Supporting Information for

Syntheses of Novel Azobenzene and Stilbene Heterobifunctional Cores Suitable for Stepwise Functionalization via CuAAC, Cross-coupling and Alkylation Approaches

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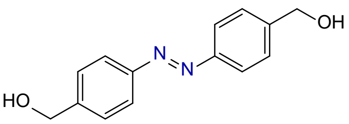
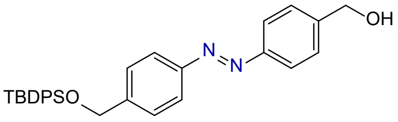
Contents

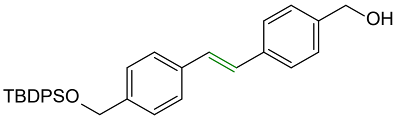
Synthesis and characterization of novel compounds



(E)-4,4'-dihydroxymethylazobenzene ***4***. A mixture of azobenzene bis(bromide) **1** (7.97 g, 21.7 mmol), $CaCO_3$ (21.7 g, 21.7 mmol), dioxane (144 mL) and water (144 mL) was refluxed for 48 h. The mixture was cooled to room temperature and the orange precipitate was filtered, washed with dioxane/water (1:1) mixture, aqueous HCl (2 M), water and dried. Yield 4.99 g (95%), orange solid. Analytical data were the same as previously published [1].

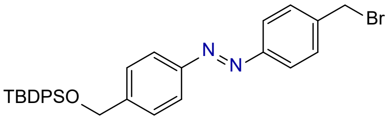


(E)-4-(tert-butyldiphenylsilyl)oxymethyl-4'-hydroxymethylazobenzene ***6****.* To a solution of azobenzene **4** (4.99 g, 20.6 mmol) in dry DMF (100 mL) imidazole (3.51 g, 51.6 mmol) and TBDPSCl (4.04 mL, 15.5 mmol) was added and the mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure. To the sticky residue water was added and then decanted twice and the remaining precipitate was dried on a rotary evaporator. The residue was subjected to column chromatography (silica, hexane/EtOAc) to yield firstly (gradient from 1:0 to 20:1) the diether as an orange solid (1.84 g, 26% in relation to starting diol, was not characterized). Further elution (gradient from 20:1 to 7:1) gave the product as an orange viscous oil (4.25 g, 43% in relation to starting diol) and (gradient from 7:3 to 1:0) a portion of starting diol contaminated with imidazole which was washed with Et_2O and dried to afford azobenzene **4** (0.477 g, 10% in relation to starting diol). Analytical data were the same as previously published [2].

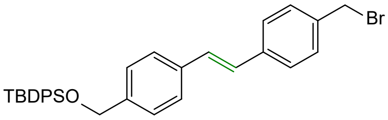


(E)-4-[(tert-butyldiphenylsilyl)oxy]methyl-4'-hydroxymethylstilbene ***7*** was prepared as described for compound **6** from stilbene **5** (0.420 g, 1.75 mmol), imidazole (0.298 g, 4.38 mmol) and TBDPSCl (0.319 g, 1.23 mmol) in dry DMF (5 mL). The product was purified by column chromatography (silica, gradient from hexane to hexane/EtOAc 4:1). Yield 0.368 g (44%), transparent viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.68 (m, 4H; ArH_{Ph}), 7.55–7.47 (m, 4H; ArH_{stil}), 7.47–7.32 (m, 10H; ArH), 7.14 (d, 1H, $^3J = 16.6$ Hz; CH), 7.10 (d, 1H $^3J = 16.6$ Hz; CH), 4.79 (s, 2H; $CH_2OTBDPS$), 4.71 (d, 2H, $^3J = 5.8$ Hz; $C\underline{H}_2OH$), 1.67 (t, 1H, $^3J = 5.8$ Hz; OH), 1.11 (s,

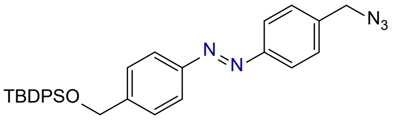
9H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 140.62, 140.10, 136.85, 135.90 (C$_{Ar}$), 135.54 (CH$_{Ar}$), 133.44 (C$_{Ar}$), 129.59 (CH$_{Ar}$), 128.58, 127.77 (CH$_{stil}$), 127.70, 127.34, 126.59, 126.37, 126.31 (CH$_{Ar}$), 65.31 (CH$_2$OH), 65.09 (CH$_2$OTBDPS), 26.82 ($\underline{C}$(CH$_3$)$_3$), 19.30 (C($\underline{C}$H$_3$)$_3$) ppm. APPI-MS *m*/*z*: 478.2321 [M]$^+$ for $C_{32}H_{34}O_2Si$ (478.2323).



