Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Electronic Supplementary Information

An Ultrafast Surface-Bound Photo-active Molecular Motor

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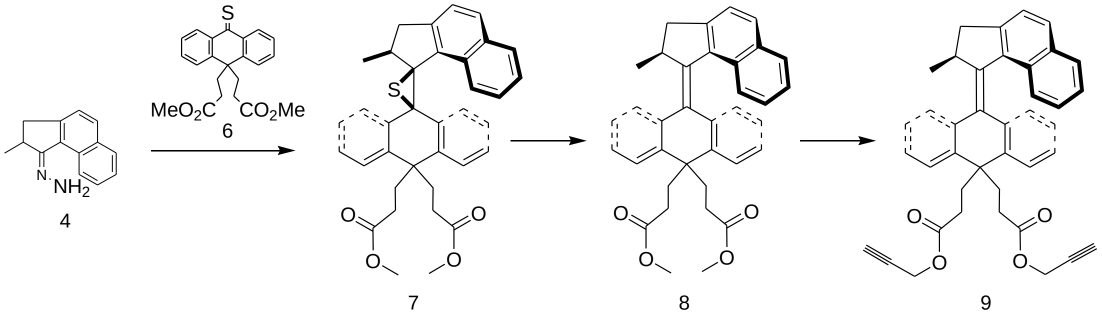
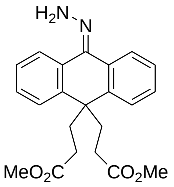
General Remarks: All commercially available reagents were used without further purification. All solvents were used after distillation. Tetrahydrofuran (THF), diethyl ether and toluene were refluxed over and distilled from sodium-benzophenone. Dichloromethane was refluxed over and distilled from P_2O_5. Dimethylformamide (DMF) was distilled from CaH_2 under reduced pressure. Chromatography: silica gel, Merck type 9385 230-400 mesh. TLC: silica gel 60, Merck, 0.25 mm, impregnated with a fluorescent indicator (254 nm). Melting points were recorded on a Büchi B-545 melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were measured on a ESI-TOF MS. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 a Varian Mercury Plus, or a Varian Inova 400. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintet), integration, coupling constant in Hz. UV-vis spectra were obtained using Hewlet-Packard HP 8543 FT or a Jasco V-630 spectrophotometer in a 1 cm quartz cuvette. Spectroscopic ellipsometry measurements were performed on a J.A. Woollam VASE ellipsometer. Samples for ellipsometry were prepared on silicon wafers (Wafer World Inc.) containing a thin layer of SiO_2 (approximately 2 nm, exact value measured for each sample) and measured in three different locations and the results averaged. A refractive index value of 1.5 was used for the organic layer. ATR-IR spectra of the surfaces were obtained using a Spectrum 400 FT-IR (Perkin Elmer) equipped with a Pike Veemax II attachment and a liquid nitrogen cooled MCT detector. Spectra were taken with parallel-polarized light and an incident reflection angle of 65° while samples were in intimate contact with a germanium crystal. Samples were cleaned with lens tissue immediately before measuring. Contact angles were measured on a Data Physics contact angle goniometer. The contact angle was calculated using software provided by the company. The contact angle was measured at three different locations on each surface and the results averaged. Fluorescence spectra were obtained using a Jobin Yvon Fluorolog 3 spectrofluorometer. Surfaces were measured in front face mode. Modified surfaces were prepared according to a previously published procedure.[15]

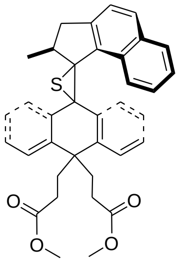


Dimethyl 3,3'-(10-hydrazono-9,10-dihydroanthracene-9,9-diyl)dipropanoate (4)



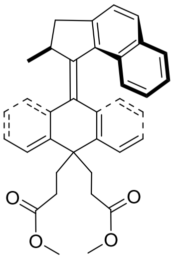
N_2H_4•H_2O (0.4 mL) was added dropwise to a suspension of thioketone **3** (440 mg, 1.16 mmol) suspended in THF (2 mL) and EtOH (15 mL). The mixture turned from blue-green to yellow as all of the material dissolved (~ 1 min). After stirring 1 h, the mixture was diluted with water. The mixture was extracted with EtOAc (2x 20 mL), dried (Na_2SO_4), and reduced *in vacuo* to give an oil. This crude product was purified by flash chromatography (Pentane:EtOAc, 2:1→1:1) to give the desired product as an oil which solidified upon standing (340 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.86 (*A*BMN ddd, 1H, *J* = 6.8, 9.9, 16.8 Hz), 1.96 (A*B*MN ddd, 1H, *J* = 6.8, 9.9, 16.8 Hz), 2.35-2.48 ((AB*MN* m, 2H), 3.52 (s, 6H), 5.95 (br s, 2H), 7.28-7.48 (m, 5H), 7.64 (dd, 1H, *J* = 8.0, 1.2 Hz), 7.90 (dd, 1H, *J* = 7.6, 1.6 Hz), 8.17 (dd, 1H, *J* = 7.6, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.3, 141.6, 140.3, 137.7, 136.6, 129.1, 128.7, 128.1, 126.9, 126.8, 126.6, 125.9, 124.6, 124.3, 51.2, 45.6, 37.3, 29.3; HRMS calcd $C_{22}H_{24}N_2O_4$ 380.1736, found 380.1719.

