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London, Gabor; Chen, Kuang-Yen; Carroll, Gregory T.; Feringa, B.L.

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Supporting Information

Towards Dynamic Control of Wettability by Using Functionalized Altitudinal Molecular Motors on Solid Surfaces

Gábor London, Kuang-Yen Chen, Gregory T. Carroll, and Ben L. Feringa*[a]

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General remarks

General remarks for synthetic procedures

Reagents were purchased from Aldrich, Acros, Merck or Fluka and were used as provided unless otherwise stated. All solvents were reagent grade and were dried and distilled before use according to standard procedures. All reactions were performed in oven- or flame-dried round bottomed or Schlenk flasks fitted with rubber septa under a positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation 30–40 °C. Flash column chromatography was performed as described by Still et al. (Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. 1978, 43, 2923-2925.) Chromatography: silica gel, Merck type 9385 230-400 mesh.
TLC: silica gel 60, Merck, 0.25 mm, impregnated with a fluorescent indicator (254 nm).

General remarks for instrumentation

Mass spectra (HRMS) were recorded on an AEI MS-902. Melting points were recorded on a Büchi B-545 melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 a Varian Mercury Plus, or a Varian Inova 500 operating at 299.97, 399.93, and 499.98 MHz, respectively, for the ^{1}H nucleus, and at 75.43, 100.57 and 124.98 MHz for the ^{13}C nucleus.
Chemical shifts for protons are reported in parts per million scale (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents $CHCl_3$: δ 7.26, $CDHCl_2$: δ 5.32, DMSO δ 2.5). Chemical shifts for carbon are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintet), coupling constant in Hz, integration. Irradiation experiments were performed using a Spectroline model ENB-280C/FE lamp at λ = 365 nm, ± 30 nm. NMR samples were placed 2-3 cm from the lamp. UV spectra were obtained using Hewlet-Packard HP 8543 FT or a Jasco V-630 spectrophotometer in a 1 cm quartz cuvette. Contact angles were measurured on a LINOS contact angle goniometer. The contact angle was measured at three different locations on each surface and the results averaged.

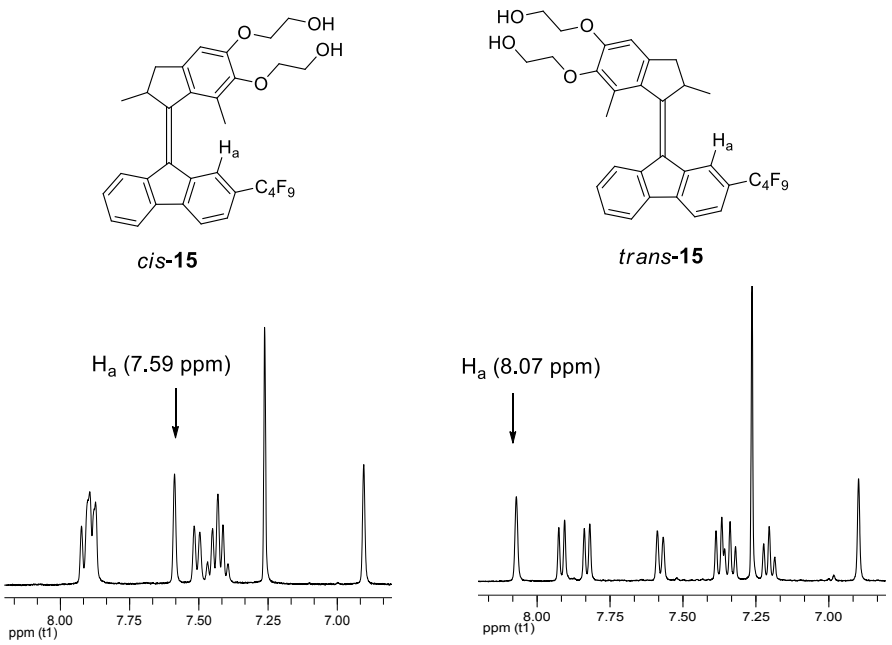
Preparation of azide terminated monolayer[1,2]

1.25 mL of the hydrolysis solution containing 0.04 g 11-azidoundecyltrimethoxy silane[2] 6 ml THF and 31 µl double-distilled H_2O and 4 µl 37% HCl was added to 25 mL cyclohexane to give a slighty hazy solution. The piranha-cleaned quartz slides were immersed into this solution overnight. After the assembly the slides were sonicated in DMF, toluene and MeOH for 2 min each and dried under a stream of Ar.

Procedure for the interfacial 1,3-dipolar cycloaddition[1,2]

Compounds **16** and **17** were grafted to the azide monolayer **SAM-1** by immersing the slide into a 1 mM solution of *cis*- and *trans*-**16** and **17** in DMF containing 1 mol% $CuSO_4$•$5H_2O$ and 5 mol% sodium-ascorbate relative to the alkyne moieties. The azide functionalized slides were immersed for 12 h at rt. The modified quartz substrates (**MS-1** and **MS-2**) were sonicated in DMF, water and MeOH for 2 min each and then dried under a stream of Ar.

a



b

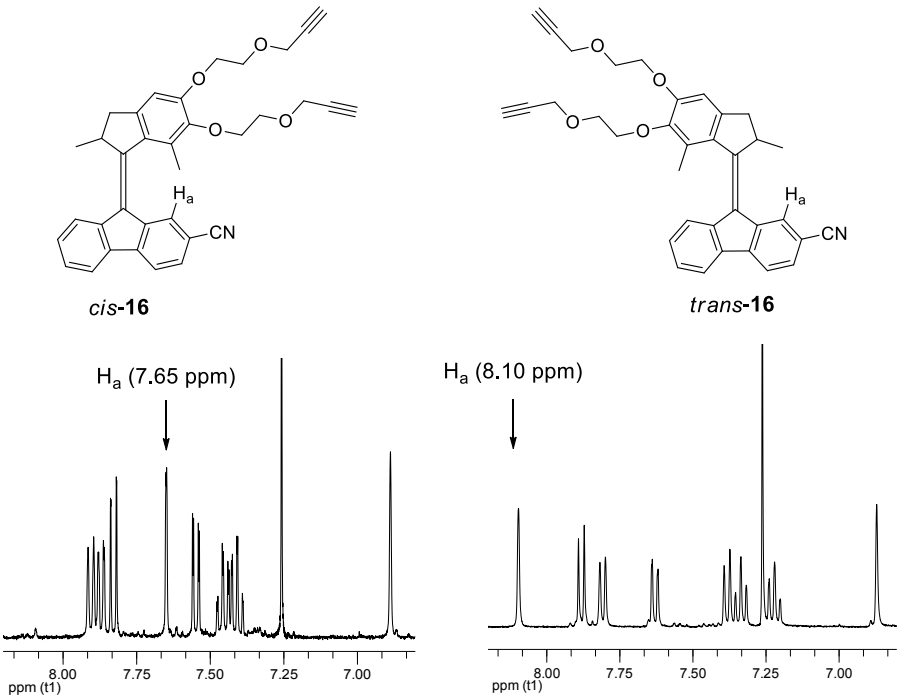


Figure S1 (a) Partial ^{1}H NMR spectra of *cis*-**15** and *trans*-**15** in $CDCl_3$. (b) Partial ^{1}H NMR spectra of *cis*-**16** and *trans*-**16** in $CDCl_3$. *Cis*- and *trans*-isomers were assigned based on the singlet absorption of H_a of the aromatic lower half. In previously reported motors containing substituted fluorene lower halves the absorption of H_a appears at higher field in the *cis*-form compared to the *trans*-isomer.[3-6]

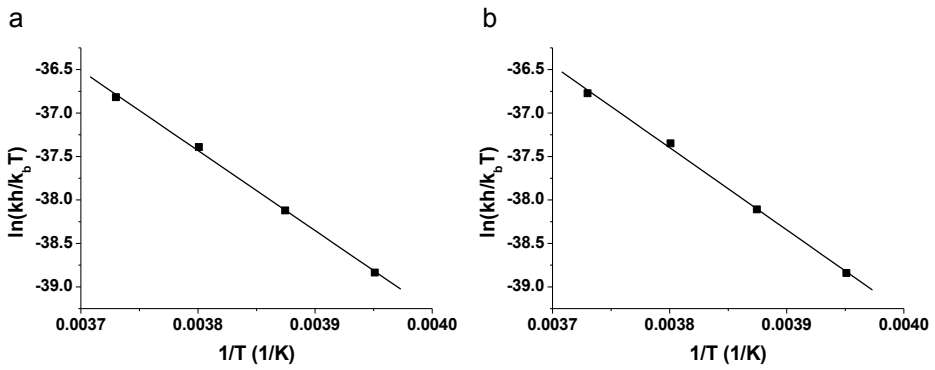


Figure S2 (a) Eyring plot of the conversion of unstable-*trans*-**16** to stable-*trans*-**16** and (b) Eyring-plot of the conversion of unstable-*cis*-**16** to stable-*cis*-**16** *via* thermal helix inversion.

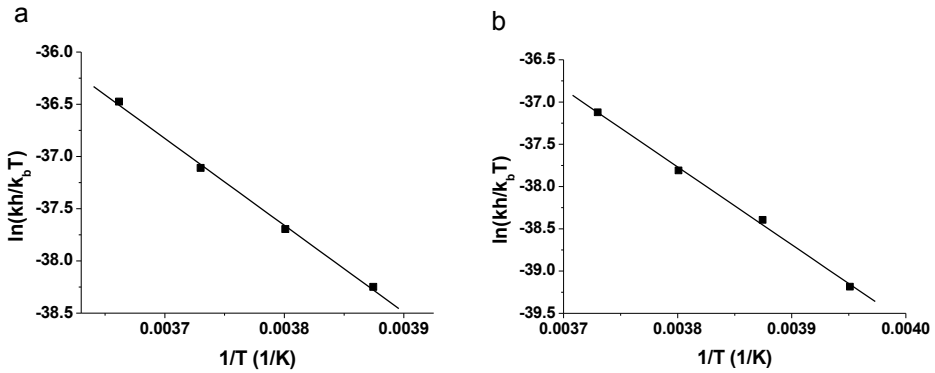


Figure S3 (a) Eyring plot of the conversion of unstable-*trans*-**17** to stable-*trans*-**17** and (b) Eyring-plot of the conversion of untable-*cis*-**17** to stable-*cis*-**17** *via* thermal helix inversion.

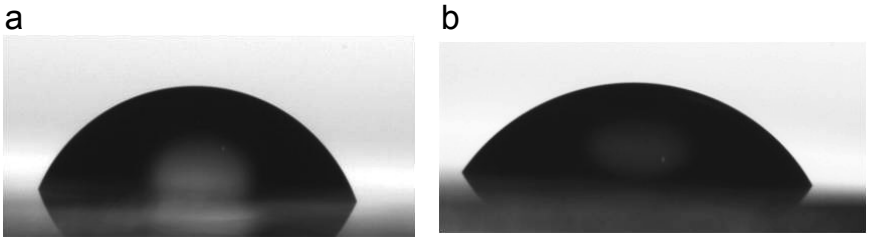


Figure S4 Water droplets on quartz surfaces modified by the attachment of (a) *cis*-**16** and (b) *trans*-**16** containing a cyano-group on the rotor part. Water contact angles of 67(±1°) and 60(±1°) were measured for *cis*-**16** and *trans*-**16** isomers, respectively.

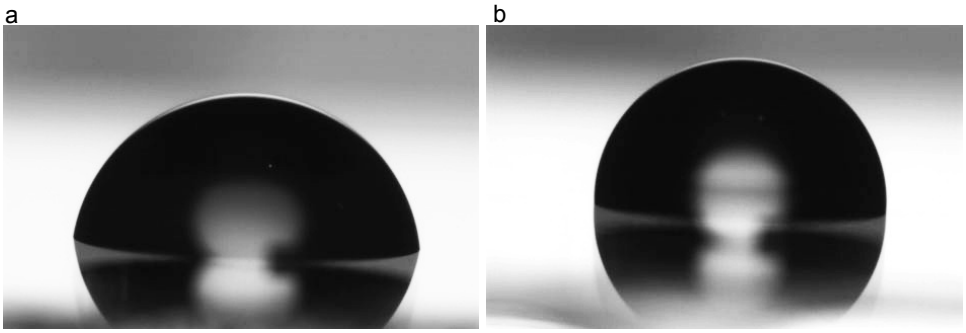


Figure S5 Water droplets on quartz surfaces modified by the attachment of perfluorobutyl-motor *cis*-**17** (a) and *trans*-**17** (b). Water contact angles of 80(±2°) and 92(±1°) were measured for *cis*-**17** and *trans*-**17** isomers, respectively.

Synthesis of compounds and intermediates

The synthesis of compounds **2**[4,7], **3**[4], **4**[4] and **5**[1] has been reported earlier.

(*Cis/trans*)-Diester-bromo motor (7) 2-bromodiazofluorenone (**4**) (1.23 g, 4.7 mmol) was added to a solution of thioketone 5 (1.64 g, 4.3 mmol) in toluene (30 mL). The mixture was heated up to 55°C for 3 h. The formation of the episulfide was monitored by ^{1}H NMR spectroscopy by following the shift of the aromatic proton of the thioketone from 6.66 ppm to 6.35 and 6.37 ppm (*E/Z* isomers of the episulfide). After the conversion of the thioketone was complete, PPh_3 (1.2 g, 4.7 mmol) was added to the episulfide solution and the mixture was heated for an additional 2 h at 75°C. The reaction mixture was cooled to rt and concentrated *in vacuo*. EtOAc (60 mL) was added to the mixture, which resulted in the precipitation of PPh_3S as yellow crystals. The precipitate was filtered and the procedure was repeated once more. The solvent was removed under reduced pressure. The product was obtained as a mixture of *cis* and *trans* isomers (42 : 58) after column chromatography (SiO_2, n-hexane : EtOAc = 4 : 1) as a yellow solid (1.6 g, 2.93 mmol, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30-1.34 (m, 9H major, 9H minor), 2.23 (s, 3H, major), 2.24 (s, 3H, minor), 2.54 (d, *J* = 14.7 Hz, 1H major, 1H minor), 3.29 (dd, *J* = 5.8, 14.76 Hz, 1H major, 1H minor), 4.04-4.15 (m, 1H major, 1H minor), 4.26-4.33 (m, 4H major, 4H minor), 4.67 (d, *J* = 15.8 Hz, 1H major), 4.70 (d, *J* = 15.7 Hz, 1H minor), 4.74 (s, 2H, major), 4.75 (s, 2H, minor), 4.83 (d, *J* = 15.7 Hz, 1H, minor), 4.90 (d, *J* = 15.8 Hz, 1H, major), 6.75 (s, 1H, major), 6.77 (s, 1H, minor), 7.17 (t, *J* = 7.6 Hz, 1H, major), 7.29 (t, *J* = 7.5 Hz, 1H, major), 7.32-7.41 (m, 1H major, 3H minor), 7.45-7.48 (m, 1H major, 1H minor), 7.61 (d, *J* = 8.1 Hz, 1H, minor), 7.66 (d, *J* = 8.1 Hz, 1H, major), 7.71 (d, *J* = 7.3 Hz, 1H, major), 7.76-7.79 (m, 1H, minor), 7.82-7.85 (m, 1H, minor), 7.95 (s, 1H, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.2, 16.2, 18.8, 18.9, 41.3, 41.4, 44.7, 44.8, 60.9, 61.0, 61.4, 65.8, 65.9, 68.1, 69.3, 69.7, 108.2, 108.4, 119.1, 119.6, 120.2, 120.3, 120.4, 120.7, 123.6, 123.7, 126.4, 126.7, 126.8, 126.9, 127.0, 127.1, 128.1, 128.4, 129.3, 129.4, 131.9, 132.1, 134.0, 134.2, 137.4, 137.9,

138.4, 138.7, 139.2, 139.3, 141.3, 143.5, 143.7, 145.1, 145.6, 151.2, 151.7, 152.8, 152.9, 168.4, 168.5, 169.3, 169.5; HRMS (ESI) calcd for $C_{32}H_{32}O_6Br$ 591.1377 (MH^+), found 591.1379.
One of the isomers (*trans*) could be crystallized from Et_2O. ^1H NMR (400 MHz, $CDCl_3$) δ 1.29-1.35 (m, 9H), 2.23 (s, 3H), 2.55 (d, *J* = 14.9 Hz, 1H), 3.29 (dd, *J* = 5.5, 15.1 Hz, 1H), (quin, *J* = 6.5 Hz, 1H), 4.26-4.33 (m, 4H), 4.67 (d, *J* = 15.9 Hz, 1H), 4.74 (s, 2H), 4.90 (d, *J* = 15.8 Hz, 1H), 6.75 (s, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 1H) 7.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.2, 16.2, 18.9, 41.4, 44.8, 60.9, 61.4, 65.8, 69.3, 108.2, 119.1, 120.5, 120.8, 123.6, 126.7, 127.0, 127.1, 128.5, 129.3, 132.1, 134.3, 137.5, 138.2, 138.5, 141.3, 143.5, 145.1, 151.3, 152.8, 168.5, 169.6.

(*Cis/trans*)-Diester-cyano motor (8) A solution of (*cis/trans*)-**7** (546 mg, 1.00 mmol) in N, N-dimethylacetamide (22 mL) was added to a mixture of $Pd_2(dba)_3$ (18.5 mg, 0.02 mmol, 2 mol%), dppf (22.3 mg, 0.04 mmol, 4 mol%), Zn powder (13.1 mg, 0.20 mmol, 20 mol%) and $Zn(CN)_2$ (235.0 mg, 2.00 mmol, 200 mol%) purged with argon and the mixture was heated at 150°C for 5 h. The reaction mixture was cooled to rt, diluted with EtOAc (50 mL), and washed with saturated aq Na_2CO_3 (60 mL), brine (20 mL), dried (Na2SO4) and concentrated *in vacuo*. Purification by column chromatography (SiO_2, n-hexane : EtOAc = 4 : 1) afforded the product as a mixture of *trans* and *cis* isomers (~ 2 : 1) as a yellow solid (479 mg, 0.89 mmol, 89%). *Cis/trans* mixture: ^1H NMR (400 MHz, $CDCl_3$) δ 1.29-1.36 (m, 9H major, 9H minor), 2.23 (s, 3H, major), 2.25 (s, 3H, minor), 2.57 (d, *J* = 14.8 Hz, 1H, minor), 2.58 (d, *J* = 14.8 Hz, 1H, major), 3.31 (dd, *J* = 5.7, 14.6 Hz, 1H major, 1H minor), 4.04-4.16 (m, 1H major, 1H minor), 4.26-4.34 (m, 4H major, 4H minor), 4.68 (d, *J* = 15.9 Hz, 1H, major), 4.75 (s, 2H, major), 4.76 (s, 2H, minor), 4.84 (d, *J* = 3.6 Hz, 2H, minor), 4.92 (d, *J* = 15.9 Hz, 1H, major), 6.76 (s, 1H, major), 6.79 (s, 1H, minor), 7.26 (m, 1H, major), 7.35 (dt, *J* = 1.0, 7.5 Hz, 1H, major), 7.40 (d, *J* = 7.7 Hz, 1H, major), 7.43-7.47 (m, 2H, minor) 7.57 (dd, *J* = 1.4, 7.9 Hz, 1H minor), 7.63 (dd, *J* = 1.3, 7.9 Hz, 1H, major), 7.65 (br s, 1H, minor), 7.80 (d, *J* = 7.3 Hz, 1H, major) 7.83 (d, *J* = 7.4 Hz, 1H, minor), 7.85-7.91 (m, 2H, minor) 7.88 (d, *J* = 7.9 Hz, 1H, major), 8.09 (s, 1H, major); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 14.2, 16.2, 18.9, 19.2, 41.4, 44.9, 45.2, 60.9, 61.0, 61.5, 65.7, 65.9, 69.2, 69.3, 108.2, 108.5, 109.4, 109.5, 119.6, 119.8, 120.0, 120.1, 120.2, 120.6, 123.8, 123.82, 127.0, 127.1, 127.2, 127.3, 127.5, 127.6, 128.4, 128.5, 130.1, 130.4, 132.1, 132.3, 133.6, 133.9, 137.3, 137.7, 137.8, 138.3, 139.5, 140.1, 142.6, 143.3, 143.8, 143.9, 145.1, 145.4, 151.6, 151.8, 154.5, 154.7, 168.4, 169.5, 169.6; HRMS (ESI) calcd for $C_{33}H_{31}NO_6Na$ 560.2044 (MNa^+), found 560.2022.
One of the isomers (*trans*) could be crystallized from Et_2O: ^1H NMR (400 MHz, $CDCl_3$) δ 1.30-1.36 (m, 9H), 2.23 (s, 3H), 2.58 (d, *J* = 14.8 Hz, 1H), 3.31 (dd, *J* = 5.9, 14.7 Hz, 1H), 4.07 (quin, *J* = 6.4 Hz, 1H), 4.30 (m, 4H), 4.68 (d, *J* = 15.9 Hz, 1H), 4.75 (s, 2H), 4.92 (d, *J* = 15.9 Hz, 1H), 6.76 (s, 1H), 7.26 (m, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.63 (dd, *J* = 1.2, 7.9 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 8.09 (s, 1H).

2-(Perfluorobutyl)-9H-fluoren-9-one (10) A suspension of Cu-bronze (2.6 g, 40.6 mmol) in DMSO (30 mL, dried over 4 Å molecular sieves for 12 h) was heated at 125 °C for 15 min. Iodononafluorobutane (3.5 mL, 20.3 mmol) in DMSO (5 mL) was added dropwise and the mixture was stirred for 45 min at 125 °C. Next, 2-bromofluorenone 2 (1.0 g, 3.9 mmol) in DMSO (10 mL) was added dropwise and the mixture was stirred for an additional 6 h at the same temperature. The mixture was diluted with diethyl ether (50 mL), and was filtered over celite to remove Cu-bronze. The organic phase was washed with water (5 × 100 mL) and brine, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, n-heptane : dichloromethane 10 : 1 → 5 : 1, dry-loaded on celite) to give **10** as yellow crystals (1.1 g, 2.8 mmol, 72 %). Mp 96-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* =7.1 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.7 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.4, 121.2, 122.7 (t, *J* = 6.5 Hz), 124.7, 129.6 (t, *J* = 24.6 Hz), 130.3, 133.2 (t, *J* = 6.5 Hz), 134.3, 134.4, 135.1, 142.9, 147.7, 192.1. Peaks corresponding to *C*F3 are not observed due to the low intensity of the peaks in the region they are expected (~ 115 ppm).[8] HRMS (APCI) calcd for $C_{17}H_8F_9O$ 399.0433 (MH^+), found 399.0423.

(E/Z)-(2-(Perfluorobutyl)-9H-fluoren-9-ylidene)hydrazine (11) To a solution of ketone **10** (1.0 g, 2.5 mmol) in MeOH : DCM (4:1, 25 mL), $N_2H_4 \bullet H_2O$ (8 mL) was added and the solution was heated at 45°C for 3 h. Addition of water (10 mL) to the hot mixture followed by cooling to room temperature resulted in the precipitation of a pale yellow solid. The solid was filtered, washed with cold MeOH and dried on air. The product **11** (151 mg, 0.37 mmol, 64 %) was obtained as a mixture of *E/Z* isomers (~ 1 : 1.5) as a pale yellow solid and was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 (br s, 2H, major), 6.58 (br s, 2H, minor), 7.36-7.42 (m, 2H, major), 7.43-7-53 (m, 2H, minor), 7.56 (d, *J* = 8.0 Hz ,1H, minor), 7.67 (d, *J* = 8.0 Hz, 1H, major), 7.71-7.74 (m, 1H, major), 7.76-7.79 (m, 1H major, 1H minor), 7.87 ($t_{apparent}$, *J* = 8.7 Hz, 1H major, 1H minor), 7.94 (d, *J* = 7.1 Hz, 1H, minor), 7.98 (s, 1H, minor), 8.07 (s, 1H, major); ^{13}C NMR (100 MHz, CDCl3) δ 119.4 (t, *J* = 5.6 Hz), 119.5, 120.3, 120.4, 121.0, 121.3, 123.3 (t, *J* = 6.3 Hz), 125.3, 126.7 (t, *J* = 6.6 Hz), 128.3 ($d_{apparent}$, *J* = 7.1 Hz), 128.7, 128.9, 129.2, 129.8, 130.0, 130.6, 136.9, 138.0, 138.4, 139.6, 141.4, 143.4, 143.8, 144.5; HRMS (ESI) calcd for $C_{17}H_{10}F_9N_2$ 413.0695 (MH^+), found 413.0690.
Minor-isomer was isolated (SiO_2, n-heptane : EtOAc 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (br s, 2H) 7.44-7.53 (m, 2H), 7.56 (d, J = 8.2 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.98 (s, 1H).

9-diazo-2-(Perfluorobutyl)-9H-fluorene (12) MnO_2 (0.5 g, 5.75 mmol) was added to a stirred solution of hydrazone **11** (760 mg, 1.84 mmol) in THF (10 mL) after which the color of the

solution turned to red. The mixture was stirred for an additional 30 min and then filtered over a plug of celite. The solvent was removed under reduced pressure and the solid residue was immediately used in the next step.