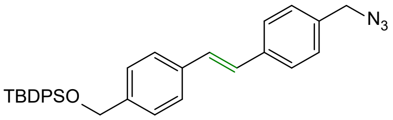
(E)-4-[(tert-butyldiphenylsilyl)oxy]methyl-4'-bromomethylazobenzene ***8***. To a mixture of alcohol **6** (3.61 g, 7.52 mmol), PPh$_3$ (2.96 g, 11.3 mmol) and dry THF (60 mL) NBS (2.01 g, 11.3 mmol) was added and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica, gradient from hexane to hexane/dichloromethane 1:1). Yield 4.00 g (98%), orange viscous oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.93–7.87 (m, 4H; ArH$_{azo}$), 7.74–7.68 (m, 4H; ArH$_{Ph}$), 7.57–7.48 (m, 4H; ArH$_{azo}$), 7.48–7.36 (m, 6H; ArH$_{Ph}$), 4.86 (s, 2H; CH$_2$OTBDPS), 4.56 (s, 2H; CH$_2$Br), 1.13 (s, 9H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 152.39, 151.70, 144.57, 140.34 (C$_{Ar}$), 135.54 (CH$_{Ar}$), 133.29 (C$_{Ar}$), 129.85, 129.79, 127.77, 126.50, 123.21, 122.91 (CH$_{Ar}$), 65.20 (CH$_2$OTBDPS), 32.78 (CH$_2$Br), 26.83 ($\underline{C}$(CH$_3$)$_3$), 19.32 (C($\underline{C}$H$_3$)$_3$) ppm. ESI-MS *m*/*z*: 545.1440 [M+H]$^+$ for $C_{30}H_{31}BrN_2OSi$ (545.1441).



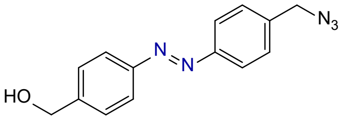
(E)-4-[(tert-butyldiphenylsilyl)oxy]methyl-4'-bromomethylstilbene ***9*** was prepared as described for compound **8** from stilbene **7** (1.26 g, 2.64 mmol), PPh$_3$ (1.04 g, 3.97 mmol) and NBS (0.705 g, 3.96 mmol) in dry THF (40 mL). Yield 1.15 g (33%), transparent viscous oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.79–7.72 (m, 4H; ArH$_{Ph}$), 7.55–7.49 (m, 4H; ArH$_{stil}$), 7.50–7.36 (m, 10H; ArH), 7.17 (d, 1H, ^3J = 16.4 Hz; CH), 7.11 (d, 1H ^3J = 16.4 Hz; CH), 4.82 (s, 2H; CH$_2$OTBDPS), 4.54 (s, 2H; CH$_2$Br), 1.15 (s, 9H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 140.84, 137.64, 136.83, 135.73 (C$_{Ar}$), 135.54 (CH$_{Ar}$), 133.43 (C$_{Ar}$), 129.70, 129.42 (CH$_{Ar}$), 129.31 (CH$_{stil}$), 127.71 (CH$_{Ar}$), 127.42 (CH$_{stil}$), 126.78, 126.46, 126.32 (CH$_{Ar}$), 65.30 (CH$_2$OTBDPS), 33.54 (CH$_2$Br), 26.82 ($\underline{C}$(CH$_3$)$_3$), 19.31 (C($\underline{C}$H$_3$)$_3$) ppm. APPI-MS *m*/*z*: 542.1460 [M]$^+$ for $C_{32}H_{33}BrOSi$ (542.1458).



(E)-4-[(tert-butyldiphenylsilyl)oxy]methyl-4'-azidomethylazobenzene ***10***. To a solution of bromide **8** (0.715 g, 1.32 mmol) in acetone (35.1 mL) a solution of NaN_3 (0.129 g, 1.98 mmol) in water (3.9 mL) was added and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the residue was parted between dichloromethane and water. The organic layer was separated, washed with brine, dried and concentrated to dryness. Yield 0.666 g (quantitative), orange viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.92 (m, 4H; ArH_{azo}), 7.79–7.73 (m, 4H; ArH_{Ph}), 7.56–7.51 (m, 2H; ArH_{azo}), 7.51–7.39 (m, 8H; ArH), 4.89 (s, 2H; $CH_2OTBDPS$), 4.45 (s, 2H; CH_2N_3), 1.17 (s, 9H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.43, 151.66, 144.51, 137.98 (C_{Ar}), 135.52 (CH_{Ar}), 133.25 (C_{Ar}), 129.78, 128.81, 127.76, 126.47, 123.22, 122.89 (CH_{Ar}), 65.17 ($CH_2OTBDPS$), 54.35 (CH_2N_3), 26.82 ($\underline{C}(CH_3)_3$), 19.31 ($C(\underline{C}H_3)_3$) ppm. ESI-MS *m*/*z*: 506.2365 $[M+H]^+$ for $C_{30}H_{31}N_5OSi$ (506.2371).

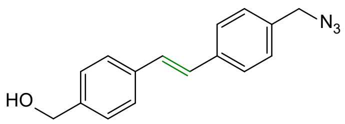


(E)-4-[(tert-butyldiphenylsilyl)oxy]methyl-4'-azidomethylstilbene ***11*** was prepared as described for compound **10** from stilbene **9** (0.273 g, 0.505 mmol), NaN_3 (0.0492 g, 0.757 mmol) in a mixture of acetone (13.5 mL) and water (1.5 mL). Yield 0.240 g (94%), transparent viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.71 (m, 4H; ArH_{Ph}), 7.58–7.50 (m, 4H; ArH_{stil}), 7.50–7.31 (m, 10H; ArH), 7.17 (d, 1H, ^3J = 16.4 Hz; CH), 7.12 (d, 1H ^3J = 16.4 Hz; CH), 4.82 (s, 2H; $CH_2OTBDPS$), 4.36 (s, 2H; CH_2N_3), 1.15 (s, 9H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.79, 137.52, 135.77 (C_{Ar}), 135.54 (CH_{Ar}), 134.43, 133.43 (C_{Ar}), 129.69 (CH_{Ar}), 129.14 (CH_{stil}), 128.59, 127.71 (CH_{Ar}), 127.47 (CH_{stil}), 126.81, 126.43, 126.32 (CH_{Ar}), 65.31 ($CH_2OTBDPS$), 54.54 (CH_2N_3), 26.82 ($\underline{C}(CH_3)_3$), 19.30 ($C(\underline{C}H_3)_3$) ppm. APPI-MS *m*/*z*: 503.2381 $[M]^+$ for $C_{32}H_{33}N_3OSi$ (503.2387).