Episulfide (7)



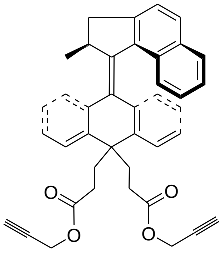
Bis(trifluoroacetoxy)iodobenzene (1.10 g, 2.56 mmol) was added to a solution of hydrazone **4** (420 mg, 2.00 mmol) in DMF and stirred at –50 °C. After the solution was stirred for 15 sec, thioketone **6** (1.0 equiv, precooled solution in $CHCl_3$ at ~0 °C) was added. The mixture was allowed to warm to rt, stirred overnight (2 h is sufficient), then diluted with water. Std workup gave a brown oil which was purified by flash chromatography (4:1, Hex:EtOAc, R_f ~0.3) to give an off-white foam (640 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (d, 3H, *J* = 7.2 Hz), 1.60-1.95 (m, 6H), 2.05-2.20 (m, 1H), 2.31 (d, 1H, *J* = 16.8 Hz), 2.50-2.71 (m, 2H), 3.00 (dd, 1H, = 7.0, 16.8 Hz), 3.59 (s, 3H), 3.67 (s, 3H), 6.83 (t, 1H, *J* = 7.6 Hz), 6.92 (t, 1H, *J* = 7.6 Hz), 7.01 (d, 1H, *J* = 7.6 Hz), 7.02 (d, 1H, *J* = 8.4 Hz), 7.22 (t, 1H, *J* = 8.0 Hz), 7.30-7.42 (m, 3H), 7.49 (apparent t, 2H, *J* = 9.2 Hz), 7.57 (d, 1H, *J* = 8.0 Hz), 7.96 (d, 1H, *J* = 7.2 Hz), 8.27 (d, 1H, *J* = 8.0 Hz), 9.42 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 22.7 (CH_3), 29.0 (CH_2), 29.1 (CH_2), 29.7 (CH_2), 37.1 (CH_2), 38.0 (CH), 38.7 (CH_2), 45.1 (C), 51.3 (CH_3), 51.4 (CH_3), 61.1 (C), 73.3 (C), 123.2 (CH), 123.8 (CH), 124.4 (CH), 124.5 (CH), 125.1 (CH), 125.2 (CH), 125.5 (CH), 125.8 (CH), 127.1 (CH), 127.3 (CH), 127.5 (CH), 128.7 (CH), 129.2 (CH), 131.6 (C), 131.7 (C), 132.1 (CH), 132.9 (C), 134.0 (C), 138.0 (C), 140.9 (C), 141.5 (C), 142.1 (C), 173.1 (C), 174.0 (C); HRMS (EI) calcd for $C_{36}H_{34}O_4S$; 562.2178, found 562.2152.

Dimethyl 3,3'-(10-(2-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-ylidene)-9,10-dihydroanthracene-9,9-diyl)dipropanoate (8)



A solution of episulfide **7** (640 mg, 1.21 mmol) and triphenylphosphine (600 mg, 2.29 mmol) in *p*-xylene (~5 mL) was heated at 130 °C for 16 h. The mixture was cooled, reduced *in vacuo* and purified by flash chromatography (4:1; Heptane:EtOAc) to give the product as a white solid (550 mg, 86%). mp 167-169°C; ^{1}H NMR (400 MHz, $CDCl_3$) 0.76 (d, 3H, *J* = 6.8 Hz), 2.21 (t, 1H, *J* = 8.2 Hz), 2.48-2.52 (m, 4H), 2.58 (d, 1H, *J* = 15.6 Hz), 2.82 (ddd, 1H, *J* = 7.8,), 3.45 (s, 3H), 3.63 (dd, 1H, *J* = 6.2, 15.4 Hz), 3.69 (s, 3H), 4.74 (quin, 1H, *J* = 6.4 Hz), 6.61 (t, 1H, *J* = 7.6 Hz), 6.67 (d, 1H, *J* = 8.4 Hz), 6.84 (dd, 1H, *J* = 1.0, 7.8 Hz), 7.11 (dt, 1H, *J* = 1.2, 8.1 Hz), 7.14 (t, 1H, *J* = 8.0 Hz), 7.28 (d, 1H, *J* = 5.6 Hz), 7.29 (d, 1H, *J* = 5.6 Hz), 7.41 (d, 1H, *J* = 8.0 Hz), 7.47 (d, 2H, *J* = 7.6 Hz), 7.69 (d, 1H, *J* = 7.6 Hz), 7.70 (d, 1H, *J* = 8.0 Hz), 7.92 (t, 1H, *J* = 4.4 Hz), ^{13}C NMR (APT, 100 MHz, $CDCl_3$): 18.6 (CH_3), 27.3 (CH_2), 29.3 (CH_2), 30.4 (CH_2), 35.5 (CH_2), 37.6 (CH), 39.5 (CH_2), 46.8 (C), 51.4 (CH_3), 51.6 (CH_3), 123.8 (CH), 123.9 (CH), 124.1 (CH), 125.2 (CH), 125.5 (CH), 125.6 (CH), 125.8 (CH), 126.0 (CH), 126.3 (CH), 126.4 (CH), 127.2 (CH), 127.5 (C), 127.8 (CH), 128.2 (CH), 128.9 (C), 129.8 (C), 132.9 (C), 135.7 (C), 139.4 (C), 139.6 (C), 140.2 (C), 141.1 (C), 144.7 (C), 146.0 (C), 173.3 (C), 174.2 (C); HRMS (EI) calcd for $C_{36}H_{34}O_4$; 530.2457, found 562.2440.

Molecular motor (9)



To a 2-necked round bottom equipped with a condenser was added compound **8** (250 mg, 0.471 mmol), freshly distilled propargylic alcohol (5 mL) and NaCN (2.2 mg, 0.047 mmol). Under N_2, the solution was stirred under reflux overnight. After cooling it back to room temperature, the solution was passed through a short silica gel plug. The crude material was purified by flash chromatography (1:5 EtOAc/Heptane) to give a slightly yellowish solid (220 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.86 (m, 1H), 7.71 (dd, , 2H *J* = 8.0, 5.2 Hz), 7.44 (t, 3H, *J* = 7.6 Hz), 7.37 – 7.28 (m, 2H), 7.15 (td, 2H, *J* = 14.0, 6.9 Hz), 6.88 – 6.79 (m, 1H), 6.74 (t, 1H, *J* = 7.1 Hz), 6.69 – 6.54 (m, 2H), 4.72 (d, 2H, *J* = 2.5 Hz), 4.48 (m, 3H), 3.64 (dd, 1H, *J* = 15.6, 6.1 Hz), 2.82 (dd, 2H, *J* = 12.8, 7.2 Hz), 2.66 – 2.40 (m, 6H), 2.34 – 2.12 (m, 3H), 0.75 (d, 3H, *J* = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 172.3, 146.4, 145.2, 141.3, 140.6, 139.6, 139.7, 136.0, 133.3, 130.2, 129.3, 128.6, 128.2, 128.1, 127.7, 127.6, 126.7, 126.5, 126.3, 125.9, 125.5, 124.6, 124.3, 124.23, 124.18, 75.2, 75.1, 74.94, 74.91, 52.3, 52.1, 47.1, 39.9, 38.0, 35.6, 30.7, 29.9, 29.7, 19.1.