(Cis/trans)-Diester-perfluorobutyl motor (9) Diazofluorene **12** was dissolved in toluene (5 mL) and added to a solution of thioketone **5**[1] (560 mg, 1.47 mmol) in toluene (10 mL). The mixture was heated at 75°C for 3 h. The formation of the episulfide was monitored by ^{1}H NMR spectroscopy by following the shift of the absorption of the aromatic proton of the thioketone from 6.66 to 6.34 and 6.39 ppm in the episulfide isomers (*cis/trans*). After the conversion of the thioketone was complete, PPh_3 (0.8 g, 3.05 mmol) was added to the episulfide solution, followed by an additional 1 h stirring at 75°C. The mixture was cooled to rt and the solvent was evaporated under reduced pressure. The crude product was dissolved in Et_2O and CH_3I (2 mL, 32 mmol) was added. The solution was stirred for 2 h at rt, the precipitate was filtered and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (SiO_2, n-heptane → n-heptane : Et_2O 3 :1) to give **9** as a mixture of isomers (1.4 : 1) as a yellow oil (792 mg, 1.08 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28-1.36 (m, 9H major, 9H minor), 2.21 (s, 3H major), 2.25 (s, 3H minor), 2.56 (d, *J* = 14.8 Hz, 1H major), 2.58 (d, *J* = 14.7 Hz, 1H minor), 3.32 (dd, *J* = 4.7, 14.8 Hz, 1H major, 1H minor), 4.06-4.18 (m, 1H major, 1H minor), 4.24-4.34 (m, 4H major, 4H minor), 4.52 (d, *J* = 15.6 Hz, 1H major), 4.68 (d, *J* = 15.8 Hz, 1H minor), 4.75 (s, 2H major, 2H minor), 4.87 (d, *J* = 15.8 Hz, 1H major), 4.92 (d, *J* = 16.1 Hz, 1H minor), 6.77 (s, 1H minor), 6.79 (s, 1H major), 7.24 (t, *J* = 7.4 Hz, 1H minor), 7.34 (t, *J* = 7.4 Hz, 1H minor), 7.39-7.46 (m, 3H major, 1H minor), 7.50 (d, *J* = 7.9 Hz, 1H major), 7.56-7.59 (m, 1H major, 1H minor), 7.81 (d, *J* = 7.6 Hz, 1H minor), 7.85-7.91 (m, 2H major, 1H minor), 8.06 (s, 1H minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 13.8, 13.9, 15.5, 16.1, 18.5, 18.6, 41.2, 41.3, 44.8, 44.9, 60.6, 60.7, 61.1, 61.2, 65.5, 65.6, 69.1, 69.3, 108.0, 108.4, 115.6-116.6 (m, *C*F_3), 119.1, 119.4, 119.8, 120.3, 121.5 (t, *J* = 6.9 Hz), 121.8 (t, *J* = 6.4 Hz), 123.6, 123.7, 124.8 (t, *J* = 6.2 Hz), 125.1 (t, *J* = 4.8 Hz), 126.0 (t, *J* = 23.7 Hz), 126.3 (t, *J* = 23.6 Hz), 126.8, 127.1, 127.7, 127.9, 128.0, 128.2, 131.6, 132.1, 133.7, 133.9, 137.5, 137.9, 138.2, 139.3, 139.9, 142.2, 142.7, 143.6, 143.9, 145.0, 145.5, 151.3, 151.9, 153.3, 153.7, 168.2, 169.1, 169.4; HRMS (ESI) calcd for $C_{36}H_{31}F_9O_6Na$ 753.6039 (MNa^+), found 753.1856.

(Cis/trans)-Dihydroxy-cyano motor (14) A solution of (*cis/trans*)-**8** (339 mg, 0.63 mmol) in THF (22 mL) was added to a suspension of $LiBH_4$ (14.4 mg, 0.66 mmol) in THF (3 mL) and the mixture was stirred at rt for 90 min. The mixture was diluted with EtOAc (25 mL) and washed with H_2O (20 mL), brine (10mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, EtOAc) afforded **14** as a mixture of isomers (1 : 1.7) as a yellow solid (152 mg, 0.34 mmol, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (d, *J* = 6.6 Hz, 3H, minor), 1.37 (d, *J* = 6.7 Hz, 3H, major), 2.18 (s, 3H, minor), 2.19 (s, 3H, major), 2.61 (d, *J* = 14.9

Hz, 1H, minor), 2.62 (d, *J* = 14.8 Hz, 1H, major), 3.34 (dd, *J* = 5.70, 14.8 Hz, 1H major, 1H minor), 3.92-4.23 (m, 9H major, 8H minor), 4.28-4.32 (m, 1H, minor) 6.90 (s, 1H, major) 6.91 (s, 1H, minor), 7.22 (t, *J* = 7.6 Hz, 1H, major), 7.33-7.38 (m, 2H, major), 7.41-7.49 (m, 2H, minor), 7.56 (dd, *J* = 1.3, 7.9 Hz, 1H, minor), 7.63-7.65 (m, 1H major, 1H minor), 7.81-7.85 (m, 1H major, 1H minor), 7.87-7.89 (m, 1H, minor) 7.89 (d, *J* = 7.9 Hz, 1H, major), 7.91 (d, *J* = 7.8 Hz, 1H, minor), 8.10 (s, 1H, major); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 154.8, 153.4, 153.0, 145.6, 144.6, 144.5, 143.2, 142.8, 140.2, 139.6, 138.5, 137.8, 137.4, 133.3, 133.0, 132.2, 131.9, 130.1, 129.985, 128.6, 128.1, 127.3, 127.3, 127.2, 127.1, 127.0, 123.8, 123.4, 120.7, 120.3, 120.2, 120.1, 119.9, 119.8, 109. 6, 109.1, 108.3, 108.1, 74.4, 74.3, 70.6, 70.6, 64.4, 62.2, 62.0, 61.0, 45.0, 44.8, 41.6, 41.5, 19.2, 18.9, 16.1, 15.9; HRMS (ESI) calcd for $C_{29}H_{27}NO_4Na$ 476.1832 (MNa^+), found 476.1843.

(Cis/trans)-Dihydroxy-perfluorobutyl motor (15) A suspension of $LiBH_4$ (66 mg, 3 mmol) in THF (5 mL) was added to a solution of motor (*cis/trans*)-**9** (660 mg, 0.9 mmol) in THF (15 mL) and the mixture was heated at 40 °C for 3 h. The reaction was quenched with H_2O (10 mL) and the mixture was extracted with EtOAc until the aqueous phase was colorless. The combined organic layers were washed with water and brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, Et_2O → EtOAc). One of the isomers could be precipitated by adding Et_2O to the product mixture. The rest of the *cis* and *trans* isomer mixture was separated by column chromatography (SiO_2, Et_2O)

***Cis*-15** (140 mg, 0.22 mmol, 24 %) was obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, *J* = 6.7 Hz, 3H), 2.18 (s, 3H), 2.59 (d, *J* = 14.7 Hz, 1H), 3.35 (dd, *J* = 5.6, 14.91 Hz, 1H), 3.37 (br s, OH), 3,75 (br s, O*H*), 3.86 ($t_{apparent}$, *J* = 10.4 Hz, 1H), 3.91-4.00 (m, 3H), 4.04-4.10 (m, 1H), 4.12-4.27 (m, 4H), 6.90 (s, 1H), 7.39-7.47 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.87-7.92 (m, 3H).

The protons of the terminal OH-groups could be observed in DMSO-d_6. ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.29 (d, *J* = 6.5 Hz, 3H), 2.07 (s, 3H), 2.61 (d, *J* = 14.8 Hz, 1H), 3.69 (br dd, *J* = 5.1, 9.7 Hz, 2H), 3.81 (br dd, *J* = 4.1, 8.6 Hz, 2H), 3.94-4.02 (m, 2H), 4.09 (q, *J* = 6.5 Hz, 1H), 4.12-4.18 (m, 2H), 4.75 (t, *J* = 5.3, O*H*), 4.93 (t, *J* = 5.2 Hz, O*H*), 7.13 (s, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.51-7.55 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 8.11 (d, *J* = 7.4 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H). (1H is not observed due to overlap with DMSO peak at 3.33 ppm.); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 18.9, 41.6, 45.1, 60.9, 61.8, 70.5, 74.4, 108.3, 119.3, 120.4, 121.6 (t, *J* = 7.1 Hz), 123.8, 125.3 (t, *J* = 5.3 Hz), 126.1 (t, *J* = 23.6 Hz), 126.9, 127.9, 128.1, 131.9, 133.3, 137.7, 138.0, 140, 2, 142.4, 144.6, 145.7, 153.2, 154.2.

***Trans*-15** (200 mg, 0.31 mmol, 34%) was obtained as a yellow solid.

^{1}H NMR (400 MHz, CDCl3) δ 1.36 (d, *J* = 6.7 Hz, 3H), 2.21 (s, 3H), 2.62 (d, *J* = 14.7 Hz, 1H), 3.54 (dd, *J* = 5.7, 14.9 Hz, 1H), 3.73 (br s, O*H*), 3.91-4.24 (m, 9H), 6.89 (s, 1H), 7.20 (t, *J* = 7.6

Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 8.07 (s, 1H).
The protons of the terminal OH-groups could be observed in DMSO-d_6. ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.29 (d, *J* = 6.6 Hz, 3H), 2.09 (s, 3H), 2.63 (d, *J* = 15.1 Hz, 1H), 3.70 (q, *J* = 5.2 Hz, 2H), 3.79 (q, *J* = 5.0 Hz, 2H), 3.92-3.97 (m, 1H), 3.98-4.05 (m, 1H), 4.08-4.19 (m, 3H), 4.77 (t, *J* = 5.4 Hz, O*H*), 4.91 (t, *J* = 5.4 Hz, O*H*), 7.11 (s, 1H), 7.30-7.33 (m, 2H), 7.37-7.41 (m, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 8.02 (s, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 8.22 (d, *J* = 7.9 Hz, 1H). (1H is not observed due to overlap with DMSO peak at 3.33 ppm.); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 18.8, 41.6, 44.9, 61.0, 62.1, 70.5, 74.4, 108.1, 119.5, 120.0, 121.9 (t, *J* = 7.0 Hz), 123.4, 124.9 (t, *J* = 6.3 Hz), 126.6 (t, *J* = 23.7 Hz), 127.1, 127.6, 128.0, 132.1, 133, 5, 137.8, 138.5, 139.5, 142.6, 144.4, 145.6, 152.9, 153.7; HRMS (ESI) calcd for $C_{32}H_{27}F_9O_4Na$ 669.5304 (MNa^+), found 669.1622.

(*Cis/trans*)-Dialkyne-cyano motor (16) A solution of (*cis/trans*)-**14** (160 mg, 0.35 mmol) in THF (14 mL) was added dropwise to the suspension of NaH (95%, 35 mg, 1.36 mmol) in THF (6 mL) and the mixture was stirred at rt for 30 min. To this mixture propargyl bromide (80 % in toluene, 170 μL, 1.53 mmol,) was added. The solution was stirred at rt for 12 h. The mixture was diluted with EtOAc (25 mL) and washed with H_2O (20 mL), brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (SiO_2, n-hexane : EtOAc = 4 : 1) afforded the product as a mixture of *cis* and *trans* isomers as a yellow solid (118 mg, 0.22 mmol, 63%).
85 mg (0.16 mmol) of the isomer mixture was separated by column chromatography (SiO_2, toluene : Et2O 20 : 1).
***Cis*-16** (26 mg, 0.05 mmol, 31%, R_f= 0.45) was obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (d, *J* = 6.7 Hz, 3H), 2.16 (s, 3H), 2.41 (t, *J* = 2.4 Hz, 1H), 2.49 (t, *J* = 2.4 Hz, 1H), 2.58 (d, *J* = 14.8 Hz, 1H), 3.32 (dd, *J* = 5.7, 14.7 Hz, 1H), 3.92-3.94 (m, 2H), 4.00 (t, *J* = 4.77 Hz, 2H), 4.12 ($quin_{apparent}$, *J* = 8.0 Hz, 1H), 4.23-4.30 (m, 4H), 4.31-4.32 (m, 4H), 6.88 (s, 1H), 7.40 (dt, *J* = 1.1, 7.4 Hz, 1H), 7.45 (dt, *J* = 1.5, 7.6 Hz, 1H), 7.55 (dd, *J* = 1.4, 7.9 Hz, 1H), 7.65 ($d_{apparent}$, *J* = 0.8 Hz, 1H), 7.83 (dd, *J* = 0.5, 7.9 Hz, 1H), 7.87 ($dd_{apparent}$, *J* = 0.9, 7.3 Hz, 1Hz), 7.90 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1 19.0, 41.5, 45.0, 58.4, 58.6, 68.1, 68.2, 69.3, 72.0, 74.4, 74.8, 108.5, 109.2, 119.7, 119.9, 120.7, 123.8, 126.8, 127.2, 128.5, 130.0, 131.8, 132.8, 137.7, 137.9, 140.2, 142.6, 144.0, 146.2, 153.7, 155.5.
***Trans*-16** (40 mg, 0.075 mmol, 47%, R_f=0.55) was obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (d, *J* = 6.7 Hz, 3H), 2.18 (s, 3H), 2.43 (t, *J* = 2.3 Hz, 1H), 2.49 (t, *J* = 2.3 Hz, 1H), 2.59 (d, *J* = 14.8 Hz, 1H), 3.32 (dd, *J* = 5.9, 14.8 Hz, 1H), 3.89-3.93 (m, 2H), 3.99 (t, *J* = 4.7 Hz, 2H), 4.03-4.16 (m, 2H), 4.22-4.38 (m, 3H), 4.30 (d, *J* = 2.3 Hz, 2H), 4.32 (d, *J* = 2.4 Hz, 2H), 6.87 (s, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.63 (dd, *J* = 0.8, 7.9 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 8.09 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.0, 19.3, 41.5, 45.0, 58.3, 58.6, 68.0, 68.2, 69.3, 71.6, 74.6,

74.8, 108.3, 109.5, 120.0, 120.1, 120.3, 123.6, 127.1, 127.1, 127.2, 128.2, 130.0, 132.1, 133.0, 137.3, 138.6, 139.6, 143.2, 143.9, 145.8, 153.3, 155.3; HRMS (APCI) calcd for $C_{35}H_{31}NO_4$ 529.2253, found 530.2324 (MH^+).

Irradiation experiment to generate unstable isomer of motor *trans*-16:

Motor *cis*-**16** (~2 mg) was dissolved in CD_2Cl_2 (~1 mL). This sample was placed in an NMR tube and irradiated at 365 nm at -55ºC at a distance of 2-3 cm from the centre of the lamp. 1H NMR spectra of the sample were taken before, during and after irradiation at -55ºC. No further changes were observed after 7 h of irradiation. The relative integration of the absorptions from the two isomers revealed a photostationary state of unstable-*trans*-**16** to stable-*cis*-**16** of 5 : 1. After warming the sample to rt, only the stable forms were observed by ^{1}H NMR spectroscopy.

stable-*cis*-**16** ^{1}H NMR (500 MHz, CD_2Cl_2, -55°C) δ 1.28 (d, *J* = 6.5 Hz, 3H), 2.08 (s, 3H), 2.51 (s, 1H), 2.56-2.60 (m, 2H), 3.28 (dd, *J* = 5.4, 14.7 Hz, 1H), 3.80-3.88 (m, 2H), 3.95 (t, *J* = 3.6 Hz, 2H), 4.06-4.13 (m, 2H), 4.16-4.24 (m, 3H), 4.27 (s, 2H), 4.29 (d, *J* = 1.4 Hz, 2H), 6.89 (s, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.57 (s, 2H), 7.85-7.91 (m, 3H).

unstable-*trans*-**16** ^{1}H NMR (500 MHz, CD_2Cl_2, -55°C) δ 1.42 (d, *J* = 6.4 Hz, 3H), 1.93 (s, 3H), 2.50-2.60 (absorptions in this region could not be resolved due to overlap with remaining stable-*cis*-**16**), 2.98 (dd, *J* = 5.30, 16.4 Hz, 1H), 3.42 (dd, *J* = 8.2, 16.3 Hz, 1H), 3.72-4.13 (absorptions in this region could not be resolved due to overlap with remaining stable-*cis*-**16**), 4.20 (d, *J* = 2.2 Hz, 2H), 4.21-4.25 (absorptions in this region could not be resolved due to overlap with remaining stable-*cis*-**16**), 4.28 (d, *J* = 2.2 Hz, 2H), 6.83 (s, 1H), 7.19-7.23 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.98 (s, 1H).

Irradiation experiment to generate unstable isomer of motor *cis*-16:

Motor *trans*-**16** (~2 mg) was dissolved in CD_2Cl_2 (~1 mL). This sample was placed in an NMR tube and irradiated at 365 nm at -55ºC at a distance of 2-3 cm from the centre of the lamp. ^{1}H NMR spectra of the sample were taken before, during and after irradiation at -55ºC. No further changes were observed after 7 h of irradiation. The relative integration of the absorptions from the two isomers revealed a photostationary state of unstable-*cis*-**16** to stable-*trans*-**16** of 3.5 : 1. After warming the sample to rt, only the stable forms were observed by ^{1}H NMR spectroscopy.

stable-*trans*-**16** ^{1}H NMR (500 MHz, CD_2Cl_2, -55°C) δ 1.29 (d, *J* = 6.5 Hz, 3H), 2.09 (s, 3H), 2.52 (s, 1H), 2.57-2.60 (m, 2H), 3.28 (dd, *J* = 5.5, 14.7 Hz, 1H), 3.77-3.86 (m, 2H), 3.92-3.95 (m, 2H), 3.99-4.06 (m, 2H), 4.18-4.32 (m, 3H), 4.24 (s, 2H), 4.29 (s, 2H), 6.88 (s, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.3-7.34 (m, 2H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 8.09 (s, 1H)

unstable-*cis*-**16** ^{1}H NMR (500 MHz, CD_2Cl_2, -55°C) δ 1.45 (d, *J* = 6.4 Hz, 3H), 1.92 (s, 3H), 2.48-2.50 (m, 1H), 2.55-2.60 (absorptions in this region could not be resolved due to overlap with remaining stable-*trans*-**16**), 2.98 (dd, *J* = 5.3, 16.0 Hz, 1H), 3.41 (dd, *J* = 8.2, 16.3 Hz, 1H),

3.74-4.31 (absorptions in this region could not be resolved due to overlap with remaining stable-*trans*-**16**), 4.22 (d, *J* = 2.2 Hz, 2H), 6.83 (s, 1H), 7.30-7.35 (absorptions in this region could not be resolved due to overlap with remaining stable-*trans*-**16**), 7.39 (t, *J* = 7.7 Hz, 1H), 7.47 (s, 1H), 7.53 (dd, *J* = 0.7, 7.9 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H)

***Cis*-Dialkyne-perfluorobutyl motor (*cis*-17)** A suspension of NaH (100 mg, 50% in oil, 2.1 mmol) in THF (2 mL) was cooled to 0ºC and a solution of *cis*-**15** (140 mg, 0.22 mmol) in THF (5 mL) was added dropwise. Then, propargyl bromide (0.15 mL, 80 % in toluene, 1.35 mmol) was added to this mixture and the resulting solution was stirred at rt for 12 h. The reaction was quenched with water (10 mL) and the mixture was extracted with EtOAc until the yellow color of the aqueous phase had disappeared. The organic phase was washed with water (10 mL) and brine (10 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, n-pentane : DCM 2 : 1 → 2 : 3) to give the product as a yellow solid (100 mg, 0.14 mmol, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (d, *J* = 6.7 Hz, 3H), 2.16 (s, 3H), 2.42 (t, *J* = 2.3 Hz, 1H), 2.49 (t, *J* = 2.3 Hz, 1H), 2.57 (d, *J* = 14.6 Hz, 1H), 3.33 (dd, *J* = 5.8, 14.41 Hz, 1H), 3.92 (t, *J* = 4.5 Hz, 2H), 3.99-4.01 (m, 2H), 4.07-4.18 (m, 2H), 4.23-4.37 (m, 7H), 6.88 (s, 1H), 7.38-7.46 (m, 2H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.61 (s, 1H), 7.86-7.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 19.0, 41.5, 45.1, 58.3, 58.6, 67.9, 68.2, 69.2, 71.8, 74.2, 74.7, 108.5, 119.1, 120.4, 121.7 (t, *J* = 6.5 Hz), 123.8, 125.1 (t, *J* = 5.8 Hz), 126.1 (t, *J* = 23.2 Hz), 126.7, 127.5, 128.0, 131.7, 133.0, 137.7, 138.0, 140.2, 142.2, 144.0, 146.2, 153.5, 154.7; HRMS (APCI) calcd for $C_{38}H_{32}F_9O_4$ 723.2151 (MH^+), found 723.2152.

Irradiation experiment to generate unstable isomer of motor *trans*-17:
Motor *cis*-**17** (~2 mg) was dissolved in CD_2Cl_2 (~1 mL). This sample was placed in an NMR tube and irradiated at 365 nm at -55ºC at a distance of 2-3 cm from the centre of the lamp. ^{1}H NMR spectra of the sample were taken before, during and after irradiation at -55ºC. No further changes were observed after 7 h of irradiation. The relative integration of the absorptions from the two isomers revealed a photostationary state of stable-*cis*-**17** to unstable-*trans*-**17** of 1 : 2.5. After warming the sample to rt, only the stable form was observed by ^{1}H NMR spectroscopy.
<u>stable-*cis*-**17**</u> ^{1}H NMR (500 MHz, CD_2Cl_2, -55°C) δ 1.29 (d, *J* = 6.6 Hz, 3H), 2.06 (s, 3H), 2.52 (t, *J* = 2.3 Hz, 1H), 2.55-2.58 (m, 2H), 3.28 (dd, *J* = 5.3, 14.6 Hz, 1H) 3.79-3.85 (m, 2H), 3.9-4.0 (m, 4H), 4.10 (quin, *J* = 6.0 Hz, 1H), 4.14-4.25 (m, 2H), 4.26 (t, *J* = 2.4 Hz, 2H), 4.29 (d, *J* = 2.3 Hz, 2H), 6.88 (s, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.44 ($t_{apparent}$, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.51 (s, 1H), 7.89-7.92 (m, 3H).
<u>unstable-*trans*-**17**</u> ^{1}H NMR (500 MHz, CD_2Cl_2, -55°C) δ 1.41 (d, *J* = 6.3 Hz, 3H), 1.95 (s, 3H), 2.50-2.51 (m, 1H), 2.55-2.59 (absorptions in this region could not be resolved due to overlap with remaining stable-*cis*-**17**), 3.40 (dd, *J* = 8.4, 16.1 Hz, 1H), 3.72-4.29 (absorptions in this

region could not be resolved due to overlap with remaining stable-*cis*-**17**), 6.82 (s, 1H), 7.19-7.22 (m, 2H), 7.28-7.31 (m, 1H), 7.32-7.51 (absorptions in this region could not be resolved due to overlap with remaining stable-*cis*-**17**), 7.82 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.89-7.94 (absorptions in this region could not be resolved due to overlap with remaining stable-*cis*-**17**).

***Trans*-Dialkyne-perfluorobutyl motor (*trans*-17)** A suspension of NaH (100 mg, 50% in oil, 2.1 mmol) in THF (2 mL) was cooled to 0ºC and a solution of *trans*-**15** (90 mg, 0.14 mmol) in THF (4 mL) was added dropwise. Then, propargyl bromide (0.1 mL, 80 % in toluene, 0.9 mmol) was added to this mixture and the resulting solution was stirred at rt for 5 h. The reaction was quenched with water (10 mL) and the mixture was extracted with EtOAc until the yellow color of the aqueous phase had disappeared. The organic phase was washed with water (10 mL) and brine (10 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, n-pentane : DCM 1 : 1 → 1 : 2) to give the product as a yellow solid (80 mg, 0.11 mmol, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, J = 6.7 Hz, 3H), 2.19 (s, 3H), 2.43 (t, J = 2.4 Hz, 1H), 2.49 (t, J = 2.4 Hz, 1H), 2.59 (d, J = 14.7 Hz, 1H), 3.33 (dd, J = 6.0, 14.6 Hz, 1H), 3.88-3.95 (m, 2H), 3.99 (t, J = 4.7 Hz, 2H), 4.06-4.17 (m, 3H), 4.22-4.37 (m, 2H), 4.30 (d, J = 2.4 Hz, 2H) 4.32 (d, J = 2.4 Hz, 2H), 6.87 (s, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 7.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1, 18.9, 41.5, 44.9, 58.3, 58.6, 68.0, 68.2, 69.3, 71.6, 74.5, 74.7, 108.3, 119.5, 119.9, 121.9 (t, J = 7.1 Hz), 123.6, (t, J = 6.6 Hz), 126.5 (t, J = 23.8 Hz), 127.0, 127.7, 127.8, 132.0, 133.2, 137.6, 138.5, 139.5, 142.6, 143.7, 145.8, 153.1, 154.2; HRMS (APCI) calcd for $C_{38}H_{32}F_9O_4$ 723.2151 (MH^+), found 723.2152.

Irradiation experiment to generate unstable isomer of motor *cis*-17:

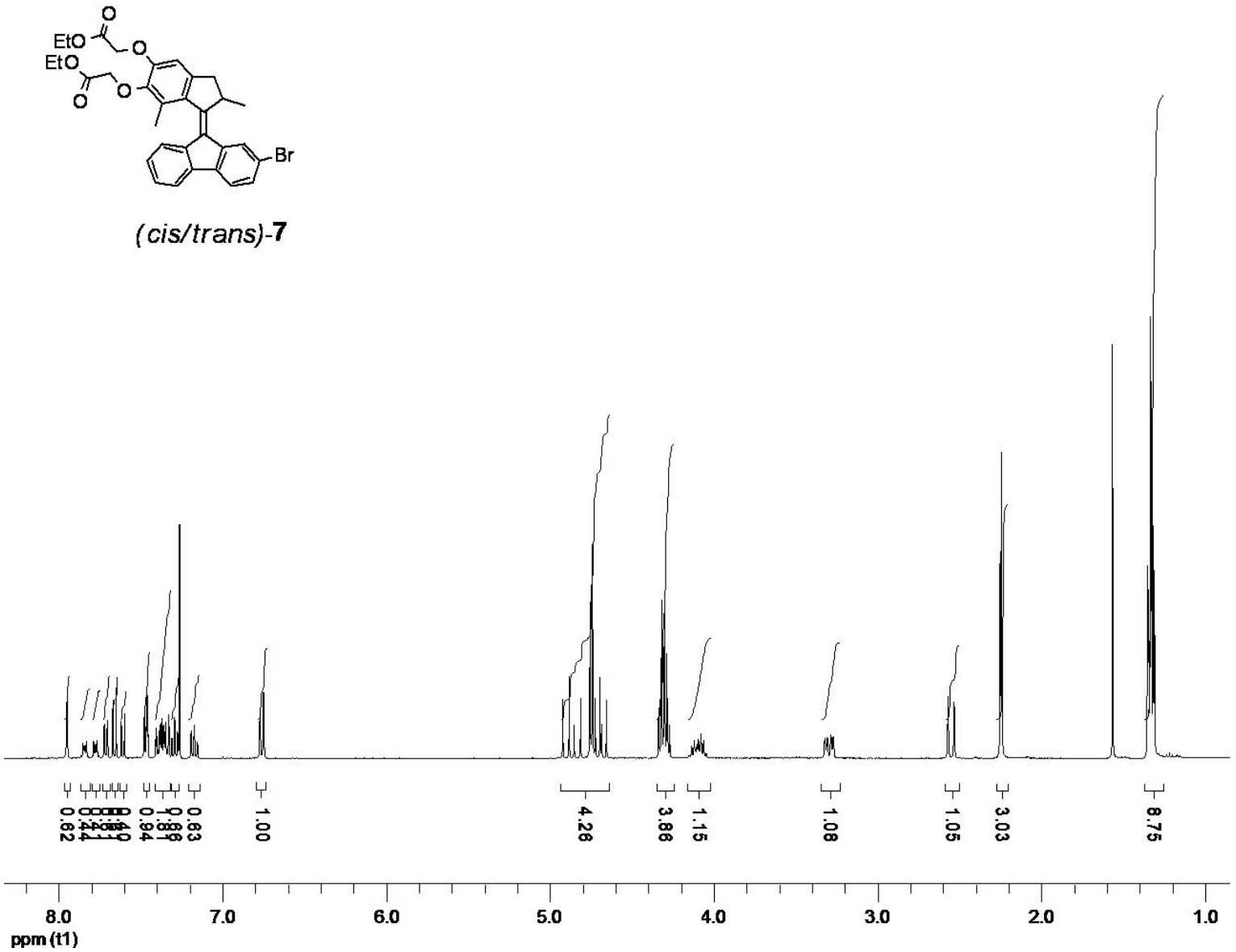
Motor *trans*-**17** (~2 mg) was dissolved in CD_2Cl_2 (~1 ml). This sample was placed in an NMR tube and irradiated at 365 nm at -55ºC at a distance of 2-3 cm from the centre of the lamp. ^{1}H NMR spectra of the sample were taken before, during and after irradiation at -55ºC. No further changes were observed after 7 h of irradiation. The relative integration of the absorptions from the two isomers revealed a photostationary state of stable-*trans*-**17** to unstable-*cis*-**17** of 1 : 2. After warming the sample to rt, only the stable forms were observed by ^{1}H NMR spectroscopy.