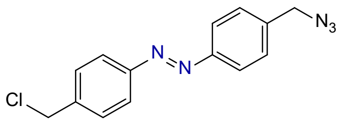


(E)-4-hydroxymethyl-4'-azidomethylazobenzene ***12***. To a solution of azobenzene **10** (0.101 g, 0.200 mmol) in THF (3 mL) a solution of TBAF (6.3 mg, 0.02 mmol) in water (0.03 mL) was added and the mixture was stirred at room temperature overnight. The solvent was reduced under reduced pressure and the product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 33:1).

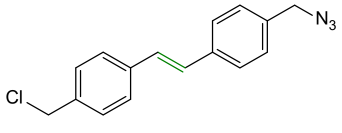
Yield 0.0534 g (quantitative), orange solid. M.p. 187–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.90 (m, 4H; ArH), 7.55–7.50 (m, 2H; ArH), 7.50–7.44 (m, 2H; ArH), 4.80 (d, 2H, ^3J = 5.7 Hz; CH_2O), 4.44 (s, 2H; CH_2N_3), 1.76 (t, 1H, ^3J = 5.7 Hz; OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.37, 152.00, 144.02, 138.18 (C_{Ar}), 128.86, 127.42, 123.29, 123.14 (CH_{Ar}), 64.86 (CH_2O), 54.37 (CH_2N_3) ppm. ESI-MS *m*/*z*: 268.1196 $[M+H]^+$ for $C_{14}H_{13}N_5O$ (268.1193).



(E)-4-hydroxymethyl-4'-azidomethylstilbene ***13*** was prepared as described for compound **12** from stilbene **11** (0.998 g, 1.98 mmol), TBAF (0.0624 g, 0.198 mmol) in a mixture of THF (30.0 mL) and water (0.3 mL). Yield 0.477 g (91%), white solid. M.p. 170–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.49 (m, 4H; ArH), 7.40–7.35 (m, 2H; ArH), 7.34–7.29 (m, 2H; ArH), 7.14 (d, 1H, ^3J = 16.6 Hz; CH), 7.10 (d, 1H, ^3J = 16.6 Hz; CH), 4.71 (s, 2H; CH_2O), 4.35 (s, 2H; CH_2N_3), 1.66 (br. s, 1H; OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.40, 137.35, 136.57, 134.59 (C_{Ar}), 128.83 (CH_{stil}), 128.63 (CH_{Ar}), 127.99 (CH_{stil}), 127.38, 126.87, 126.73 (CH_{Ar}), 65.13 (CH_2O), 54.55 (CH_2N_3) ppm. APPI-MS *m*/*z*: 265.1207 $[M]^+$ for $C_{16}H_{15}N_3O$ (265.1210).

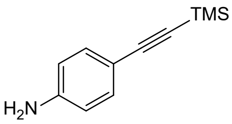


(E)-4-chloromethyl-4'-azidomethylazobenzene ***14**.* A mixture of alcohol **12** (0.175 g, 0.655 mmol), $SOCl_2$ (0.057 mL, 0.786 mmol), dry DMF (1.30 µL, 0.0168 mmol) in dry dichloromethane (8.30 mL) was stirred at room temperature overnight. The reaction was quenched with saturated aqueous $NaHCO_3$, the organic layer was separated, washed with brine, dried and concentrated to dryness. Yield 0.178 g (95%), orange solid. M.p. 108–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.89 (m, 4H; ArH), 7.58–7.52 (m, 2H; ArH), 7.51–7.45 (m, 2H; ArH), 4.66 (s, 2H; CH_2Cl), 4.44 (s, 2H; CH_2N_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.24, 152.23, 140.30, 138.39 (C_{Ar}), 129.36, 128.82, 123.34, 123.23 (CH_{Ar}), 54.30 (CH_2N_3), 45.62 (CH_2Cl) ppm. APPI-MS *m*/*z*: 285.0775 $[M]^+$ for $C_{14}H_{12}ClN_5$ (285.0776).

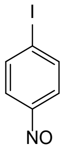


(E)-4-chloromethyl-4'-azidomethylstilbene ***16*** was prepared as described for compound **12** from stilbene **11** (0.419 g, 1.58 mmol), $SOCl_2$ (0.138 g, 0.190 mmol), DMF (3.2 µL, 0.0414 mmol) in dry dichloromethane (20.0 mL). Yield 0.443 g (99%), white solid. M.p.

