced pressure. Finally, the residue was purified by column chromatography on silica gel.

Conditions B: To a solution of the allene **5** (1 mmol) in dichloromethane (10 mL) at room temperature trifluoroacetic acid (1 mmol) was added. The reaction mixture was stirred at room temperature for 10 min. Then, saturated $NaHCO_3$ solution (10 mL) was added. After separation of the organic phase the aqueous one was extracted with dichloromethane (2 x 15 mL). The organic layers were combined, washed with brine (30 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified column chromatography on silica gel.

Indene-1,4-dioxepane *trans*-6a (R^1 = H, R^2 = $C(CH_3)_3$, n = 1): *conditions A*; (hexanes/ethyl acetate 9:1); (0.15 g, 62%); colorless prism; mp 108-110 ºC (from diethyl ether); δ_H (300 MHz; $CDCl_3$) 0.96 (s, 9H), 3.65-3.71 (m, 1H), 3.96-4.06 (m, 3H), 4.19 (s, 1H), 5.00 (s, 1H), 6.51 (s, 1H), 7.14-7.19 (m, 2H), 7.23-7.28 (m, 1H), 7.41-7.43 (m, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 26.5, 36.8 (s), 72.3, 72.7, 85.0, 87.6, 120.7, 124.1, 125.9, 128.8, 130.3, 142.5 (s), 143.2 (s), 151.9 (s) ppm; IR (Nujol): ν_{max}/cm^{-1} 1610, 1358, 1283; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}$: 183.1168 $[M+H-C_2H_6O_2]^+$; found 183.1171.

Indene-1,4-dioxepane *cis*-6a (R^1 = H, R^2 = $C(CH_3)_3$, n = 1): *see Table 1*; **(**hexanes/ethyl acetate 9:1); mp 106-108 ºC (from diethyl ether); δ_H (400 MHz; $CDCl_3$) 1.14 (s, 9H), 3.11 (dd, *J* = 10.0, 13.6 Hz, 1H), 3.51-3.55 (m, 1H), 3.62-3.68 (m, 1H), 3.82-3.86 (m, 2H), 5.08 (s, 1H), 6.87 (s, 1H), 7.19-7.31 (m, 3H), 7.50 (d, *J* = 7.2 Hz, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 27.1, 34.9 (s), 67.6, 72.0, 82.7, 86.7, 121.4, 123.6, 125.8, 128.7, 128.9, 142.9 (s), 143.9 (s), 149.3 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1479, 1438, 1292; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}$: 183.1168 $[M+H-C_2H_6O_2]^+$; found 183.1172.

Indene-1,4-dioxepane *cis/trans*-6b (R^1 = OCH_3, R^2 = CH_3, n = 1): *conditions A*; (hexanes/ethyl acetate 9:1); (0.14 g, 60%); colorless oil; *cis*/*trans* ratio 1:3; δ_H (300 MHz; $CDCl_3$) 1.45 (d, *J* = 6.3 Hz, 3H), 1.55 (d, *J* = 6.3 Hz, 3H), 3.46 (dd, *J* = 0.9, 6.9 Hz, 1H), 3.67-3.90 (m, 10H), 3.95-4.13 (m, 3H), 4.52 (q, *J* = 6.3 Hz, 1H), 4.64-4.70 (m, 1H), 5.08 (s, 1H), 5.11 (s, 1H), 6.33 (s, 1H), 6.61 (s, H), 6.69 (dt, *J* = 2.4, 8.0 Hz, 1H), 6.79 (dt, *J* = 2.4, 8.0 Hz, 1H), 7.03-7.13 (m, 4H) ppm; δ_C (75 MHz; $CDCl_3$) 19.0, 23.5, 55.6, 69.6, 70.8, 71.5, 73.6, 74.2, 76.8, 84.8, 85.0, 110.5, 110.7, 113.7, 113.8, 121.1, 121.7, 125.9, 127.9, 135.3 (s), 144.5

(s), 145.8 (s), 150.5 (s), 155.1 (s), 158.5 (s), 158.8 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1480, 1286; HRMS (ESI): *m/z* calcd for $C_{14}H_{17}O_3$: 233.1172 $[M+H]^+$; found 233.1169.

Indene-1,4-dioxepane *trans*-6c (R^1 = H, R^2 = C_6H_5, n = 1): *conditions A*; (hexanes/diethyl ether 9:1); (0.12 g, 47%); mp 116-118 ºC (from diethyl ether); δ_H (300 MHz; $CDCl_3$) 3.87-3.95 (m, 1H), 4.12-4.15 (m, 2H), 4.20-4.26 (m, 1H), 5.26 (s, 1H), 5.53 (s, 1H), 6.23 (d, *J* = 1.2 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.15-7.21 (m, 2H), 7.27-7.40 (m, 5H), 7.45 (d, *J* = 6.9 Hz, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 73.8, 74.9, 83.5, 85.8, 120.9, 123.8, 125.8, 127.0, 128.0, 128.6, 128.7, 128.9, 142.3 (s), 142.6 (s), 155.4 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1494, 1290, 1164; HRMS (ESI): *m/z* calcd for $C_{18}H_{17}O_2$: 265.1233 $[M+H]^+$; found 265.1232.

Indene-1,5-dioxocane *trans*-7a (R^1 = H, R^2 = $C(CH_3)_3$, n = 2): *conditions A*; (hexanes/ethyl acetate 9:1); (0.11 g, 45%); colorless oil; δ_H (300 MHz; $CDCl_3$) 0.99 (s, 9H), 1.31-1.41 (m, 1H), 1.93-2.07 (m, 1H), 3.09-3.18 (m, 1H), 3.47 (dt, *J* = 2.1, 12.0 Hz, 1H), 3.69-3.76 (m, 1H), 3.98-4.05 (m, 2H), 5.19 (s, 1H), 6.64 (s, 1H), 7.17-7.30 (m, 3H), 7.49 (d, *J* = 7.6 Hz, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 27.1, 32.2, 35.5 (s), 66.2, 68.0, 83.9, 88.8, 120.6, 123.8, 125.8, 128.4, 134.4, 141.7 (s), 145.0 (s), 149.8 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1462, 1389, 1292; HRMS (ESI)M *m/z* calcd for $C_{14}H_{15}$: 183.1168 $[M+H-C_3H_8O_2]^+$; found 183.1172.

Indene-1,5-dioxocane *cis/trans*-7b (R^1 = H, R^2 = CH_3, n = 2): *conditions A*; (hexanes/diethyl ether 4:1); (0.13 g, 60%); colorless oil; *cis*/*trans* ratio 1:3; δ_H (300 MHz; $CDCl_3$) 1.29-1.34 (m, 2H), 1.46 (d, *J* = 6.6 Hz, 3H), 1.54 (d, *J* = 6.6 Hz, 3H), 1.78-1.89 (m, 1H), 1.96-2.11 (m, 1H) , 3.02-3.11 (m, 2H), 3.54 (dt, *J* = 1.8, 12.0 Hz, 3H), 3.62-3.72 (m, 3H), 3.85 (t, *J* = 5.4 Hz, 1H), 3.96-4.02 (m, 1H), 4.56 (q, *J* = 6.6 Hz, 1H), 4.61 (q, *J* = 6.6 Hz, 1H), 5.08 (s, 1H), 5.20 (s, 1H), 6.68 (s, 1H), 6.73 (s, 1H), 7.18-7.30 (m, 6H), 7.48-7.53 (m, 2H) ppm; δ_C (75 MHz; $CDCl_3$) 19.0, 23.0, 31.3, 32.4, 63.8, 65.6, 65.8, 67.6, 73.0, 75.3, 80.4, 84.8, 120.8, 121.2, 123.7, 124.0, 126.0, 128.5, 130.5, 131.8, 141.8 (s), 144.0 (s), 144.4 (s), 151.5 (s), 152.3 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1724, 1600, 1339; HRMS (ESI): m/z calcd for $C_{14}H_{17}O_2$: 217.1233 $[M+H]^+$; found 217.1233.

Indene-1,4-oxathiepane *cis*-8: *conditions A*; (hexanes/ethyl acetate 95:5); (0.16 g, 58%); colorless oil; δ_H (300 MHz; $CDCl_3$) 1.40 (s, 9H), 2.55-2.63 (m, 1H), 2.91-3.03 (m, 2H), 3.69 (s, 1H), 3.88-3.96 (m, 1H), 4.91 (s, 1H), 6.79 (d, *J* = 1.8 Hz, 1H), 7.14-7.20 (m, 2H), 7.25-7.30 (m, 1H), 7.47 (d, *J* = 7.2 Hz, 1H) ppm; δ_C (75 MHz; $CDCl_3$) 28.7, 33.2, 35.0 (s), 53.4,

67.4, 86.1, 120.9, 123.5, 125.4, 126.9, 128.8, 141.1 (s), 144.2 (s), 152.7 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1608, 1458, 1396; HRMS (ESI): *m/z* calcd for $C_{16}H_{21}OS$: 261.1308 $[M+H]^+$; found 261.1315.

Indene-1,4-dithiepane 9: *conditions B*; (hexanes/ethyl acetate 9:1); (0.23 g, 83%); colorless oil; δ_H (400 MHz; $CDCl_3$) 1.18 (s, 9H), 2.12 (ddd, *J* = 2.0, 10.0, 15.6 Hz, 1H), 2.66 (ddd, *J* = 2.0, 6.0, 15.6 Hz, 1H), 2.87-2.99 (m, 2H), 3.97 (s, 1H), 4.29 (s, 1H), 6.91 (s, 1H), 7.16-7.26 (m, 3H), 7.47 (dd, *J* = 0.8, 7.6 Hz, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 28.4, 30.3, 34.7, 35.5 (s), 52.8, 54.5, 120.9, 124.0, 125.3, 127.6, 129.4, 143.7 (s), 145.6 (s), 153.3 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1478, 1390, 1361; HRMS (ESI): *m/z* calcd for $C_{16}H_{21}S_2$: 277.1079 $[M+H]^+$; found 277.1078.

1-Methoxy-1H-indene 10: *conditions A*; (hexanes/diethyl ether 9:1); (0.15 g, 61%); colorless oil; δ_H (400 MHz; $CDCl_3$) 1.03 (s, 9H,), 3.27 (s, 3H), 3.35 (s, 3H), 3.64 (s, 1H), 5.09 (s, 1H), 6.67 (s, 1H), 7.17-7.29 (m, 3H), 7.46-7.48 (m, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 26.8, 35.7 (s), 55.0, 58.2, 85.4, 88.6, 121.2, 123.7, 125.7, 128.4, 133.5, 141.9 (s), 143.4 (s), 147.0 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1465, 1364, 1179; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}$: 183.1168 $[M+H-C_2H_8O_2]^+$; found 183.1171.

1-(Ethylthio)-1H-indene 11: *conditions B*; (hexanes/diethyl ether 9:1); (0.26 g, 99%); colorless oil; δ_H (400 MHz; $CDCl_3$) 0.98 (t, *J* = 7.6 Hz, 3H), 1.19 (t, *J* = 7.6 Hz, 3H), 1.22 (s, 9H), 1.81-1.89 (m, 1H), 1.96-2.04 (m, 1H), 2.43-2.52 (m, 1H), 2.57-2.65 (m, 1H), 3.75 (s, 1H), 4.53 (s, 1H), 6.72 (s, 1H), 7.16-7.25 (m, 3H), 7.54 (d, *J* = 7.2 Hz, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 13.9, 14.9, 21.3, 28.0, 28.8, 36.3 (s), 53.7, 54.9, 120.8, 123.9, 125.2, 127.3, 127.4, 143.4 (s), 143.9 (s), 149.5 (s) ppm; ; IR (Neat): ν_{max}/cm^{-1} 1607, 1461, 1392; HRMS (ESI): *m/z* calcd for $C_{16}H_{21}S$: 245.1358 $[M+H-C_2H_6S]^+$; found 245.1362.

1H-Indene 12a (R^1 = CH_3CH_2): *conditions B*; (hexanes/diethyl ether 4:1); (0.32 g, 83%); yellow oil; δ_H (400 MHz; $CDCl_3$) 0.94 (t, *J* = 7.2 Hz, 3H), 1.30 (s, 9H), 1.37 (t, *J* = 7.2 Hz, 3H), 2.01-2.08 (m, 1H), 2.18-2.27 (m, 1H), 2.63-2.73 (m, 2H), 4.09 (s, 1H), 5.33 (s, 1H), 6.94-6.97 (m, 1H), 7.14-7.40 (m, 8H) ppm; δ_C (100 MHz; $CDCl_3$) 14.0, 26.0, 27.7, 31.2, 37.8 (s), 47.8, 52.6, 123.7, 126.2, 127.0, 127.2, 127.6, 127.8, 128.2, 130.7, 137.8 (s), 141.7 (s), 142.7 (s), 143.8 (s), 148.5 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1475, 1458, 1392; HRMS (ESI): *m/z* calcd for $C_{24}H_{30}NaS_2$: 405.1681 $[M+Na]^+$; found 405.1677.

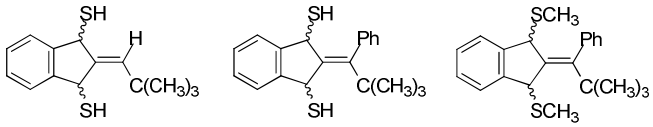
1H-Indene 12b (R^1 = $PhCH_2CH_2$): *conditions B*; (hexanes/ethyl acetate 9:1); (0.43 g, 80%); yellow oil; δ_H (300 MHz; $CDCl_3$) 1.27 (s, 9H), 2.24-2.27 (m, 1H), 2.44-2.54 (m, 3H), 2.87-3.00 (m, 4H), 4.14 (s, 1H), 5.33 (s, 1H), 6.93-7.12 (m, 4H), 7.13-7.38 (m, 15H) ppm; δ_C (75 MHz; $CDCl_3$) 31.2, 33.6, 35.3, 35.7, 35.8, 37.8 (s) , 48.4, 53.1, 123.8, 126.2, 126.3, 126.4, 127.3, 127.4, 128.0, 128.2, 128.4, 128.5, 128.6, 130.7, 137.7 (s), 140.8 (s), 140.9 (s), 141.7 (s), 142.7 (s), 143.7 (s), 149.0 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1475, 1458, 1392; HRMS (ESI): *m/z* calcd for $C_{36}H_{38}KS_2$: 573.2047 $[M+K]^+$; found 573.2047.

1H-Indene 12c (R^1 = 4-Cl-C_6H_4-CH_2): *conditions B*; (hexanes/ethyl acetate 4:1); (0.50 g, 87%); mp 119-121 ºC (from diethyl ether); δ_H (300 MHz; $CDCl_3$) 1.16 (s, 9H), 3.08 (d, *J* = 13.5 Hz, 1H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.71 (d, *J* = 13.5 Hz, 1H), 3.79 (d, *J* = 13.5 Hz, 1H), 4.05 (s, 1H), 5.19 (s, 1H), 6.45 (d, *J* = 7.2 Hz, 1H), 6.85-6.91 (m, 3H), 7.15-7.39 (m, 13H) ppm; δ_C (75 MHz; $CDCl_3$) 31.1, 36.1, 37.5, 37.7 (s), 48.4, 52.0, 123.7, 124.1, 126.4, 127.3, 127.6, 127.9, 128.0, 128.4, 128.6, 128.7, 130.3, 130.5, 130.6, 132.5 (s), 132.8 (s), 136.3 (s), 136.9 (s), 137.6 (s), 141.8 (s), 142.6 (s), 143.1 (s), 149.1 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1596, 1488, 1264; HRMS (ESI): m/z calcd for $C_{34}H_{32}Cl_2NaS_2$: 597.1215 $[M+Na]^+$; found 597.1218.

1H-Indene 12d (R^1 = 4-Br-C_6H_4-CH_2): *conditions B*; (hexanes/ethyl acetate 4:1); (0.56 g, 85 %); mp 125-127 ºC (from diethyl ether); δ_H (400 MHz; $CDCl_3$) 1.17 (s, 9H), 3.08 (d, *J* = 13.6 Hz, 1H), 3.31 (d, *J* = 13.6 Hz, 1H), 3.70 (d, *J* = 13.5 Hz, 1H), 3.79 (d, *J* = 13.5 Hz, 1H), 4.06 (s, 1H), 5.21 (s, 1H), 6.47 (d, *J* = 7.2 Hz, 1H), 6.82-6.83 (m, 2H), 6.90-6.93 (m, 1H), 7.08-7.15 (m, 1H), 7.19-7.21 (m, 2H), 7.28-7.46 (m, 10H) ppm; δ_C (100 MHz; $CDCl_3$) 31.2, 36.2, 37.6, 37.7 (s), 48.5, 52.1, 120.6, 120.9, 123.8, 124.2, 126.5, 127.3, 127.6, 128.0, 128.4, 130.5, 130.7, 130.9, 131.1 (s), 131.6, 131.7 (s), 136.9 (s), 137.5 (s), 137.7 (s), 141.9 (s), 142.6 (s), 143.1 (s), 149.2 (s) ppm; IR (Neat): ν_{max}/cm^{-1} 1589, 1361, 1070; HRMS (ESI): m/z calcd for $C_{34}H_{33}Br_2S_2$: 663.0390 $[M+H]^+$; found 663.0392.

DFT Computational Study

The 1,3-disubstituted 2-alkylidene-2,3-dihydroindenes **28**, **29** and **30** shown in Figure S1 have been used as slightly simplified models of compounds **12** in the experimental study. Their geometries have been fully optimized by DFT methods using the B3LYP functional[6] and the 6-311++G(d,p) basis set[7] as implemented in the Gaussian 09 package.[8] All the energy minima were characterized by frequency analysis.



28 **29** **30**

Figure S1. 2-Alkylidene-2,3-dihydroindenes **28**, **29** and **30**

The *cis* and *trans* diasteroisomers of **28**, **29** and **30** have been computed. Their relative energies are gathered in Table S1. In the three pairs, the *cis* diasteroisomer is always the most stable one. The difference in energy between the two diasteroisomers in each pair increases with the substitution at the exocyclic carbon atom (compare entries 1 and 2). With a methyl group linked to each S atom, entry 3, the *cis* diasteroisomer is still the most stable although in slightly lower extent.