SPECTRA:

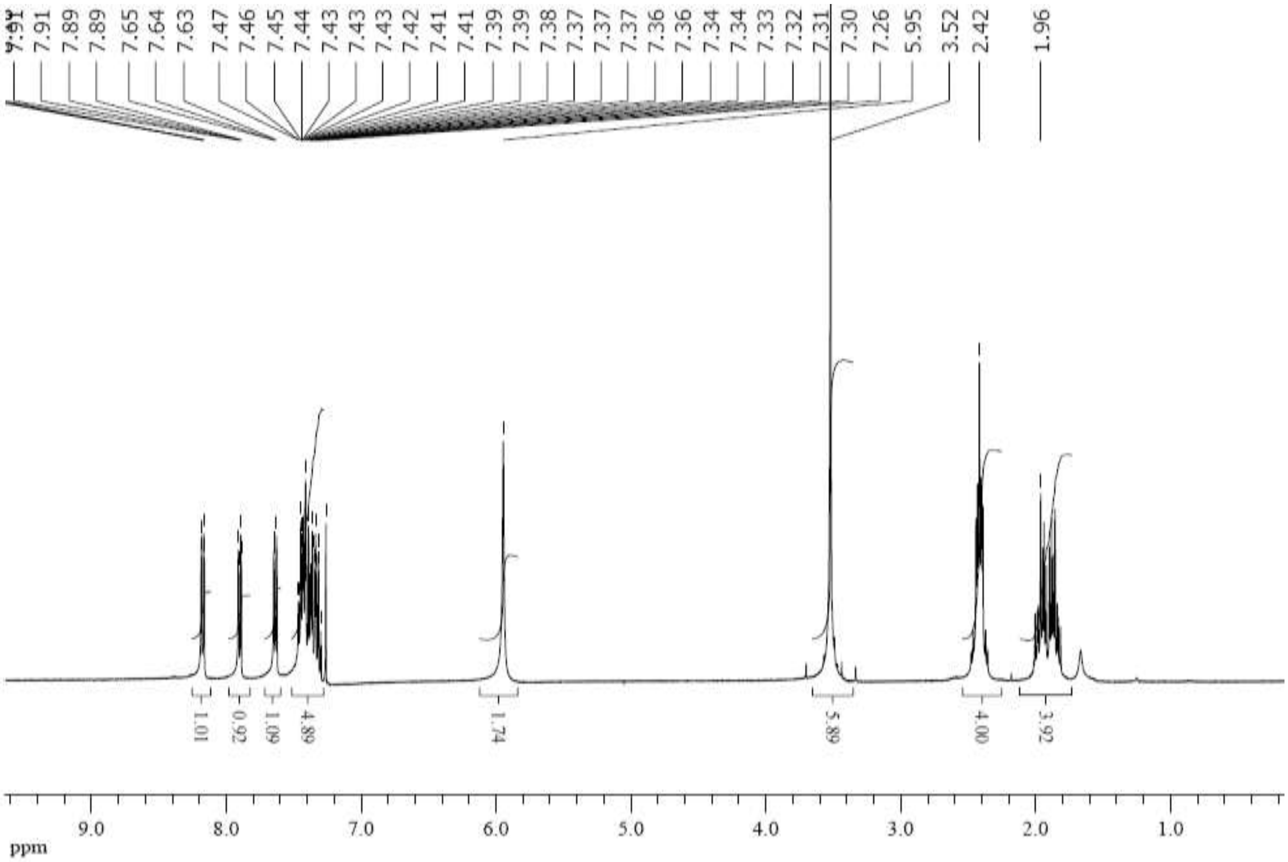


Figure 1. ^{1}H NMR of compound **4** taken at 400 MHz in $CDCl_3$.