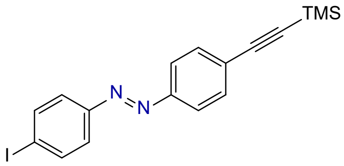
115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.48 (m, 4H; ArH), 7.42–7.37 (m, 2H; ArH), 7.35–7.30 (m, 2H; ArH), 7.12 (s, 2H; CH), 4.61 (s, 2H; CH_2Cl), 4.35 (s, 2H; CH_2N_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.24, 137.09, 136.77, 134.72 (C_{Ar}), 128.98, 128.57 (CH_{Ar}), 128.55, 128.40 (CH_{stil}), 126.89, 126.78 (CH_{Ar}), 54.44 (CH_2N_3), 46.05 (CH_2O) ppm. APPI-MS *m*/*z*: 283.0872 $[M]^+$ for $C_{104}H_{97}O_{16}$ (283.0871).



4-trimethylsilylethynylaniline ***16***. 4-Iodoaniline (2.19 g, 10.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.211 g, 0.301 mmol) and CuI (0.0572 g, 0.300 mmol) were suspended in *i*-Pr_2NH (60 mL) under Ar. After stirring for 10 min trimethylsilylacetylene (2.07 mL, 15.0 mmol) was added under Ar and the mixture was stirred at 70 °C for 9 h. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica, gradient from hexane/dichloromethane 1:1 to dichloromethane). Yield 1.84 g (97%), beige solid. Analytical data were the same as previously published [3].

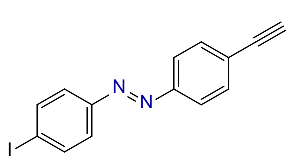


4-Iodonitrosobenzene ***17***. To a mixture of 4-iodoaniline (2.98 g, 13.6 mmol) and Ph_2Se_2 (0.205 g, 0.680 mmol) in dichloromethane (93 mL) aqueous H_2O_2 (2.34 mL, 27.2 mmol, 35 w/v%) was added and the mixture was vigorously stirred at room temperature. After 24 h another portion of H_2O_2 (2.34 mL, 27.2 mmol, 35 w/v%) was added and the stirring continued for 96 h. The organics were extracted with dichloromethane, the solvent was removed *in vacuo* and the residue was subjected to column chromatography (silica, gradient from hexane to hexane/dichloromethane 9:1). Fractions containing the product were combined and concentrated to dryness. The residue was suspended in hexane, the supernatant was collected and concentrated to dryness. Yield 1.26 g (40%), green solid. Analytical data were the same as previously published [4].

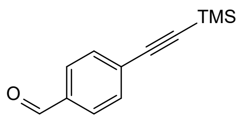


(E)-4-Iodo-4'-trimethylsilylethynylazobenzene ***18***. A mixture of aniline **16** (0.930 g, 4.92 mmol) and nitrosobenzene **17** (1.26 g, 5.41 mmol) in AcOH (39 mL) was stirred at room temperature for 48 h. The solvent was removed *in vacuo* and the residue parted between dichloromethane and saturated aqueous $NaHCO_3$. The organic layer was separated, washed with brine, dried, concentrated to dryness and the product was purified by column chromatography (silica, gradient from hexane to

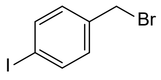
hexane/dichloromethane 19:1). Yield 1.561 g (79%), orange solid. Analytical data were the same as previously published [5].



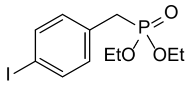
(E)-4-Iodo-4'-ethynylazobenzene ***19****.* To a solution of azobenzene **18** (0.418 g, 1.03 mmol) in THF (18.0 mL) methanol (9.0 mL) and a solution of KOH (0.087 g, 1.55 mmol) in water (4.5 mL) was added and the mixture was refluxed for 3 h. The mixture was cooled to room temperature, the solvent was removed under reduced pressure and the product was extracted with dichloromethane. Yield 0.2845 g (83%), orange solid. M.p. 190–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.83 (m, 4H; ArH), 7.69–7.60 (m, 4H; ArH), 3.24 (s, 1H; CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.89, 144.20 (C_{Ar}), 138.34 (CH_{Ar}), 133.30 (C_{Ar}), 127.43, 124.45, 123.19 (CH_{Ar}), 97.66 (C_{Ar}), 64.85 (CH_2O) ppm. ESI-MS *m/z*: 332.9885 $[M+H]^+$ for $C_{13}H_{11}IN_2O$ (338.9989).



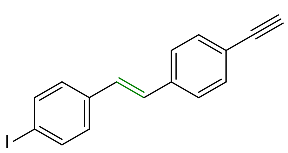
4-trimethylsilylethynylbenzaldehyde ***20****.* 4-Bromobenzaldehyde (2.035 g, 11.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.154 g, 0.219 mmol) and CuI (0.042 g, 0.220 mmol) were suspended in NEt_3 (27.5 mL) under Ar. After stirring for 10 min trimethylsilylacetylene (1.67 mL, 12.1 mmol) was added under Ar and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica, gradient from hexane to hexane/dichloromethane 1:1). Yield 2.096 g (94%), beige solid. Analytical data were the same as previously published [6].



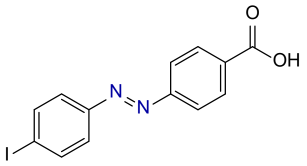
4-Iodobenzylbromide ***21****.* To a solution of 4-iodotoluene (1.65 g, 7.57 mmol) in dry CCl_4 (12 mL) at 0 °C NBS (1.37 g, 7.70 mmol) and AIBN (0.025 g, 0.152 mmol) were added and the mixture was stirred at 70 °C for 16 h. The mixture was filtrated, the solid was discarded and the filtrate was concentrated to dryness and subjected to column chromatography (silica, hexane) to yield the product as a white solid (1.99 g, 89%). Analytical data were the same as previously published [7].