Table S1. Relative energies (RE, in kJ.mol^{-1}) of the *cis* and *trans* diasteroisomers of **28**, **29** and **30**.

Entry	2,3-Dihydroindene	RE
1	*cis*_**28**	0.0
	*trans*_**28**	4.4
2	*cis*_**29**	0.0
	*trans*_**29**	24.4
3	*cis*_**30**	0.0
	*trans*_**30**	19.6

The B3LYP energies in Hartrees, the number of imaginary frequencies (NIMAG) and the Cartesian coordinates of 2-alkylidene-2,3-dihydroindenes **28**, **29** and **30** are collected in Table S2.

Table S2. B3LYP energies in Hartrees, Number of Imaginary Frequencies (NIMAG) and Cartesian Coordinates of 2-Alkylidene-2,3-dihydroindenes **28**, **29** and **30**

*cis*_**28**, B3LYP Energy= -1340.89255049 Hartree, NIMAG= 0	*trans*_**28**, B3LYP Energy= -1340.89088471 Hartree, NIMAG= 0
C,-3.1561283418,0.9856590598,0.1729834743	C,-2.6596736437,1.8698664396,0.0960029709
C,-3.2875953401,-0.4047951061,0.1041756997	C,-3.1875589365,0.6789005052,0.6016260729
C,-2.1604896505,-1.2248608662,0.0898265164	C,-2.3866571812,-0.4578039533,0.7098928923
C,-0.9000842501,-0.6364897034,0.15322345	C,-1.0552748209,-0.3841974504,0.3081424244
C,-0.7694532727,0.752660865,0.2254399111	C,-0.5241116176,0.8105584588,-0.1816553021
C,-1.8936530872,1.5748409215,0.2298446198	C,-1.3227129653,1.9438806434,-0.2962948129
H,-4.0427462605,1.609459513,0.1832756465	H,-3.2921450766,2.7469799505,0.0173621216
H,-4.2759405789,-0.8485652639,0.0611106319	H,-4.2242802783,0.6401241422,0.9166343261
H,-2.2651306452,-2.3021887057,0.0222211913	H,-2.7983437578,-1.3807841254,1.1057915263
H,-1.7911897249,2.6535155029,0.2775292903	H,-0.9054275651,2.8732159424,-0.6668423721
C,0.4526826086,-1.3061235942,0.173692626	C,-0.0160648783,-1.4726995424,0.3137866923
H,0.4818015779,-2.1461646941,0.8630890539	H,-0.0390687541,-2.0828990089,1.2113434853
C,0.685294162,1.1387602266,0.2826379137	C,0.9341191111,0.626062525,-0.5399454012
H,0.9025026221,1.901329651,1.0297714948	H,1.0348696749,0.5479107153,-1.6293398779
C,1.390842466,-0.1783035468,0.578514232	C,1.2922331036,-0.7241663554,0.1107309944
C,2.5809517937,-0.2038602487,1.1891068608	C,2.5414618874,-1.0848700804,0.4160187426
H,3.0066796427,0.7802967394,1.3944607198	H,3.2954635939,-0.3390523229,0.1669143062
S,0.8803651419,-2.1152945218,-1.4646308322	S,-0.2298161316,-2.6441390598,-1.1490947629
H,0.9258698327,-0.9684993318,-2.1748248056	H,-1.5451322353,-2.8868643633,-0.9668600621
S,1.1412173175,1.8830967684,-1.3864032828	S,2.0282915198,2.0598560435,-0.1576666383
H,2.4601328375,2.0167981059,-1.1326874406	H,1.7993293128,2.073941334,1.1726920075
C,3.519271963,-1.3155054565,1.6284184183	C,3.161957566,-2.3306209734,1.0268521272
C,2.8998588945,-2.7221166667,1.6669931764	C,2.1808645491,-3.3093850028,1.6932019603
C,4.7218786679,-1.318974411,0.6532004182	C,3.925275079,-3.0675270284,-0.1009768364
C,4.0262052651,-0.9619545781,3.0461938814	C,4.1819247959,-1.8590375007,2.0904393048
H,2.0473316596,-2.7666006582,2.35062783	H,1.6326135679,-2.8313574009,2.509913744
H,2.5816588936,-3.0527650198,0.6772471472	H,1.4663039719,-3.7255326021,0.9807322142
H,3.6445843407,-3.4376166728,2.0281879728	H,2.7403907138,-4.1459610116,2.1223494692
H,5.203223461,-0.337146466,0.6135062096	H,4.6454118183,-2.4058267907,-0.5910340347
H,5.4723330948,-2.046581873,0.9787098943	H,4.4762242611,-3.9201105011,0.309023535
H,4.4023173277,-1.5830557536,-0.3575136972	H,3.2350407718,-3.4397407345,-0.8620321393
H,4.7566985261,-1.70204595,3.3857508868	H,4.7118927215,-2.7155815748,2.517563947
H,4.5106331972,0.0189995319,3.0624932495	H,4.9260292286,-1.1856456062,1.6553845784
H,3.2025414583,-0.9431586968,3.7656410418	H,3.6828373938,-1.3277770106,2.9059890969
*cis*_**29**, B3LYP Energy= -1571.98999686 Hartree, NIMAG= 0	*trans*_**29**, B3LYP Energy= -1571.98071619 Hartree, NIMAG= 0
C,-3.2620553602,0.6483440119,0.2935353436	C,-4.5314573063,-1.704523551,0.2570937557
C,-3.2070366643,-0.6924189736,-0.1018579943	C,-4.9411957772,-0.3983136778,-0.029062599
C,-1.9849929971,-1.3565470647,-0.1912244398	C,-3.9992511545,0.6095504534,-0.2219291057
C,-0.8198244415,-0.6632861761,0.1276383134	C,-2.6443767769,0.2936064728,-0.1305886097
C,-0.8752414558,0.6724343608,0.5230451945	C,-2.236641522,-1.0125091963,0.1194202411
C,-2.0938193549,1.3429144332,0.6032057354	C,-3.1764621408,-2.0220182181,0.3217570489
H,-4.2207185403,1.1505646729,0.3581090331	H,-5.2739672951,-2.4787716853,0.4138321832
H,-4.1241479927,-1.2190374284,-0.3411575453	H,-5.9985436854,-0.1689825847,-0.0993861506
H,-1.9431613295,-2.3918212311,-0.5117636186	H,-4.3223722555,1.6235666383,-0.434929523
H,-2.1339439994,2.3856111781,0.8987465131	H,-2.858341781,-3.0417949753,0.505750064
C,0.6009207964,-1.1664672955,0.143896006	C,-1.4653744604,1.2207905388,-0.2101643001
H,0.666837877,-2.1347641959,0.6267802325	H,-1.5063429213,1.8948496247,-1.0608633402
C,0.5093258381,1.193873214,0.7986909331	C,-0.7365437933,-1.1326978308,0.0466664186
H,0.5666141357,1.8105036488,1.6912220738	H,-0.3042412666,-1.6017492121,0.9296082759
C,1.3638439817,-0.0717968681,0.8885183216	C,-0.2336570255,0.3069792355,-0.1772625971
C,2.5152627907,-0.138079466,1.5897433951	C,1.073805212,0.6456960969,-0.2475209431
S,1.2571832852,-1.527697771,-1.5772261393	S,-1.4217365457,2.2919263994,1.3459122221
H,1.2359241778,-0.246746095,-2.002030092	H,-2.7011848683,2.715408955,1.2766314111
S,0.9552158975,2.3293426445,-0.6395498706	S,-0.4153696622,-2.3184039003,-1.3759470468

H,2.1397925537,2.7421801071,-0.1430167744	H,0.8813213222,-2.5632614899,-1.1048688592
C,3.4720197132,-1.350639889,1.7675176063	C,1.6966017418,2.0308825424,-0.5940870072
C,2.8044225715,-2.7339443595,1.6237278852	C,0.7494794088,2.9923078278,-1.3418820316
C,4.6015222561,-1.253648414,0.710949739	C,2.1921936653,2.714388203,0.7038566585
C,4.1166877,-1.3206001677,3.1752346822	C,2.9245948307,1.8481774323,-1.5237079214
H,1.9313263392,-2.8347693852,2.274421409	H,0.3337220577,2.5237925645,-2.2381159152
H,2.5197458968,-2.9535010957,0.5953080529	H,-0.059620982,3.3602043112,-0.7134241219
H,3.5237567185,-3.5015938929,1.9226026473	H,1.3227265941,3.8652648582,-1.6660314152
H,5.2016059227,-0.3512100887,0.842658688	H,2.9236739097,2.093638589,1.2264814339
H,5.2740338826,-2.1114549827,0.8138360706	H,2.6777790683,3.6637323968,0.4565887623
H,4.1906954844,-1.259033515,-0.3007905458	H,1.3666606111,2.926106628,1.3851044439
H,4.7989749456,-2.1692260681,3.2748497615	H,3.3276738533,2.8344797203,-1.7684964695
H,4.6885190616,-0.409404766,3.3528356866	H,3.7240333499,1.2722747643,-1.0582764483
H,3.3627124797,-1.4047261265,3.9635755843	H,2.6488448845,1.3622080613,-2.4639519452
C,2.9867816277,1.1334467253,2.2506869545	C,2.0763487772,-0.4086978971,0.1547929191
C,3.918524028,1.9783970807,1.6325685782	C,2.262016665,-0.6723227436,1.5193882117
C,2.5032940408,1.4985102162,3.515072993	C,2.8466108261,-1.1359876774,-0.7644105254
C,4.3588324248,3.1439663602,2.2612361389	C,3.1851556954,-1.6233451283,1.9530556271
H,4.3018673485,1.7248418683,0.6511923083	H,1.6737863711,-0.1235866879,2.2468739111
C,2.9381526481,2.6635213085,4.1427428411	C,3.7668428373,-2.0904930109,-0.3341976802
H,1.779574636,0.8595384244,4.0095056765	H,2.7190071662,-0.9612124402,-1.8253238178
C,3.8714185246,3.4904588035,3.5188388456	C,3.9417810434,-2.3368248363,1.0267120847
H,5.0802502703,3.7821908022,1.762795092	H,3.3098794225,-1.8051989779,3.0148460065
H,2.5481064885,2.9247041827,5.1203971359	H,4.3461889535,-2.6434410047,-1.0654960586
H,4.2116269924,4.3967457727,4.0067613484	H,4.6589859529,-3.078254588,1.3601967528
*cis_**30***, B3LYP Energy= -1650.62962857 Hartree, NIMAG= 0	*trans_**30***, B3LYP Energy= -1650.62215681 Hartree, NIMAG= 0
C,-3.7774383608,-1.9977686429,-1.4036924713	C,-4.3658114085,-1.8650121355,0.0365916577
C,-4.3104463782,-0.7315113908,-1.6533946035	C,-4.8349544493,-0.5741395258,-0.2225761129
C,-3.5748728623,0.4166223186,-1.3536649916	C,-3.9413546632,0.4891226042,-0.3403948233
C,-2.30881141,0.2802186926,-0.7884395943	C,-2.5749239281,0.2462251672,-0.1925058127
C,-1.7715058782,-0.9882878595,-0.5496725562	C,-2.10456263,-1.0516229373,0.0000738234
C,-2.5006070408,-2.13329656,-0.856998774	C,-2.9979310595,-2.1123223941,0.1319321864
H,-4.3532717872,-2.8822045856,-1.6526199258	H,-5.0697419184,-2.6836891986,0.1360925566
H,-5.2957821291,-0.6398080761,-2.0965030003	H,-5.8991956353,-0.3996887865,-0.3349075813
H,-3.9823324609,1.3960496183,-1.5785398248	H,-4.309971275,1.4862722254,-0.5520163605
H,-2.0830813315,-3.1201924901,-0.6904103378	H,-2.6396223464,-3.1252455763,0.2775330631
C,-1.3192079219,1.3562560254,-0.4206156992	C,-1.4427319093,1.2333598125,-0.1831338586
H,-1.2938753464,2.1505179794,-1.1590587515	H,-1.5237556479,1.9885538257,-0.9610568223
C,-0.378373016,-0.8688550582,0.0030400654	C,-0.6005363991,-1.0953013889,-0.0778569572
H,0.3237499962,-1.5678793178,-0.4480374129	H,-0.1330318592,-1.5853048016,0.7773420148
C,-0.0039138773,0.5890405861,-0.2889274258	C,-0.1708255806,0.3776133648,-0.2255346925
C,1.2690820248,1.0031537907,-0.4560230039	C,1.1214401995,0.775204825,-0.2755622929
S,-1.6658466065,2.1629377085,1.2365205925	S,-1.37045059,2.1367680157,1.4693923564
S,-0.3170977736,-1.2459035434,1.8452499624	S,-0.0926911262,-2.1211008189,-1.5707452003
C,1.800310767,2.4407955889,-0.708537424	C,1.6887326801,2.1897244332,-0.5885842453
C,0.7665609637,3.4366525742,-1.2702217663	C,0.6825564728,3.1590879832,-1.2411791963
C,2.3237595771,3.0060161772,0.6364366843	C,2.2368611662,2.8388423273,0.7053788586
C,2.977755004,2.4128201204,-1.7137434212	C,2.8664056629,2.0632616002,-1.5907586367
H,0.3355750336,3.0849371173,-2.2115786949	H,0.2393814524,2.7293288408,-2.1436525218
H,-0.0312880291,3.651131864,-0.558900649	H,-0.1060774542,3.4613455503,-0.5538189142
H,1.2743697617,4.3825673371,-1.4796477921	H,1.2147798878,4.0667234455,-1.5396320571
H,3.1355688566,2.398418094,1.0407266029	H,3.0119497218,2.2216915693,1.1644585772
H,2.713150584,4.0176312048,0.4825408354	H,2.6819136768,3.8102431214,0.4673352699
H,1.5232311669,3.0571812882,1.3777689574	H,1.4391971077,2.9981787895,1.4327637034
H,3.3397983239,3.4328498801,-1.8696506994	H,3.2308858376,3.0647848087,-1.8347465997
H,3.815107852,1.8118071993,-1.3584146595	H,3.7034485452,1.4978798858,-1.1819559911
H,2.6655103959,2.0187345303,-2.685346391	H,2.5508114143,1.5880193142,-2.5240638242
C,2.3429066397,-0.0503711115,-0.3360462918	C,2.165769422,-0.2449492843,0.1117485311
C,2.9636384298,-0.3318300045,0.8868527487	C,2.3661586766,-0.4959500641,1.4770948934
C,2.7345148719,-0.7871750732,-1.4631820662	C,2.958674679,-0.9444365748,-0.8077373631
C,3.9575893038,-1.3069539632,0.9758129205	C,3.3341402719,-1.4012348141,1.9129760709
H,2.6515126633,0.1977927674,1.777449639	H,1.757001354,0.0291413405,2.2049392106
C,3.7238174654,-1.7643527543,-1.3757402744	C,3.9231010355,-1.8526563435,-0.3757543088
H,2.2575247862,-0.5908504411,-2.4174150986	H,2.8090078461,-0.7916944787,-1.8677990377
C,4.3435960763,-2.0247088972,-0.1541632061	C,4.1192297051,-2.0819195702,0.9860350745
H,4.4248743306,-1.5085066662,1.933625176	H,3.4719554947,-1.5703976856,2.9753511511
H,4.0105781927,-2.3203149801,-2.261741954	H,4.5224480872,-2.38403829,-1.1071161528
H,5.1165210321,-2.7819272952,-0.0837340876	H,4.8738526902,-2.7859267689,1.318888948
C,-3.3188918365,2.8887286698,0.9707055273	C,-2.9376270779,3.07113449,1.5035461763
H,-3.3195042309,3.5796818076,0.1248067065	H,-2.8851125725,3.7039149762,2.3910773163
H,-4.0755887874,2.1169534226,0.8300140767	H,-3.0382941774,3.7113940828,0.6244710839
H,-3.5491234784,3.4477469447,1.8789364126	H,-3.799147138,2.4099685356,1.5917070385
C,0.1525120166,-3.0108715845,1.7919487548	C,0.4739241735,-3.6585106195,-0.764563175
H,-0.6223626659,-3.6234057654,1.3284757557	H,1.3252404182,-3.4614104759,-0.1117462065

H,1.1042268186,-3.1458856675,1.2744679424 H,0.2677658743,-3.3267754794,2.8300783883	H,-0.3290808029,-4.1449577816,-0.2090834094 H,0.7918568699,-4.3237058202,-1.5690468081