<u>stable-*trans*-**17**</u> ^{1}H NMR (500 MHz, CD_2Cl_2, -55°C) δ 1.29 (d, J = 6.6 Hz, 3H), 2.09 (s, 3H), 2.52 (t, J = 2.3 Hz, 1H), 2.58 (d, J = 14.7 Hz, 1H), 2.59 (t, J = 2.5 Hz, 1H), 3.28 (dd, J = 5.6, 14.7 Hz, 1H), 3.77-3.86 (m, 3H), 3.94 (t, J = 3.9 Hz, 2H), 3.98-4.02 (m, 1H), 4.06 ($t_{apparent}$, J = 6.5 Hz, 1H), 4.17-4.32 (m, 2H) 4.24 (d, J = 2.0 Hz, 2H), 4.28 (d, J = 2.3 Hz, 2H), 6.87 (s, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.30-7.34 (m, 2H), 7.55 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.4 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.00 (s, 1H).

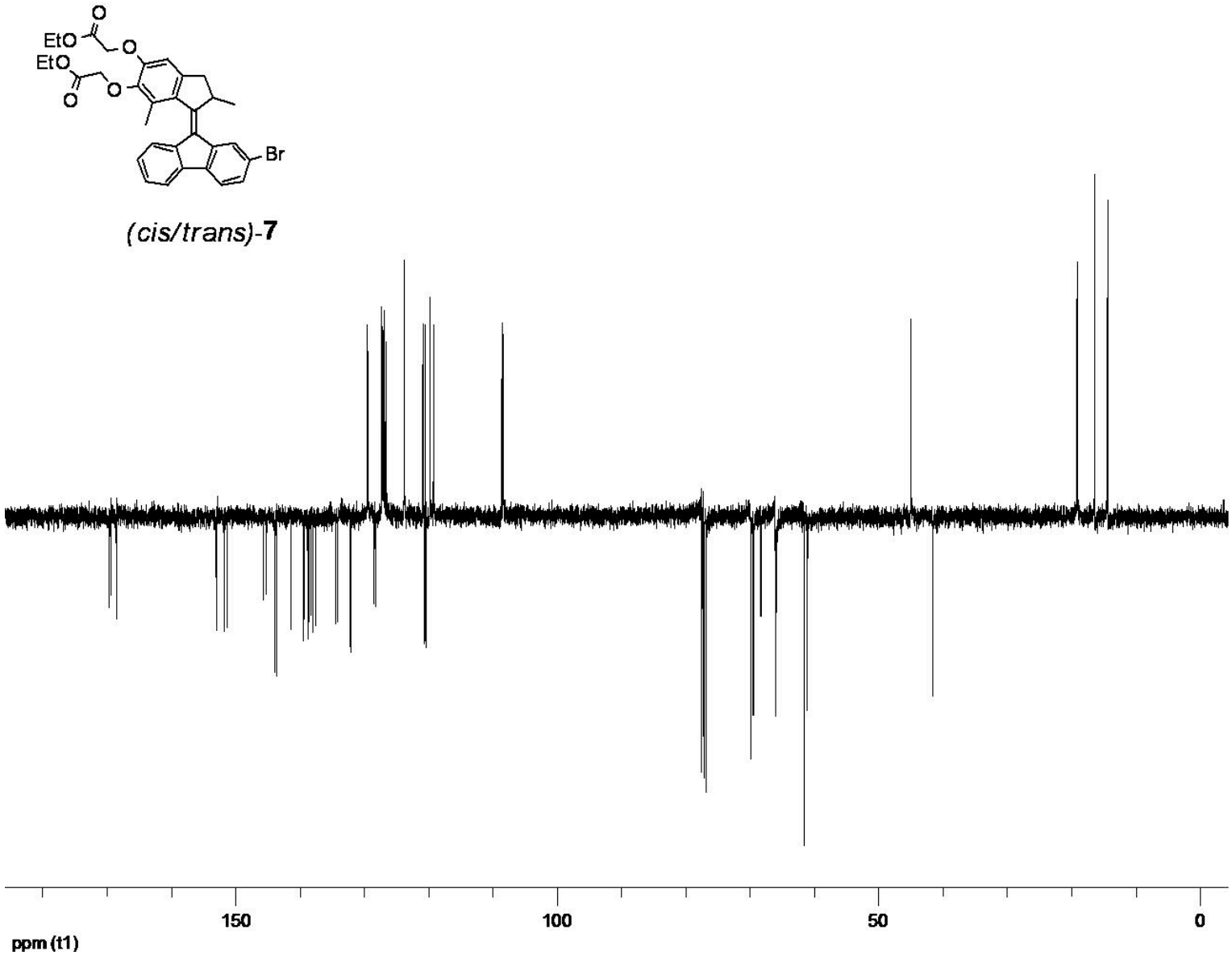
<u>unstable-*cis*-**17**</u> ^{1}H NMR (500 MHz, CD_2Cl_2, -55°C) δ 1.46 (d, J = 6.2 Hz, 3H), 1.89 (s, 3H), 2.49-2.51 (m, 1H), 2.55-2.60 (absorptions in this region could not be resolved due to overlap

with remaining stable-*trans*-**17**), 3.00 (dd, J = 5.7, 16.4 Hz, 1H), 3.41 (dd, J = 8.4, 16.3 Hz, 1H), 3.74-4.32 (absorptions in this region could not be resolved due to overlap with remaining stable-*trans*-**17**), 4.22 (s, 2H), 6.83 (s, 1H), 7.19-7.39 (absorptions in this region could not be resolved due to overlap with remaining stable-*trans*-**17**), 7.37 (s, 2H), 7.44 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.87 (d, J = 7.4 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H).

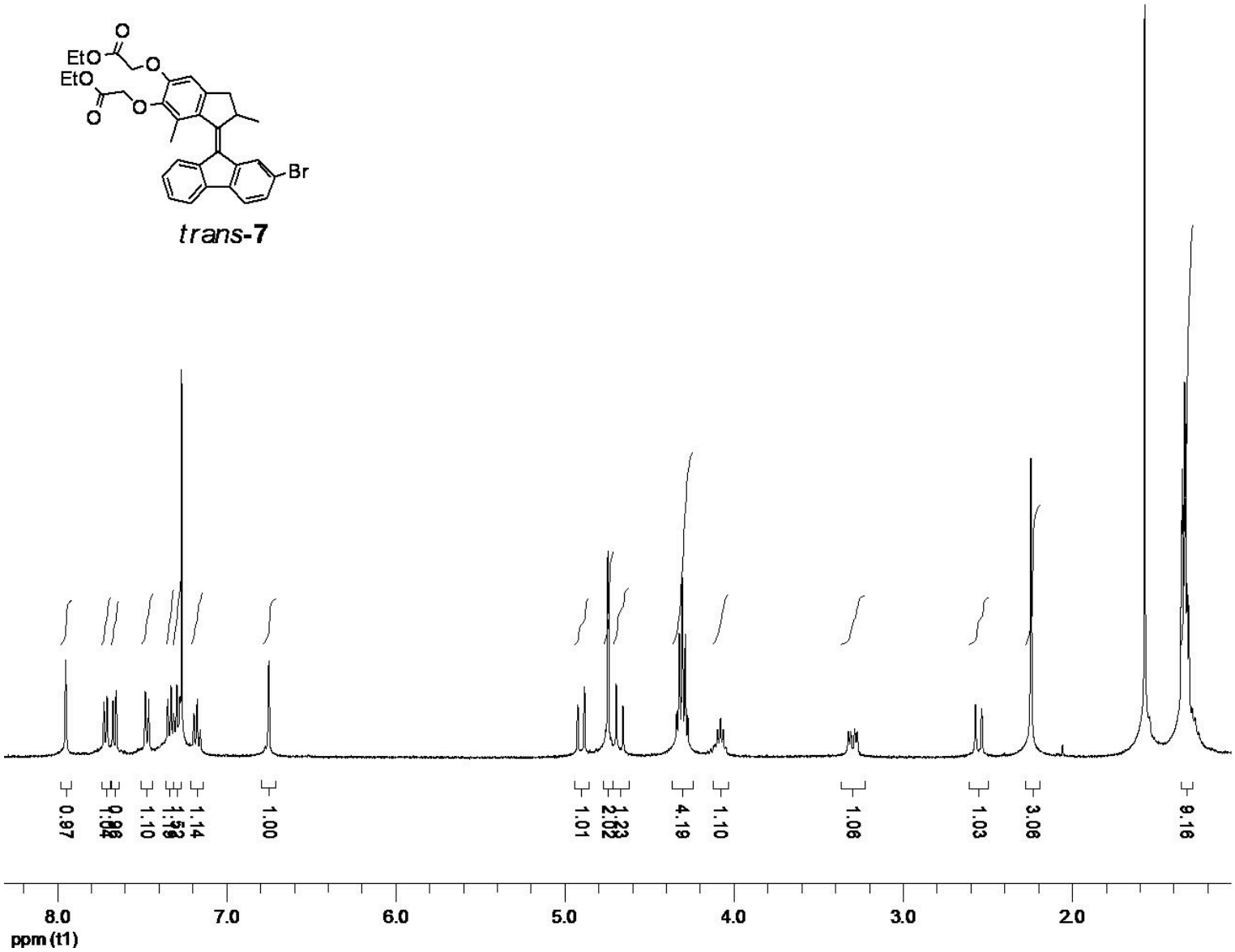
NMR Spectra



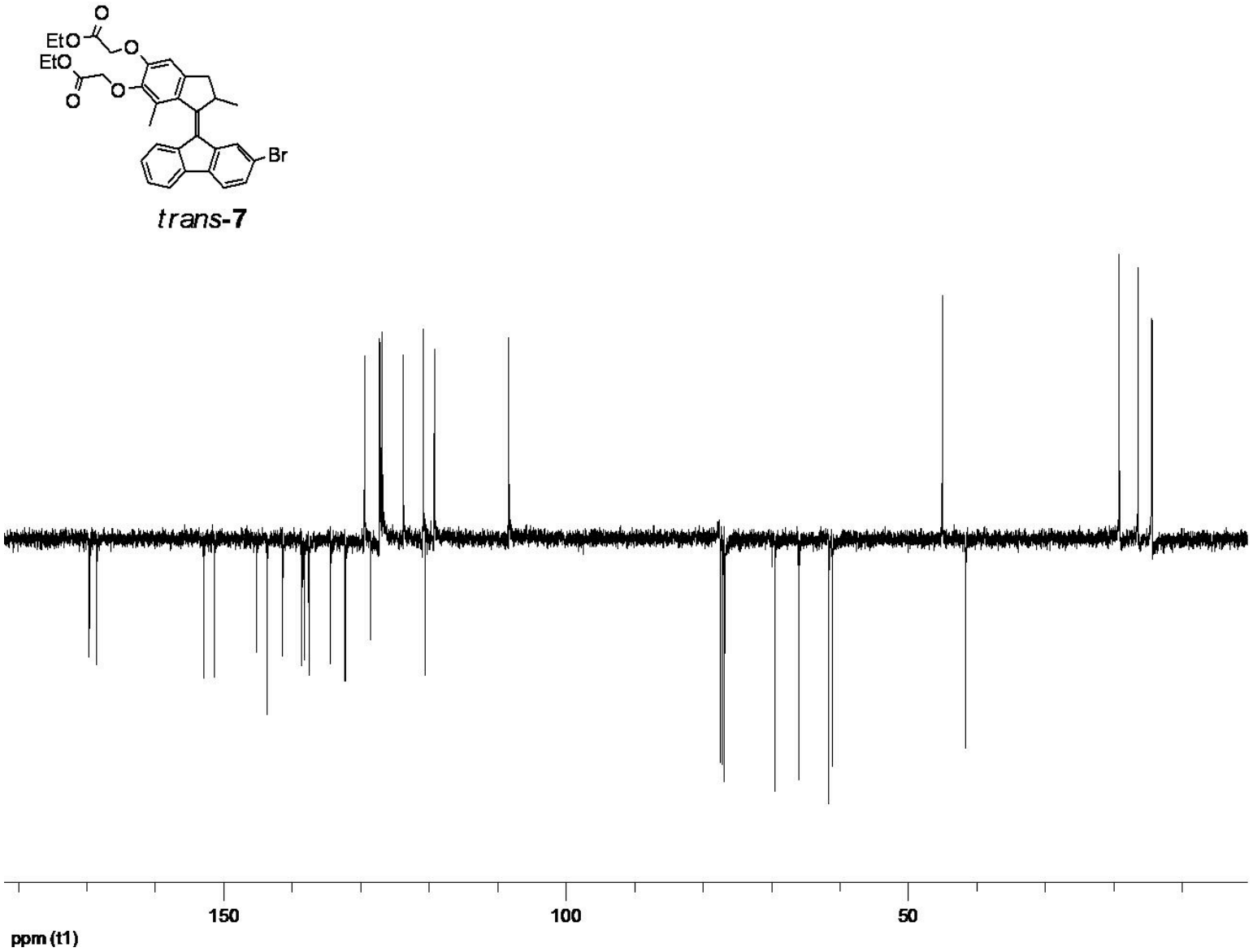
Spectrum 1 ^{1}H NMR spectrum of (*cis/trans*)-**7** in $CDCl_3$.



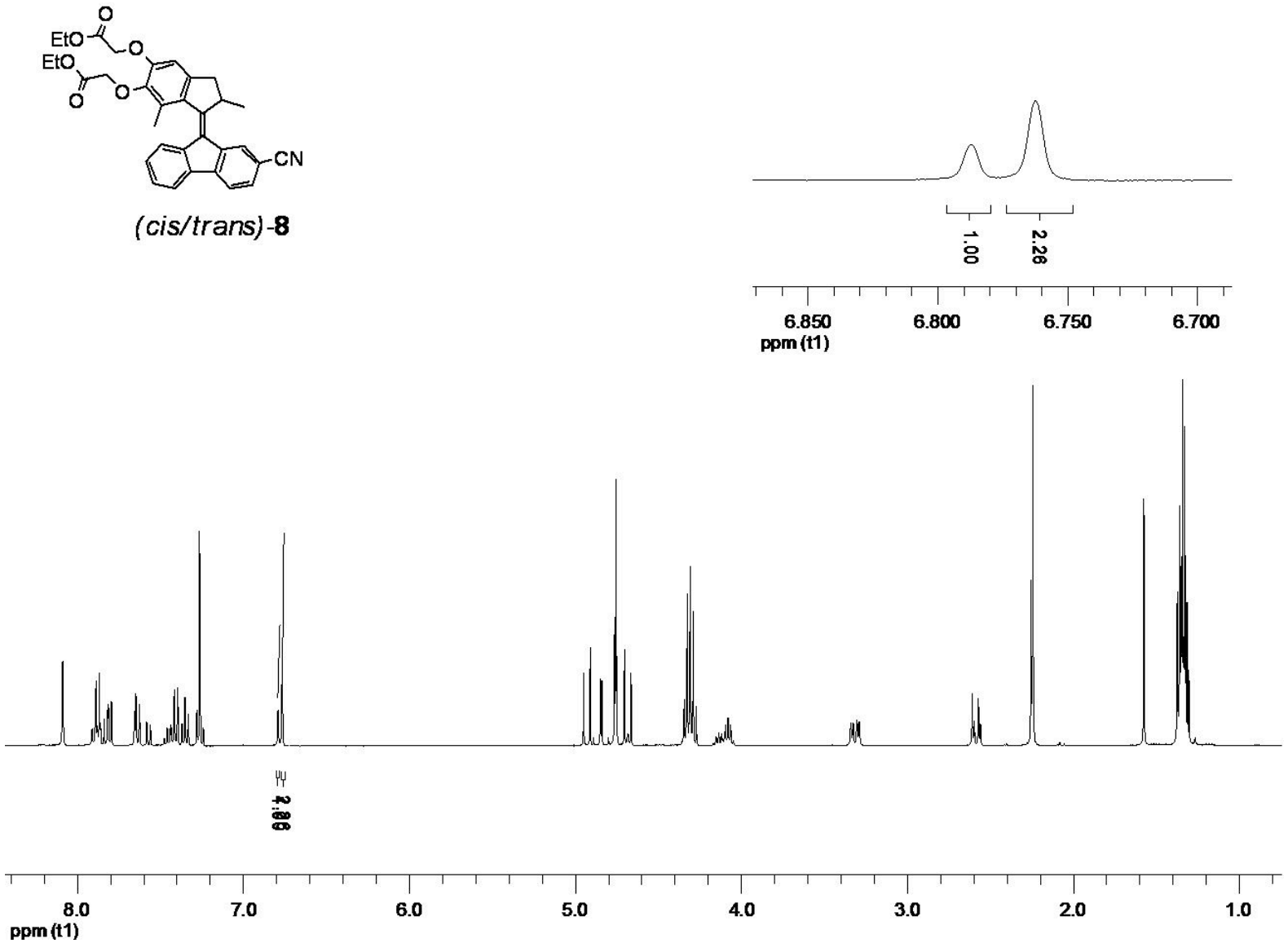
Spectrum 2 APT ^{13}C NMR spectrum of (*cis/trans*)-**7** in $CDCl_3$.



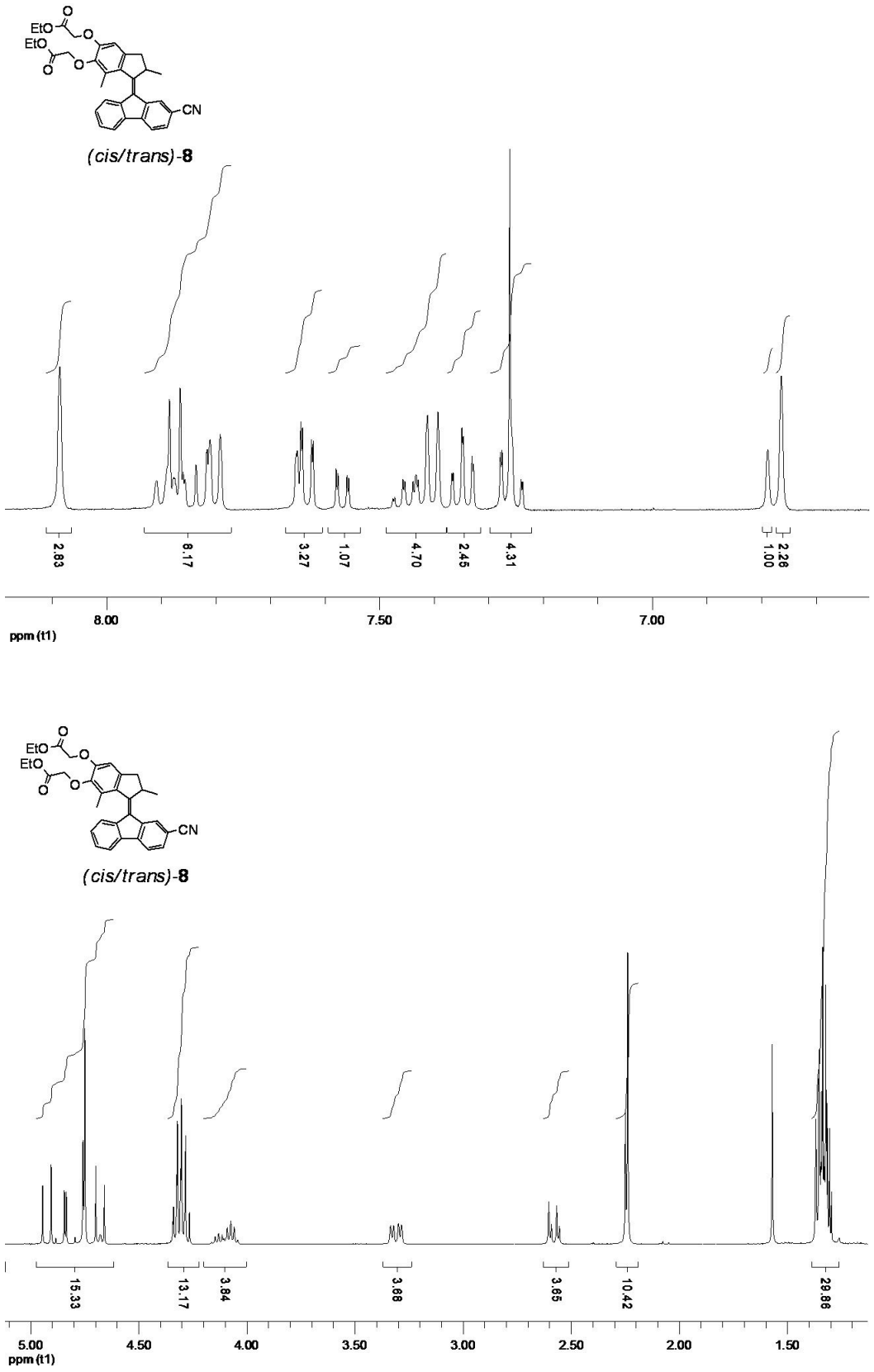
Spectrum 3 ^{1}H NMR spectrum of *trans*-**7** in $CDCl_3$.



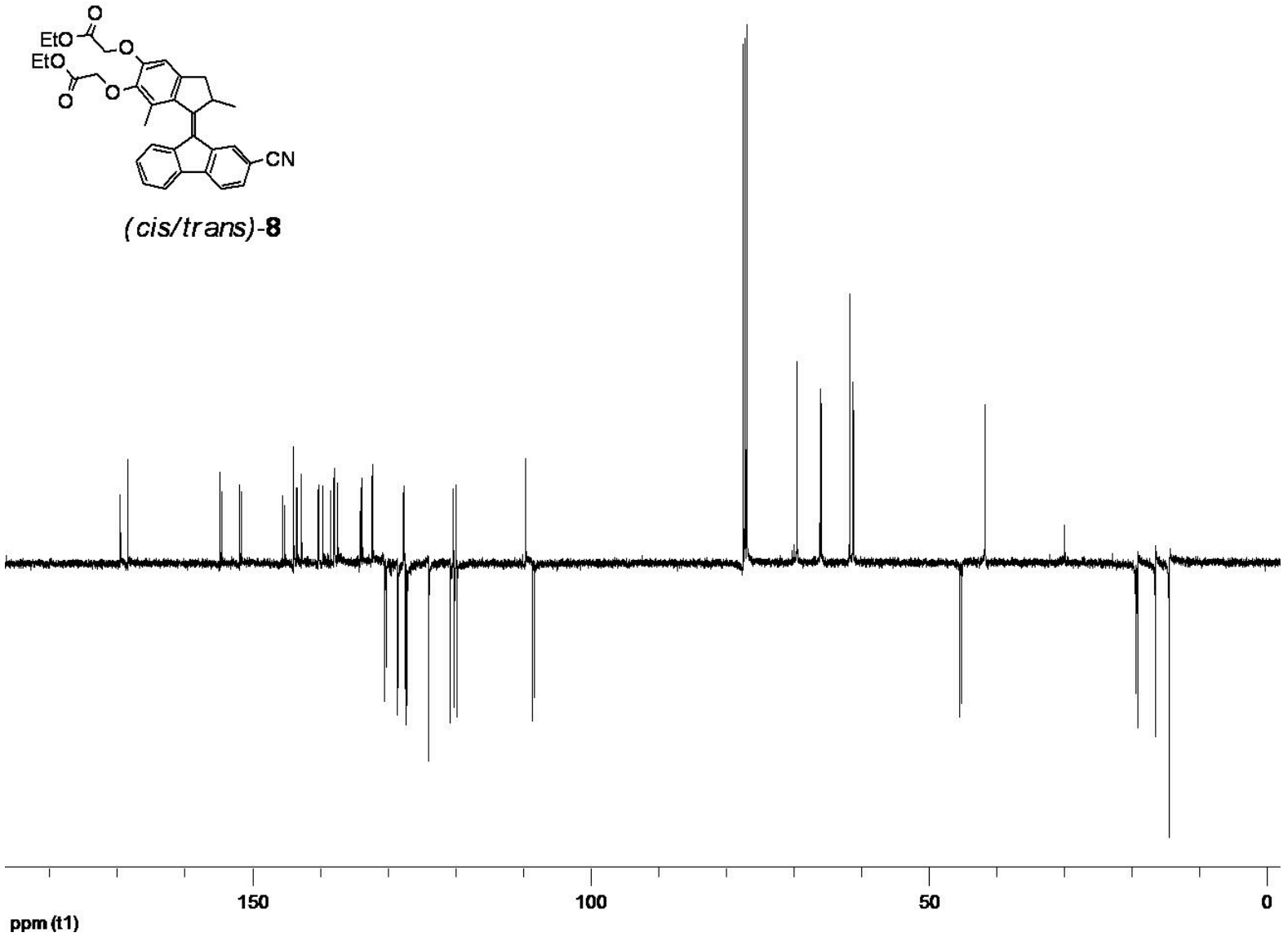
Spectrum 4 APT ^{13}C NMR spectrum of *trans*-**7** in $CDCl_3$.