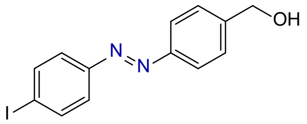
Diethyl 4-iodobenzylphosphonate ***22****.* Compound **21** (1.99 g, 6.70 mmol) was mixed with $P(OEt)_3$ (1.26 mL, 7.37 mmol) and the mixture was stirred at 150 °C for 3 h. The residue was diluted with dichloromethane, washed with saturated aqueous $NaHCO_3$, dried and concentrated to dryness. The product was purified by column chromatography (silica, hexane/EtOAc, gradient from 2:1 to 1:1). Yield 1.99 g (84%), transparent oil. Analytical data were the same as previously published [8].



(E)-4-Iodo-4'-ethynylstilbene ***23***. To a mixture of phosphonate **22** (3.54 g, 10.0 mmol) and aldehyde **20** (2.42 g, 12.0 mmol) dry THF (150 mL) and *t*-BuONa (1.92 g, 20.0 mmol) were added under Ar and the mixture was stirred at room temperature for 24 h. The solvent was evaporated and the residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with brine and concentrated to dryness. The residue was re-crystallized from dichloromethane/methanol mixture. Yield 2.40 g (73%), white solid. M.p. 206–208 °C (subl.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.66 (m, 2H; ArH), 7.51–7.43 (m, 4H; ArH), 7.27–7.22 (m, 2H; ArH), 7.08 (d, 1H, ^3J = 16.4 Hz; CH), 7.02 (d, 1H, ^3J = 16.4 Hz; CH), 3.14 (s, 1H; CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.81 (CH_{Ar}), 137.38, 136.48 (C_{Ar}), 132.49 (CH_{Ar}), 128.67, 128.58 (CH_{stil}), 128.28, 126.41 (CH_{Ar}), 121.34, 93.21 (C_{Ar}), 83.62 (C≡CH), 78.09 (C≡CH) ppm . APPI-MS *m*/*z*: 329.9901 $[M]^+$ for $C_{16}H_{11}I$ (329.9900).



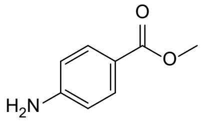
(E)-4-[2-(4-Iodophenyl)diazenyl]benzoic acid ***25***. A mixture of 4-iodoaniline (3.83 g, 17.5 mmol) and 4-nitrosobenzoic acid **24** (2.64 g, 17.5 mmol) in AcOH (120 mL) was stirred at 40 °C for 12 h. The mixture was diluted with water and filtered, the solid was washed with water, methanol and dried. Yield 5.89 g (96%), orange solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.29 (br. s, 1H, OH), 8.19–8.09 (m, 2H; ArH), 8.06–7.92 (m, 4H; ArH), 7.76–7.65 (m, 2H; ArH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6), δ = 166.70 (C=O), 154.14, 151.19 (C_{Ar}), 138.60 (CH_{Ar}), 133.10 (C_{Ar}), 130.70, 124.61, 122.71 (CH_{Ar}), 100.05 (C_{Ar}). ESI-MS *m*/*z*: 350.9639 $[M-H]^-$ for $C_{13}H_9IN_2O_2$ (350.9636).



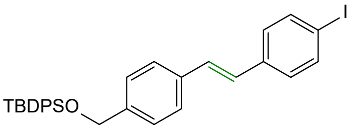
(E)-4-Iodo-4'-hydroxymethylazobenzene ***26***. *Method A.* To a suspension of $LiAlH_4$ (2.45 g, 64.5 mmol) in dry THF (340 mL) at 0 °C acid **25** (18.9 g, 53.7 mmol) was added in portions over 15 min and the resulting thick mixture was stirred at room temperature overnight. The mixture was cooled to 0 °C and the reaction was quenched by successive addition of water (2.45 mL), aqueous NaOH (3 M, 7.35 mL) and another portion of water (9.8 mL). The mixture was filtered, the filter cake was washed with hot THF several times and

dicrarded. The filtrate was concentrated to dryness and suspended in Et_2O. The resulting solid was filtered off, washed with Et_2O, dried and subjected to column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 20:1). The fractions containing the product were combined, the solvent was removed *in vacuo* and the residue was washed with a minimal amount of dichloromethane. Yield. 3.93 g (22%), orange solid.

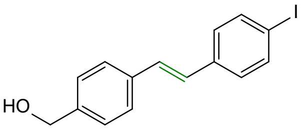
Method B. A mixture of azobenzene ester **30** (1.83 g, 5.00 mmol) and $NaBH_4$ (3.8 g, 100.0 mmol) in THF (40 mL) was stirred at 65 °C for 15 min. To the mixture methanol (40 mL) was added dropwise over 30 min and the stirring continued for 6 h. Another portion of $NaBH_4$ (3.8 g, 100.0 mmol) was added to the mixture and it was stirred at 65 °C for 18 h. After cooling the mixture to the room temperature the solvent was removed under reduced pressure and the excess of reductant was quenched with saturated aqueous NH_4Cl. The organics were extracted with dichloromethane, the extract was washed with brine, dried, concentrated to dryness and subjected to column chromatography (silica) to yield firstly (dichloromethane) the starting ester **30** as an orange solid (0.352 g, 19%). Further elution (gradient from dichloromethane to dichloromethane/ethanol 40:1) gave the product as an orange solid (1.143 g, 68%). M.p. 152–154 °C. ^1H NMR (400 MHz, DMSO-d_6): δ = 7.71–7.66 (m, 2H; ArH), 7.51–7.43 (m, 4H; ArH), 7.27–7.22 (m, 2H; ArH), 7.08 (d, 1H, ^3J = 16.4 Hz; CH), 7.02 (d, 1H, ^3J = 16.4 Hz; CH), 3.14 (s, 1H; CH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 152.27, 150.74, 146.88 (C_{Ar}), 138.45, 127.21, 124.36, 122.64 (CH_{Ar}), 98.81 (C_{Ar}), 62.50 (CH_2O) ppm. ESI-MS *m*/*z*: 338.9988 $[M+H]^+$ for $C_{13}H_{11}IN_2O$ (338.9989).