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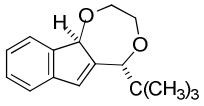
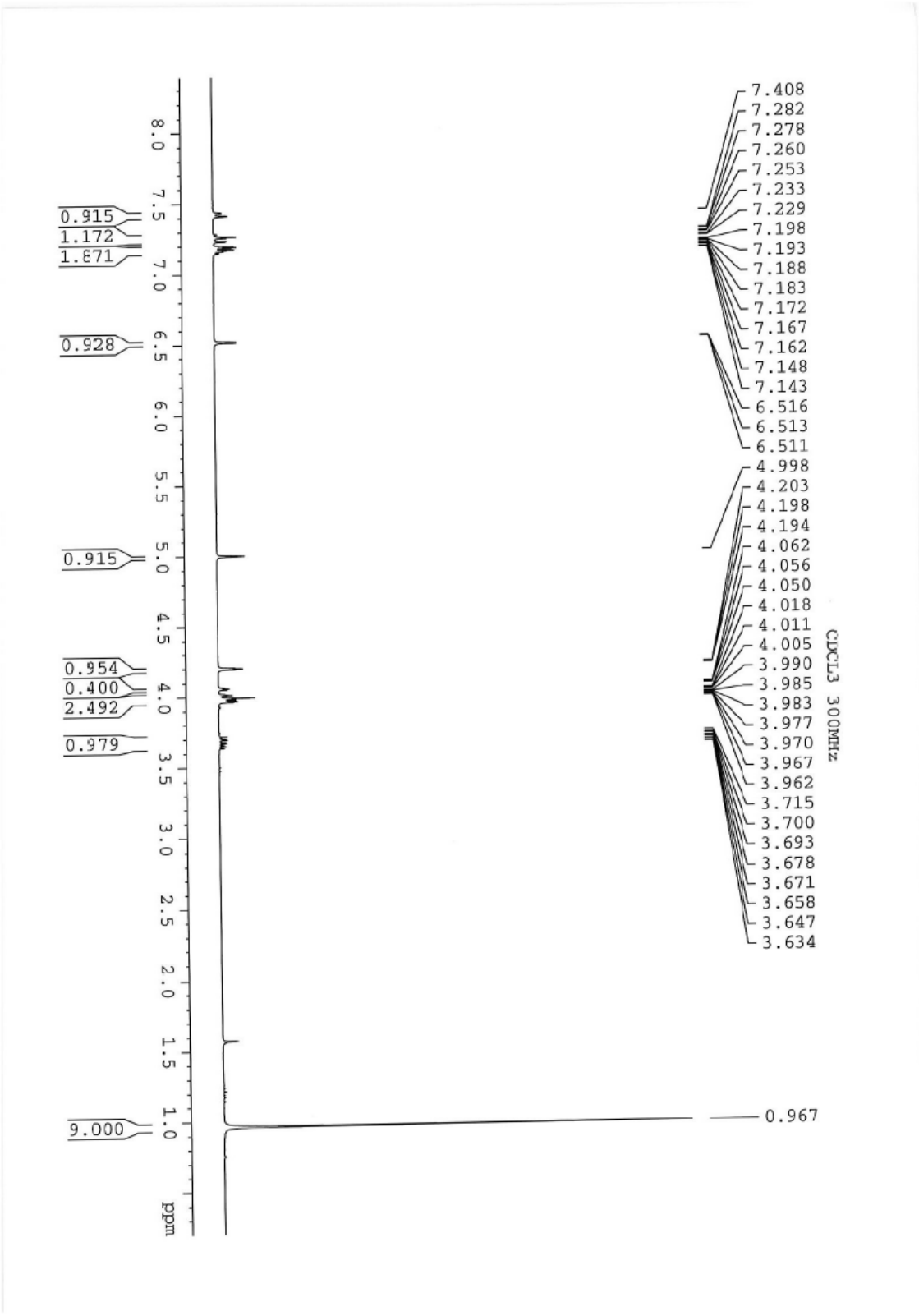
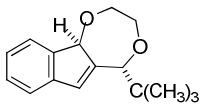
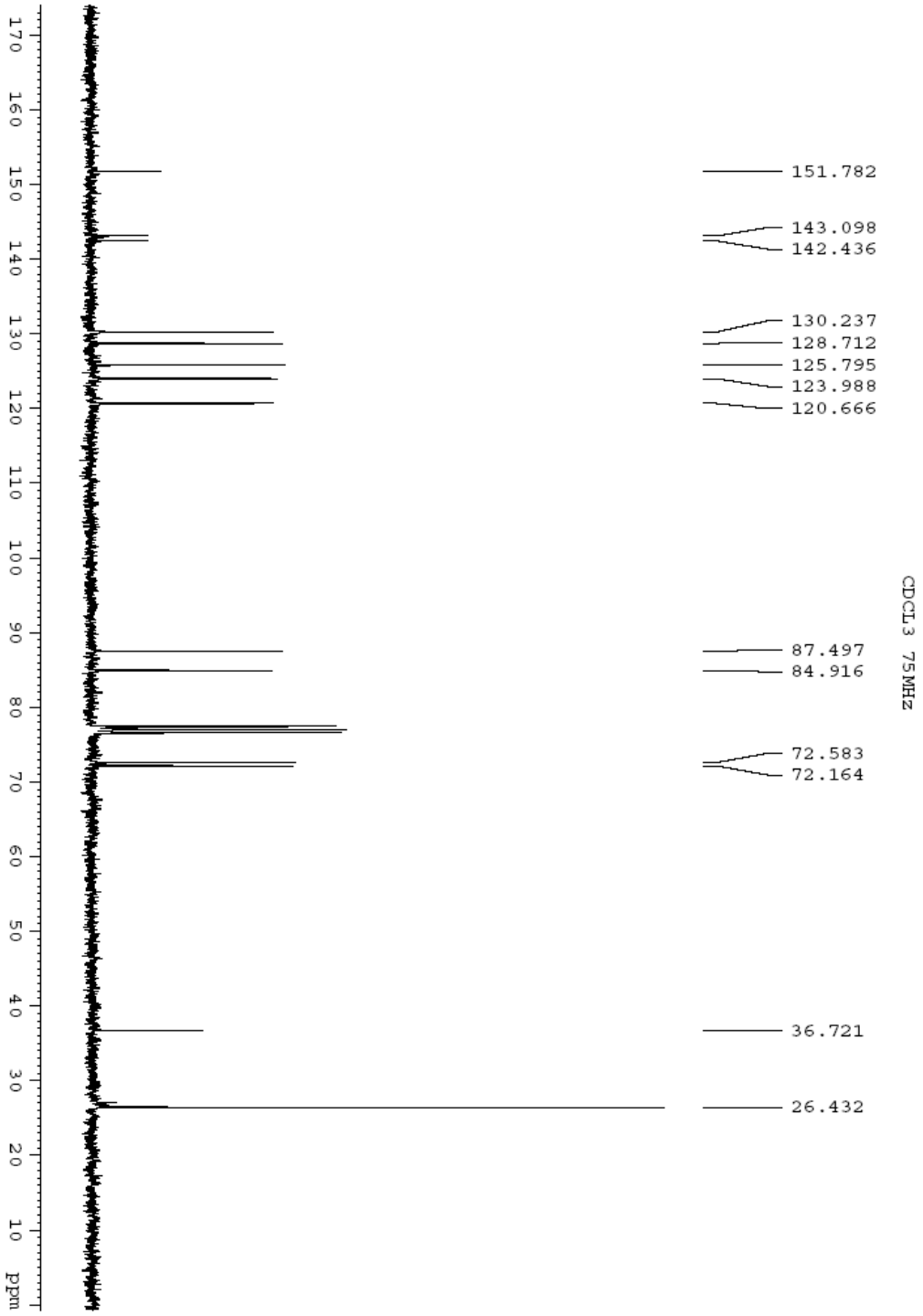
^{1}H NMR of ***trans*-6a**