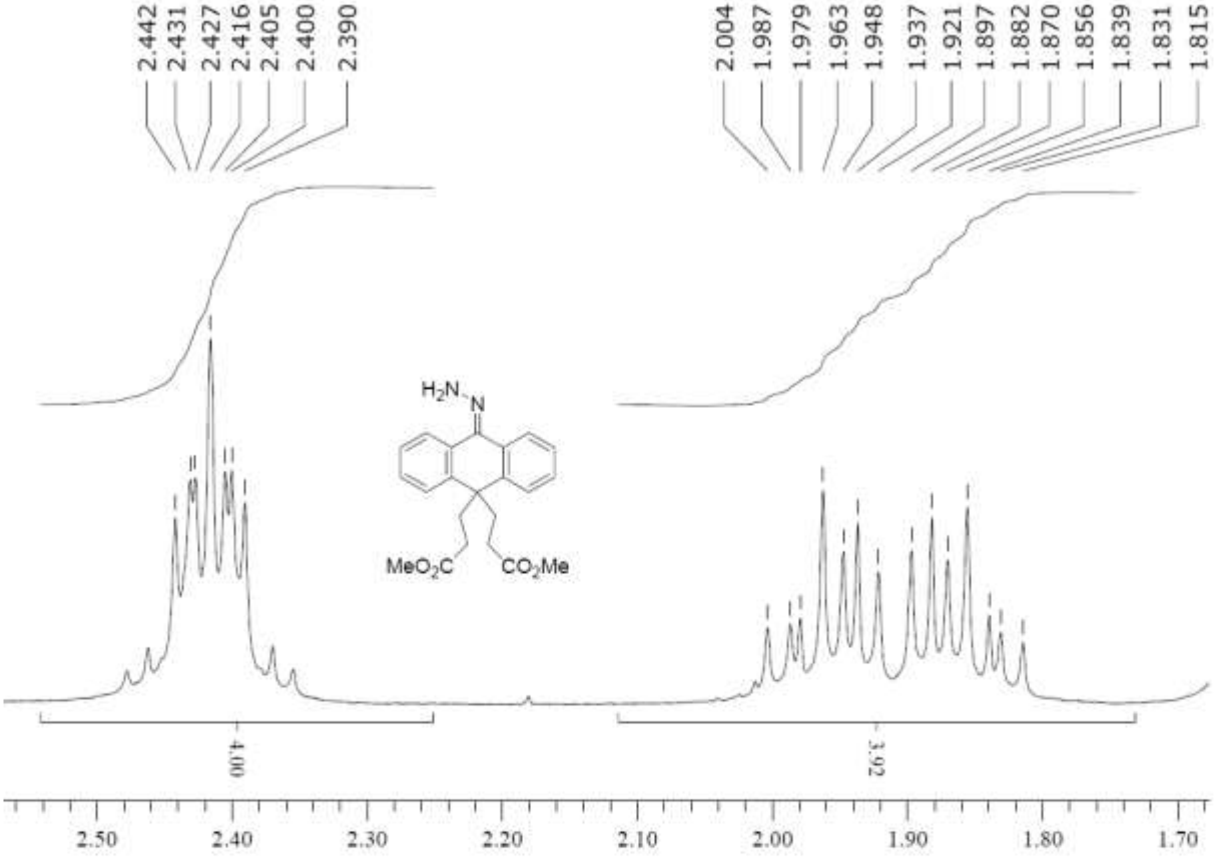


Figure 2. ^{1}H NMR of compound **4** taken at 300 MHz in $CDCl_3$ (expansion).

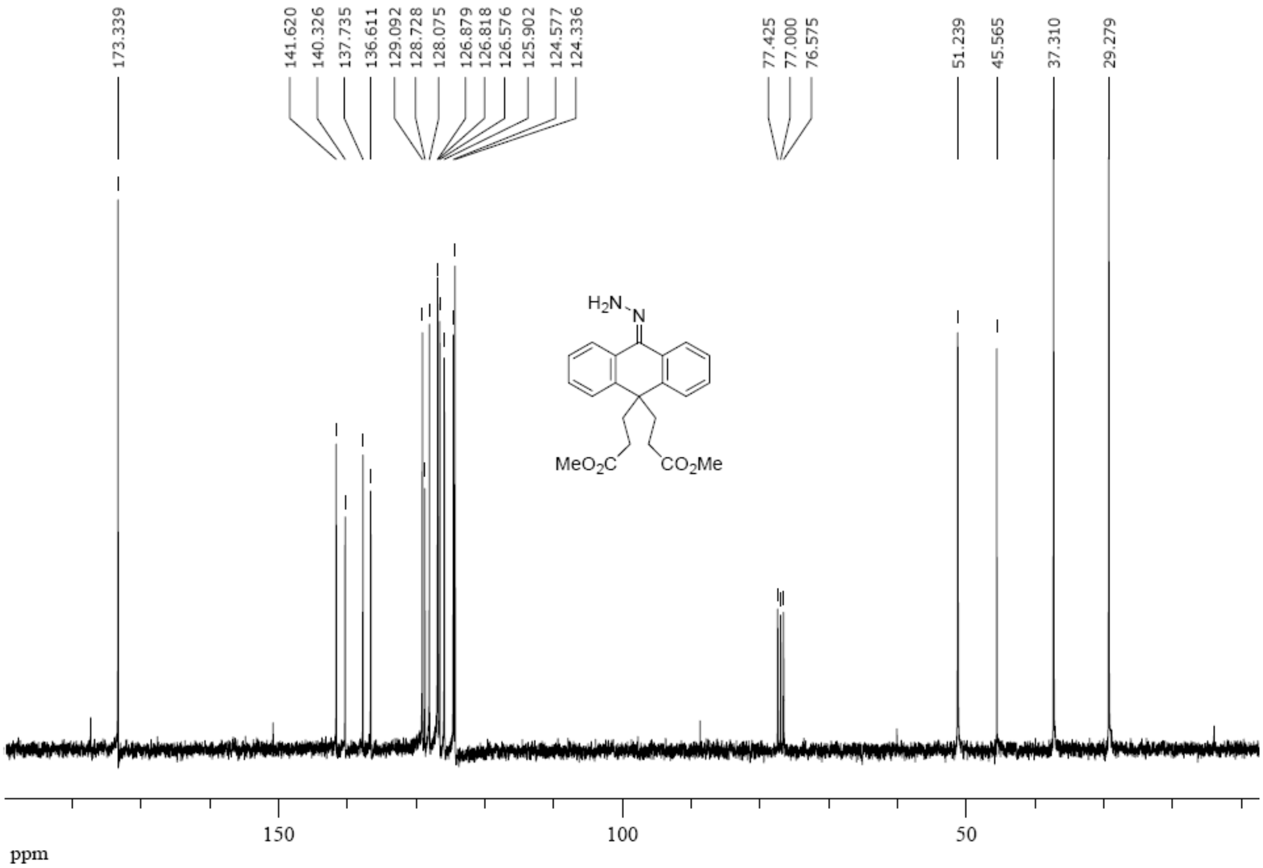


Figure 3. ^{13}C NMR of compound **4** taken at 75 MHz in $CDCl_3$.