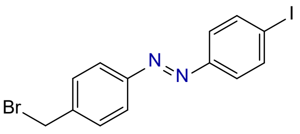
Methyl 4-aminobenzoate ***28***. To 4-aminobenzoic acid (2.74 g, 20.0 mmol) in MeOH (100 mL) $SOCl_2$ (4.38 mL, 60.0 mmol) was added dropwise at 0 °C and the mixture was stirred at room temperature overnight. The mixture was neutralized with saturated aqueous $NaHCO_3$, MeOH was evaporated and the residue was parted between dichloromethane and saturated aqueous $NaHCO_3$. The organic layer was separated, washed with brine and concentrated to dryness. Yield 2.93 g (97%), off-white solid. Analytical data were the same as previously published [9].



(E)-4-Iodo-4'-[(tert-butyldiphenylsilyl)oxy]methylstilbene ***37***. To a mixture of phosphonate **36** (1.60 g, 3.23 mmol) and 4-iodobenzaldehyde (1.124 g, 4.84 mmol) dry THF (66 mL) and *t*-BuONa (0.465 g, 4.84 mmol) were added under Ar and the mixture was stirred at room temperature for 24 h. The solvent was evaporated and the residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with brine and concentrated to dryness. The product was purified by column chromatography (silica, gradient from hexane to hexane/dichloromethane 1:1). Yield 1.39 g (75%), white solid. M.p. 115–117 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.65 (m, 6H; ArH), 7.50–7.46 (m, 2H; ArH_{stil}), 7.46–7.36 (m, 6H, ArH_{Ph}), 7.36–7.31 (m, 2H; ArH_{stil}), 7.27–7.22 (m, 2H, ArH_{stil}), 7.12 (d, 1H, ^3J = 16.4 Hz; CH), 7.00 (d, 1H, ^3J = 16.4 Hz; CH), 4.78 (s, 2H; CH_2O), 1.10 (s, 9H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.94 (C_{Ar}), 137.68 (CH_{Ar}), 136.90 (C_{Ar}), 135.54 (CH_{Ar}), 133.39 (C_{Ar}), 129.70 (CH_{Ar}), 129.32 (CH_{stil}), 128.13, 127.71 (CH_{Ar}), 126.99 (CH_{stil}), 126.46, 126.32 (CH_{Ar}), 92.61 (C_{Ar}), 65.27 (CH_2O), 26.81 ($\underline{C}(CH_3)_3$), 19.30 ($C(\underline{C}H_3)_3$) ppm . APPI-MS *m*/*z*: 574.1179 $[M]^+$ for $C_{31}H_{31}IOSi$ (574.1183).

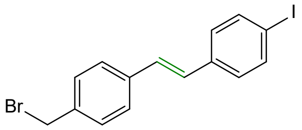


(E)-4-Iodo-4'-hydroxymethylstilbene ***38***. To a solution of stilbene **37** (1.33 g, 2.32 mmol) in THF (40 mL) a solution of TBAF (73.1 mg, 0.232 mmol) in water (0.4 mL) was added and the mixture was stirred at room temperature overnight. The solvent was reduced under reduced pressure and the product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 20:1). Yield 0.675 g (87%), white solid. M.p. 226–228 °C (subl.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.65 (m, 2H; ArH), 7.54–7.47 (m, 2H; ArH_s), 7.39–7.34 (m, 2H, ArH), 7.27–7.22 (m, 2H, ArH), 7.11 (d, 1H, ^3J = 16.3 Hz; CH), 7.02 (d, 1H, ^3J = 16.3 Hz; CH), 4.71 (d, 2H, ^3J = 5.8 Hz; $C\underline{H}_2OH$), 1.62 (t, 1H, ^3J = 5.8 Hz; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 142.41 (C_{Ar}), 137.43 (CH_{Ar}), 136.77, 135.22 (C_{Ar}), 129.18 (CH_{stil}), 128.47, 126.80 (CH_{Ar}), 126.73 (CH_{stil}), 126.39 (CH_{Ar}), 93.26 (C_{Ar}), 62.67 (CH_2O) ppm . APPI-MS *m*/*z*: 336.0007 $[M]^+$ for $C_{15}H_{13}IO$ (336.0006).