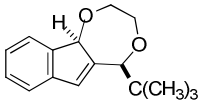


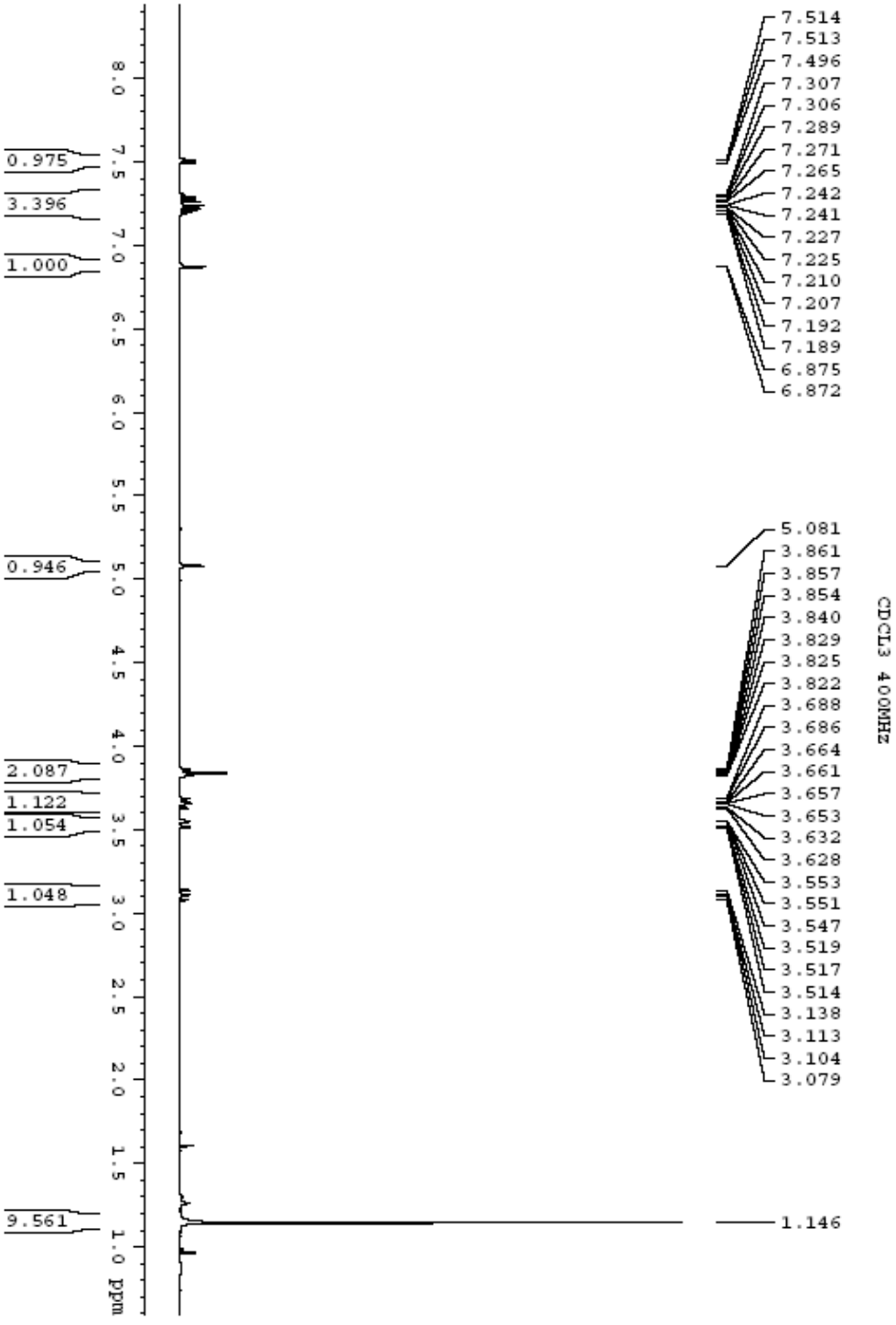
^{13}C NMR of ***trans*-6a**



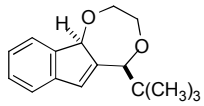


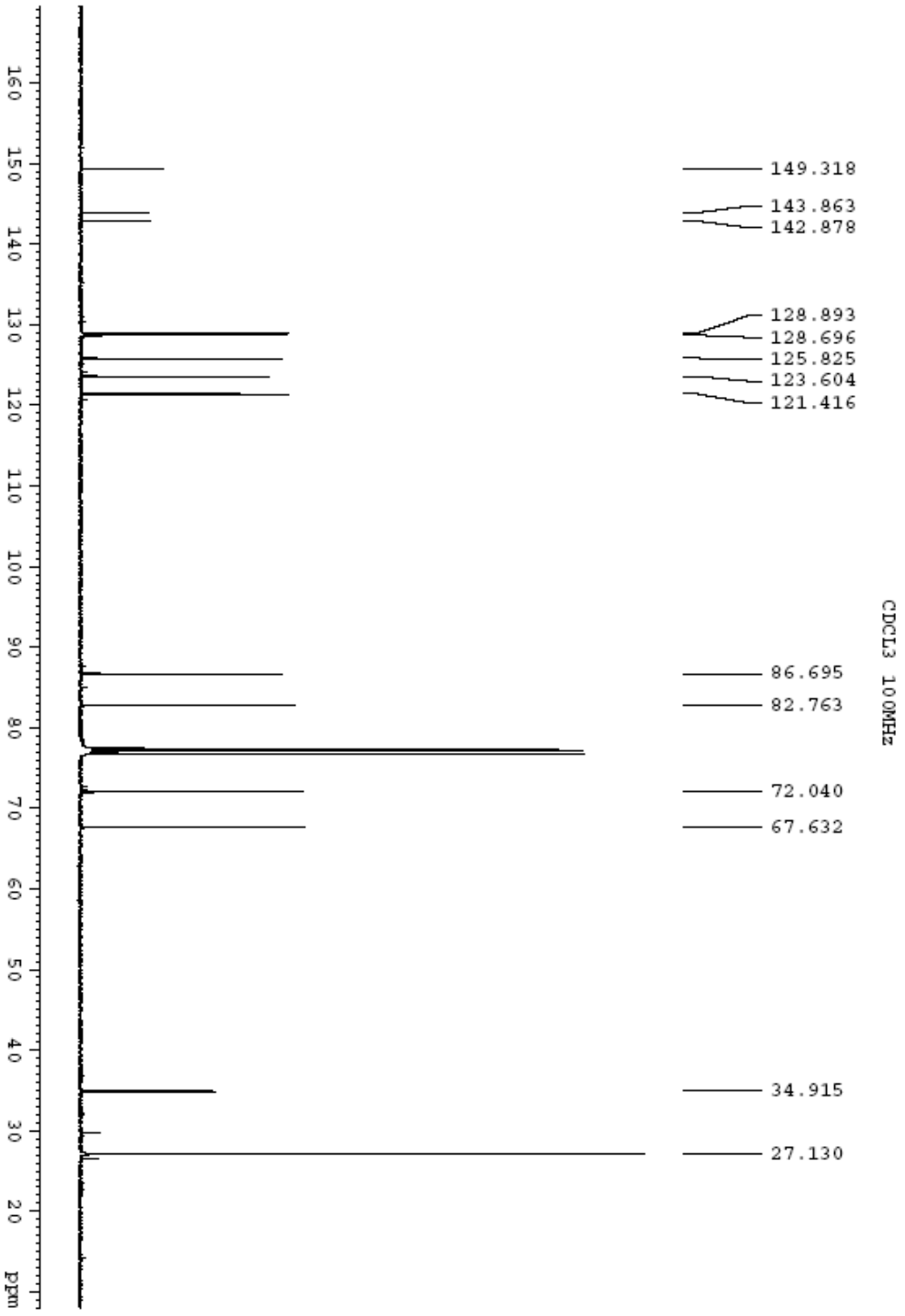
^{1}H NMR of ***cis*-6a**



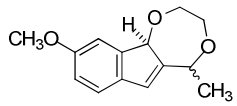


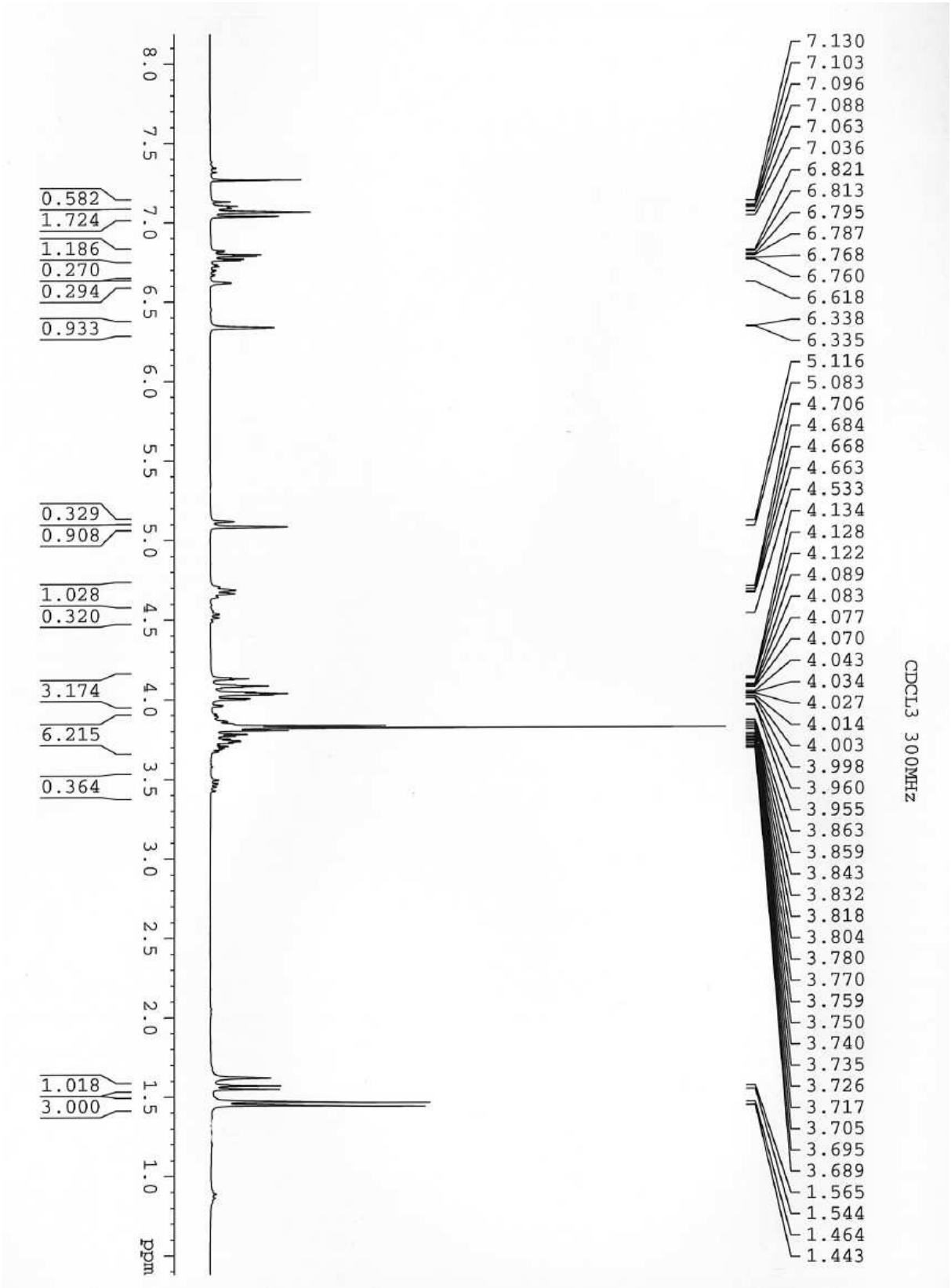
^{13}C NMR of ***cis*-6a**



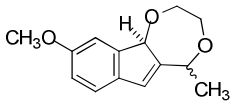


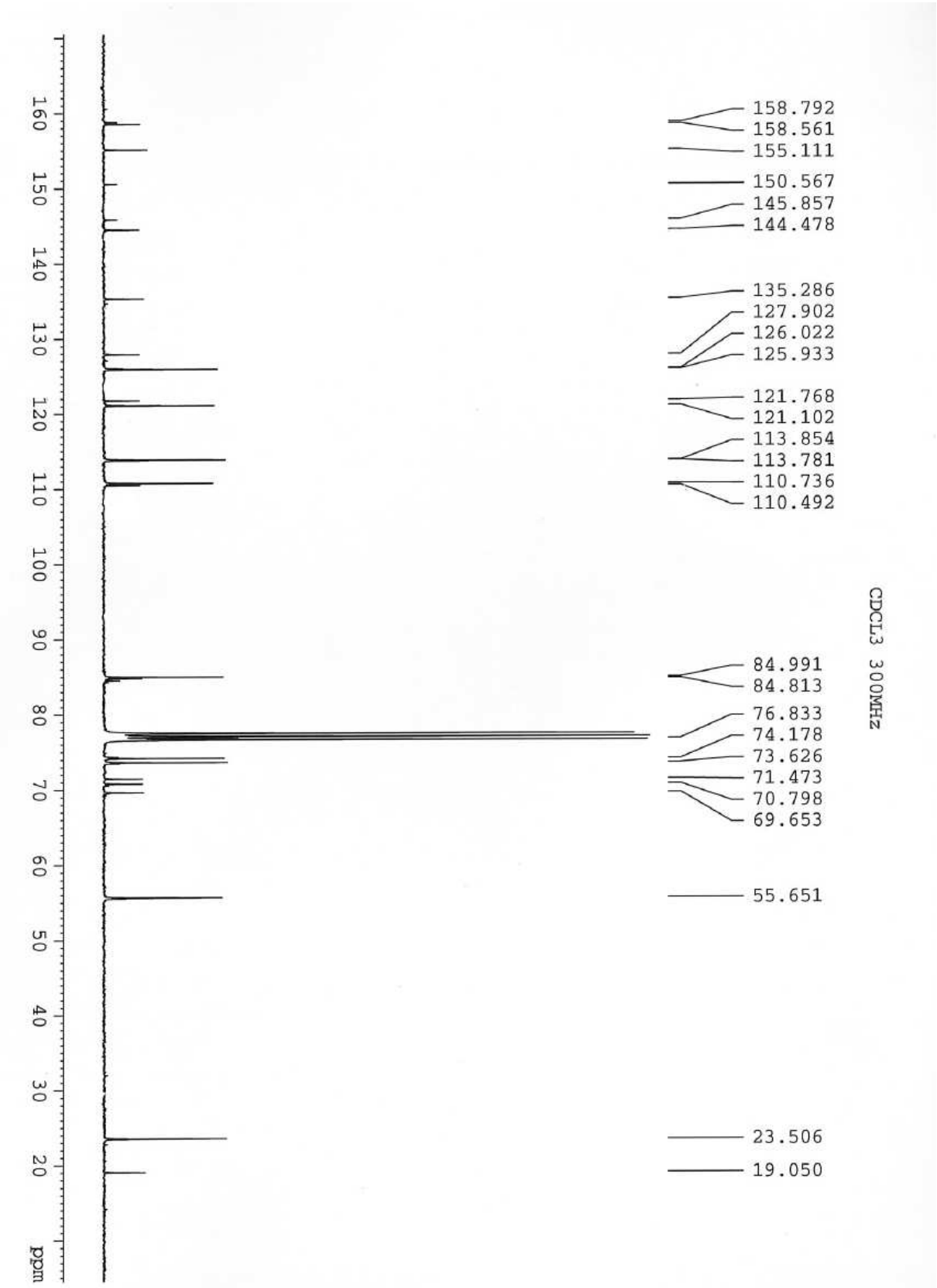
^{1}H NMR of ***cis***/***trans*-6b**



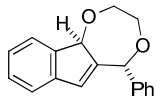


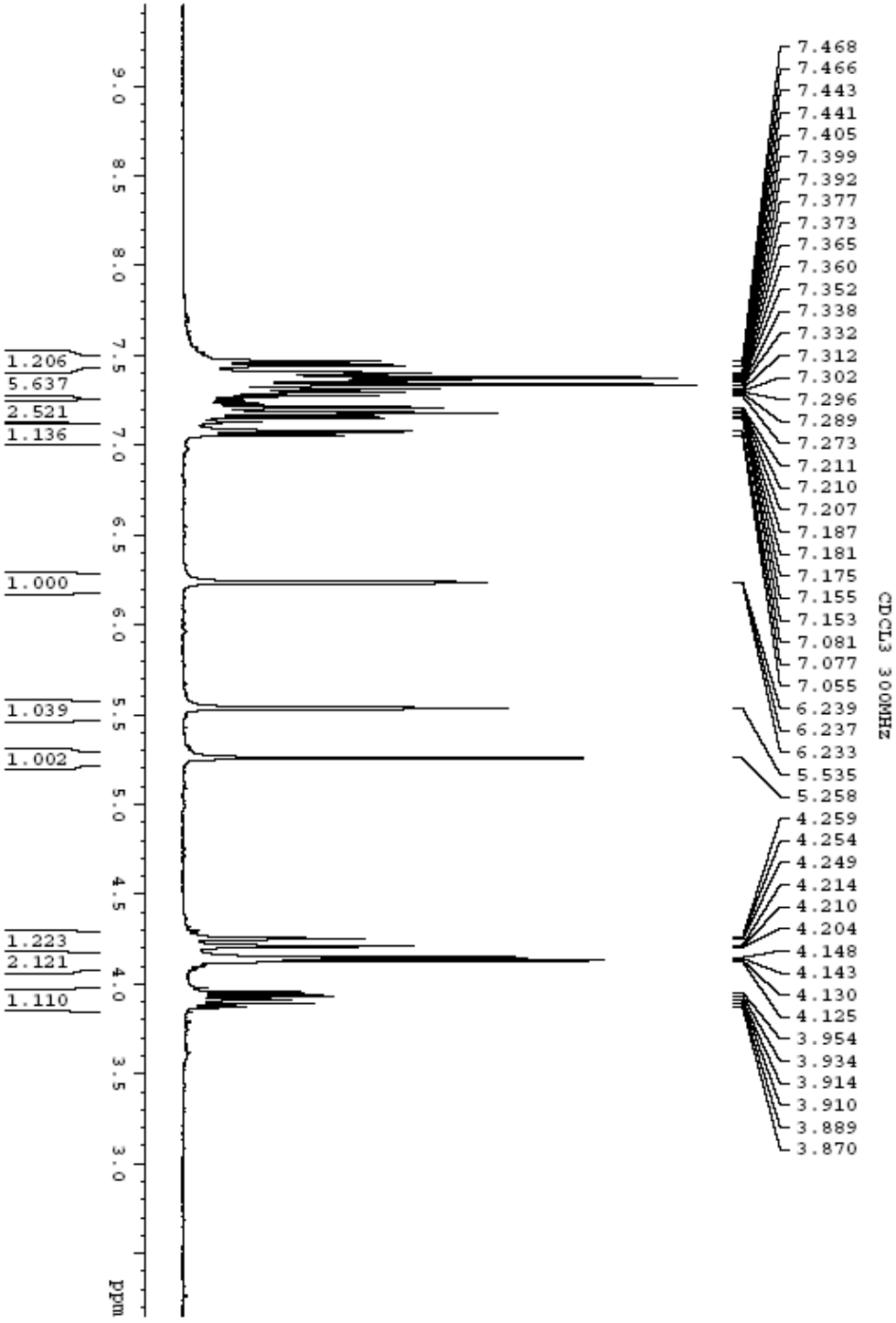
^{13}C NMR of ***cis*/*trans*-6b**



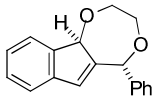


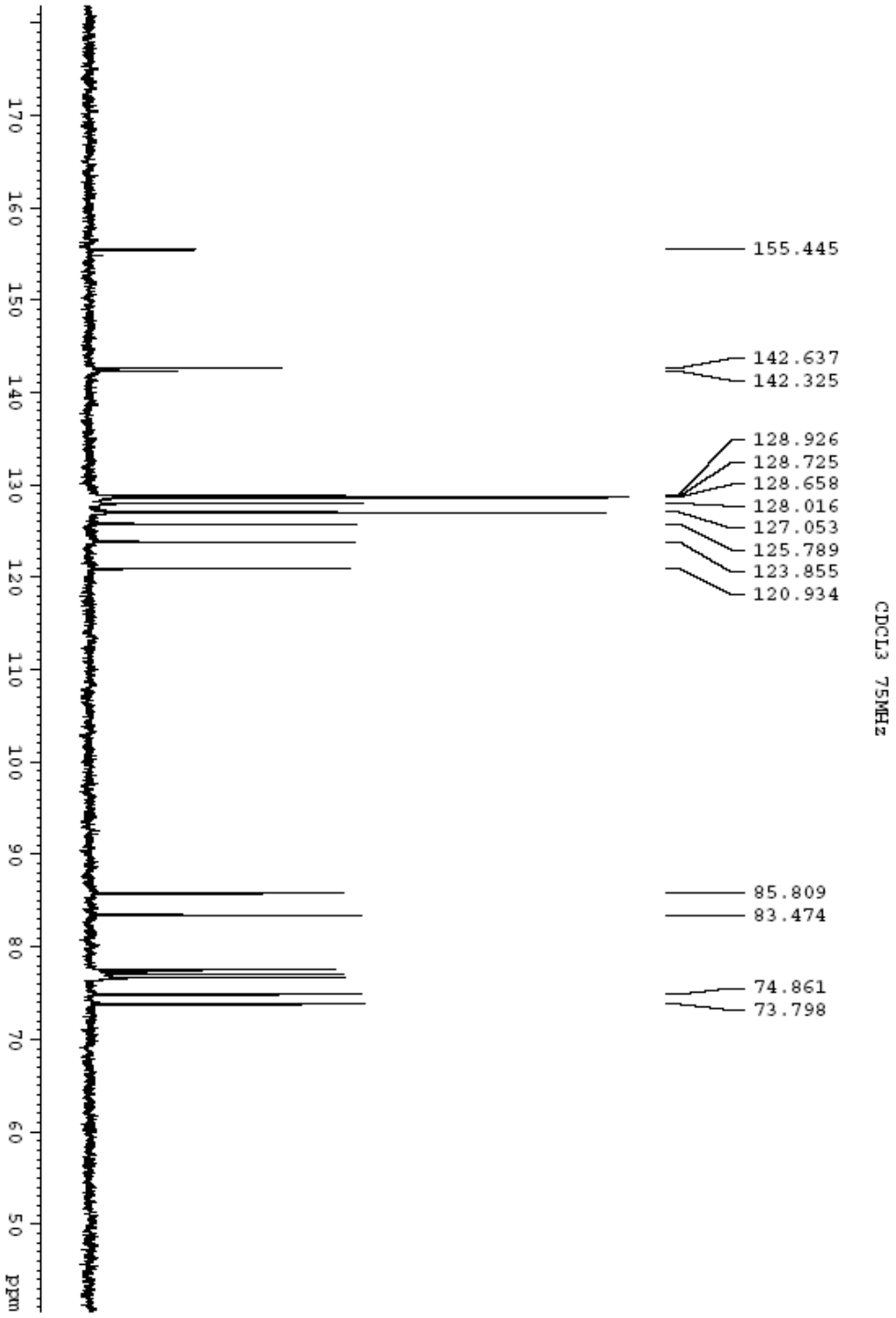
^{1}H NMR of ***trans*-6c**



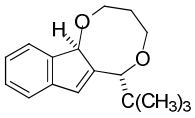


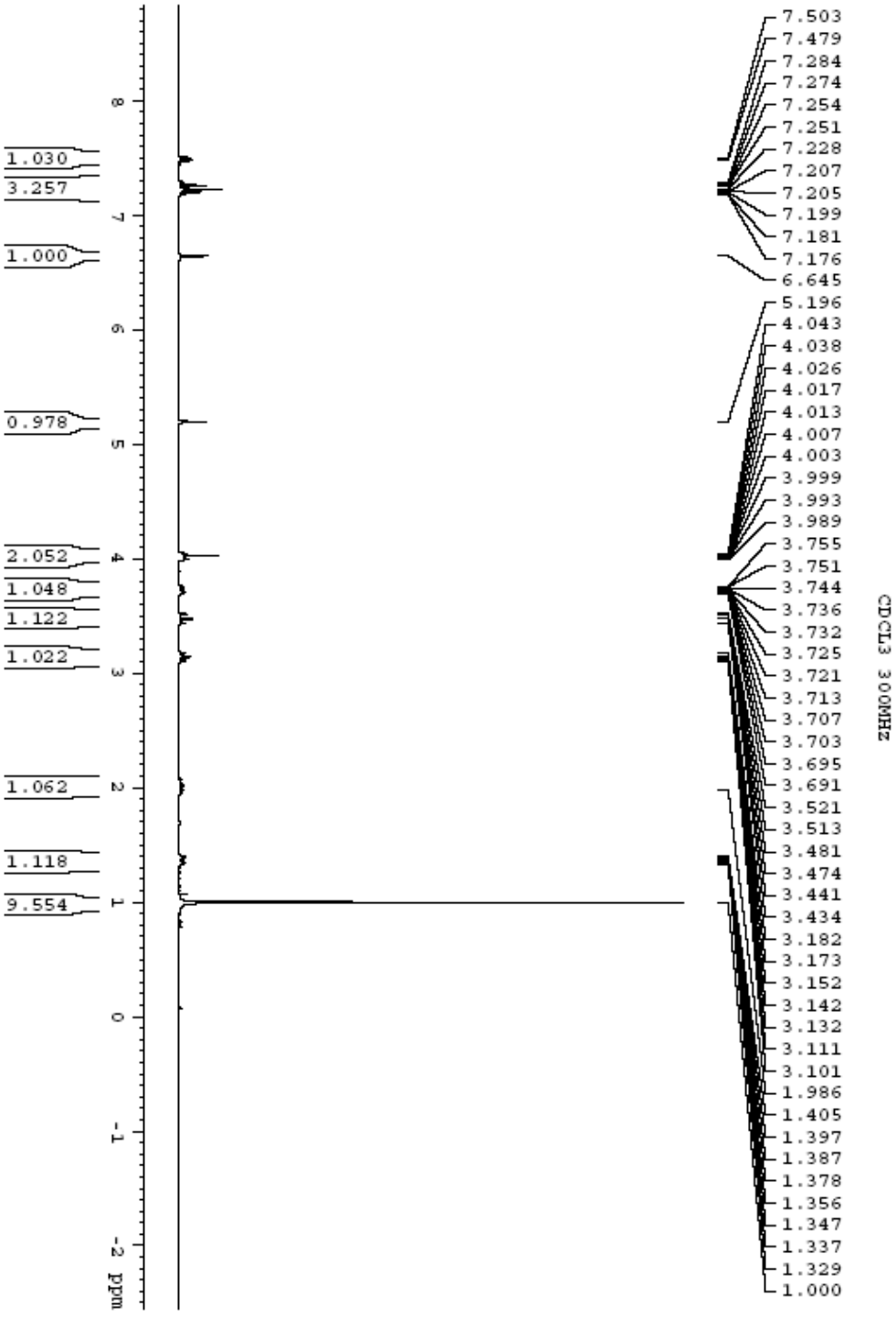