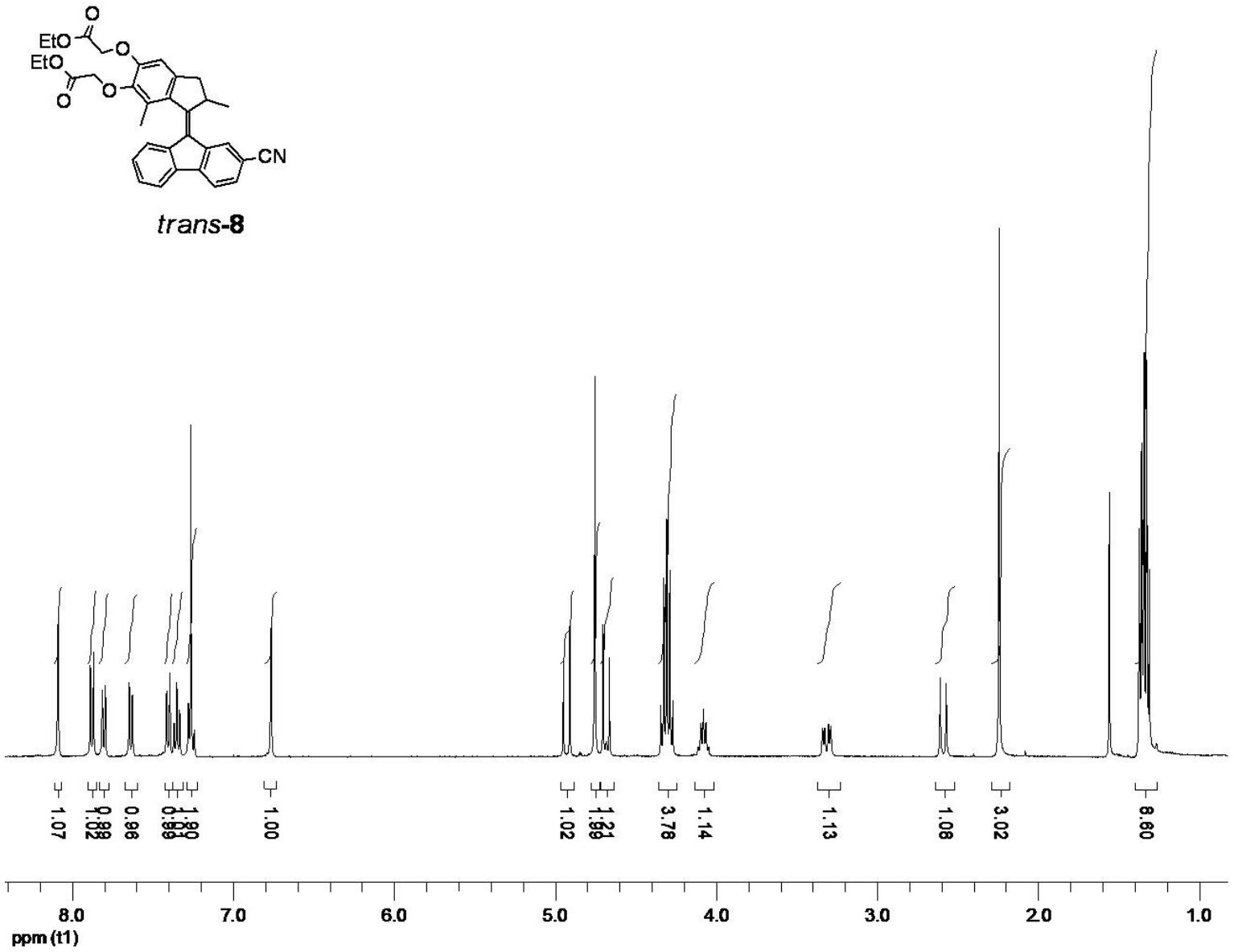
Spectrum 5 ^{1}H NMR spectrum of (*cis/trans*)-**8** in $CDCl_3$.



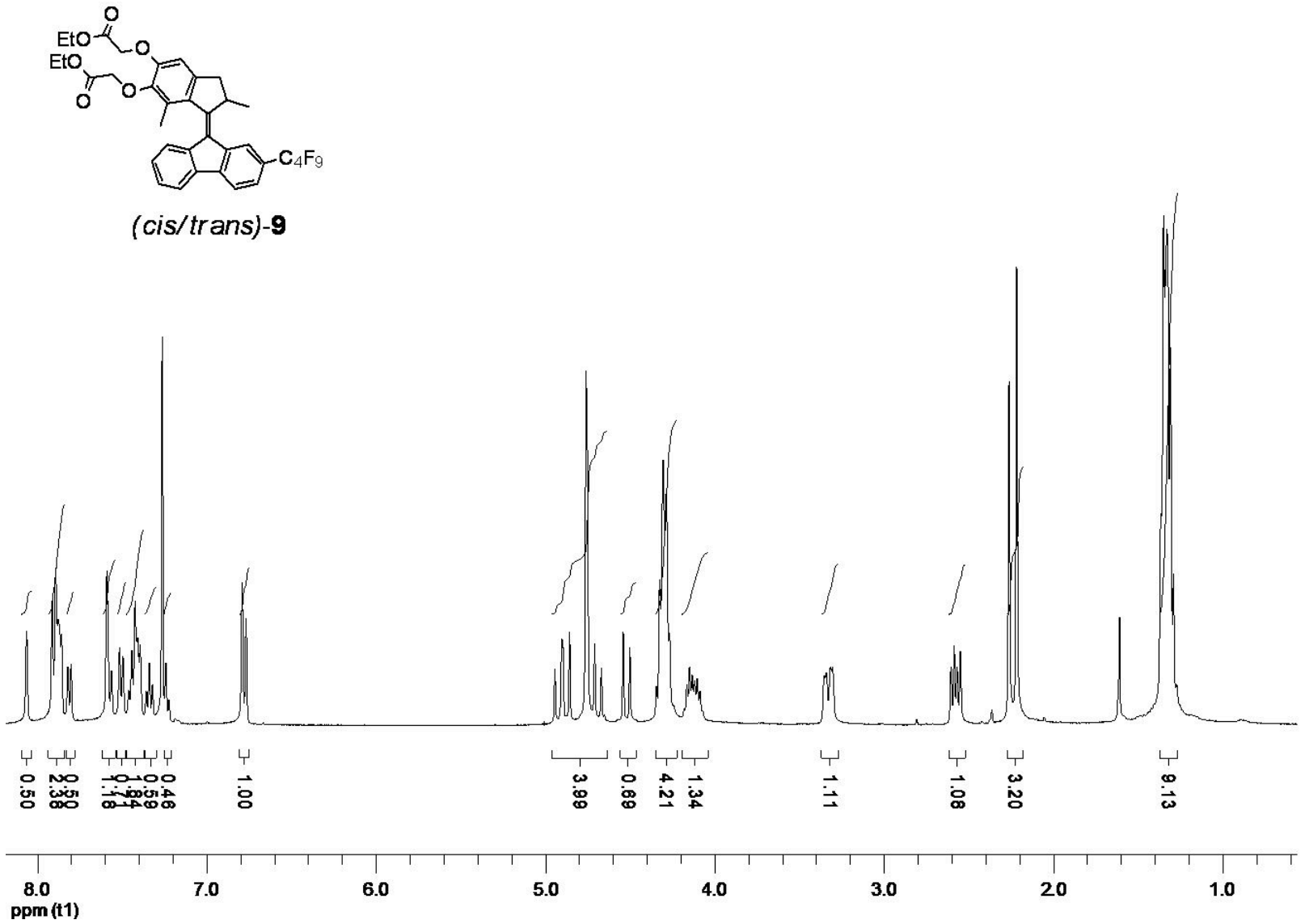
Spectrum 6 Expansion of ^{1}H NMR spectrum of (*cis/trans*)-**8** in $CDCl_3$.



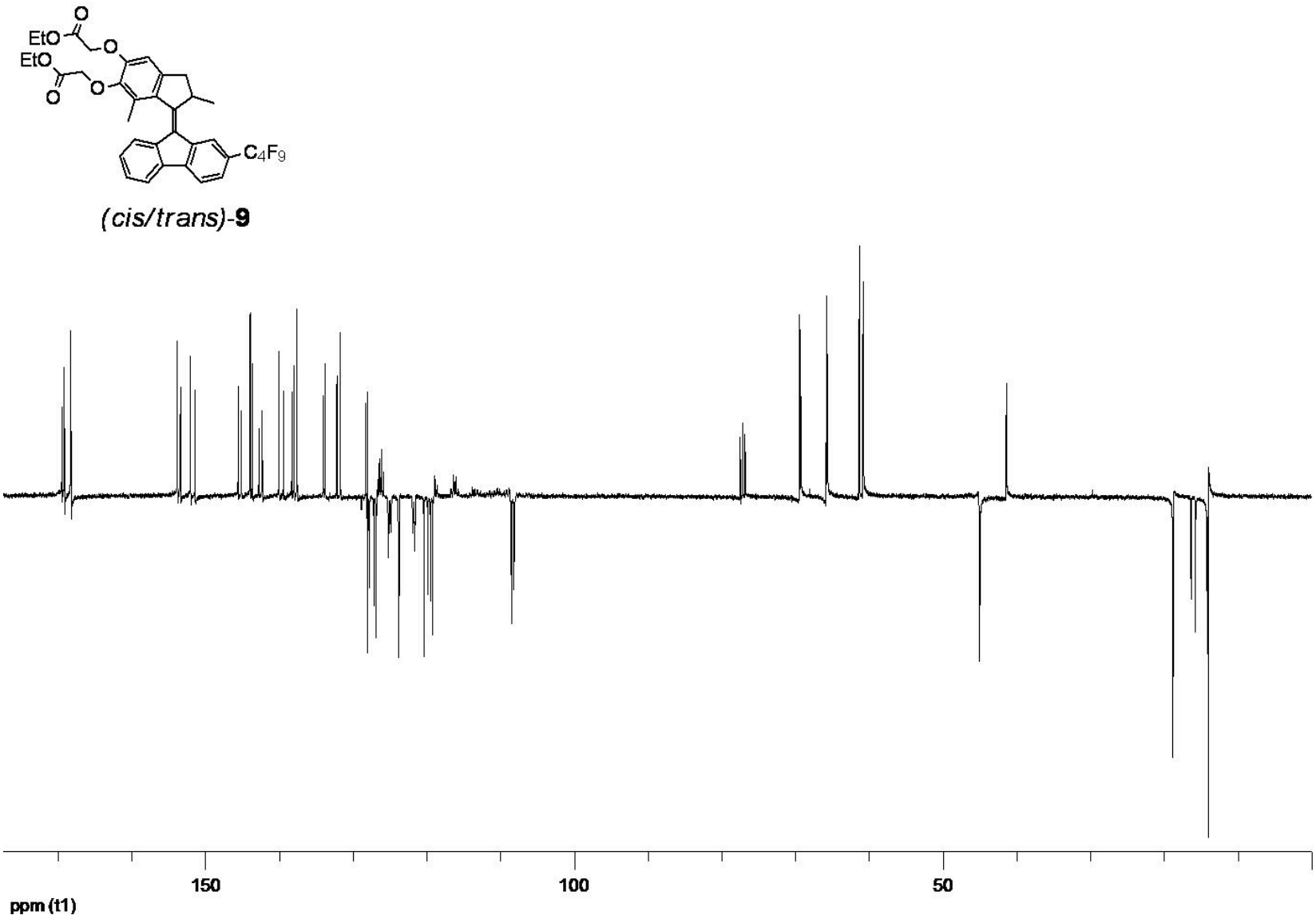
Spectrum 7 APT ^{13}C NMR spectrum of (*cis/trans*)-**8** in $CDCl_3$.



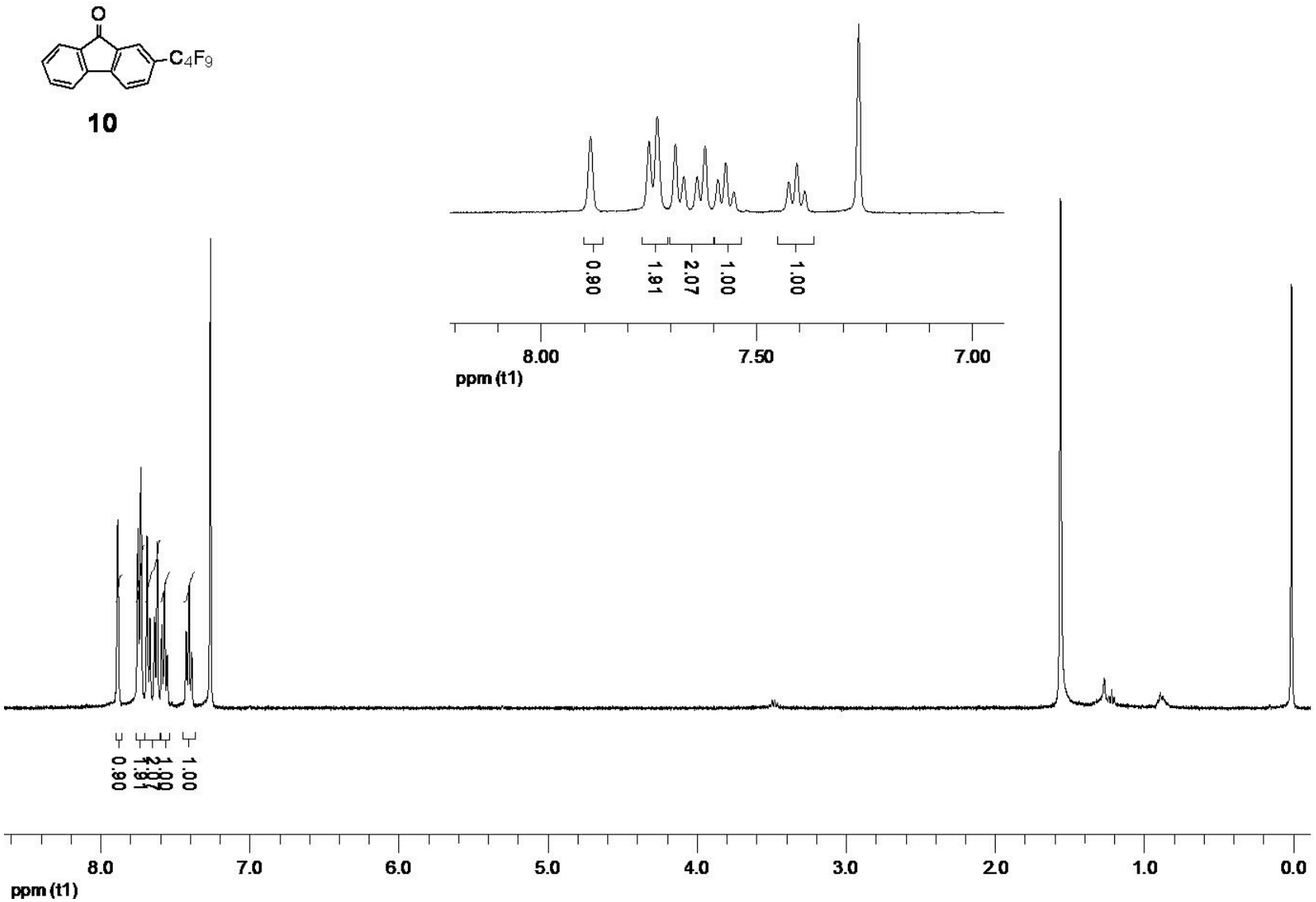
Spectrum 8 ^{1}H NMR spectrum of *trans*-**8** in $CDCl_3$.



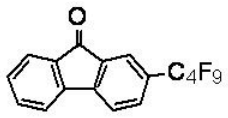
Spectrum 9 ^{1}H NMR spectrum of (*cis/trans*)-**9** in $CDCl_3$.



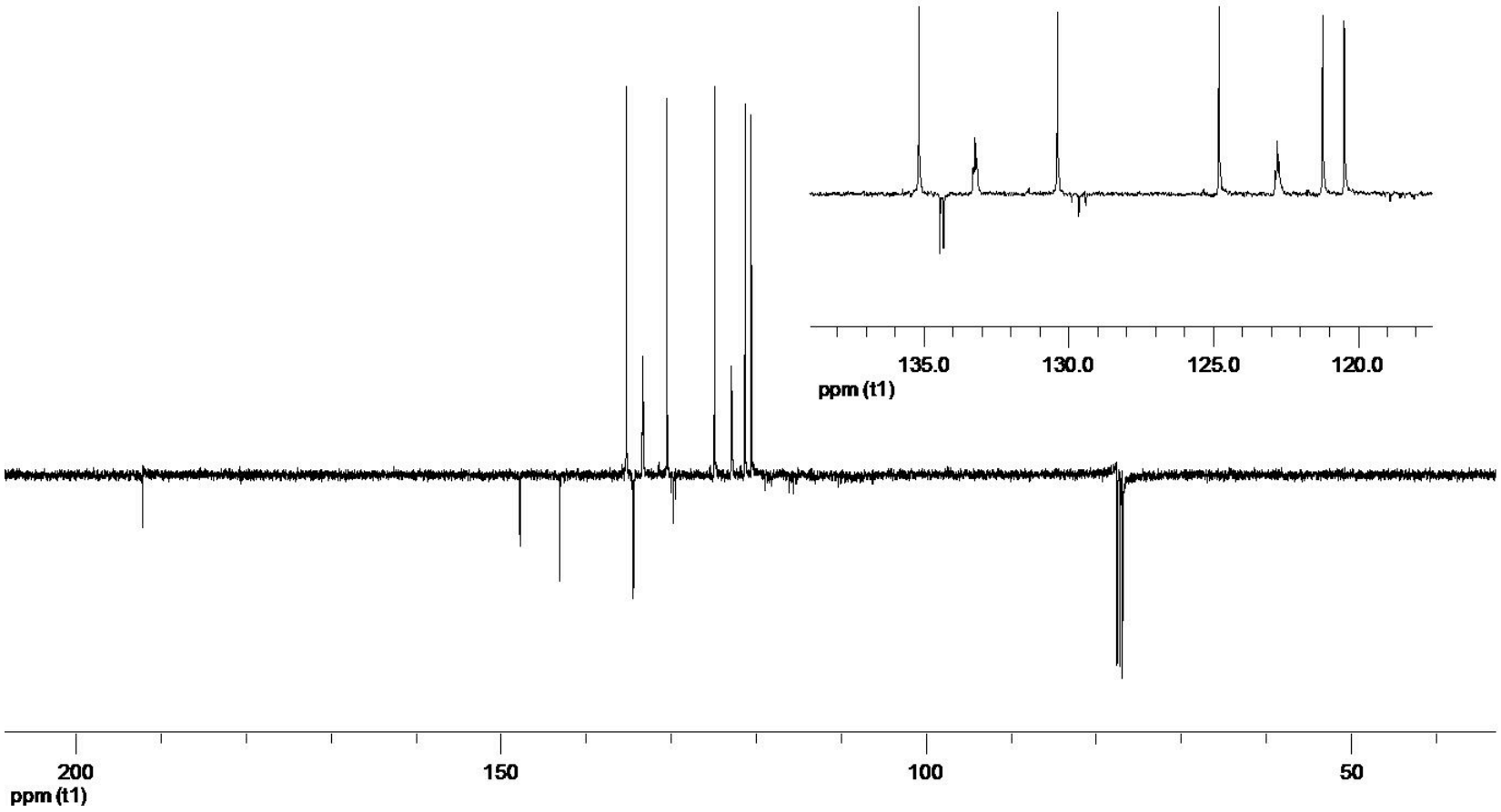
Spectrum 10 APT ^{13}C NMR spectrum of (*cis/trans*)-**9** in $CDCl_3$.



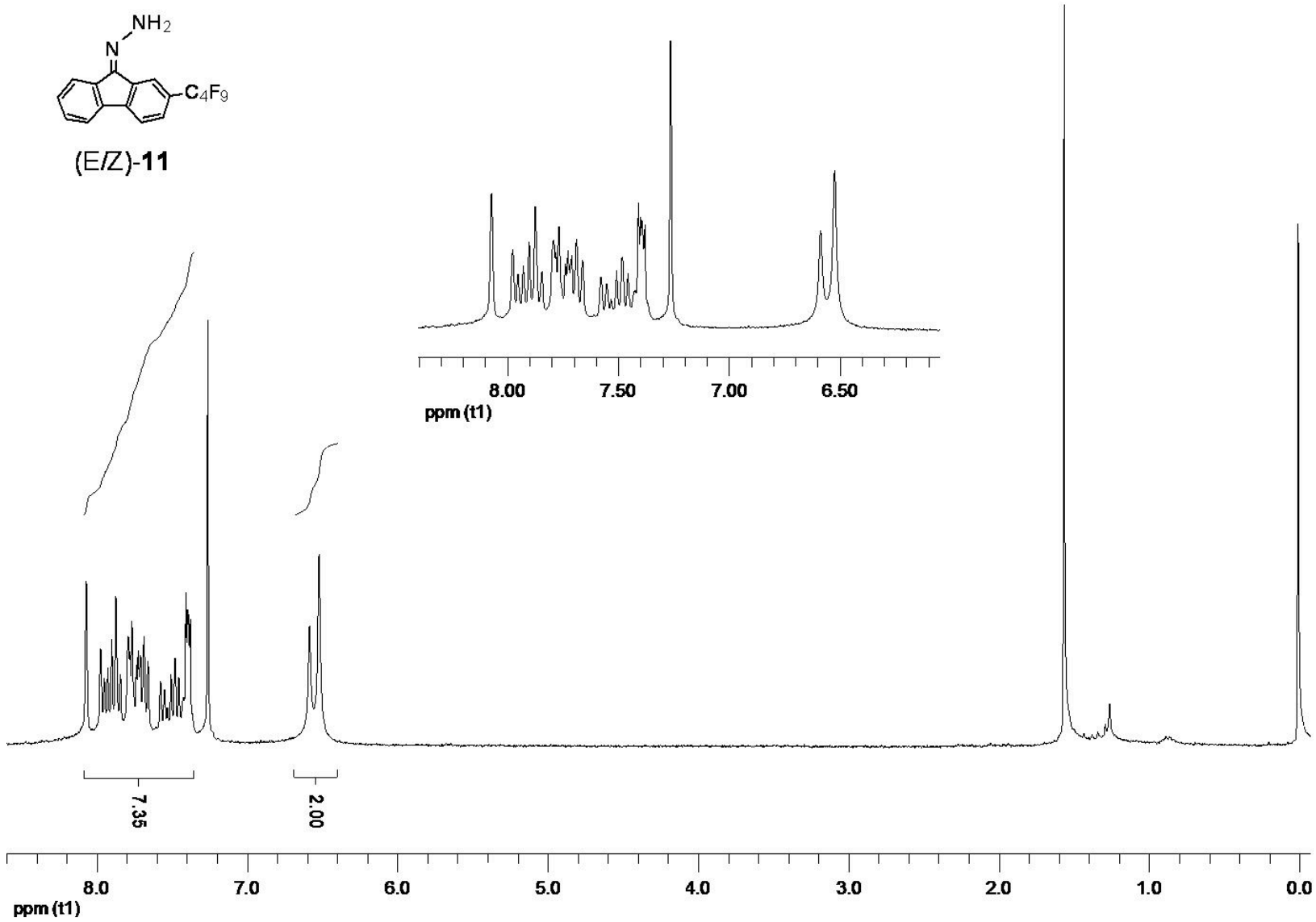
Spectrum 11 ^{1}H NMR spectrum of **10** in $CDCl_3$.