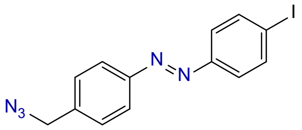


(E)-4-Iodo-4'-bromomethylazobenzene ***39***. To a mixture of alcohol **26** (2.72 g, 8.05 mmol), PPh_3 (3.16 g, 12.1 mmol) and dry THF (80 mL) NBS (2.15 g, 12.1 mmol) was added and the mixture was stirred at room temperature overnight. The solvent was removed under reduced

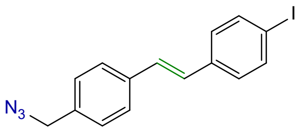
pressure and the product was re-crystallized from methanol. Yield 2.73 g (85%), orange solid. Analytical data were the same as previously published [10].



(E)-4-Iodo-4'-bromomethylstilbene ***40*** was prepared as described for compound **39** from stilbene **38** (0.675 g, 2.01 mmol), $\mathrm{PPh_3}$ (0.789 g, 3.01 mmol) and NBS (0.536 g, 3.01 mmol) in dry THF (40 mL). Yield 0.712 g (89%), white solid. M.p. 181–183 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 7.72–7.65 (m, 2H; ArH), 7.51–7.44 (m, 2H; $\mathrm{ArH_s}$), 7.42–7.35 (m, 2H, ArH), 7.27–7.22 (m, 2H, ArH), 7.09 (d, 1H, ^3J = 16.4 Hz; CH), 7.02 (d, 1H, ^3J = 16.4 Hz; CH), 4.51 (s, 2H; $\mathrm{CH_2Br}$) ppm; ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 137.76 ($\mathrm{CH_{Ar}}$), 137.31, 137.13, 136.58 ($\mathrm{C_{Ar}}$), 129.49 ($\mathrm{CH_{Ar}}$), 128.67, 128.25 ($\mathrm{CH_{stil}}$), 128.24, 126.93 ($\mathrm{CH_{Ar}}$), 93.05 ($\mathrm{C_{Ar}}$), 33.39 ($\mathrm{CH_2Br}$) ppm . APPI-MS *m*/*z*: 397.9159 $[\mathrm{M}]^+$ for $\mathrm{C_{15}H_{12}BrI}$ (397.9162).



(E)-4-Iodo-4'-azidomethylazobenzene ***41***. To a solution of bromide **39** (1.11 g, 2.77 mmol) in acetone (68.0 mL) a solution of $\mathrm{NaN_3}$ (0.271 g, 4.17 mmol) in water (4.25 mL) was added and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the residue was parted between dichloromethane and water. The organic layer was separated, washed with brine, dried and concentrated to dryness. Yield 0.966 g (96%), orange solid. M.p. 117–119 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 7.97–7.90 (m, 2H; ArH), 7.89–7.83 (m, 2H; $\mathrm{ArH_s}$), 7.69–7.62 (m, 2H, ArH), 7.49–7.43 (m, 2H, ArH), 4.43 (s, 2H; $\mathrm{CH_2N_3}$) ppm; ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 152.08, 151.74, 138.53 ($\mathrm{C_{Ar}}$), 138.32, 128.82, 124.46, 123.36 ($\mathrm{CH_{Ar}}$), 97.93 ($\mathrm{C_{Ar}}$), 54.29 ($\mathrm{CH_2N_3}$) ppm . APPI-MS *m*/*z*: 362.9977 $[\mathrm{M}]^+$ for $\mathrm{C_{13}H_{10}IN_5}$ (362.9975).



(E)-4-Iodo-4'-azidomethylstilbene ***42*** was prepared as described for compound **41** from stilbene **40** (0.360 g, 0.902 mmol) and $\mathrm{NaN_3}$ (0.088 g, 1.35 mmol) in a mixture of acetone (32.0 mL) and water (2.0 mL). Yield 0.302 g (93%), white solid. M.p. 155–157 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 7.71–7.65 (m, 2H; ArH), 7.55–7.49 (m, 2H; $\mathrm{ArH_s}$), 7.34–7.29 (m, 2H, ArH), 7.28–7.22 (m, 2H, ArH), 7.11 (d, 1H, ^3J = 16.3 Hz; CH), 7.03 (d, 1H, ^3J = 16.3 Hz; CH), 4.35 (s, 2H; $\mathrm{CH_2N_3}$) ppm; ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 137.76 ($\mathrm{CH_{Ar}}$), 137.00, 136.62, 134.90 ($\mathrm{C_{Ar}}$), 129.73 ($\mathrm{CH_{stil}}$), 128.64, 128.22 ($\mathrm{CH_{Ar}}$), 128.08 ($\mathrm{CH_{stil}}$), 126.95 ($\mathrm{CH_{Ar}}$), 92.99 ($\mathrm{C_{Ar}}$), 54.52 ($\mathrm{CH_2N_3}$) ppm . APPI-MS *m*/*z*: 361.0073 $[\mathrm{M}]^+$ for $\mathrm{C_{15}H_{12}IN_3}$ (361.0070).