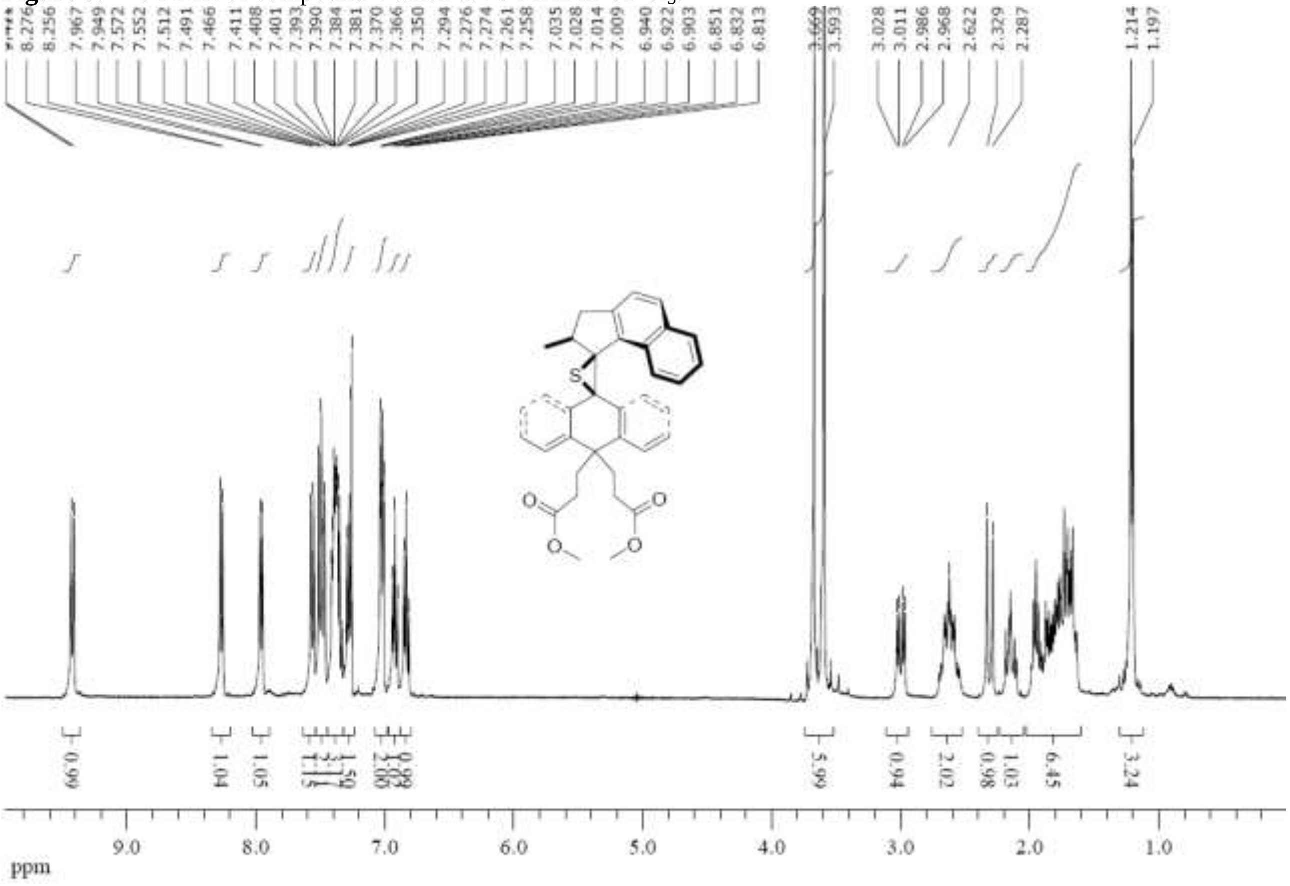


Figure 4. ^{1}H NMR spectrum of compound **7** in $CDCl_3$ taken at 400 MHz.

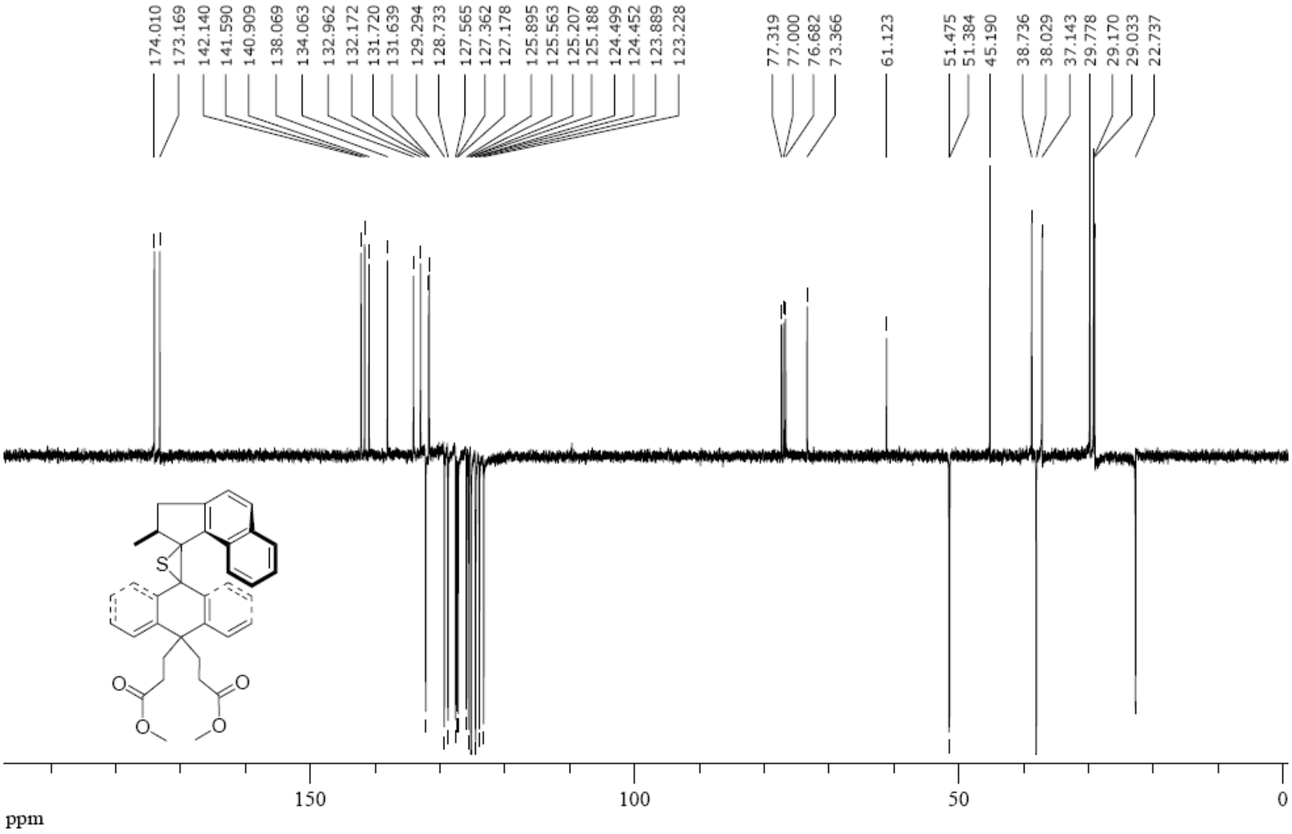


Figure 5. ^{13}C NMR spectrum of compound **7** in CDCl$_3$ taken at 100 MHz.