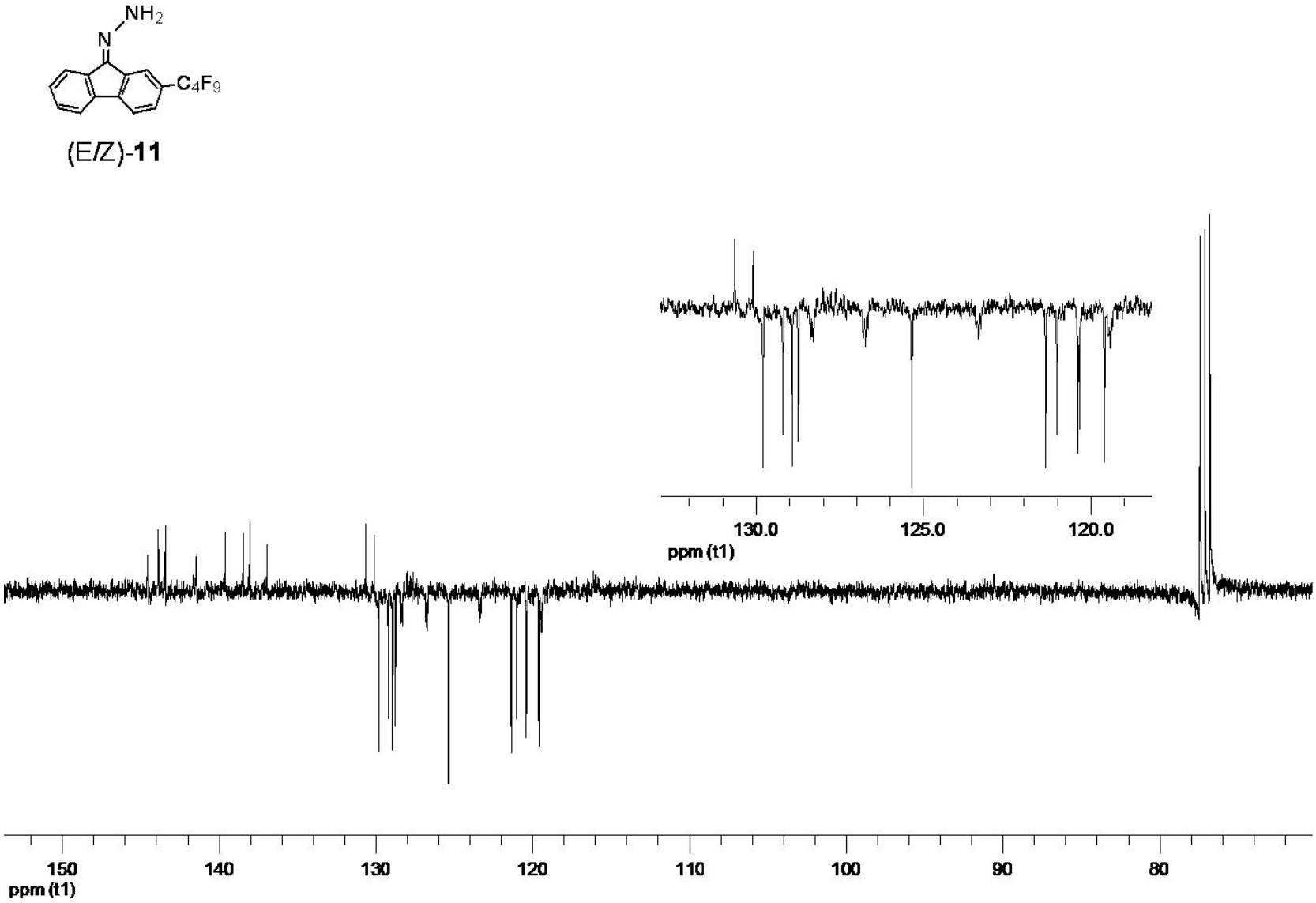
10



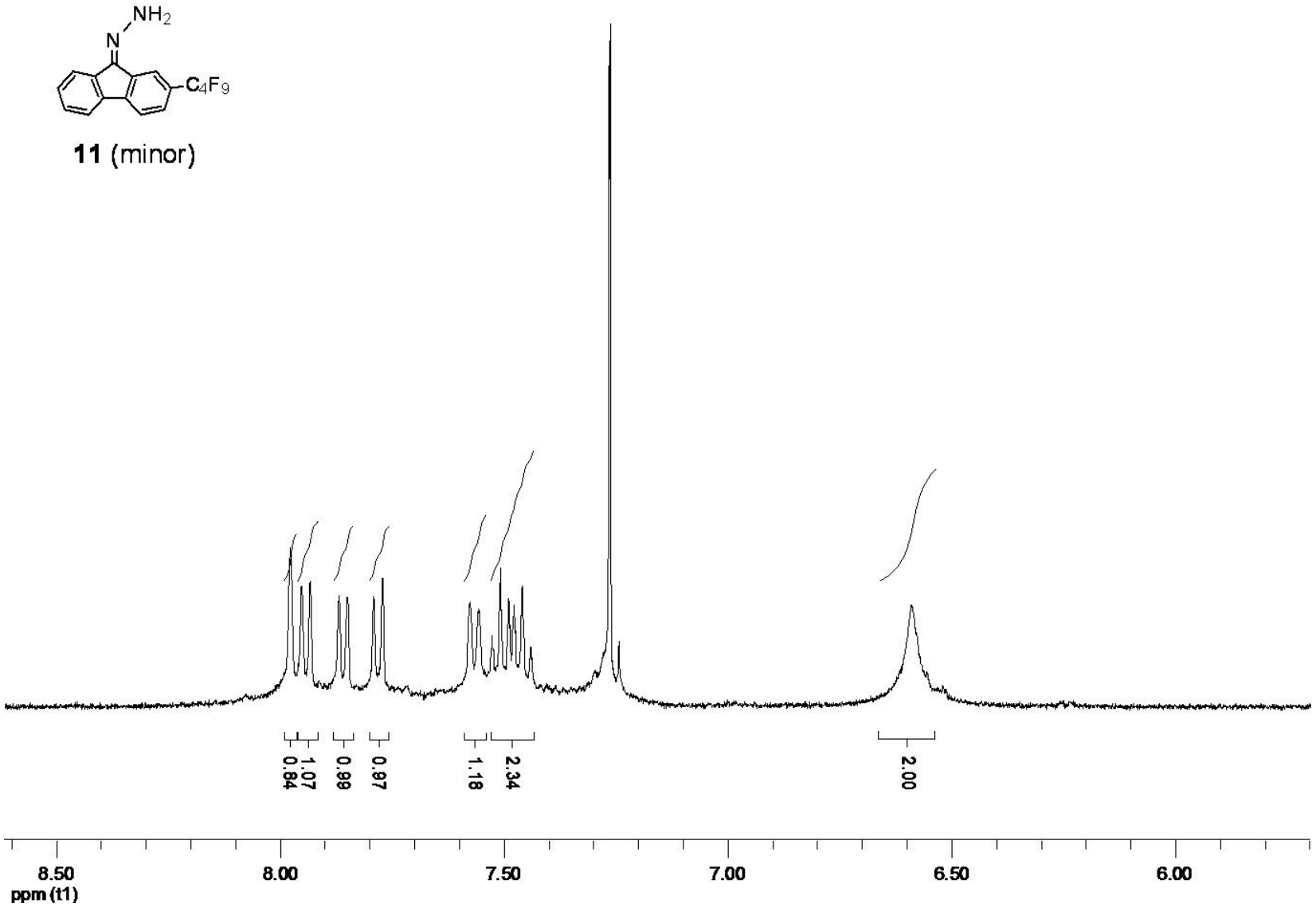
Spectrum 12 APT ^{13}H NMR spectrum of **10** in $CDCl_3$.



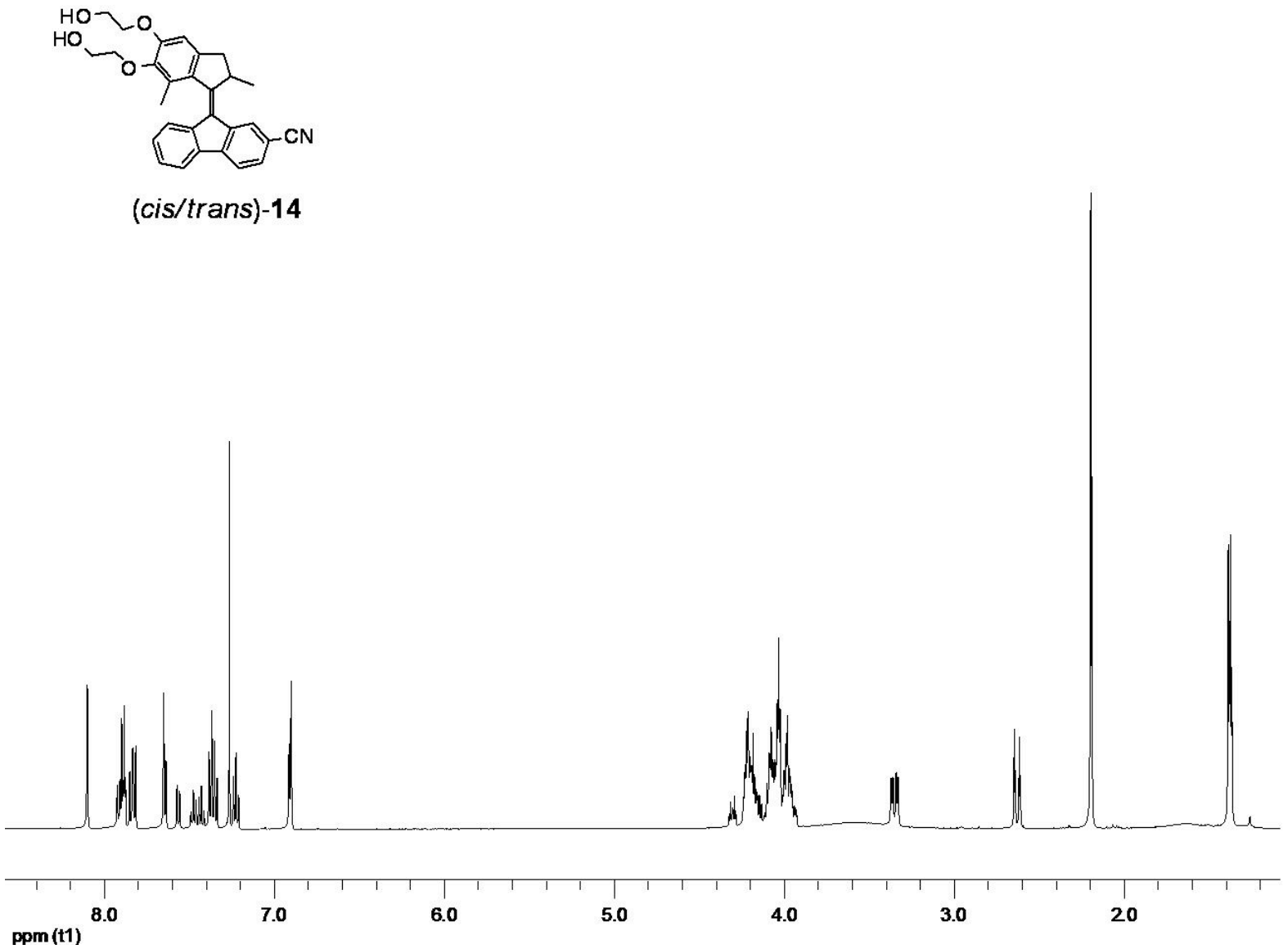
Spectrum 13 ^{1}H NMR spectrum of (*E/Z*)-**11** in $CDCl_3$.



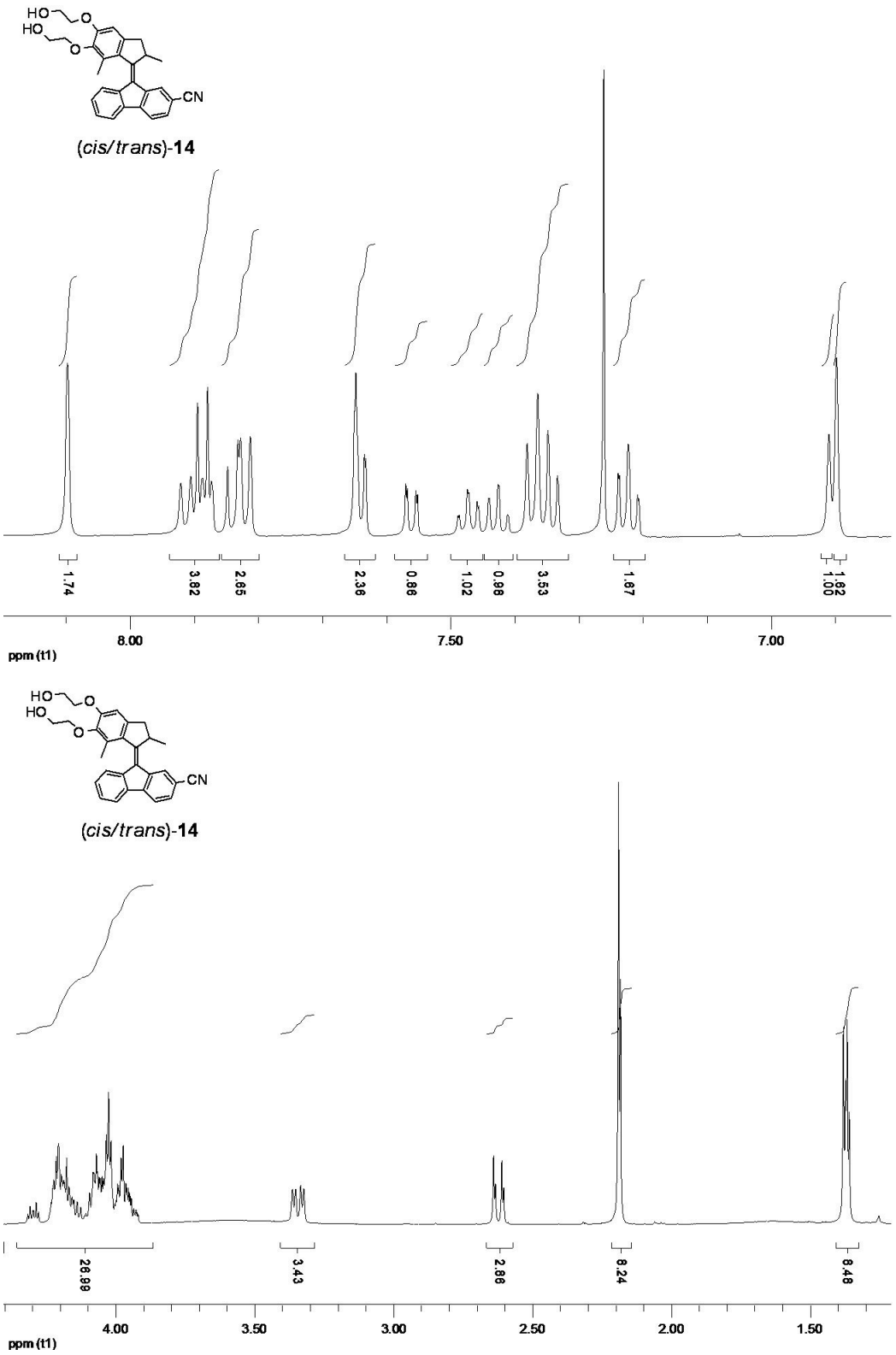
Spectrum 14 APT ^{13}C NMR spectrum of (*E/Z*)-**11** in $CDCl_3$.



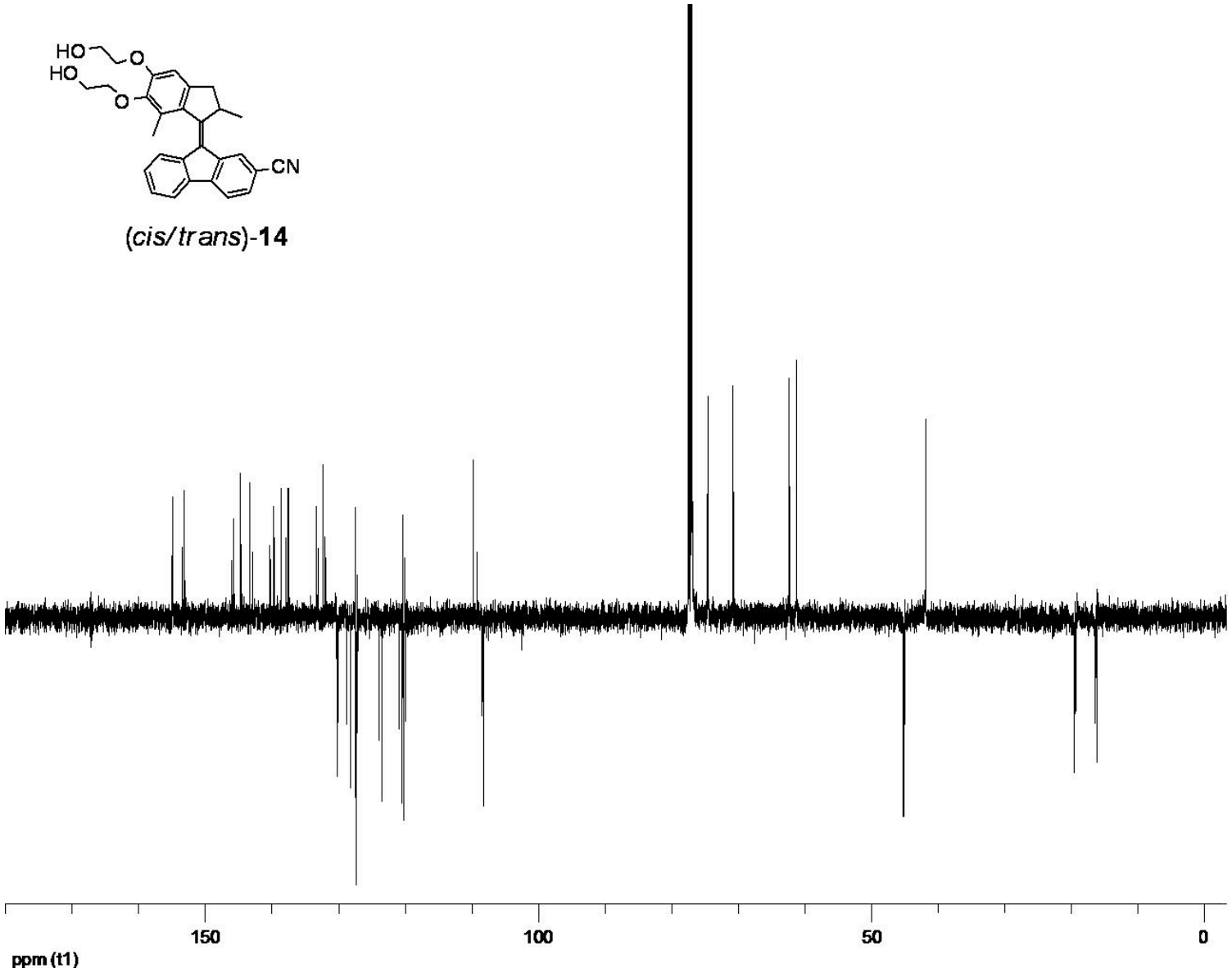
Spectrum 15 ^{1}H NMR spectrum of the minor isomer of **11** in $CDCl_3$.



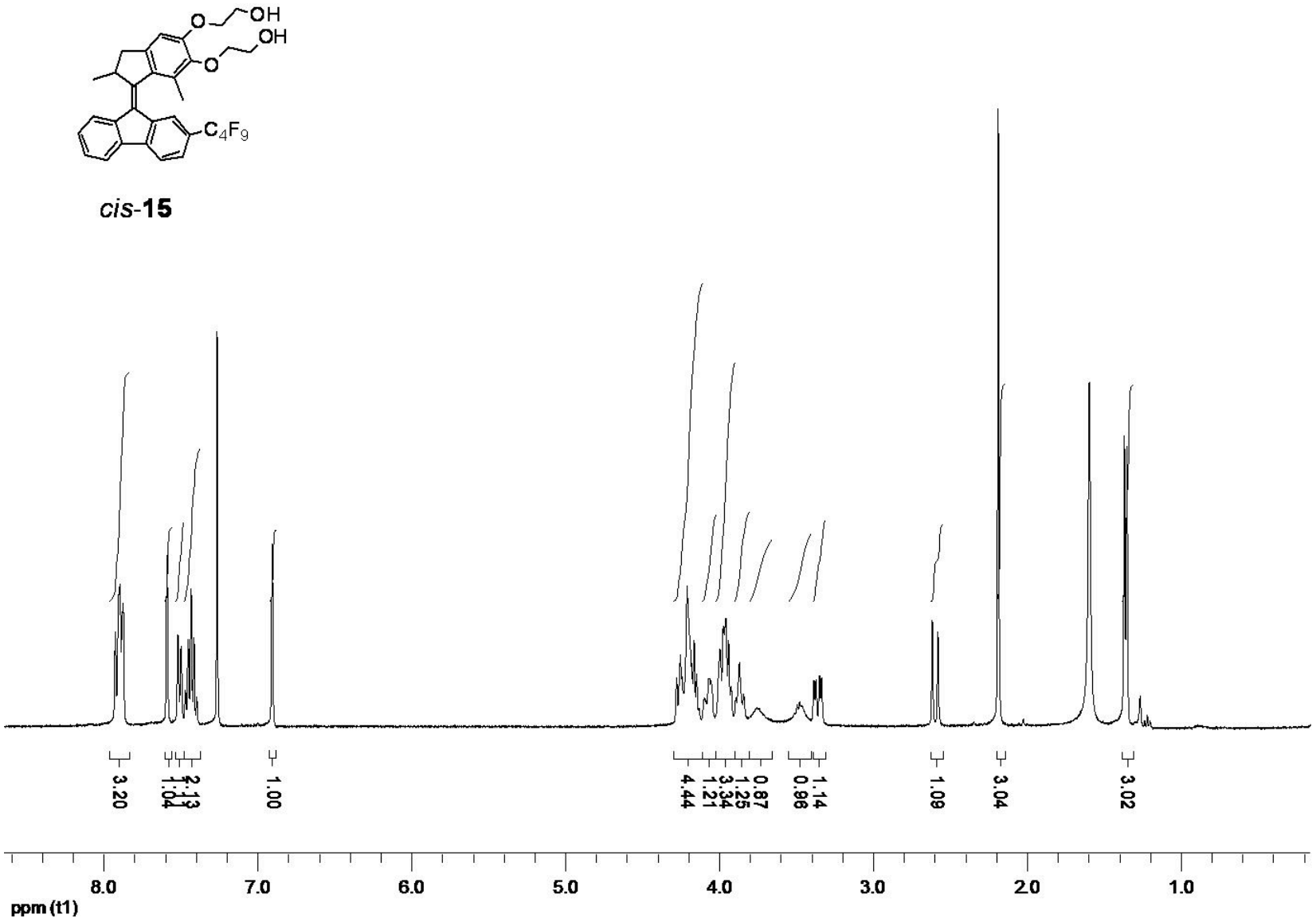
Spectrum 16 ^{1}H NMR spectrum of (*cis/trans*)-**14** in $CDCl_3$.



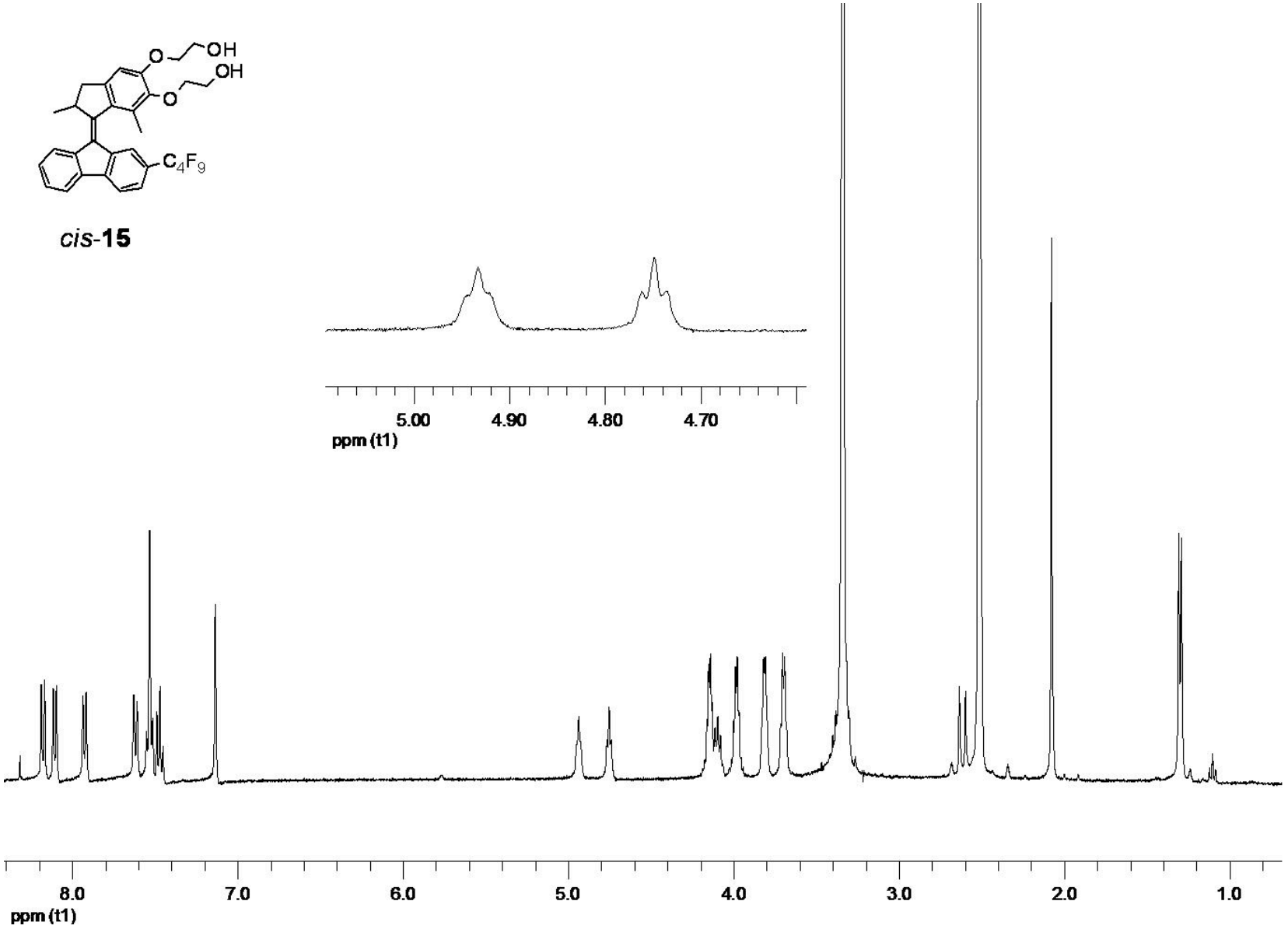
Spectrum 17 Expansion of ^{1}H NMR spectrum of (*cis/trans*)-**14** in $CDCl_3$.



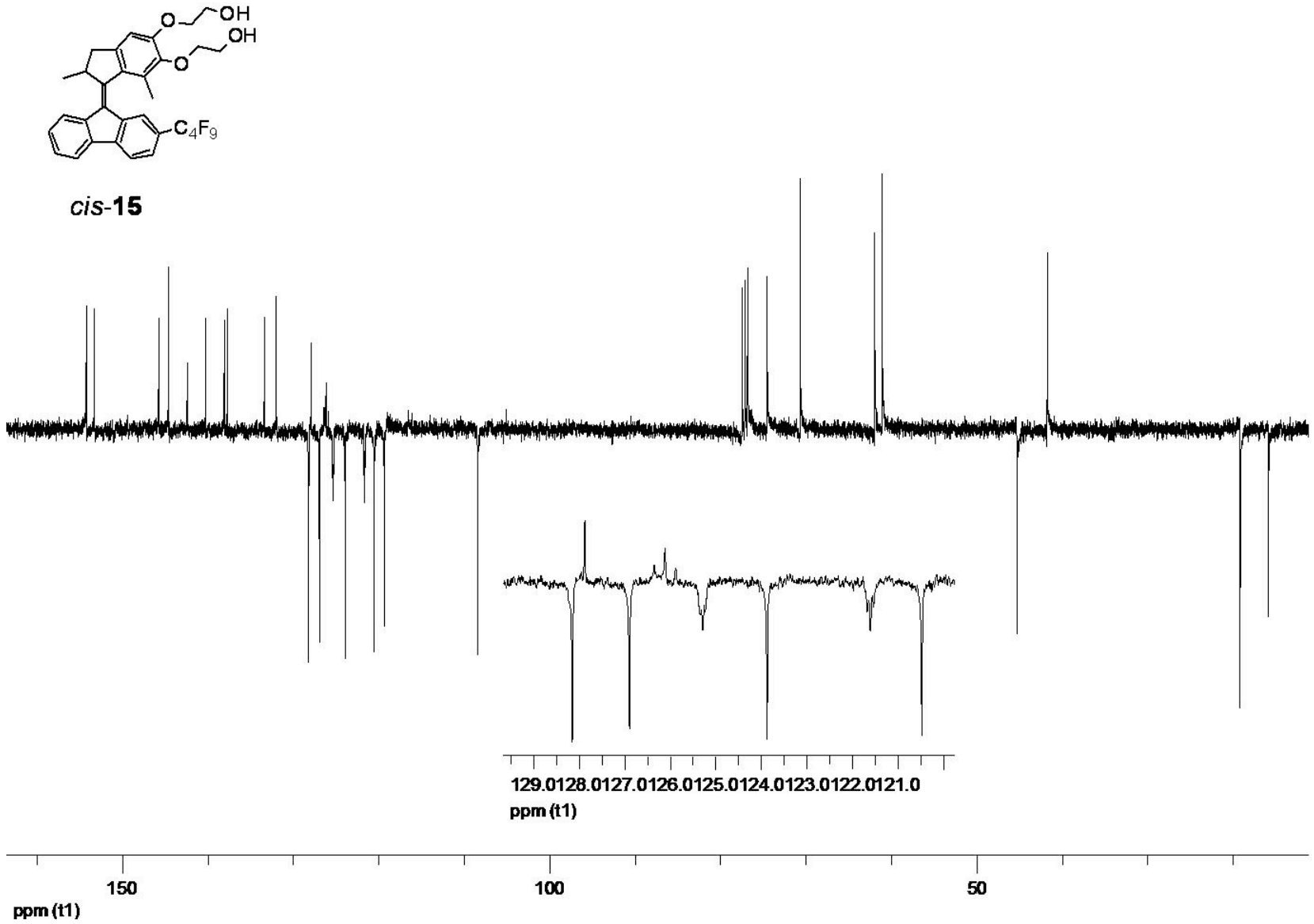
Spectrum 18 APT ^{13}C NMR spectrum of (*cis/trans*)-**14** in $CDCl_3$.