^{13}C NMR of ***trans*-6c**



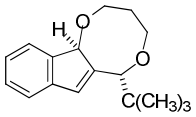


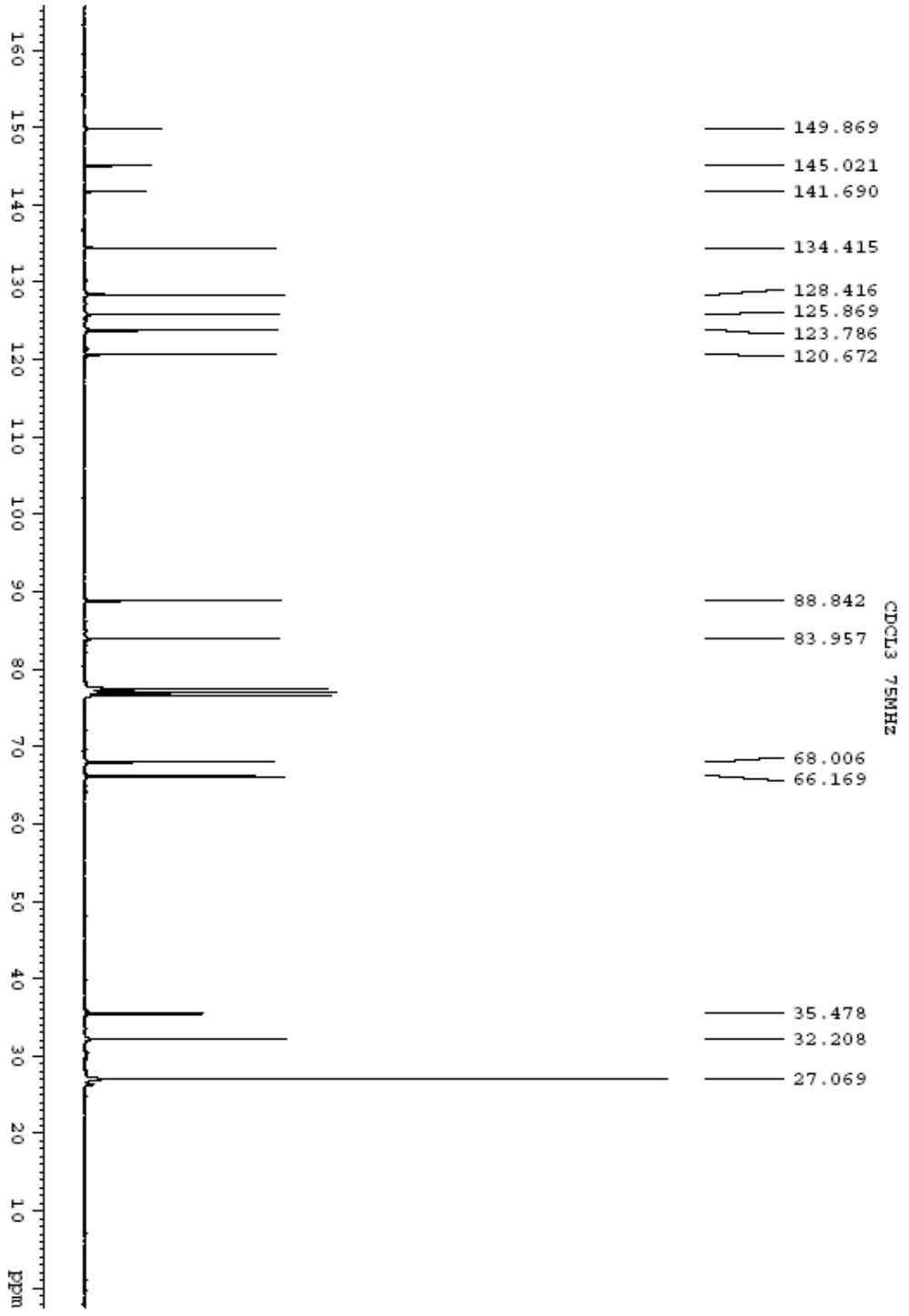
^{1}H NMR of ***trans*-7a**



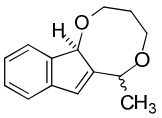


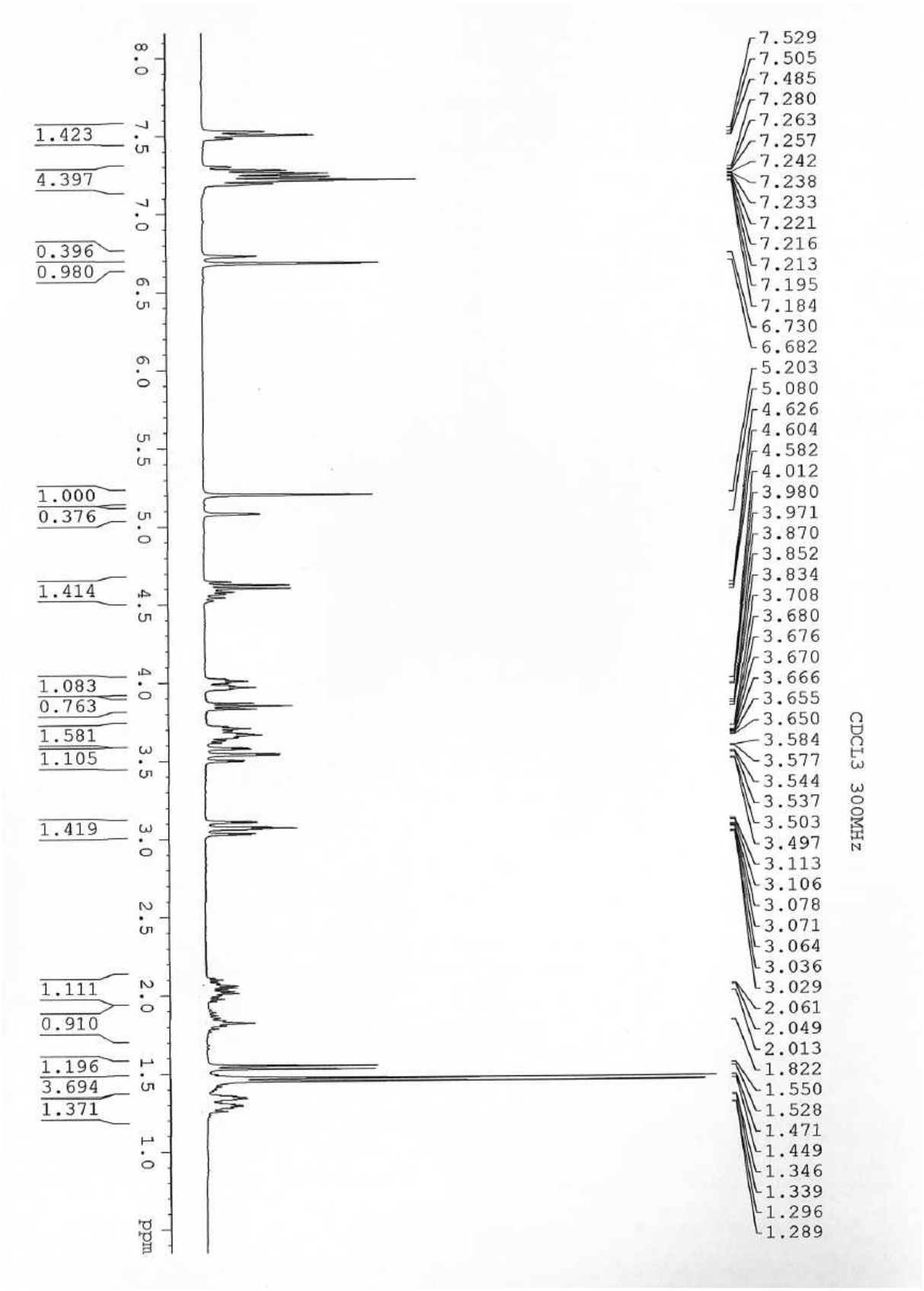
^{13}C NMR of ***trans*-7a**



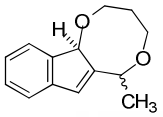


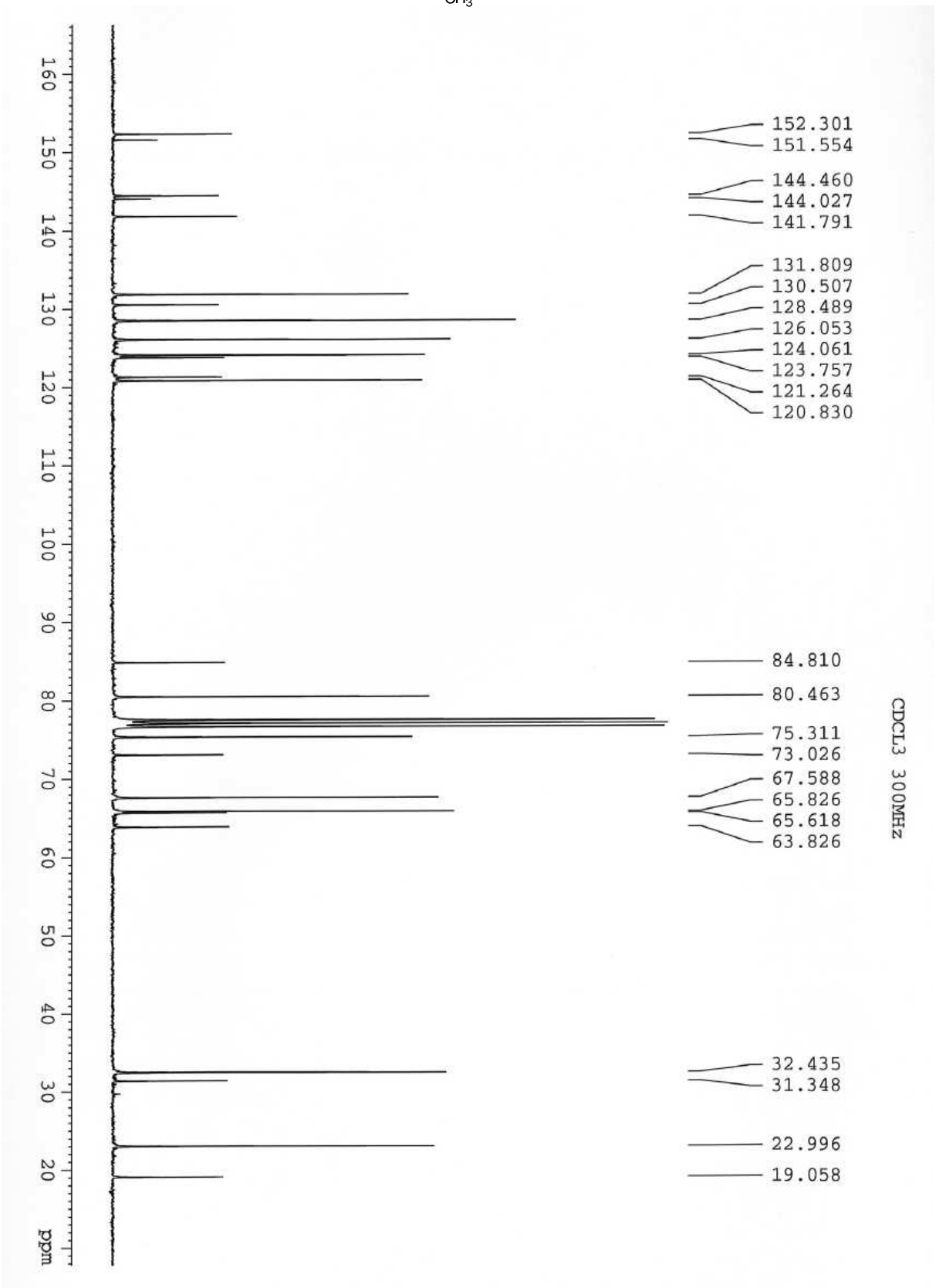
^{1}H NMR of ***cis*/*trans*-7b**



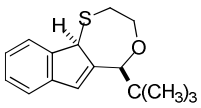


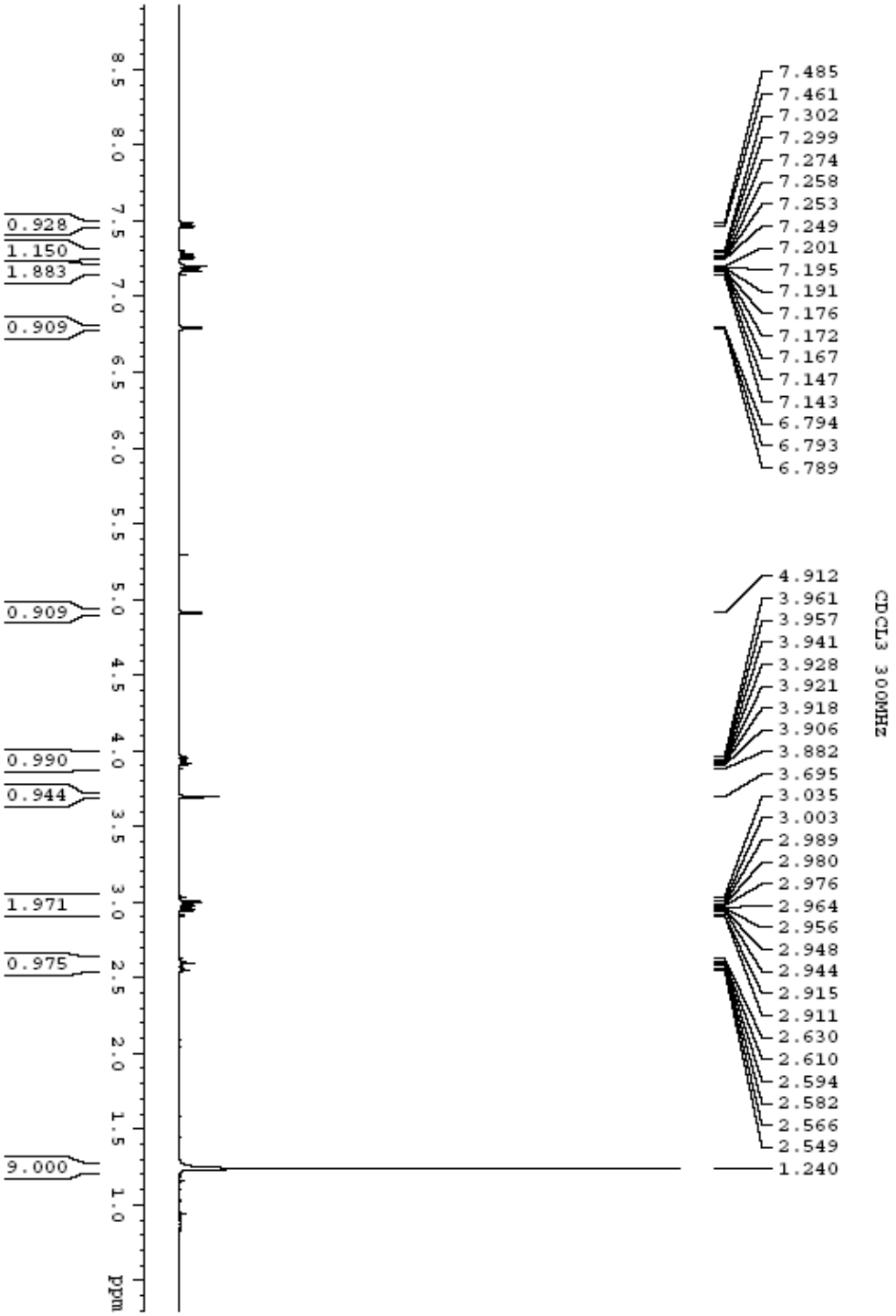
^{13}C NMR of ***cis*/*trans*-7b**



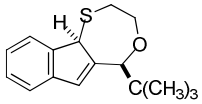


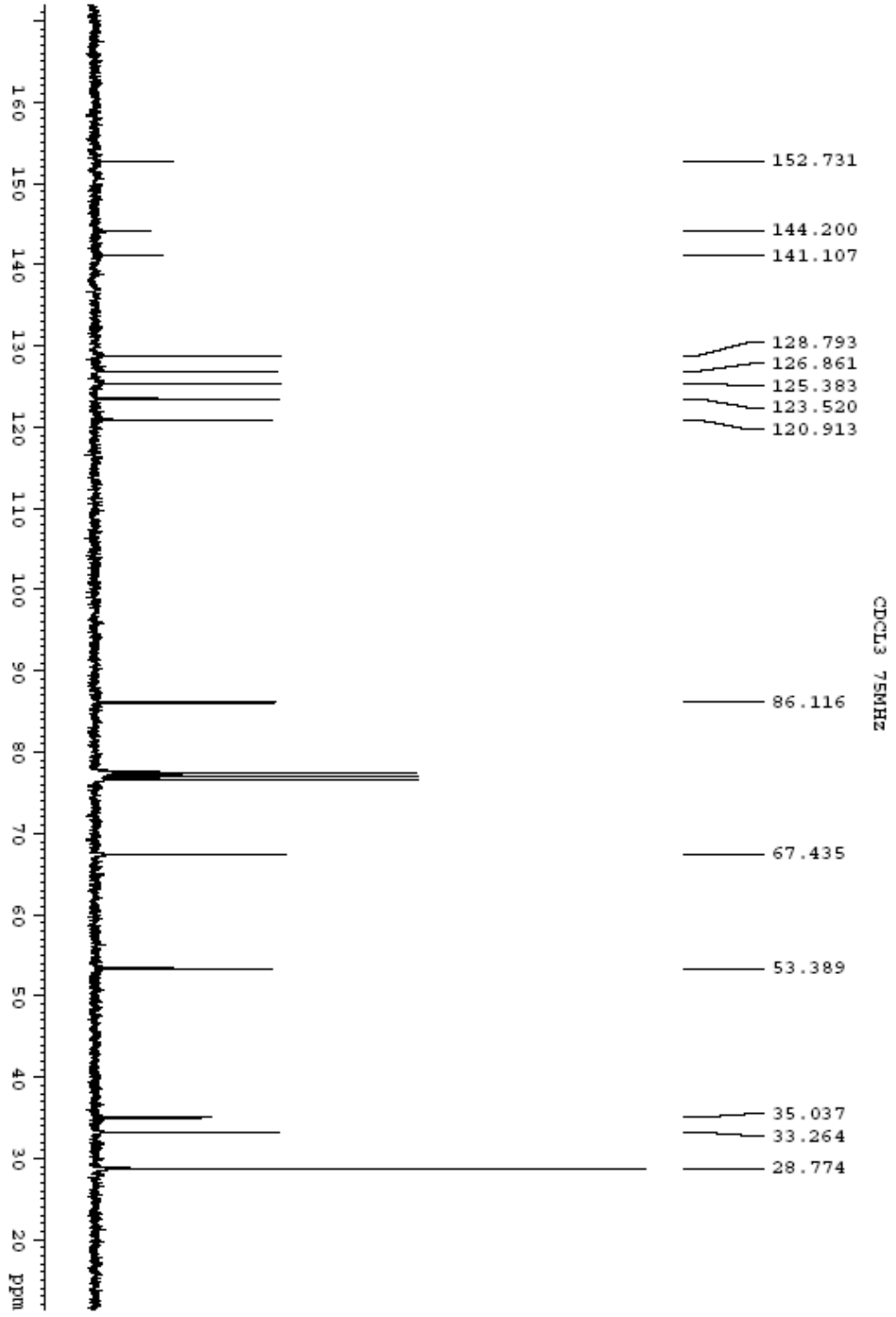
^{1}H NMR of ***cis*-8**



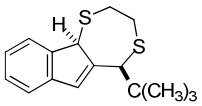


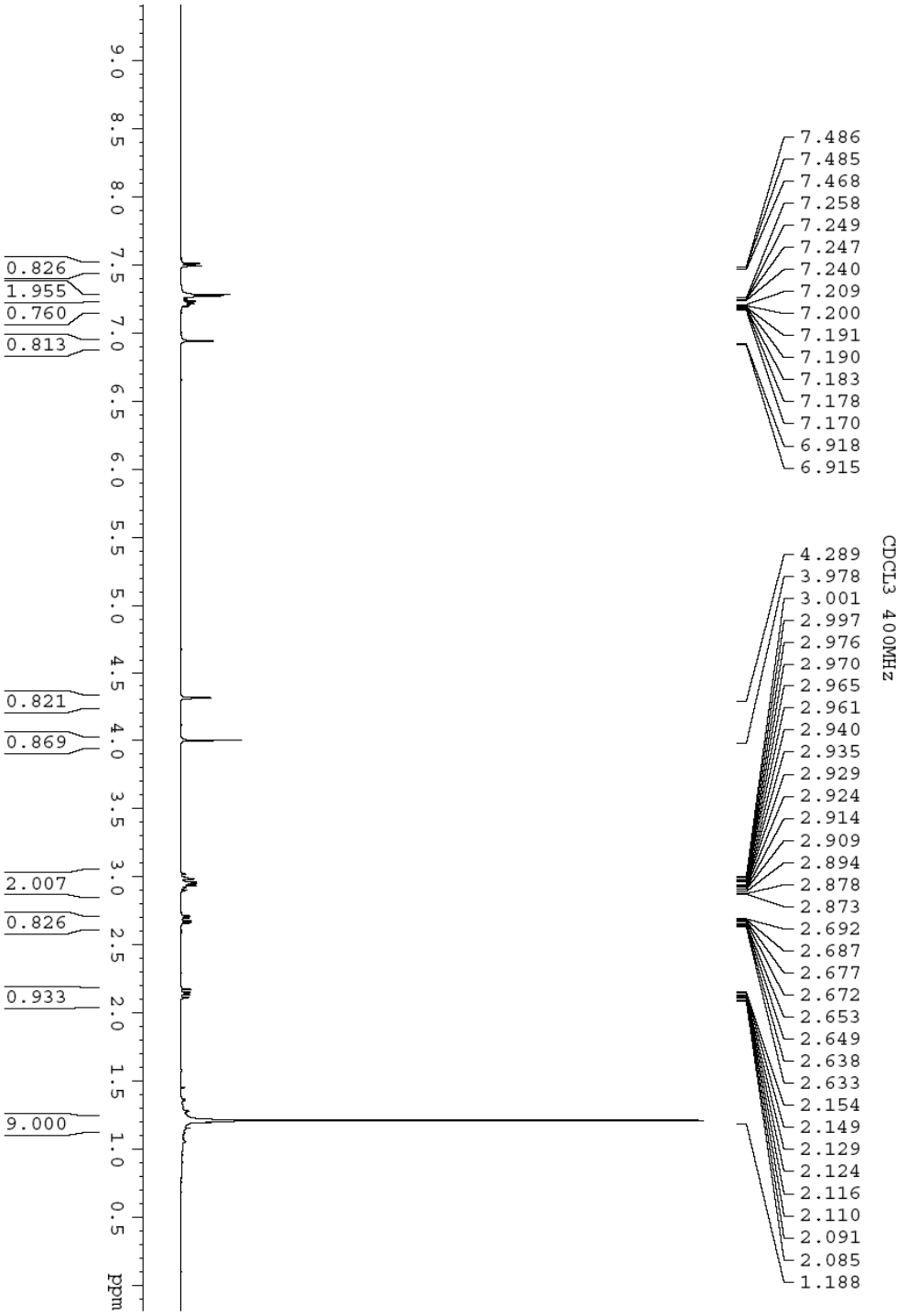
^{13}C NMR of ***cis*-8**



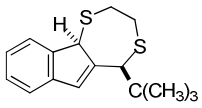


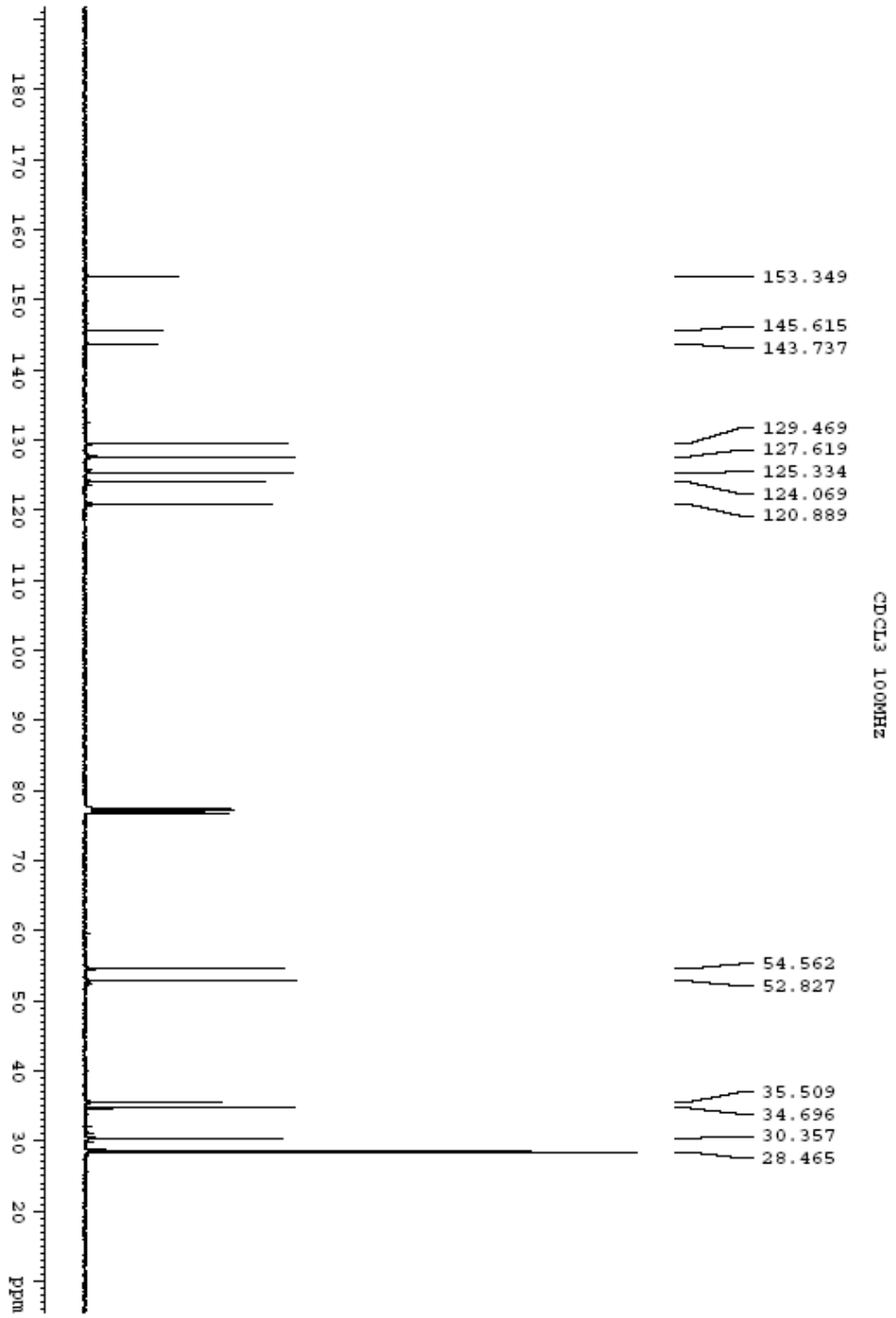