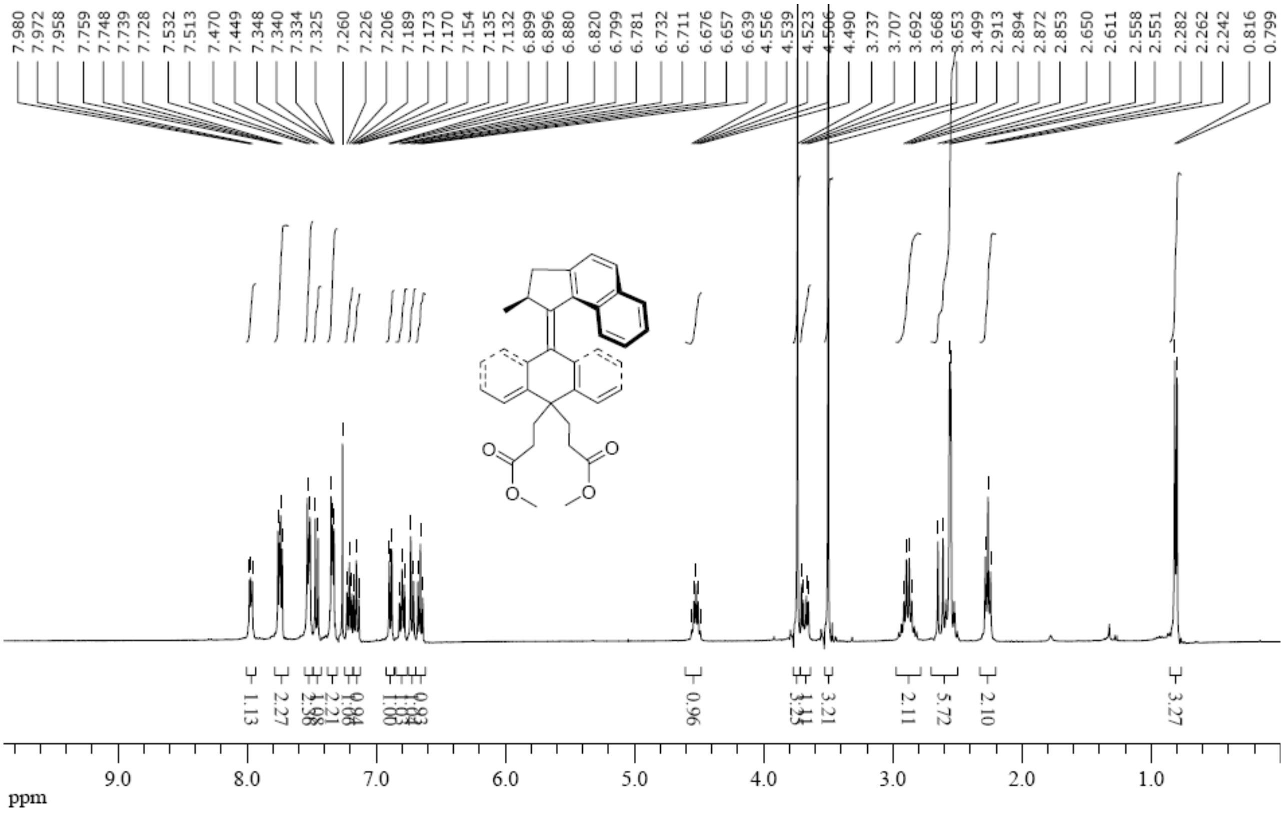


Figure 6: ^{1}H NMR spectrum of compound **8** in CDCl$_3$ taken at 400 MHz.