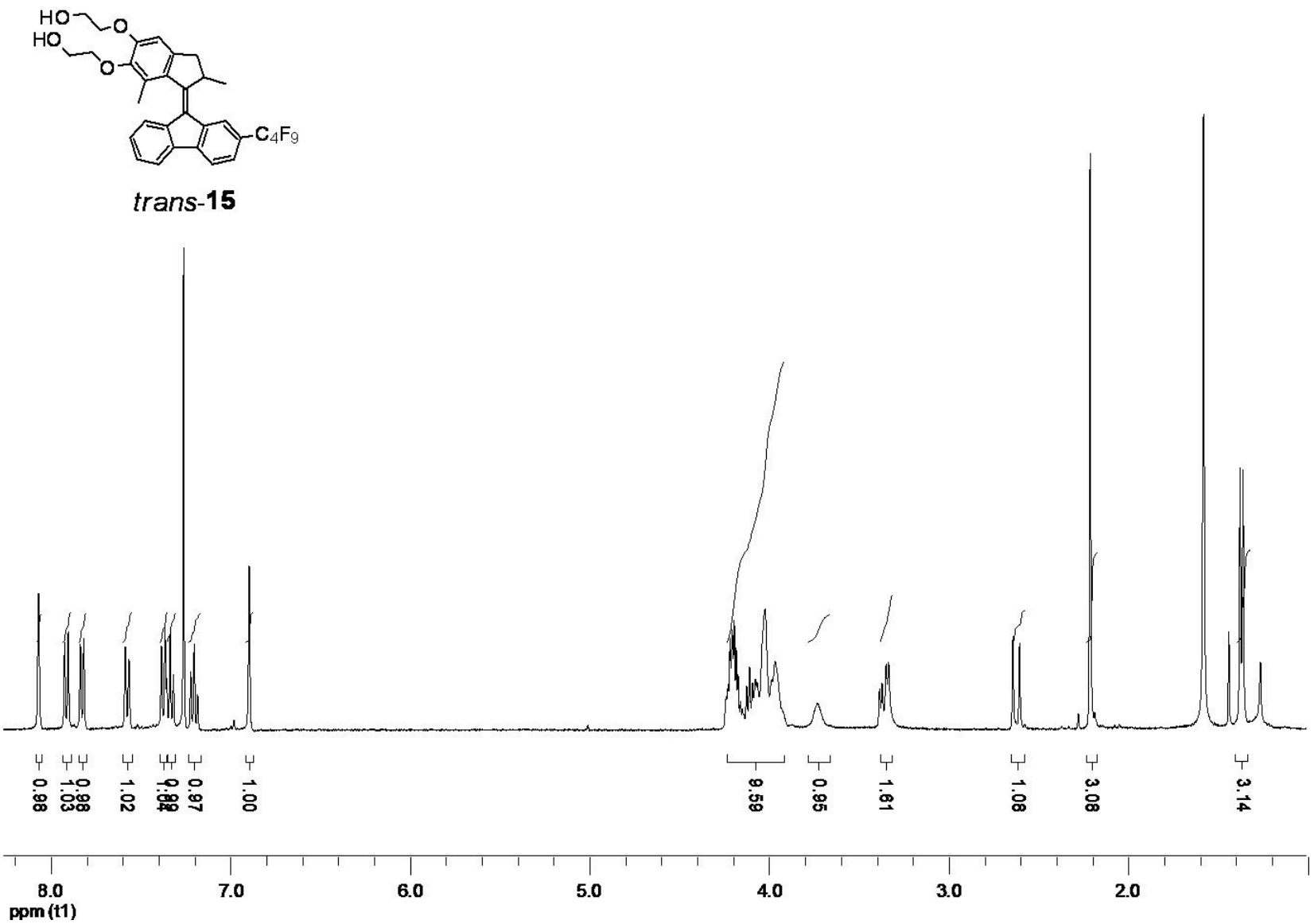
Spectrum 19 ^{1}H NMR spectrum of *cis*-**15** in $CDCl_3$.



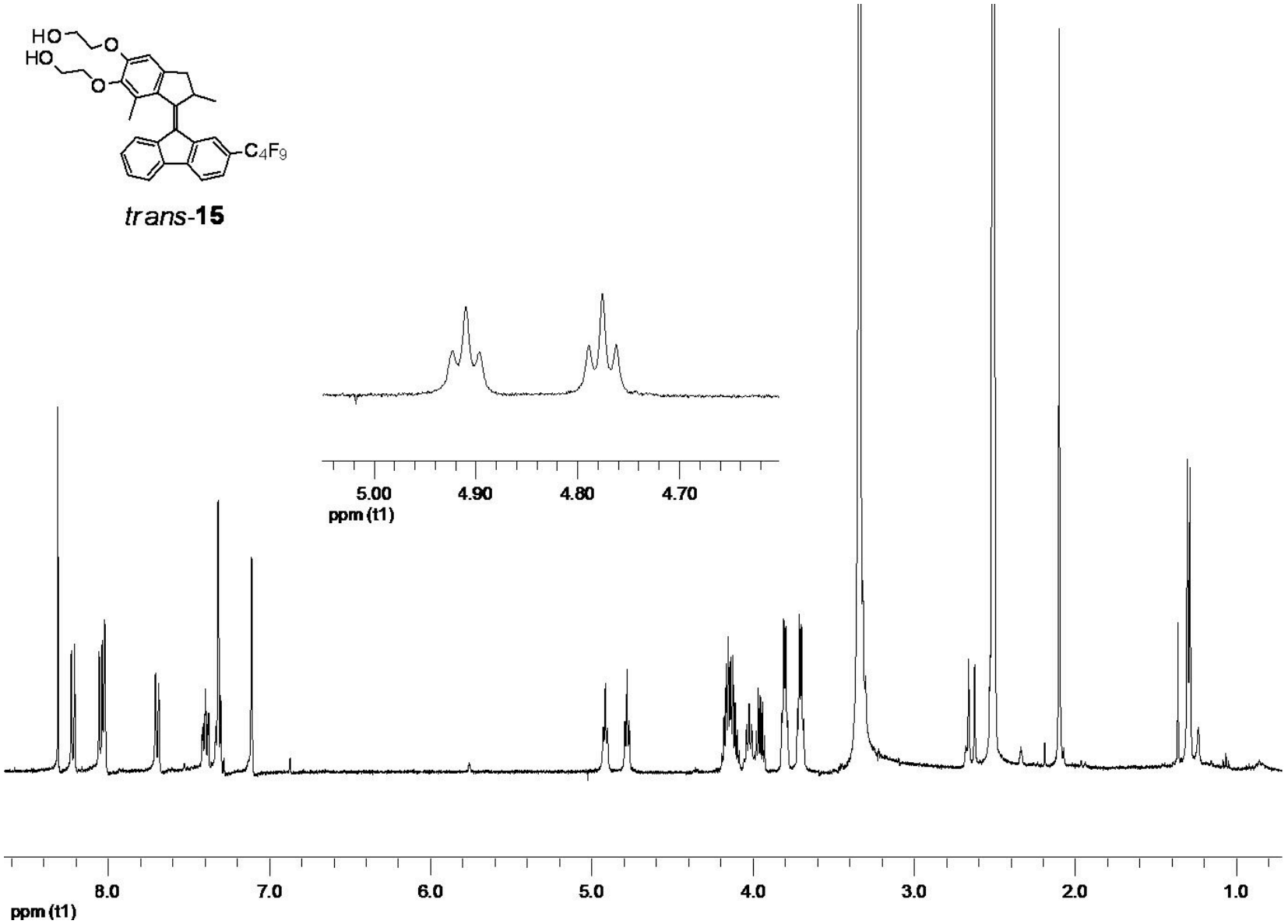
Spectrum 20 ^{1}H NMR spectrum of *cis*-**15** in DMSO-d_6. (The inset shows the O*H* proton signals.)



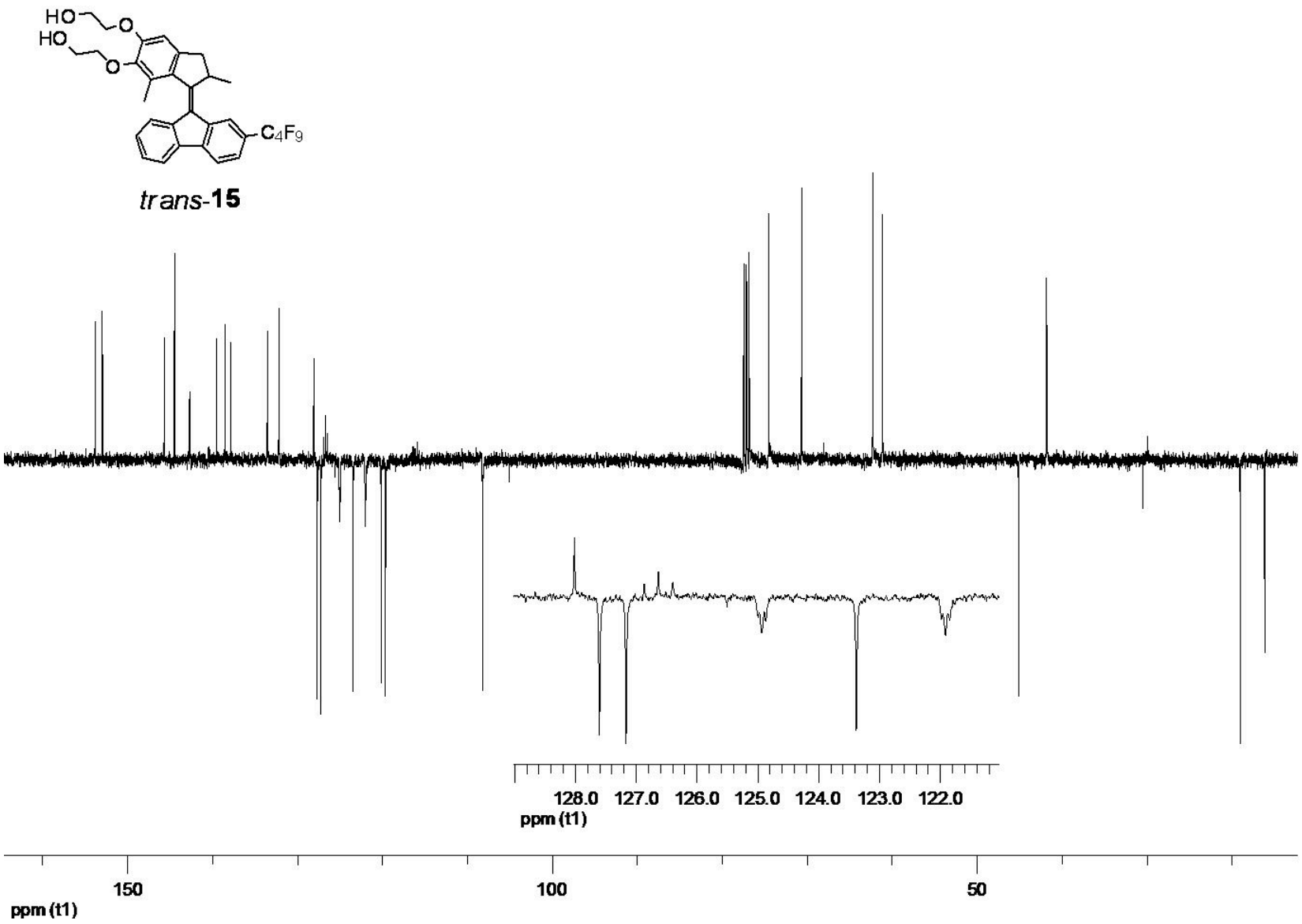
Spectrum 21 APT ^{13}C NMR spectrum of *cis*-**15** in $CDCl_3$.



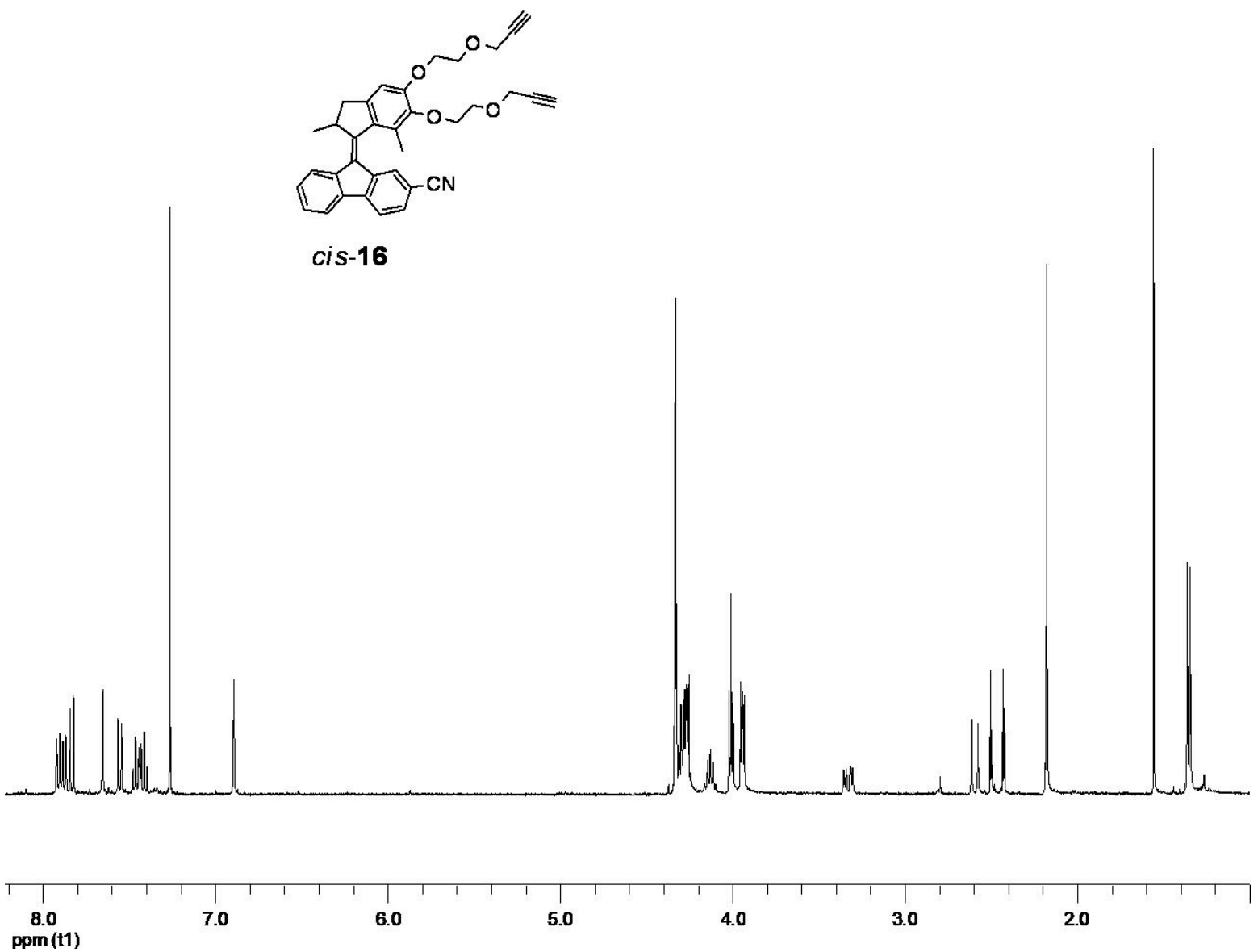
Spectrum 22 ^{1}H NMR spectrum of *trans*-**15** in $CDCl_3$.



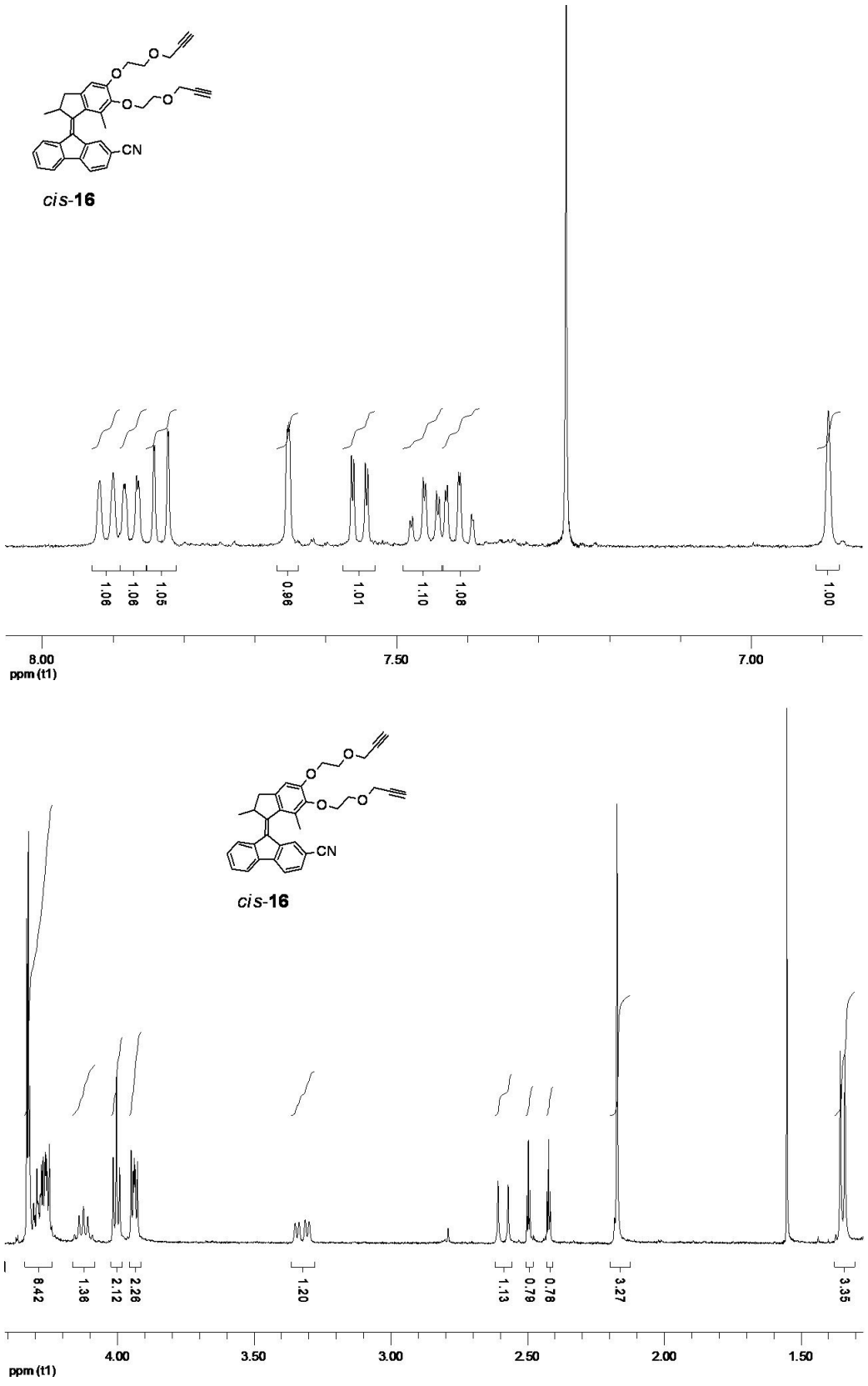
Spectrum 23 ^{1}H NMR spectrum of *trans*-**15** in DMSO-d_6. (The inset shows the O*H* proton signals.)



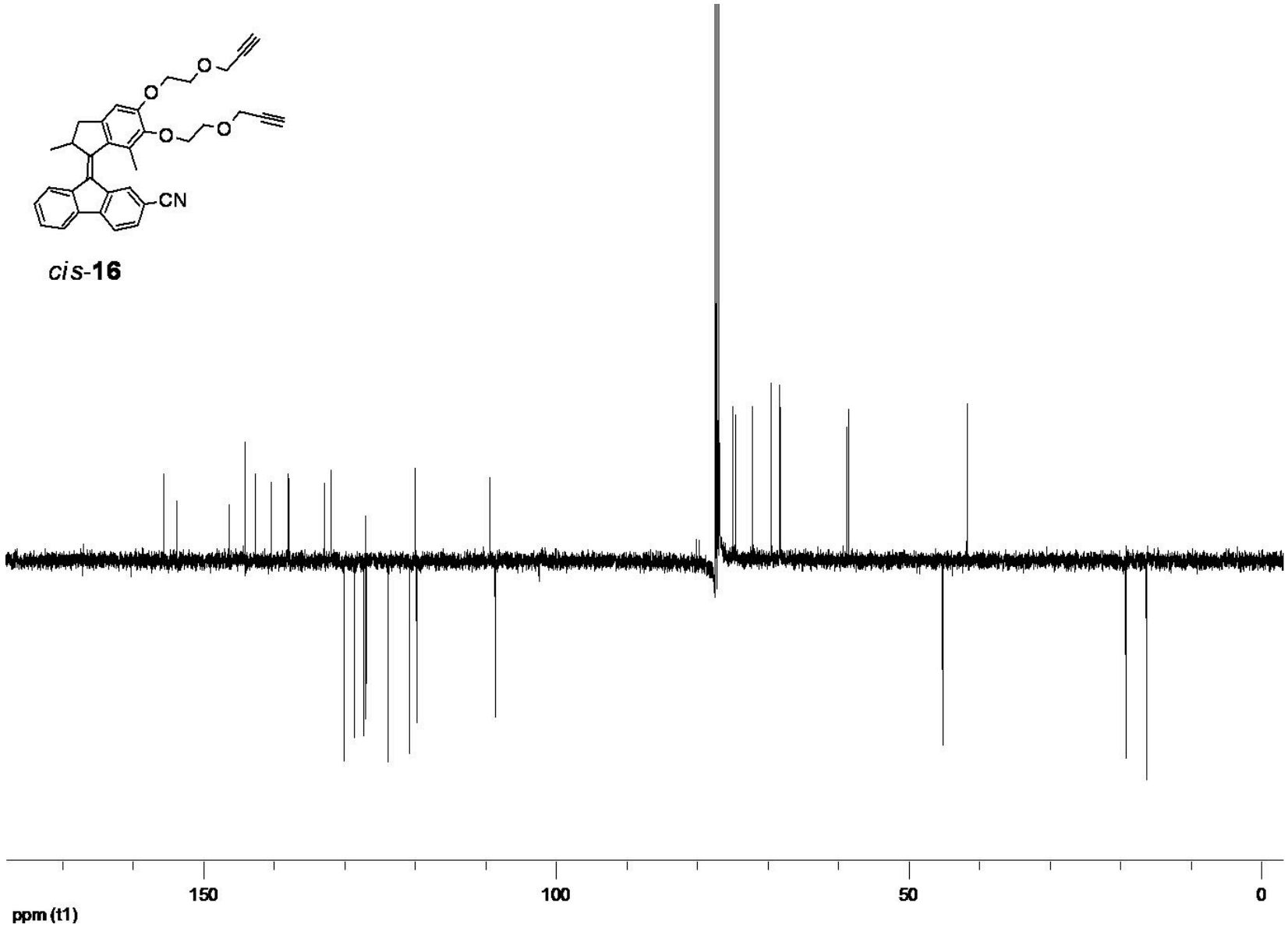
Spectrum 24 APT ^{13}C NMR spectrum of *trans*-**15** in $CDCl_3$.