^{1}H NMR of ***cis*-9**



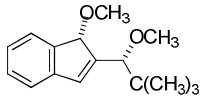


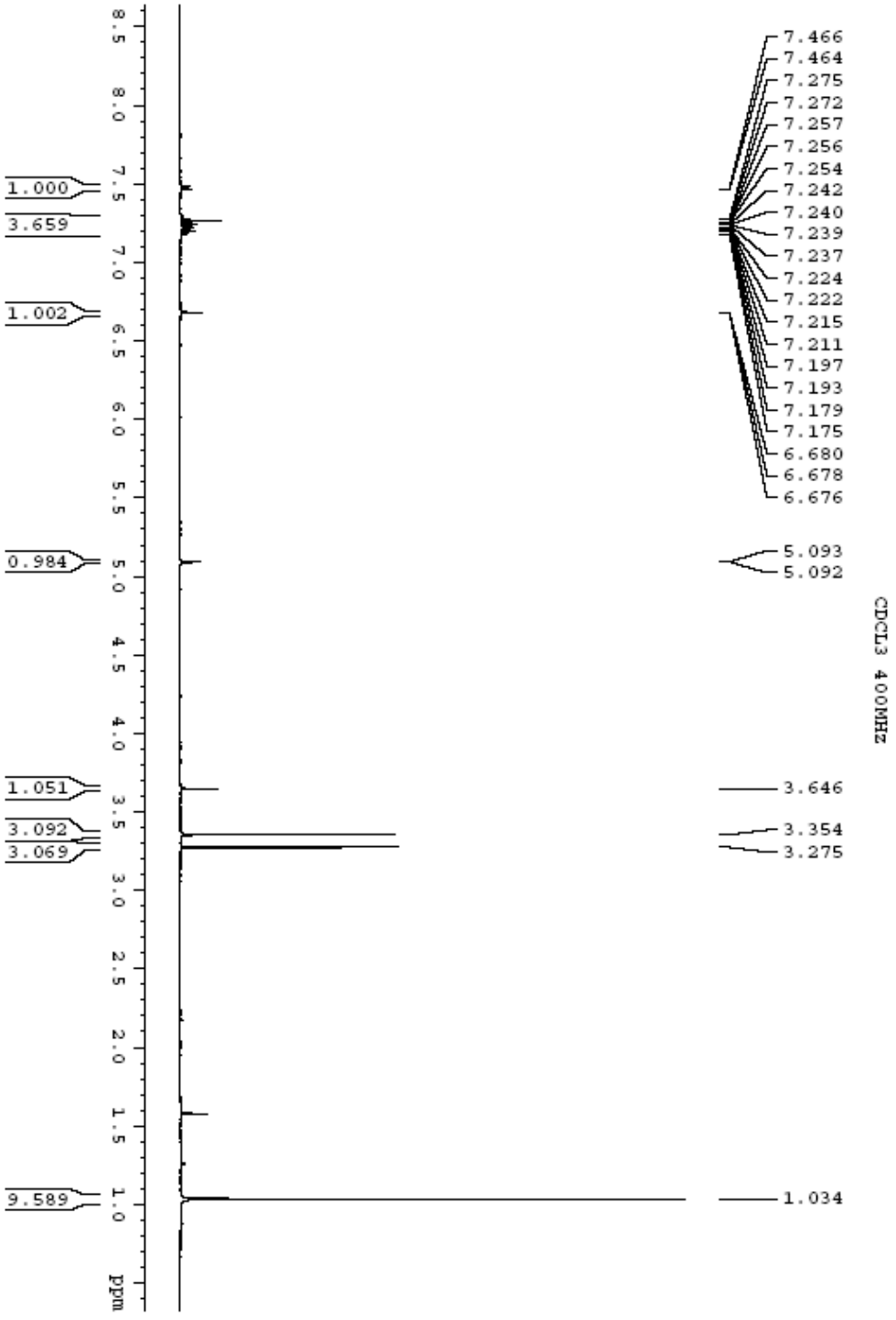
^{13}C NMR of ***cis*-9**



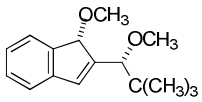


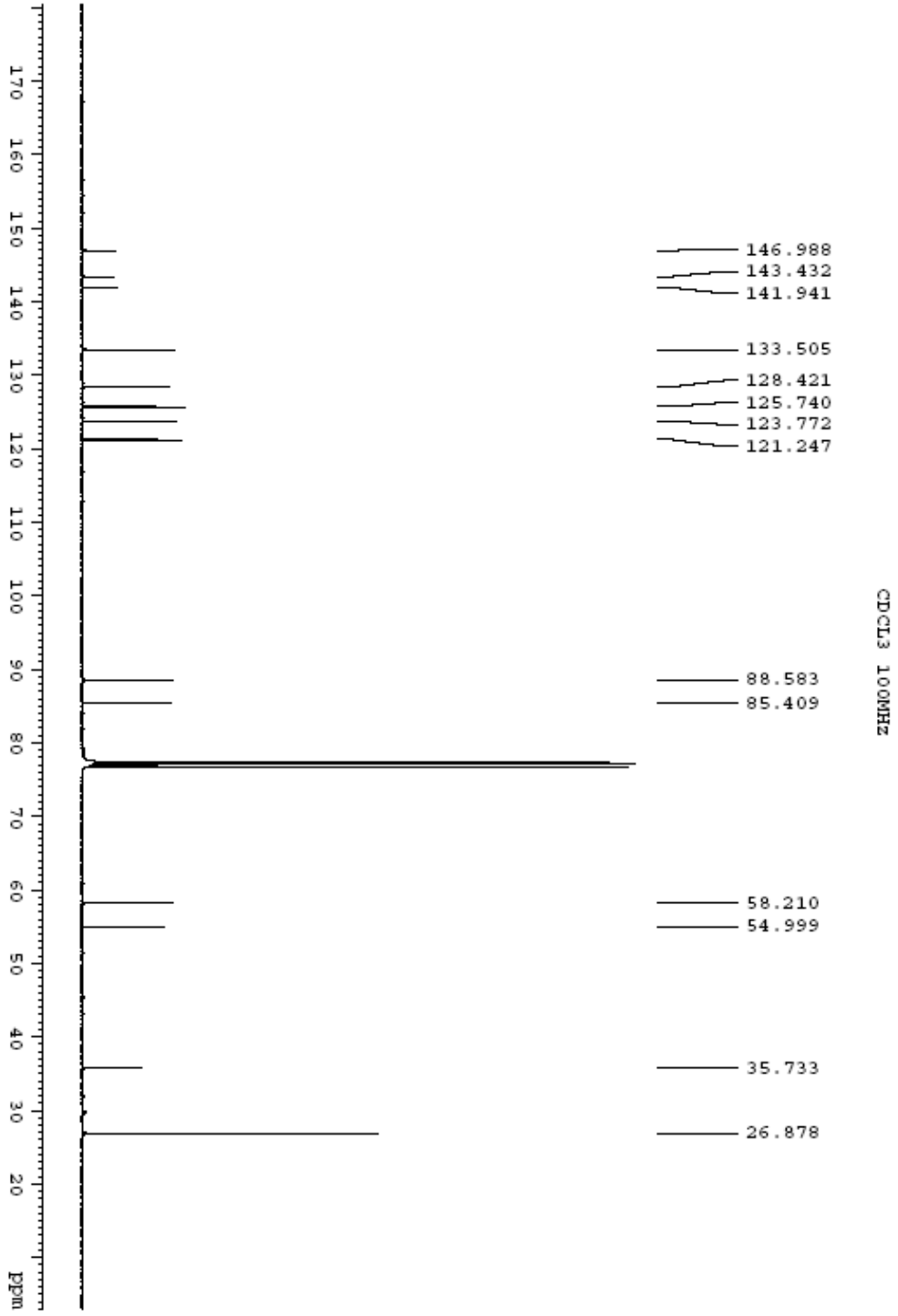
^{1}H NMR of **10**


OCH3
OCH3
C(CH3)3

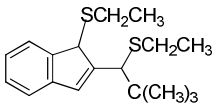

7.466
7.464
7.275
7.272
7.257
7.256
7.254
7.242
7.240
7.239
7.237
7.224
7.222
7.215
7.211
7.197
7.193
7.179
7.175
6.680
6.678
6.676
5.093
5.092
3.646
3.354
3.275
1.034
1.000
3.659
1.002
0.984
1.051
3.092
3.069
9.589
CDCL3 400MHz
ppm

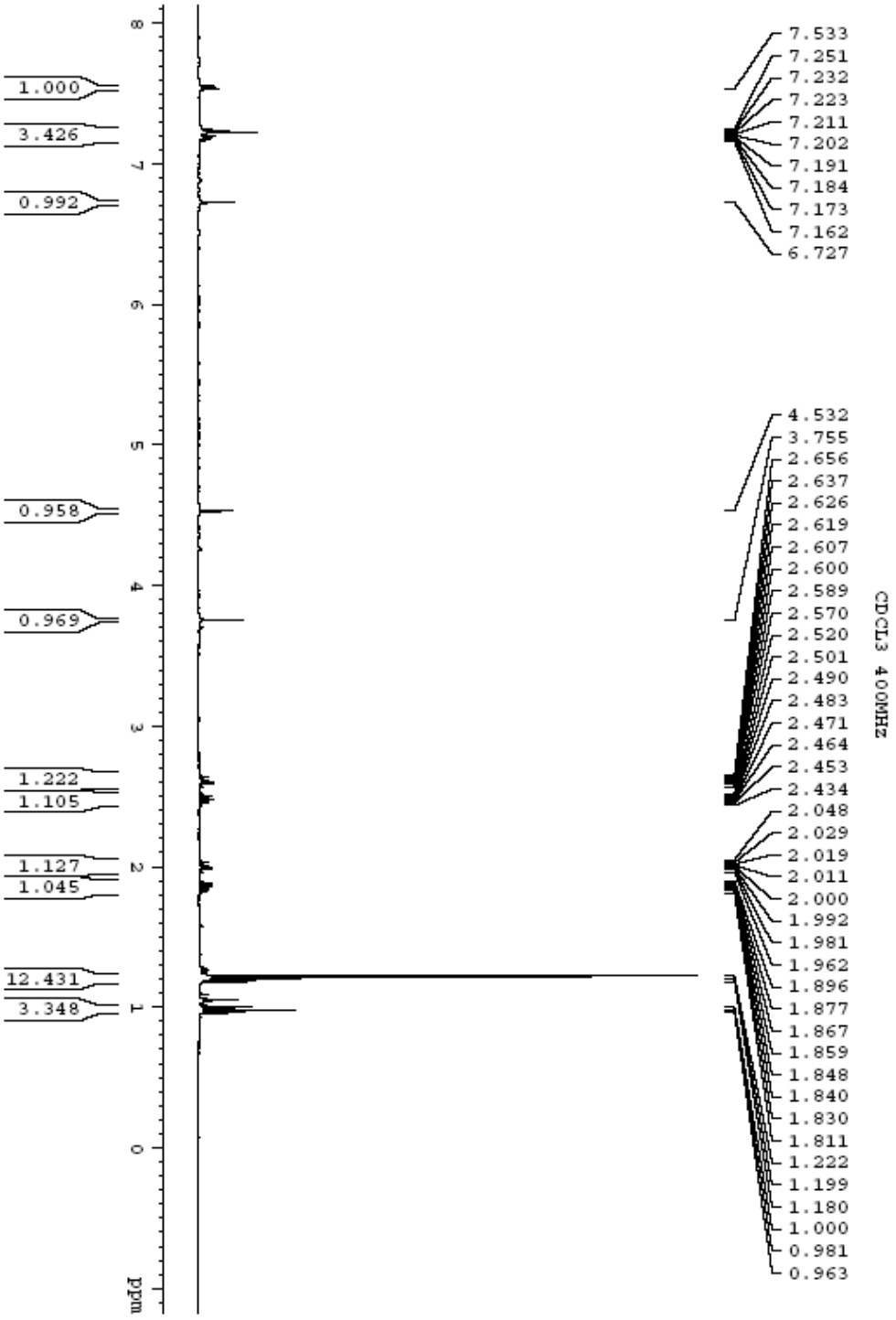
^{13}C NMR of **10**


OCH3
OCH3
C(CH3)3

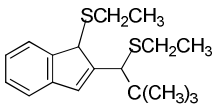

146.988
143.432
141.941
133.505
128.421
125.740
123.772
121.247
88.583
85.409
58.210
54.999
35.733
26.878
CDCL3 100MHz
ppm