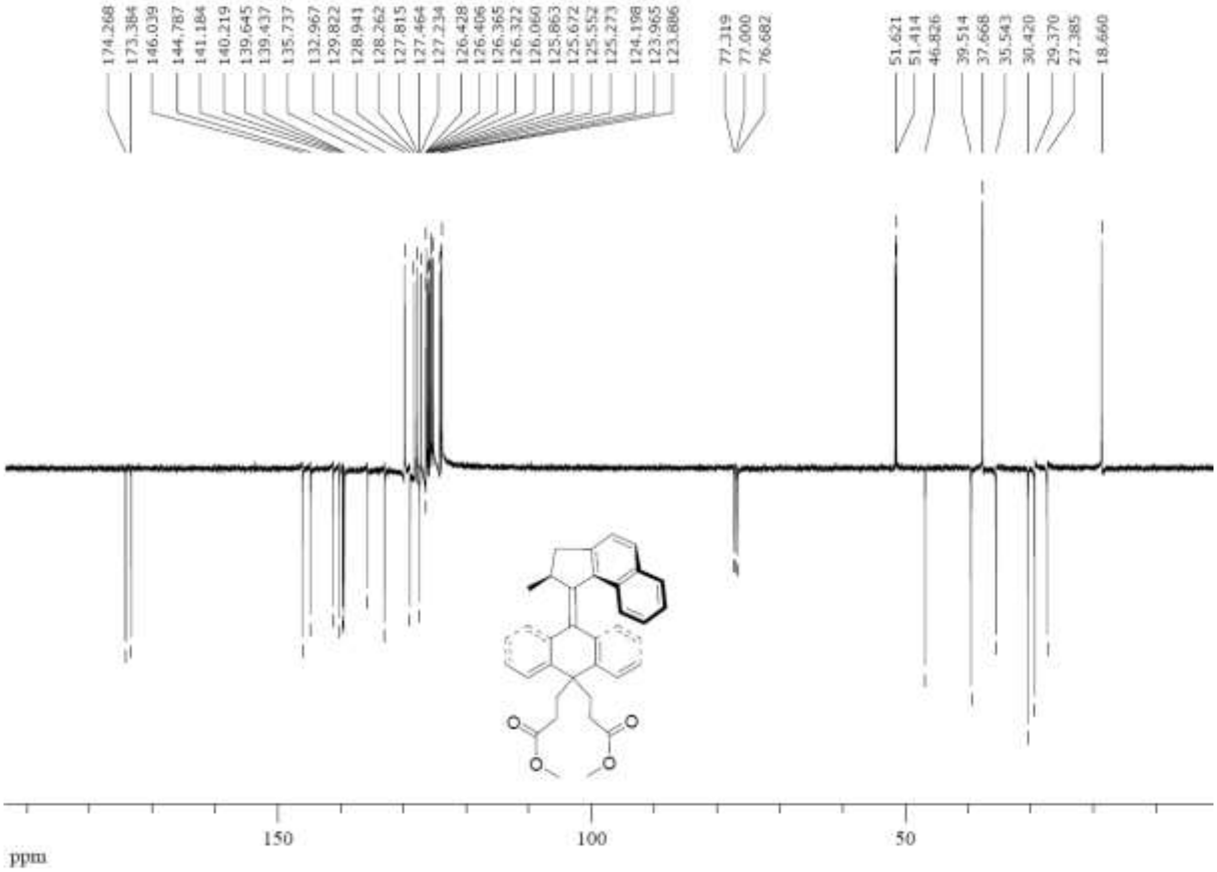


Figure 7: ^{13}C NMR spectrum of compound **8** in $CDCl_3$ taken at 100 MHz.