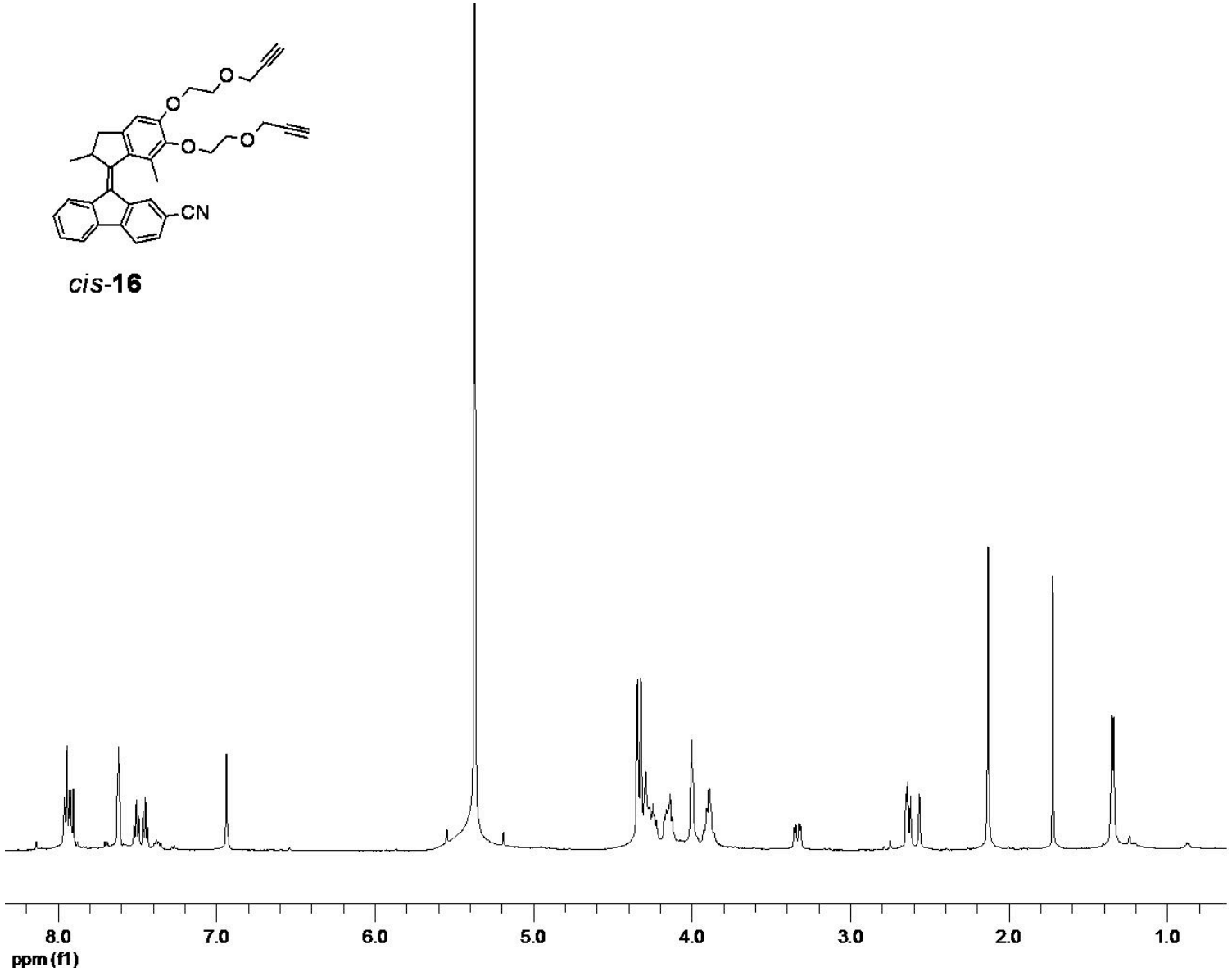
Spectrum 25 ^{1}H NMR spectrum of *cis*-**16** in $CDCl_3$.



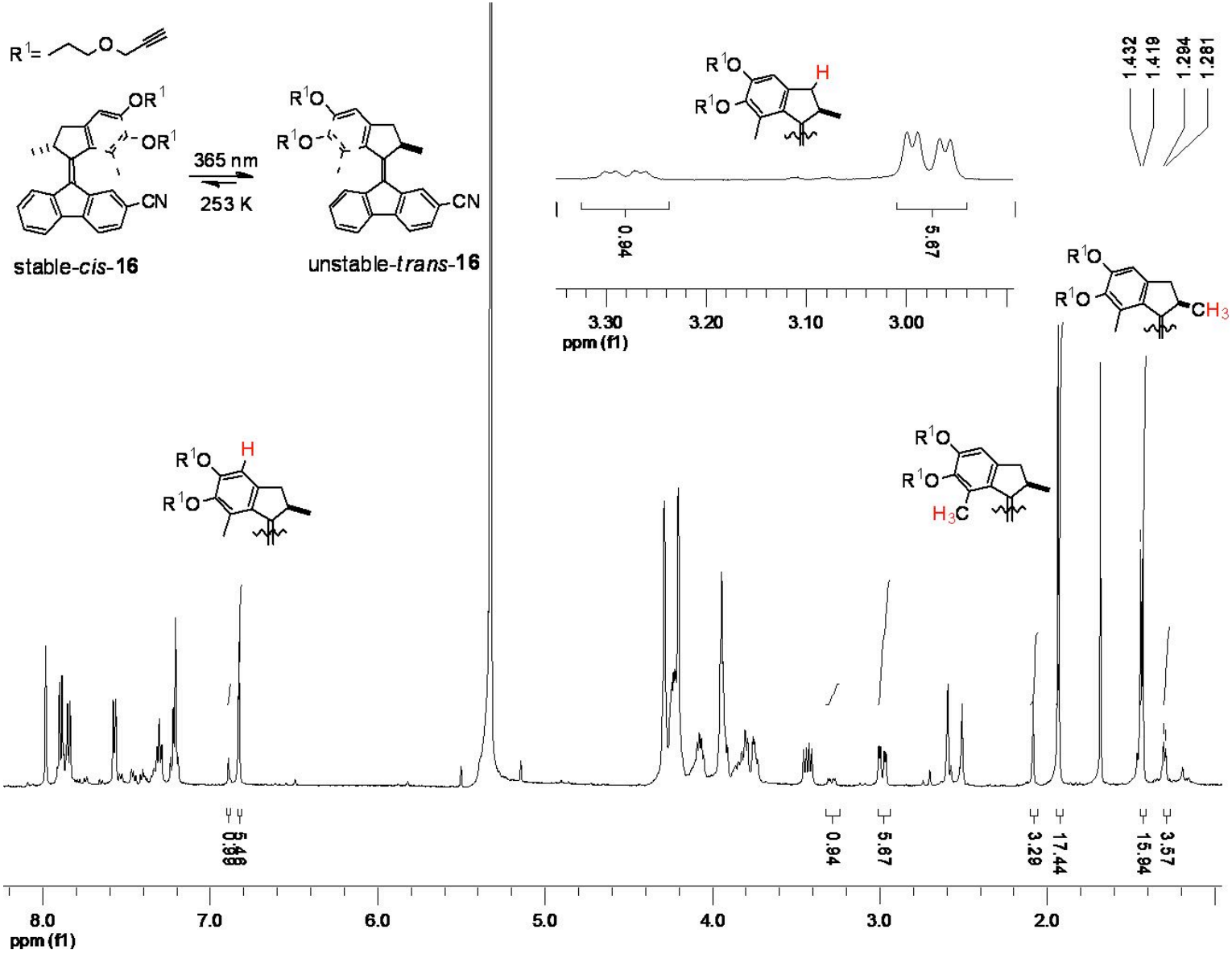
Spectrum 26 Expansion of ^{1}H NMR spectrum of *cis*-**16** in $CDCl_3$.



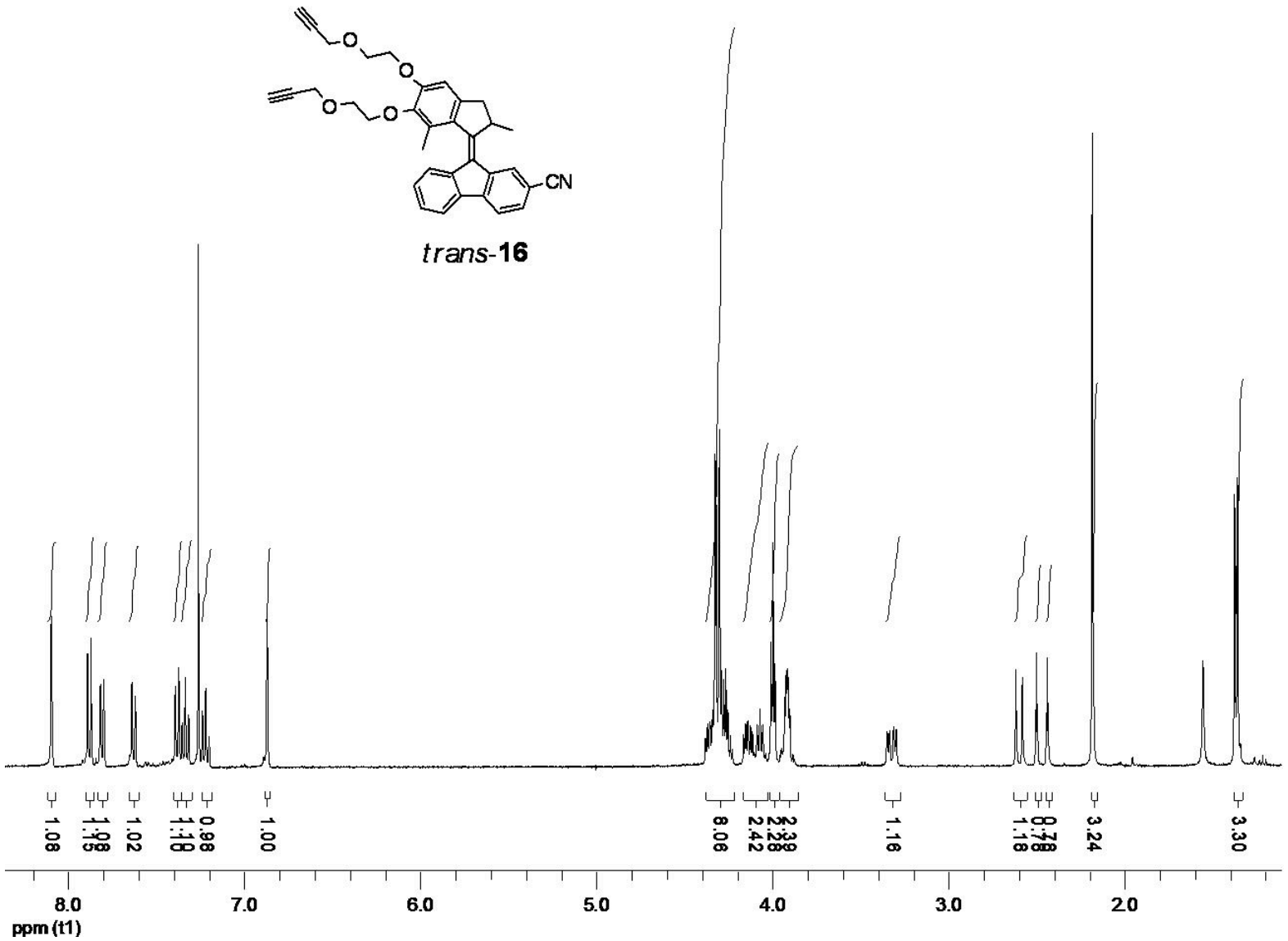
Spectrum 27 APT ^{13}C NMR spectrum of *cis*-**16** in $CDCl_3$.



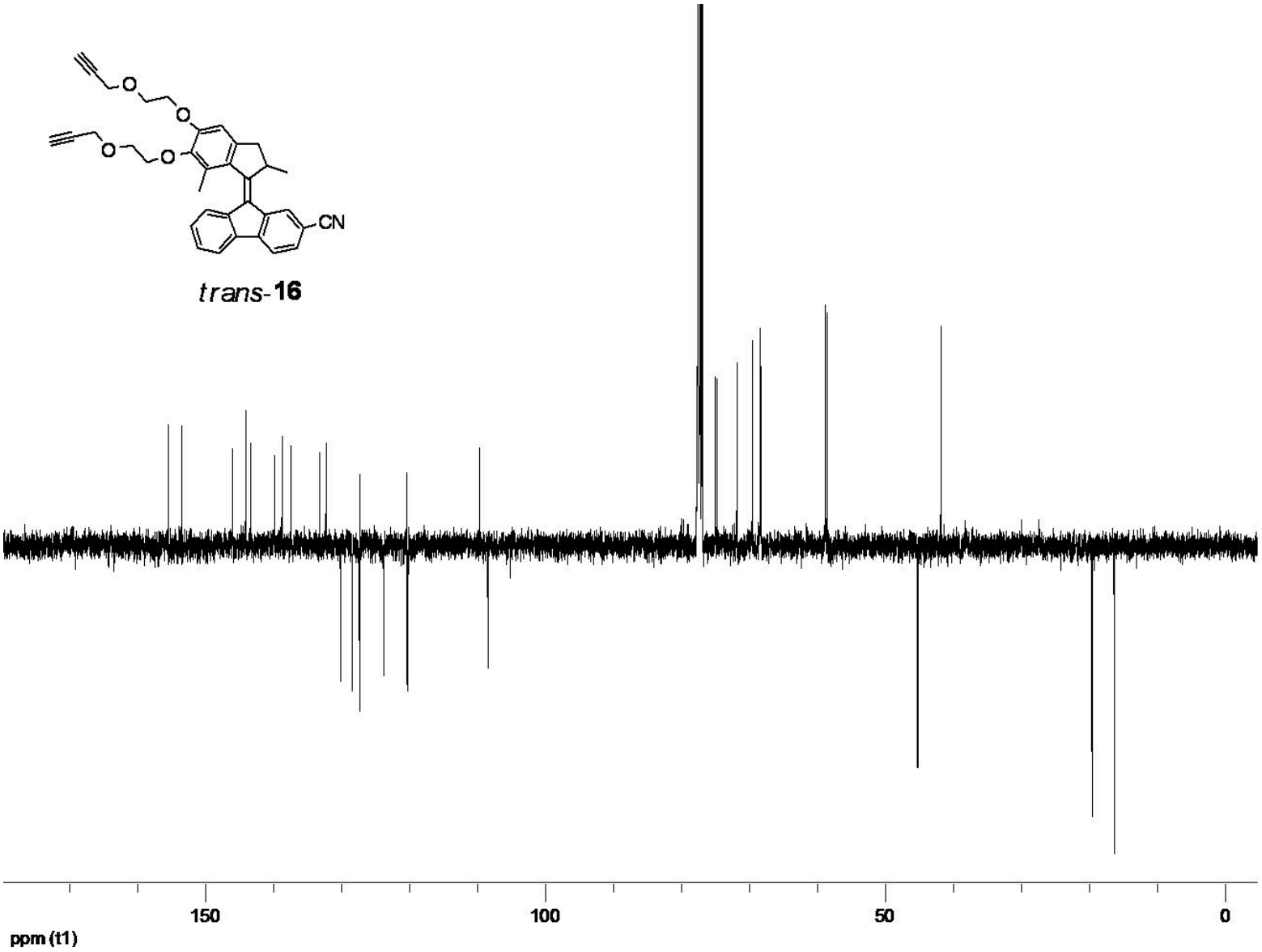
Spectrum 28 ^{1}H NMR spectrum of *cis*-**16** in CD_2Cl_2 at -55°C.



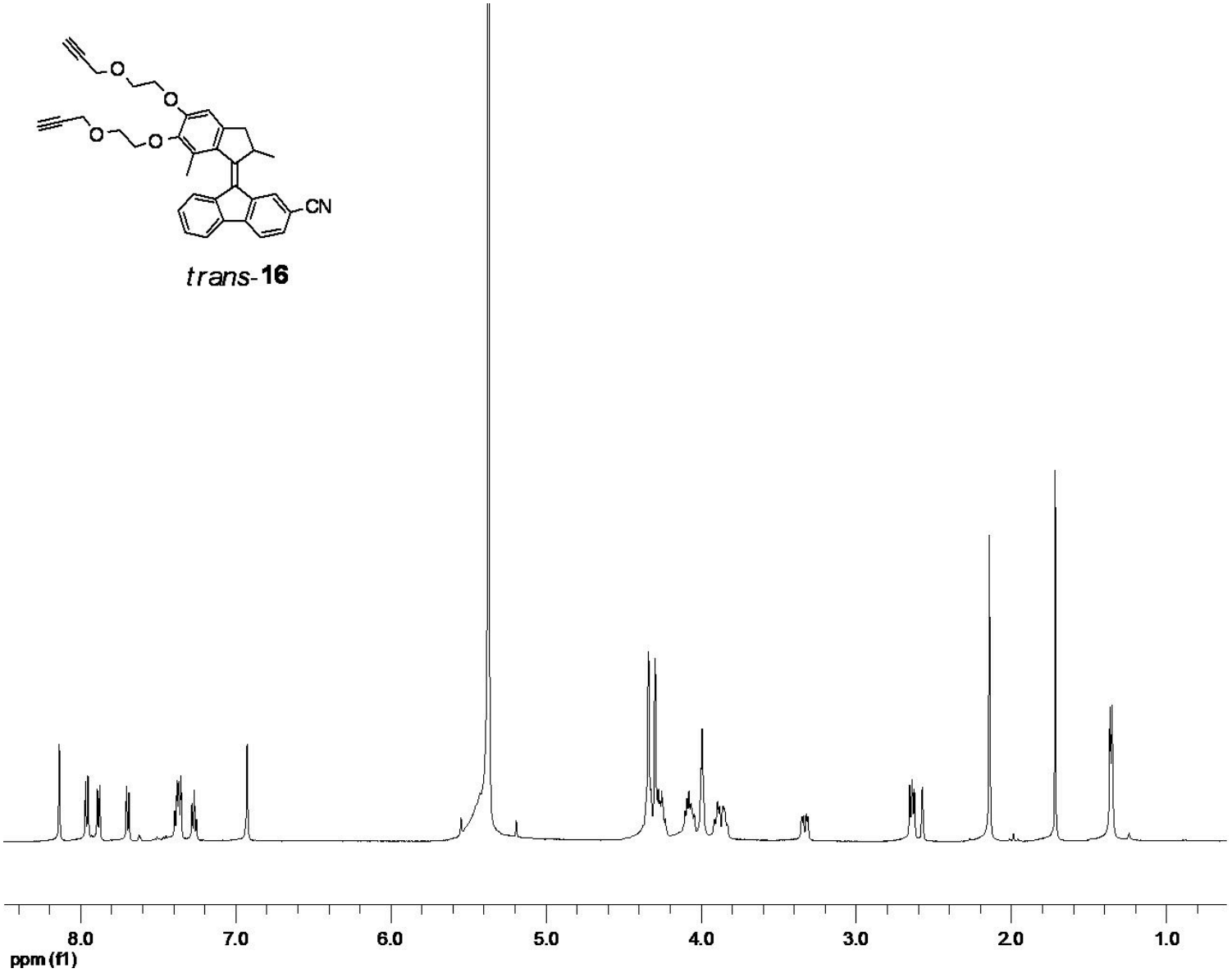
Spectrum 29 ^{1}H NMR spectrum of the photostationary state (λ=365 nm) of stable-*cis*-**16** and unstable-*trans*-**16** in CD_2Cl_2 at -55°C.



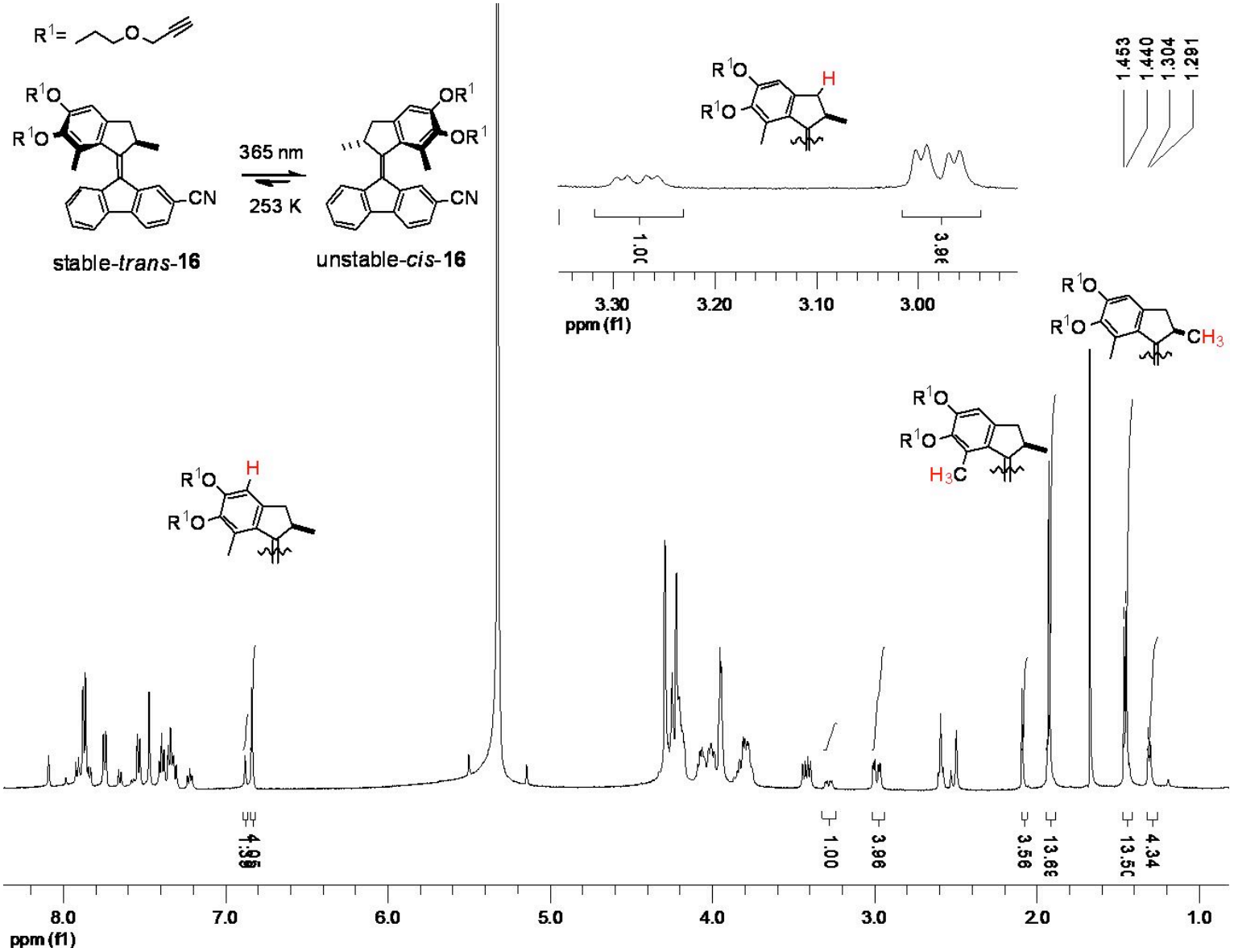
Spectrum 30 ^{1}H NMR spectrum of *trans*-**16** in $CDCl_3$.



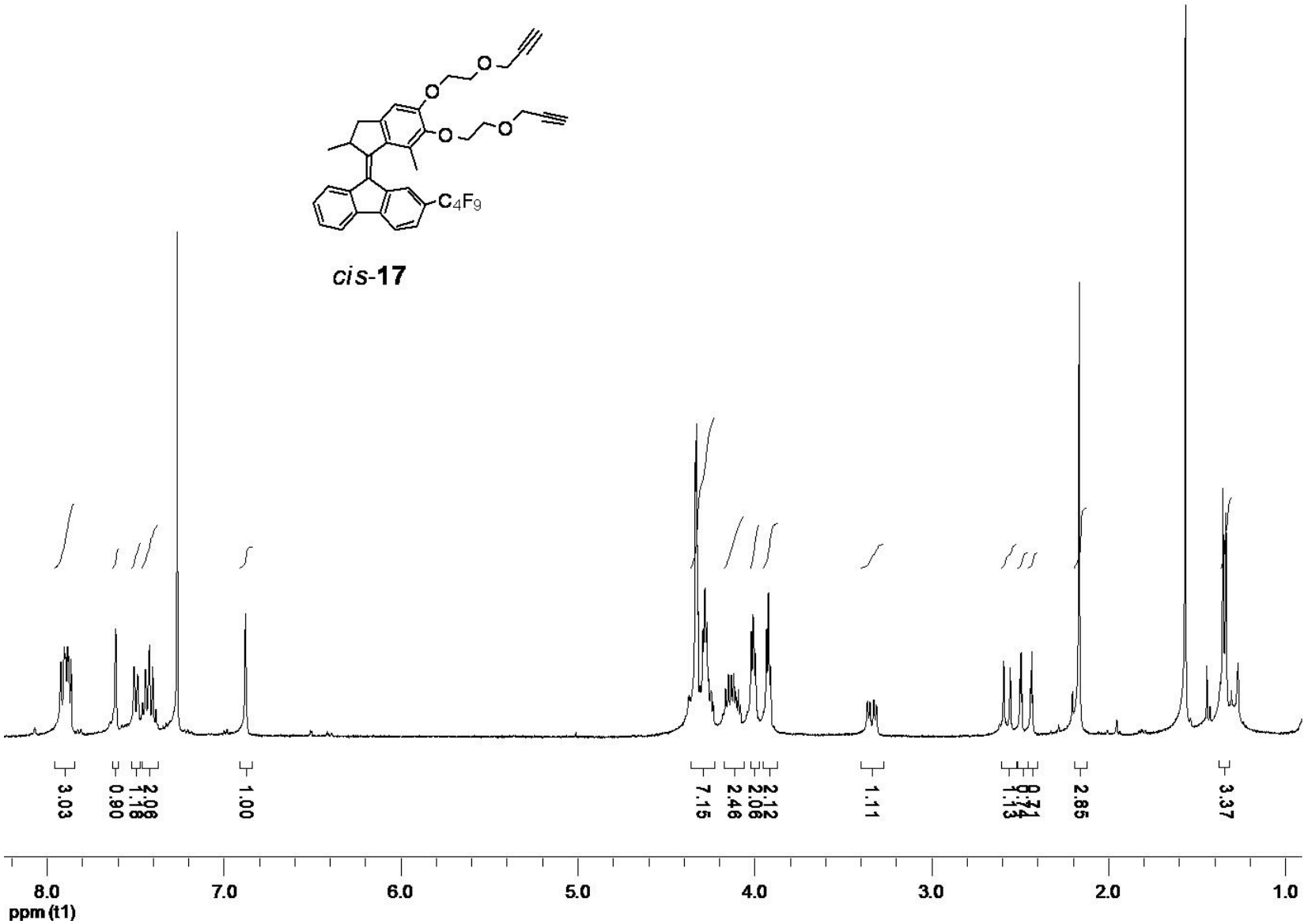
Spectrum 31 APT ^{13}C NMR spectrum of *trans*-**16** in $CDCl_3$.