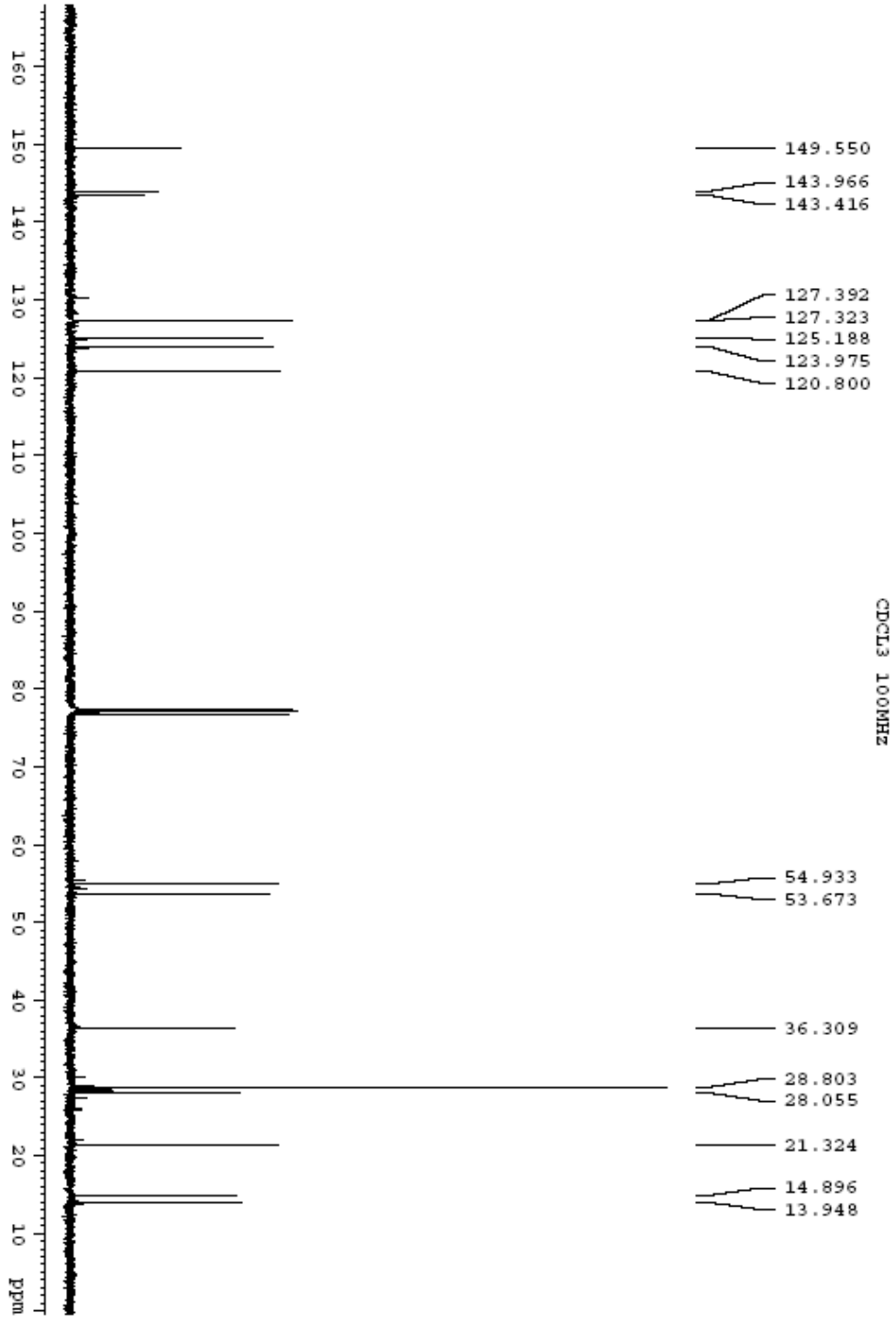
^{1}H NMR of **11**


SCH2CH3
SCH2CH3
C(CH3)3

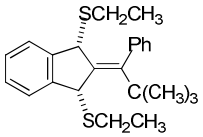

1.000
3.426
0.992
0.958
0.969
1.222
1.105
1.127
1.045
12.431
3.348
7.533
7.251
7.232
7.223
7.211
7.202
7.191
7.184
7.173
7.162
6.727
4.532
3.755
2.656
2.637
2.626
2.619
2.607
2.600
2.589
2.570
2.520
2.501
2.490
2.483
2.471
2.464
2.453
2.434
2.048
2.029
2.019
2.011
2.000
1.992
1.981
1.962
1.896
1.877
1.867
1.859
1.848
1.840
1.830
1.811
1.222
1.199
1.180
1.000
0.981
0.963
CDCL3 400MHz
ppm

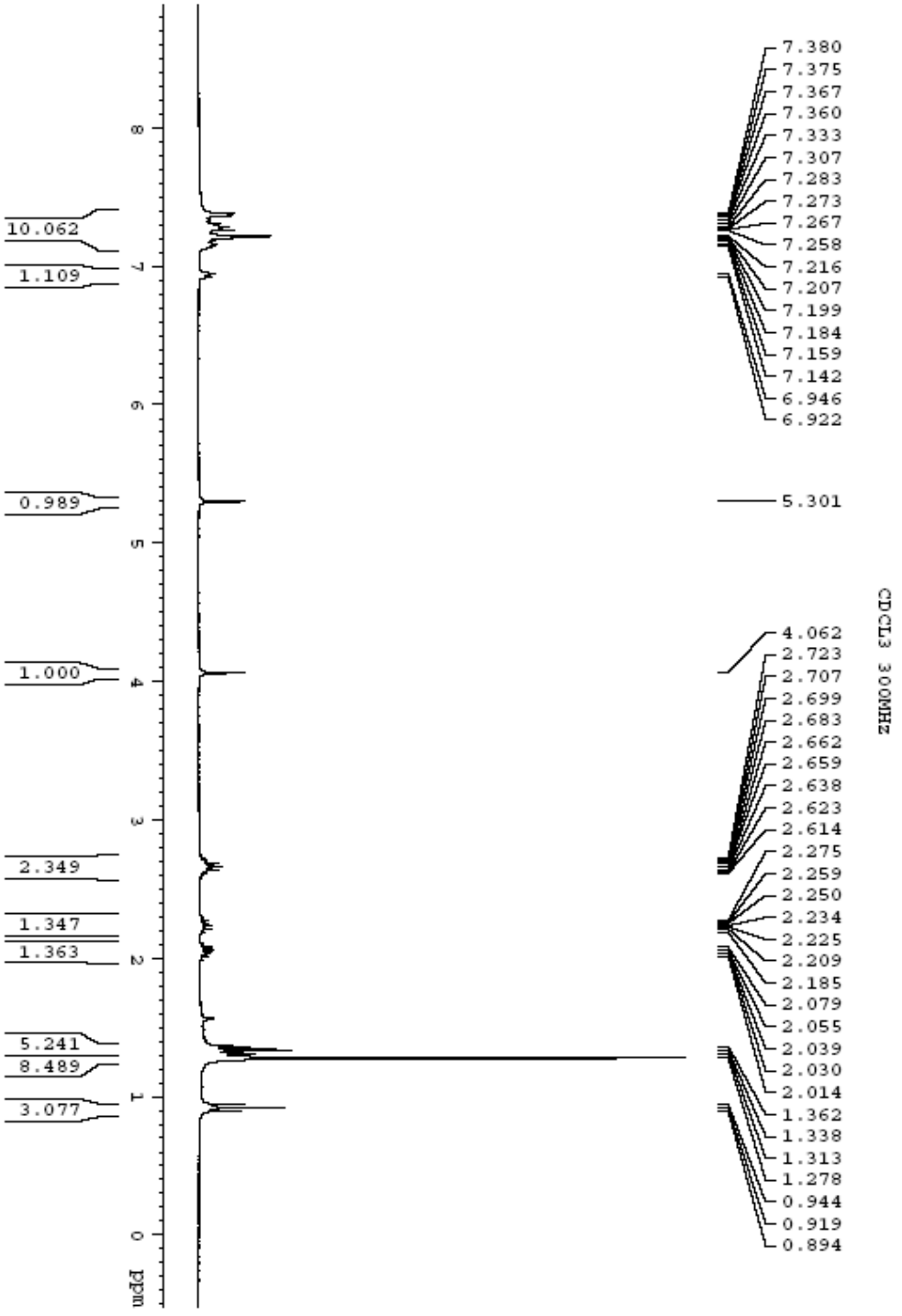
^{13}C NMR of **11**


SCH2CH3
SCH2CH3
C(CH3)3

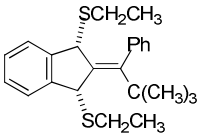

149.550
143.966
143.416
127.392
127.323
125.188
123.975
120.800
54.933
53.673
36.309
28.803
28.055
21.324
14.896
13.948
CDCL3 100MHz
ppm

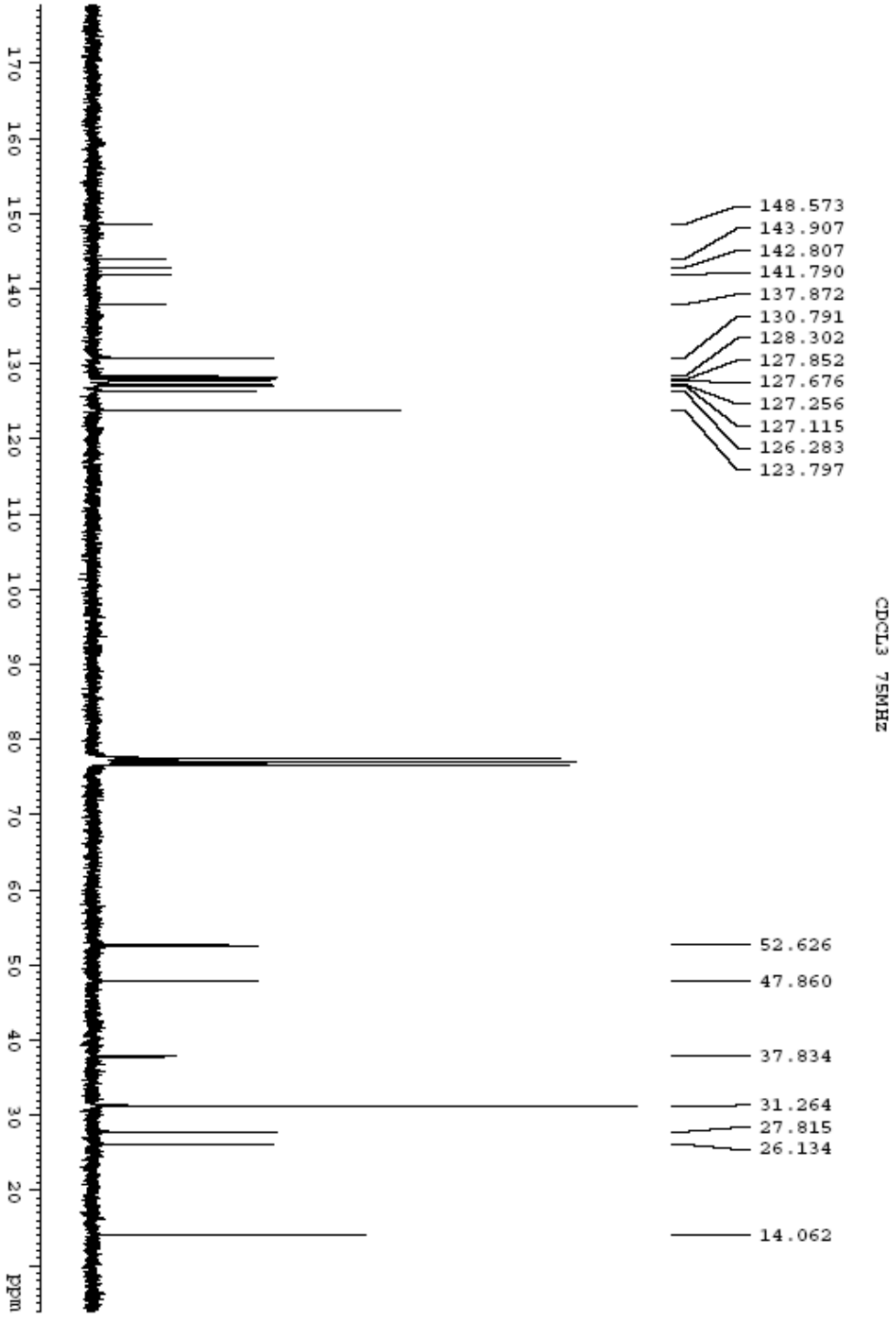
^{1}H NMR of **12a**


SCH2CH3
Ph
C(CH3)3
SCH2CH3

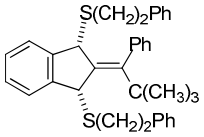

10.062
1.109
0.989
1.000
2.349
1.347
1.363
5.241
8.489
3.077
7.380
7.375
7.367
7.360
7.333
7.307
7.283
7.273
7.267
7.258
7.216
7.207
7.199
7.184
7.159
7.142
6.946
6.922
5.301
4.062
2.723
2.707
2.699
2.683
2.662
2.659
2.638
2.623
2.614
2.275
2.259
2.250
2.234
2.225
2.209
2.185
2.079
2.055
2.039
2.030
2.014
1.362
1.338
1.313
1.278
0.944
0.919
0.894
CDCL3 300MHz
ppm