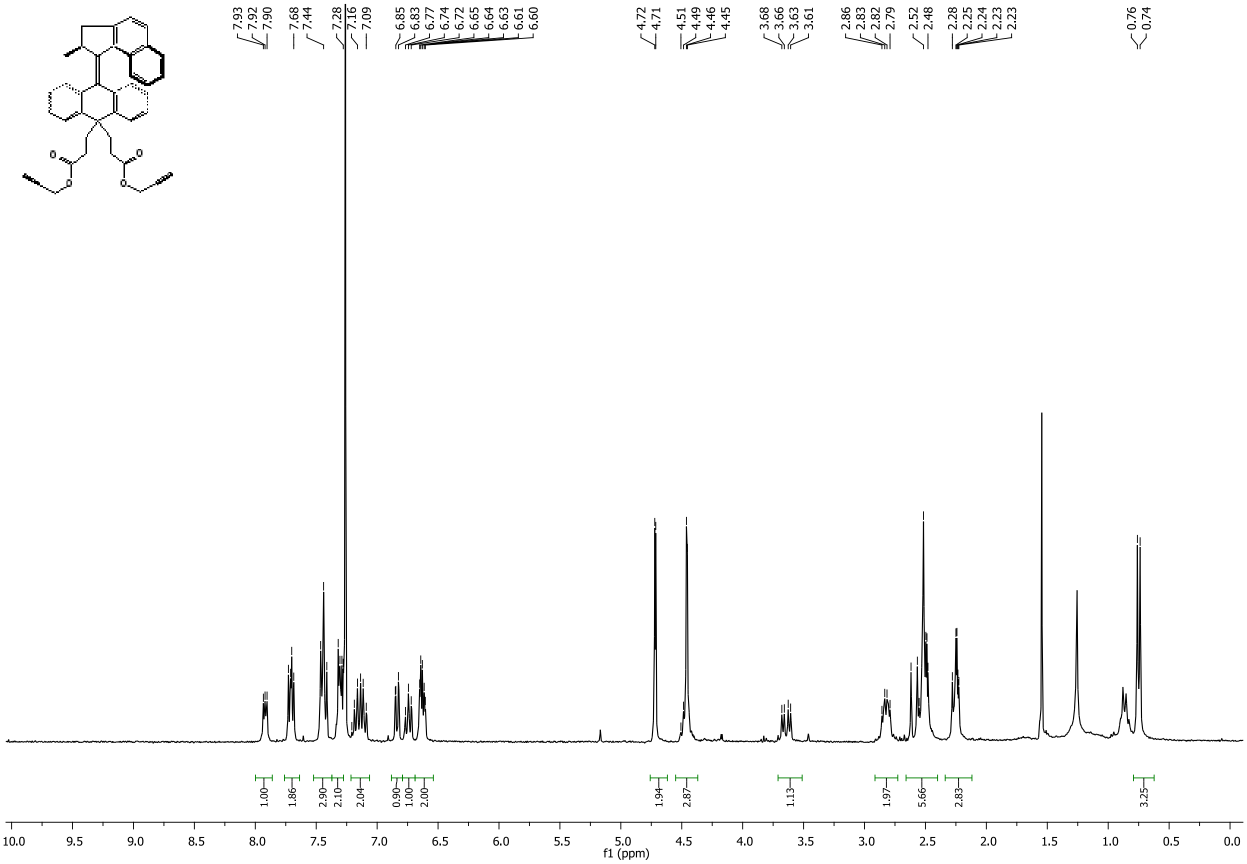


Figure 8. ^{1}H NMR spectrum of compound **9** in $CDCl_3$ taken at 400 MHz

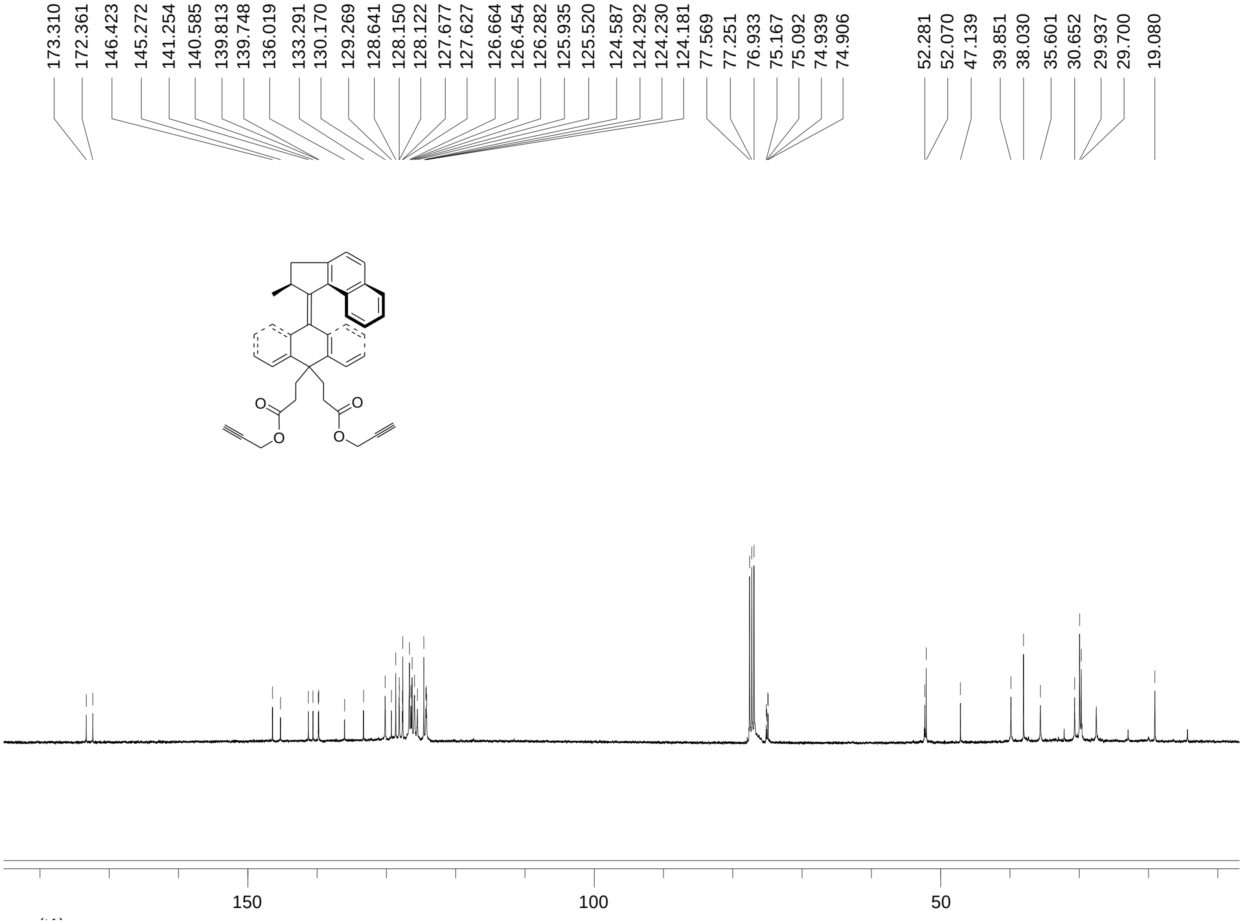


Figure 9: ^{13}C NMR spectrum of compound **9** in $CDCl_3$ taken at 100 MHz.

Instrumental Measurements

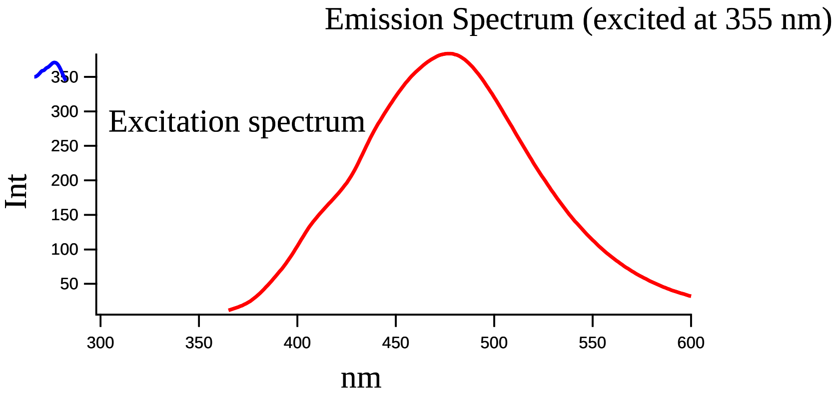


Figure 10: Excitation spectrum (blue) and emission spectrum (red, λ_{ex} = 355 nm) of **9** in DMF (c = 1.10^{-5} mol•L^{-1})

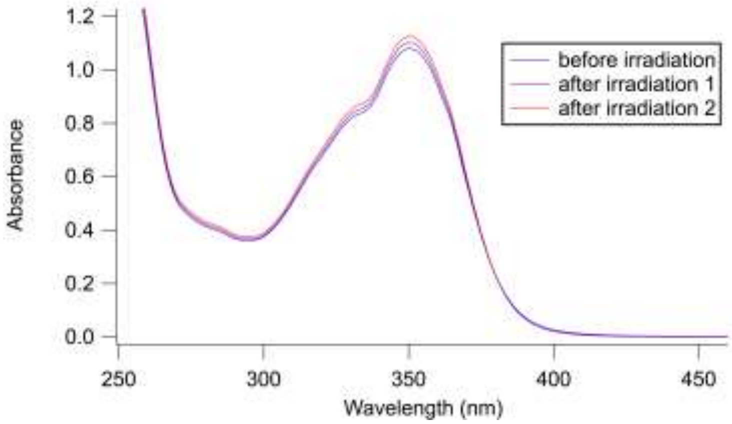


Figure 11: Steady-state absorption spectra of compound **9** in n-hexane (c = 1.10^{-5} mol•L^{-1}) before and after transient absorption measurements.

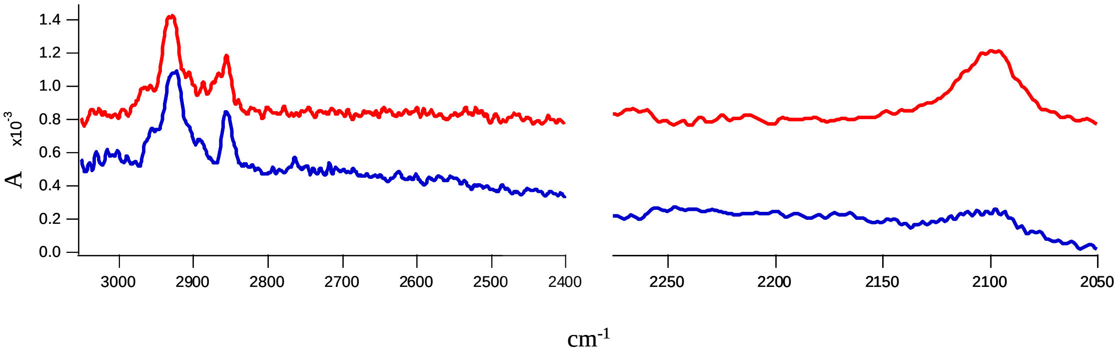


Figure 12: ATR-IR spectra of azide-functionalized SiO_2/Si wafer (red) and after reaction with **9** (blue).