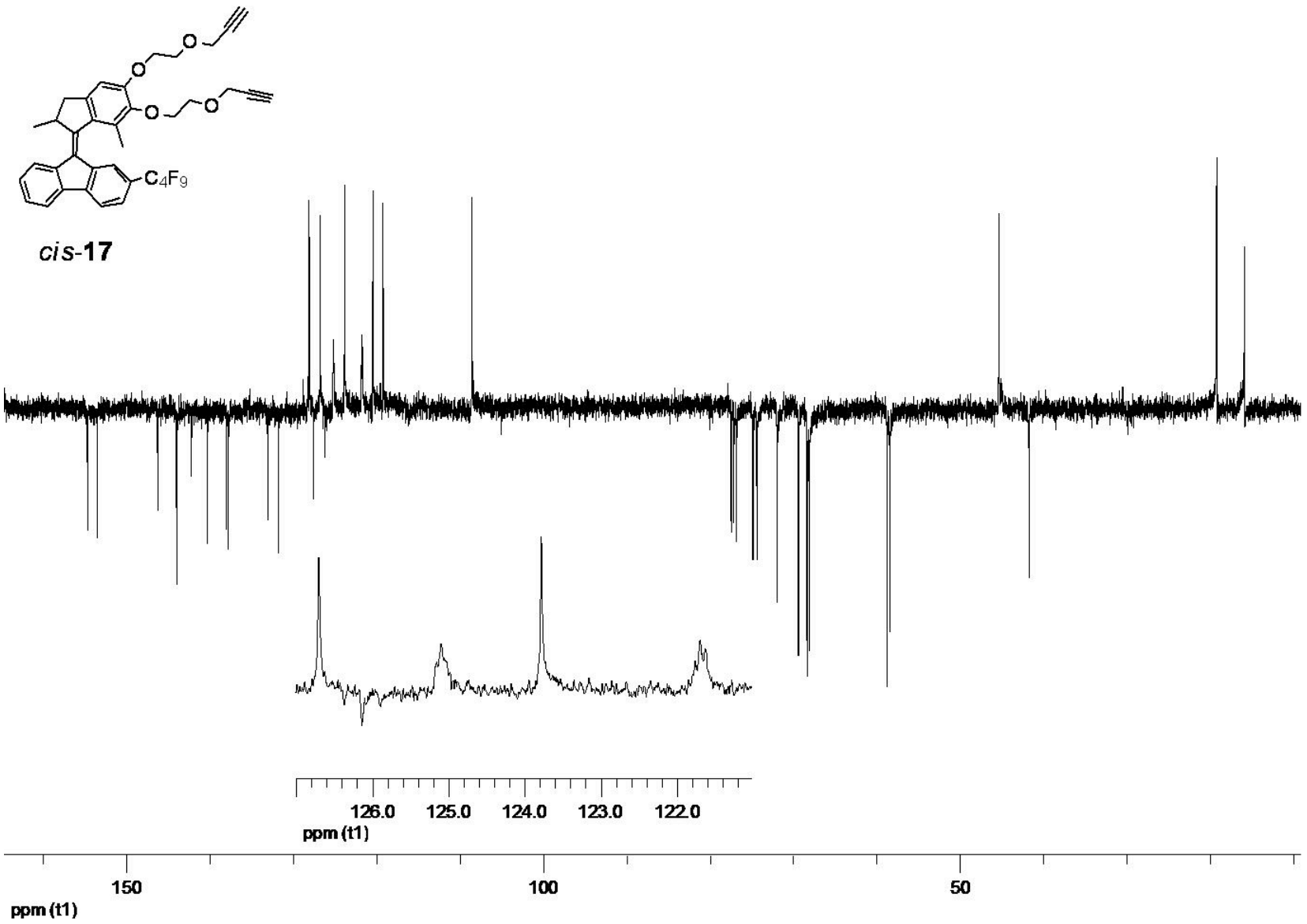
Spectrum 32 ^{1}H NMR spectrum of *trans*-**16** in CD_2Cl_2 at -55°C.



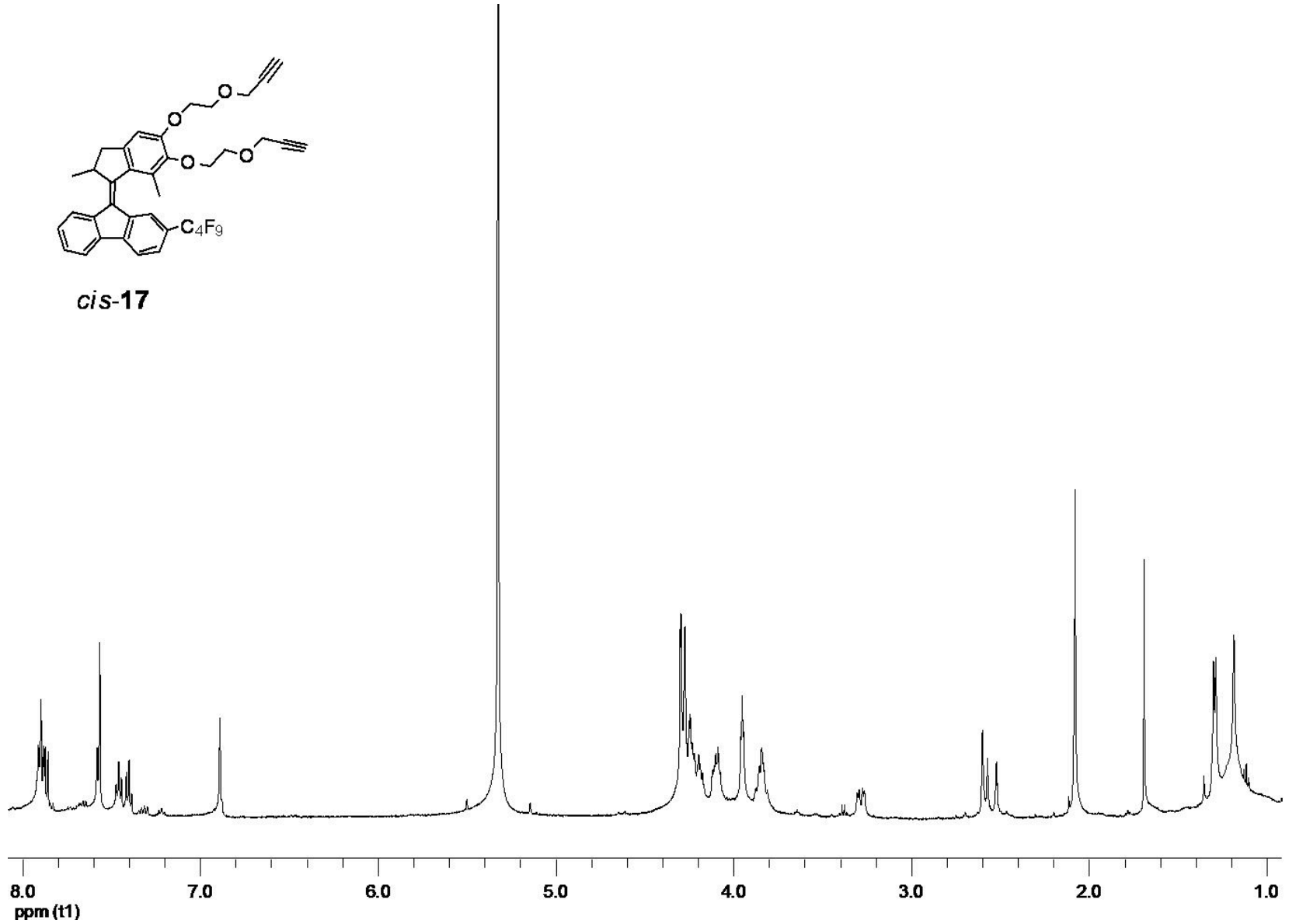
Spectrum 33 ^{1}H NMR spectrum of the photostationary state (λ=365 nm) of stable-*trans*-**16** and unstable-*cis*-**16** in CD_2Cl_2 at -55°C.



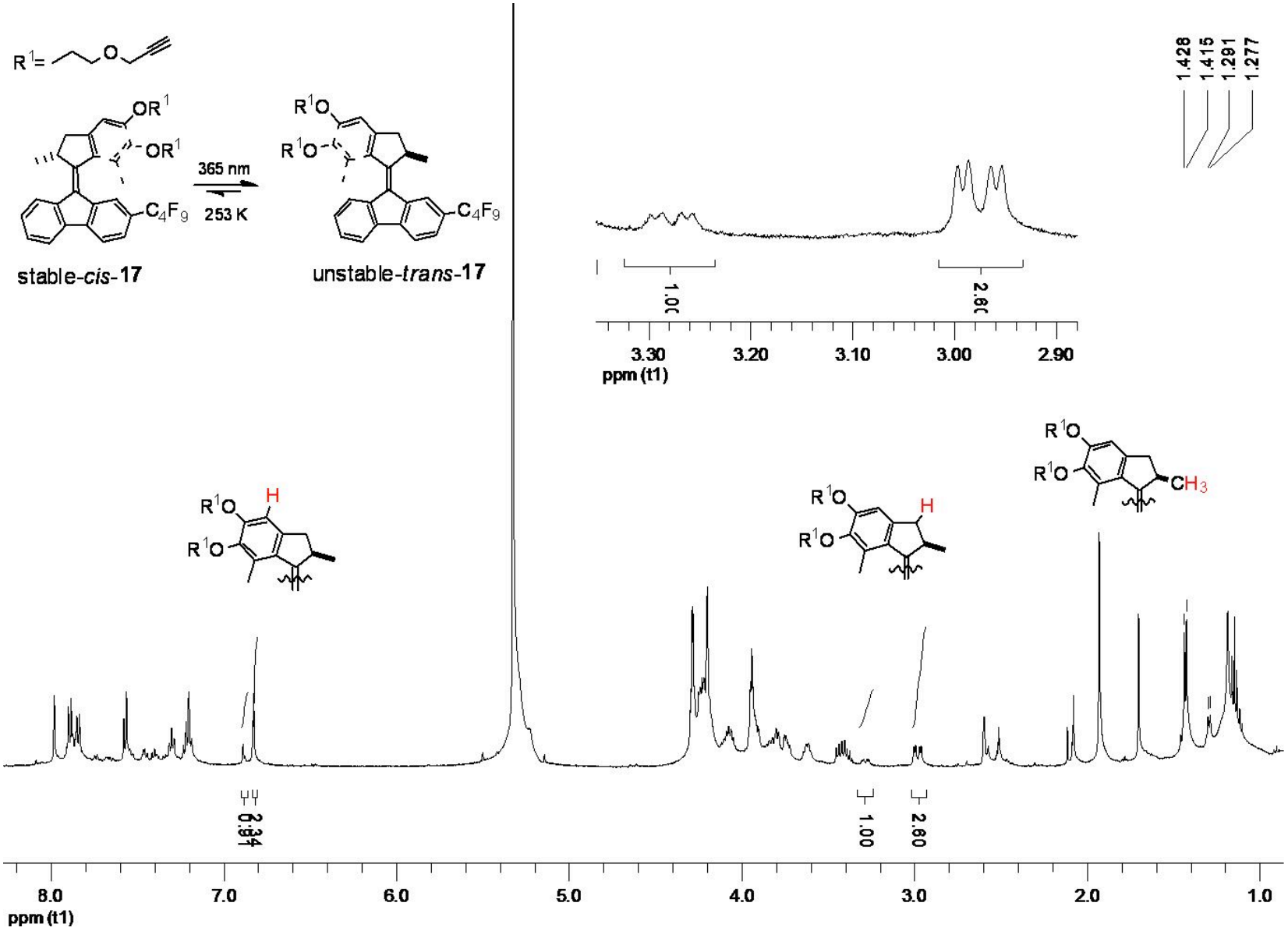
Spectrum 34 ^{1}H NMR spectrum of *cis*-**17** in $CDCl_3$.



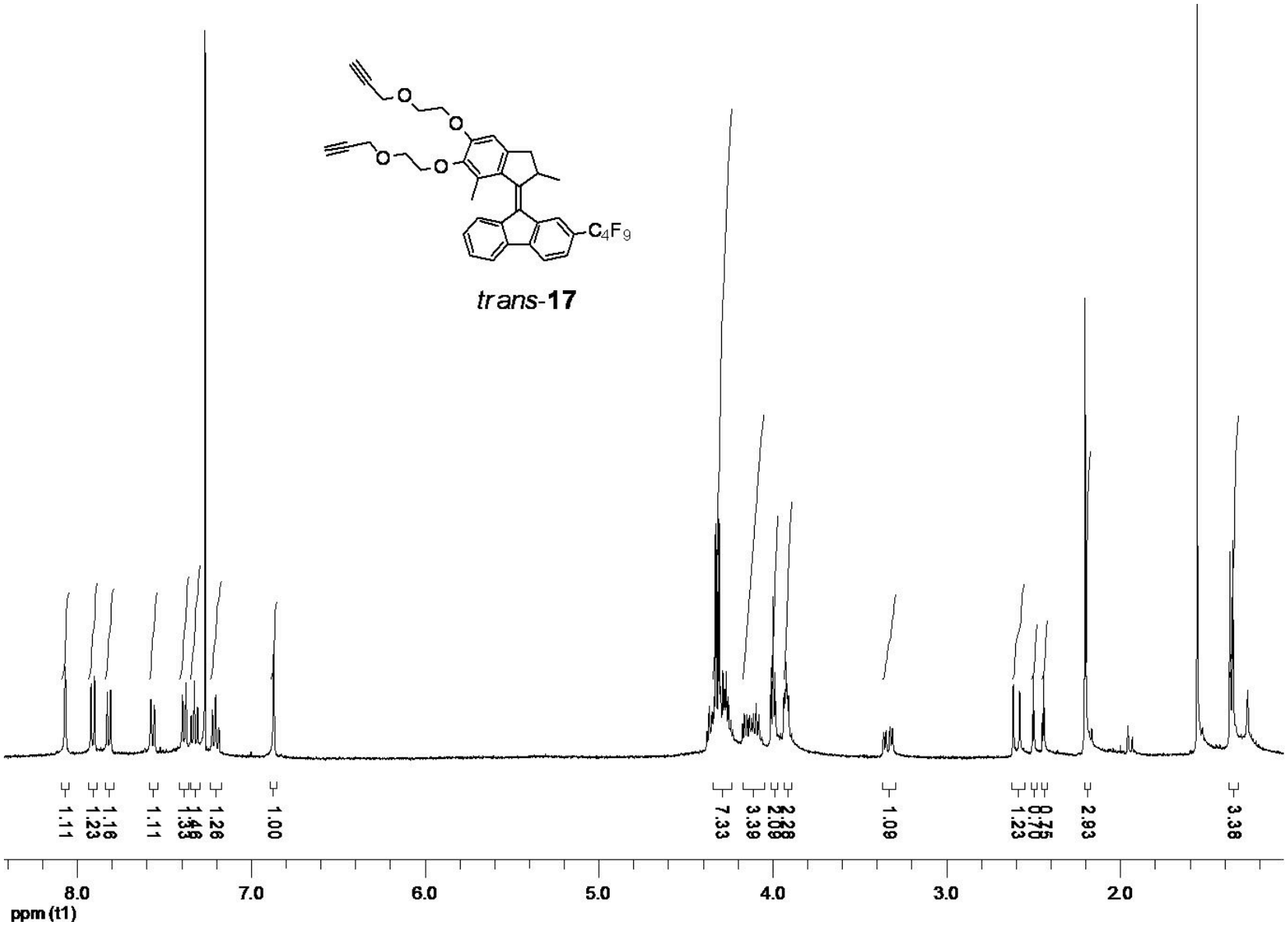
Spectrum 35 APT ^{13}C NMR spectrum of *cis*-**17** in $CDCl_3$.



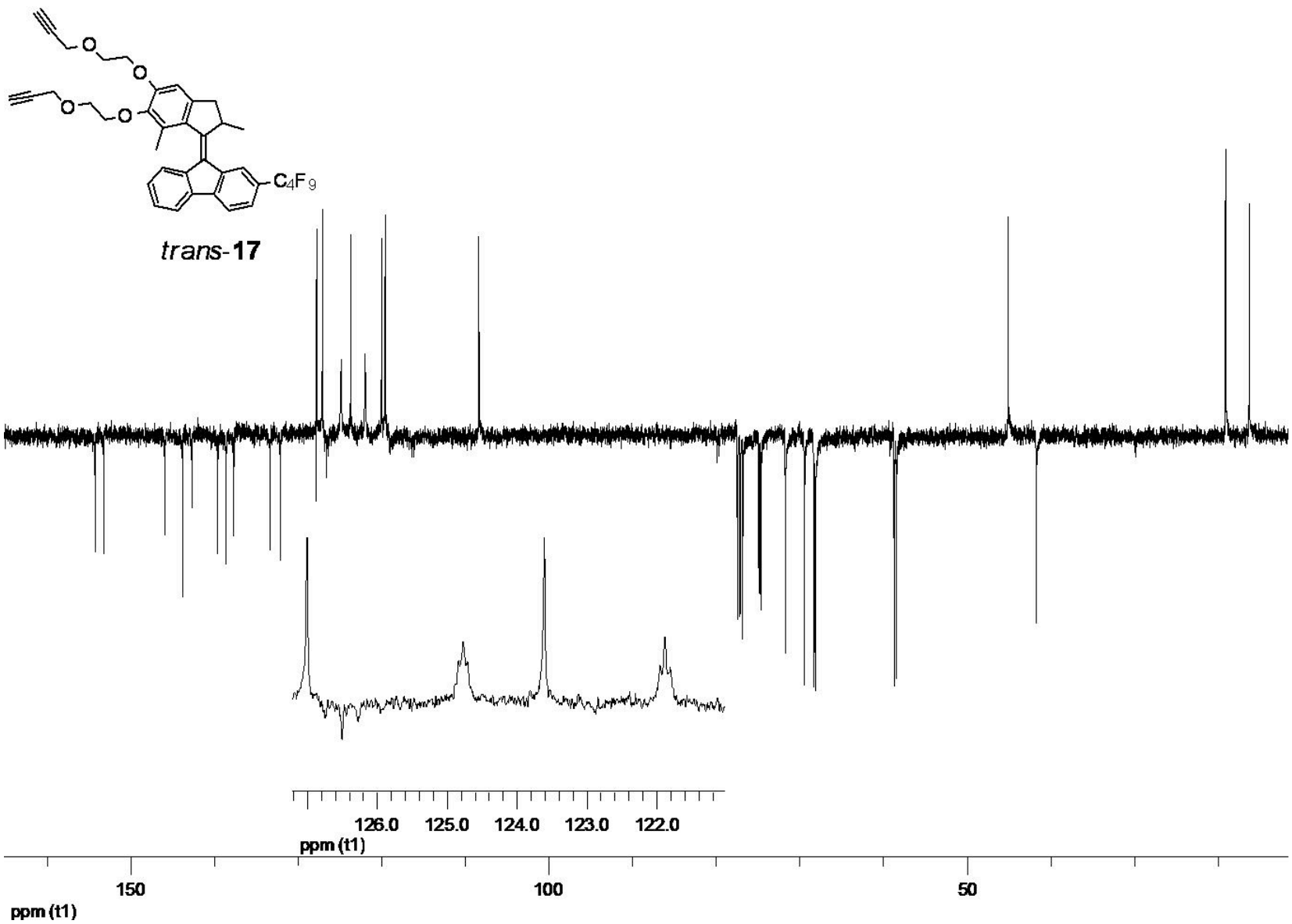
Spectrum 36 ^{1}H NMR spectrum *cis*-**17** in CD_2Cl_2 at -55°C.



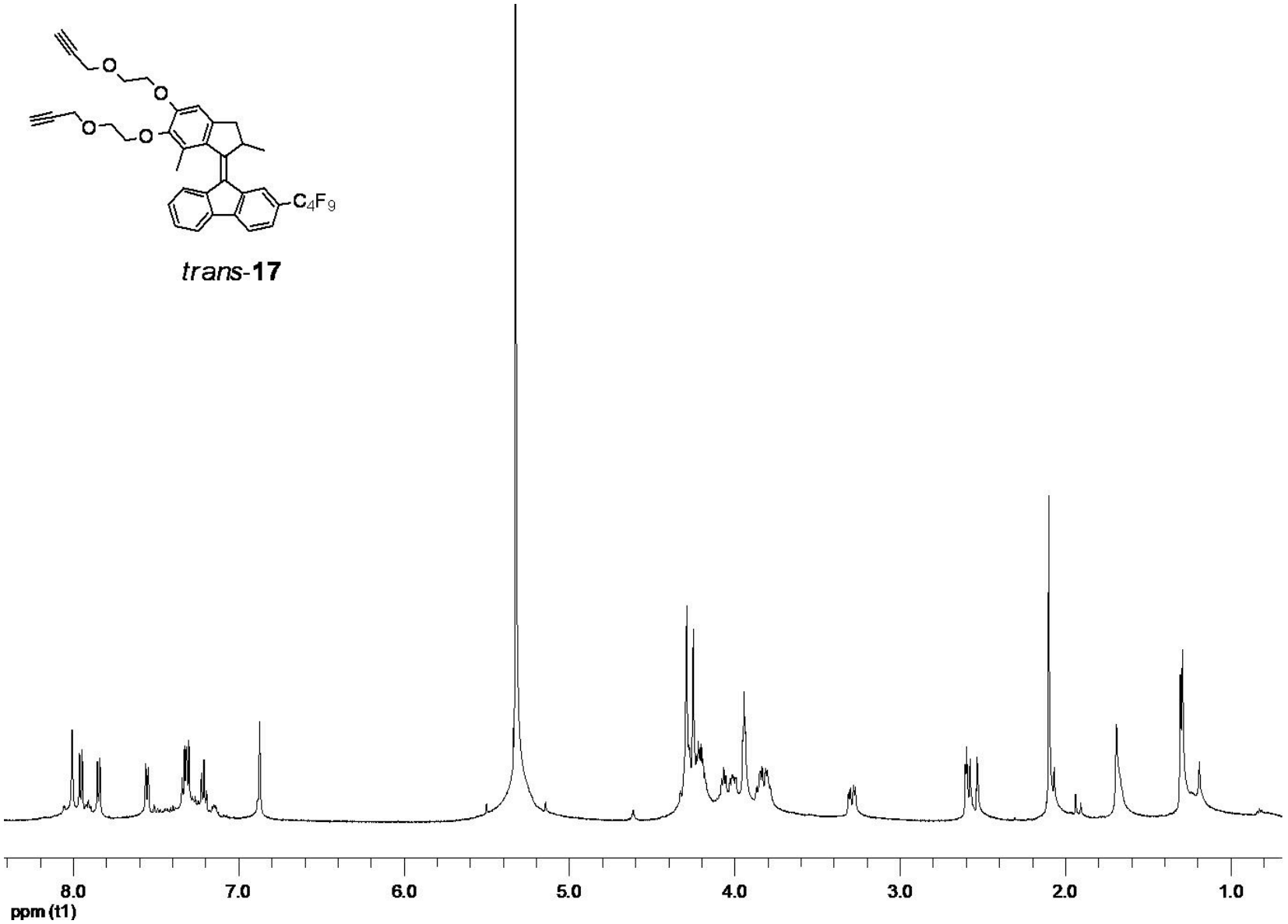
Spectrum 37 ^{1}H NMR spectrum of the photostationary state (λ=365 nm) of stable-*cis*-**17** and unstable-*trans*-**17** in CD_2Cl_2 at -55°C.



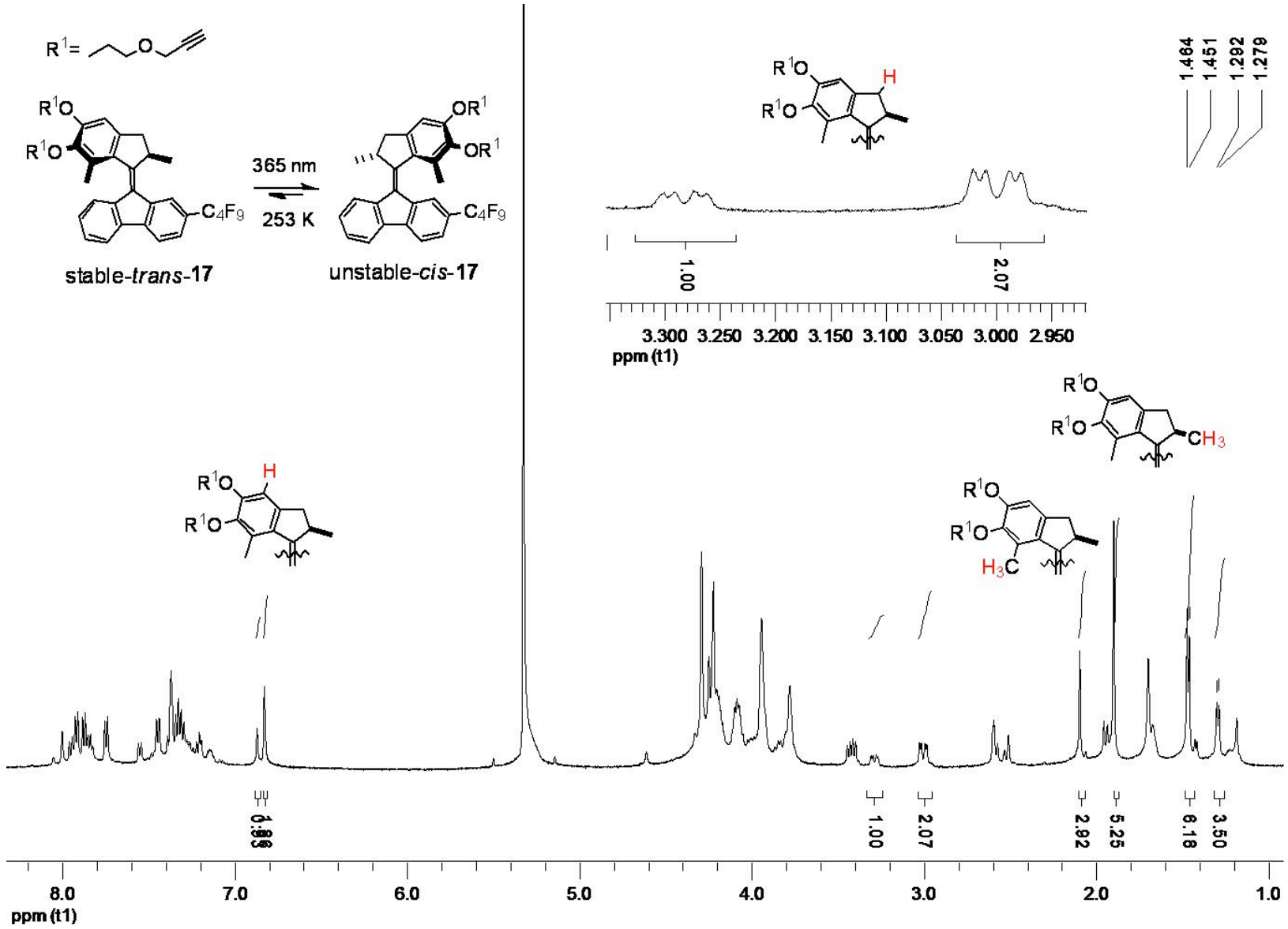
Spectrum 38 ^{1}H NMR spectrum of *trans*-**17** in $CDCl_3$.



Spectrum 39 APT ^{13}C NMR spectrum of *trans*-**17** in $CDCl_3$.



Spectrum 40 ^{1}H NMR spectrum *trans*-**17** in CD_2Cl_2 at -55°C.



Spectrum 41 ^{1}H NMR spectrum of the photostationary state (λ=365 nm) of stable-*trans*-**17** and unstable-*cis*-**17** in CD_2Cl_2 at -55°C.

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