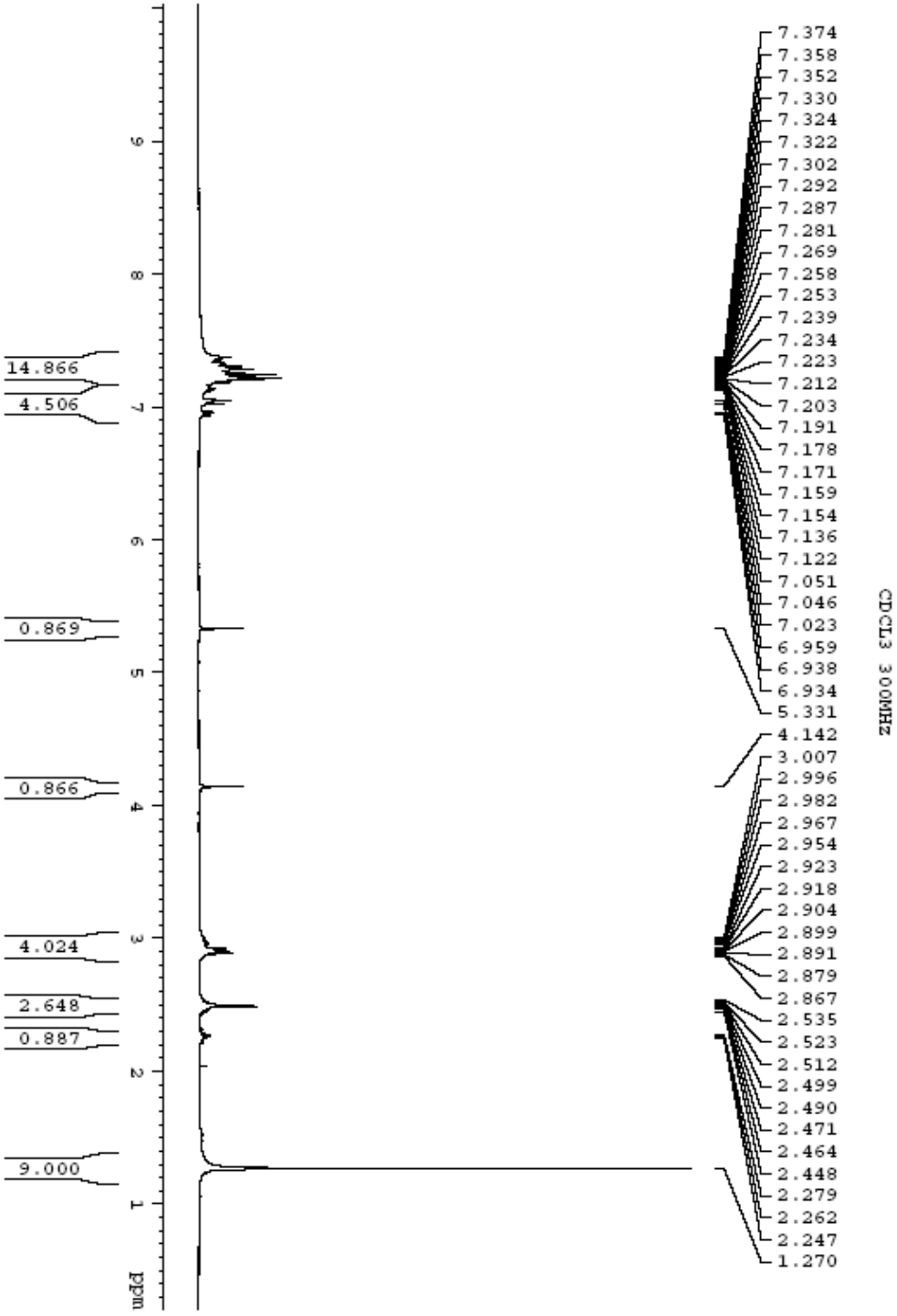
^{13}C NMR of **12a**



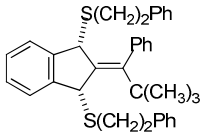


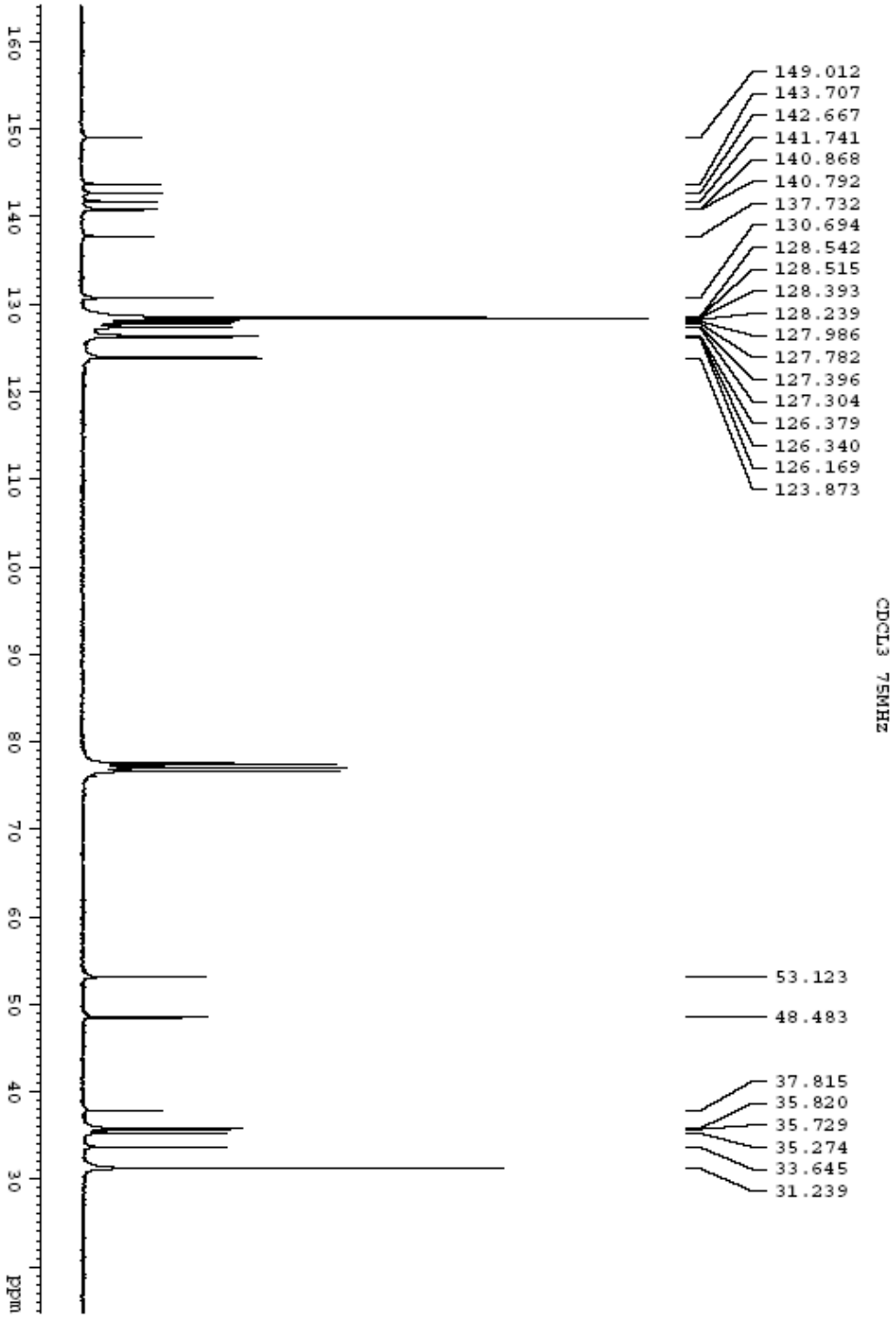
^{1}H NMR of **12b**


S(CH2)2Ph
Ph
C(CH3)3
S(CH2)2Ph

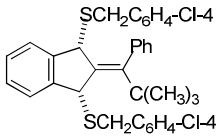

14.866
4.506
0.869
0.866
4.024
2.648
0.887
9.000
ppm
7.374
7.358
7.352
7.330
7.324
7.322
7.302
7.292
7.287
7.281
7.269
7.258
7.253
7.239
7.234
7.223
7.212
7.203
7.191
7.178
7.171
7.159
7.154
7.136
7.122
7.051
7.046
7.023
6.959
6.938
6.934
5.331
4.142
3.007
2.996
2.982
2.967
2.954
2.923
2.918
2.904
2.899
2.891
2.879
2.867
2.535
2.523
2.512
2.499
2.490
2.471
2.464
2.448
2.279
2.262
2.247
1.270
CDCL3 300MHz

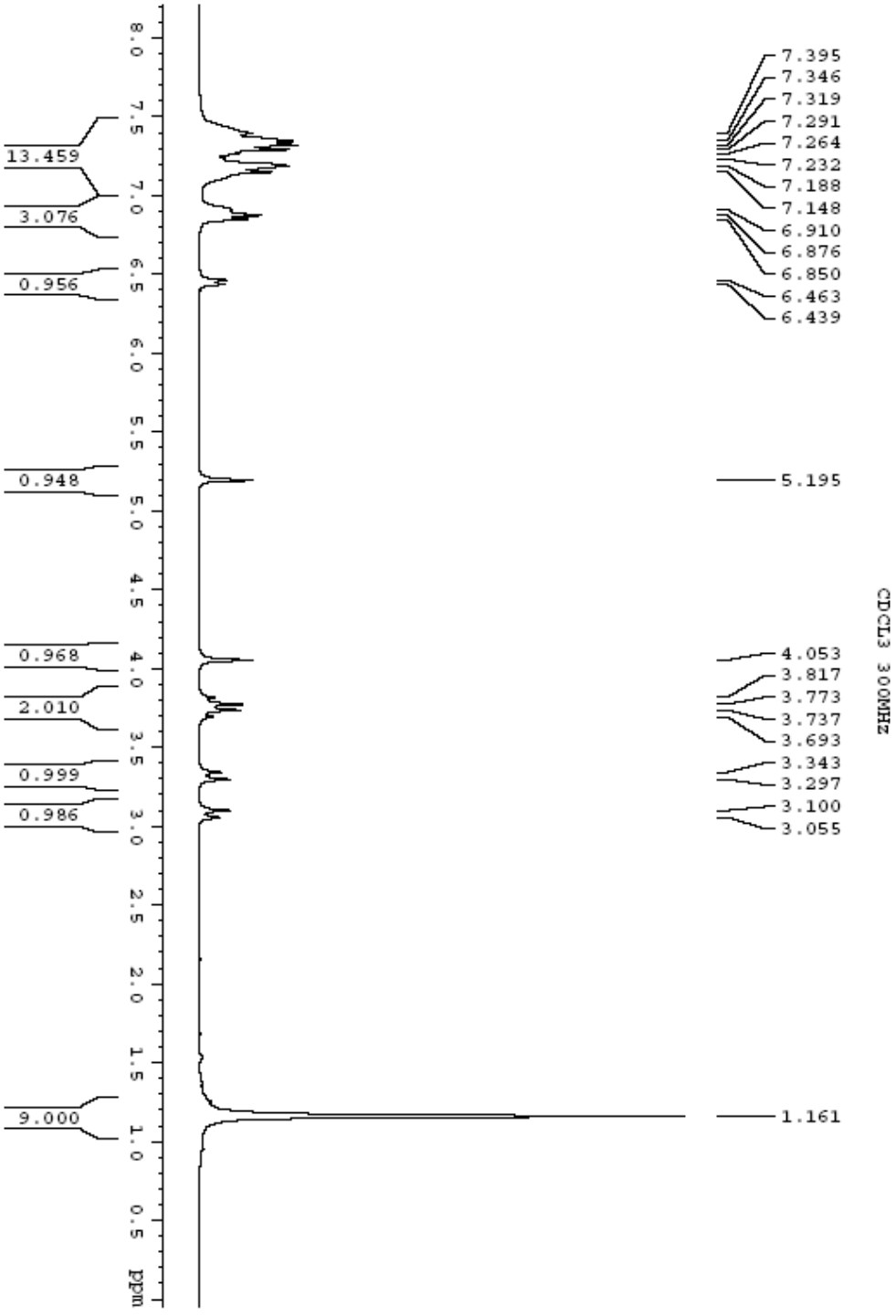
^{13}C NMR of **12b**



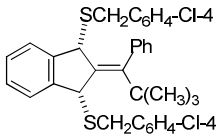


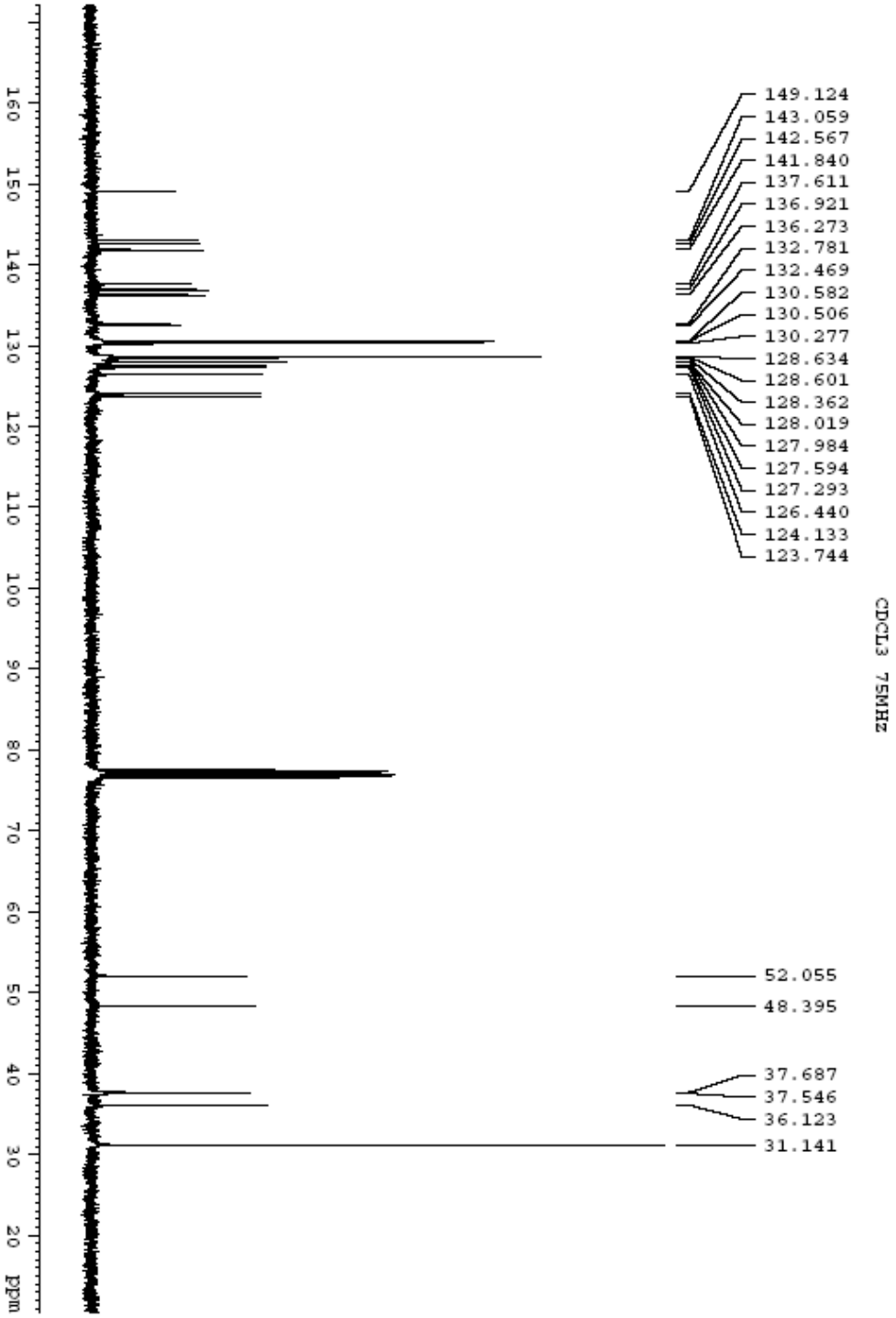
^{1}H NMR of **12c**


SCH2C6H4-Cl-4
Ph
C(CH3)3
SCH2C6H4-Cl-4

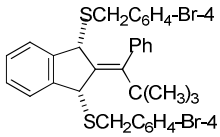

13.459
3.076
0.956
0.948
0.968
2.010
0.999
0.986
9.000
7.395
7.346
7.319
7.291
7.264
7.232
7.188
7.148
6.910
6.876
6.850
6.463
6.439
5.195
4.053
3.817
3.773
3.737
3.693
3.343
3.297
3.100
3.055
1.161
CDCL3 300MHz
ppm

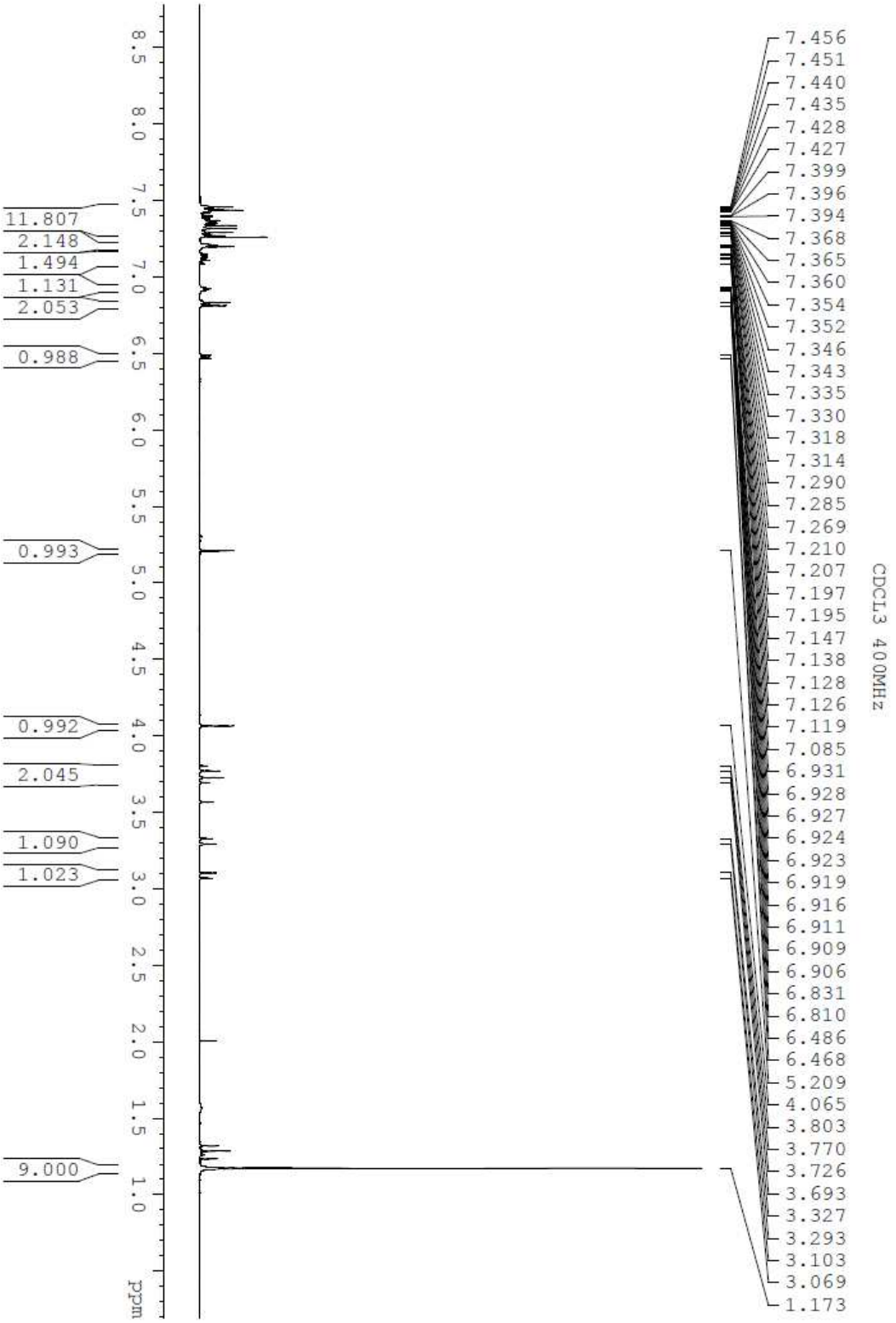
^{13}C NMR of **12c**





^{1}H NMR of **12d**


SCH2C6H4-Br-4
Ph
C(CH3)3
SCH2C6H4-Br-4


11.807
2.148
1.494
1.131
2.053
0.988
0.993
0.992
2.045
1.090
1.023
9.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
7.456
7.451
7.440
7.435
7.428
7.427
7.399
7.396
7.394
7.368
7.365
7.360
7.354
7.352
7.346
7.343
7.335
7.330
7.318
7.314
7.290
7.285
7.269
7.210
7.207
7.197
7.195
7.147
7.138
7.128
7.126
7.119
7.085
6.931
6.928
6.927
6.924
6.923
6.919
6.916
6.911
6.909
6.906
6.831
6.810
6.486
6.468
5.209
4.065
3.803
3.770
3.726
3.693
3.327
3.293
3.103
3.069
1.173
CDCL3 400MHz

^{13}C NMR of **12d**