NMR spectra of novel compounds

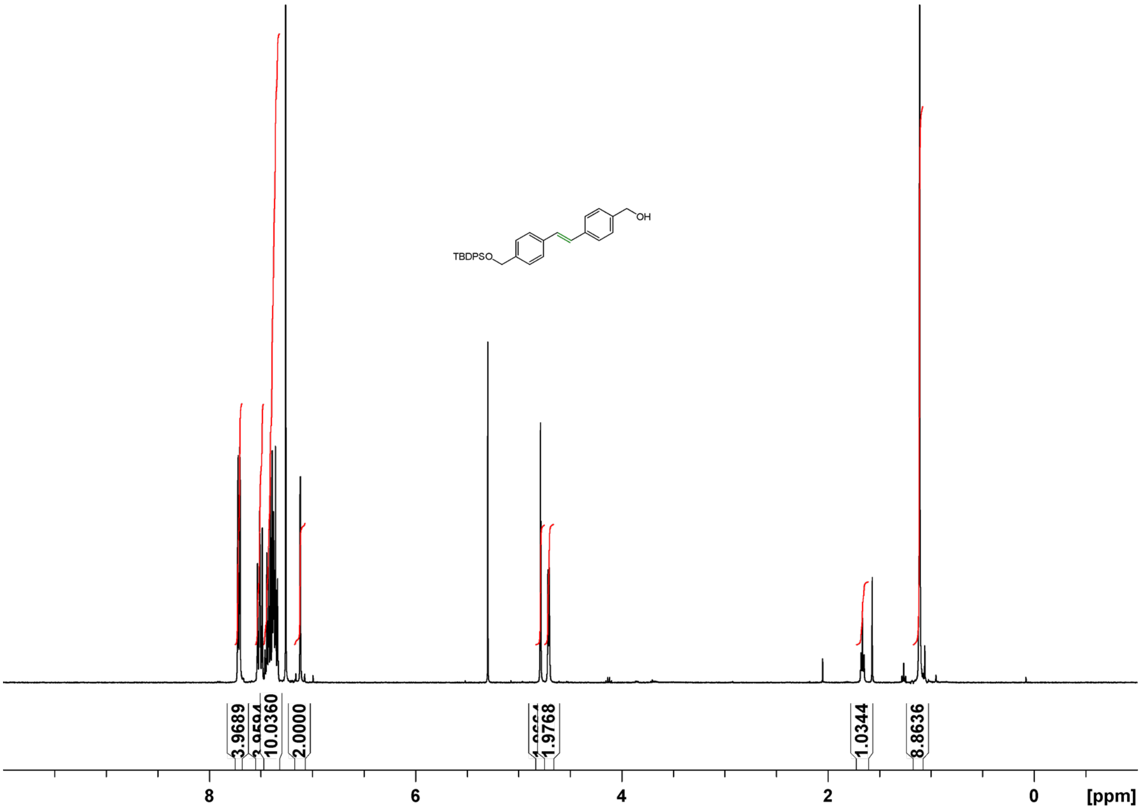


Figure S1. ^{1}H NMR spectrum of stilbene **7** (400 MHz, $CDCl_3$).

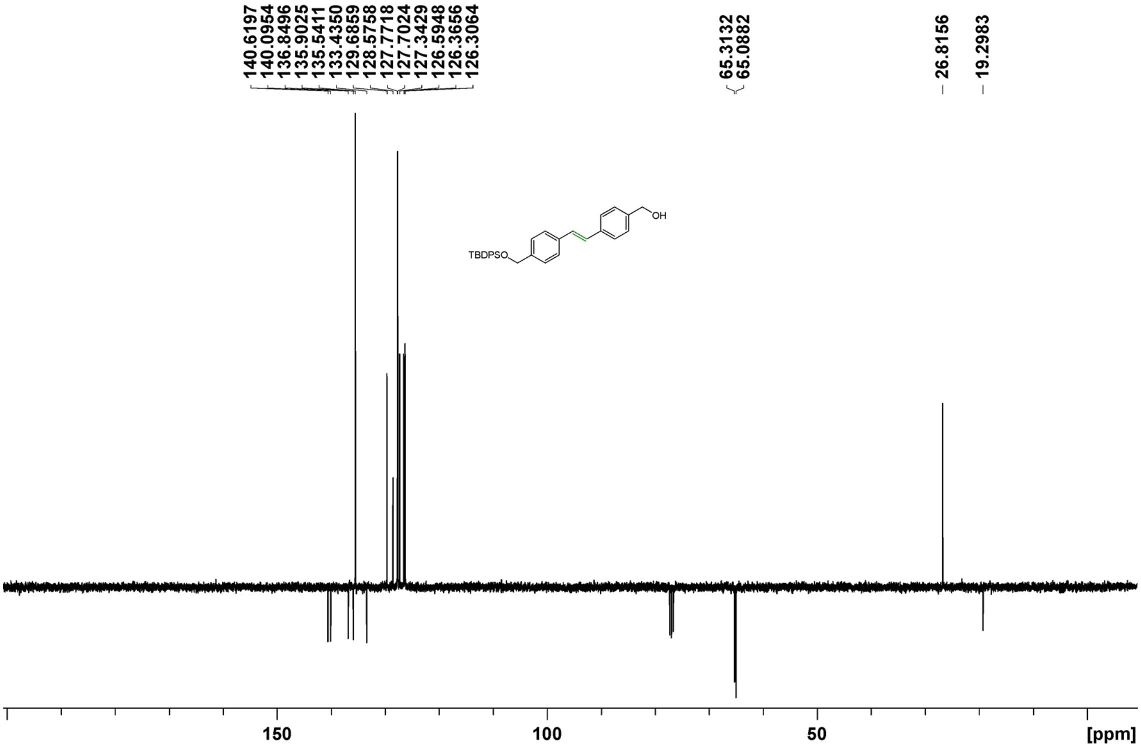


Figure S2. ^{13}C NMR spectrum (APT) of stilbene **7** (100 MHz, $CDCl_3$).

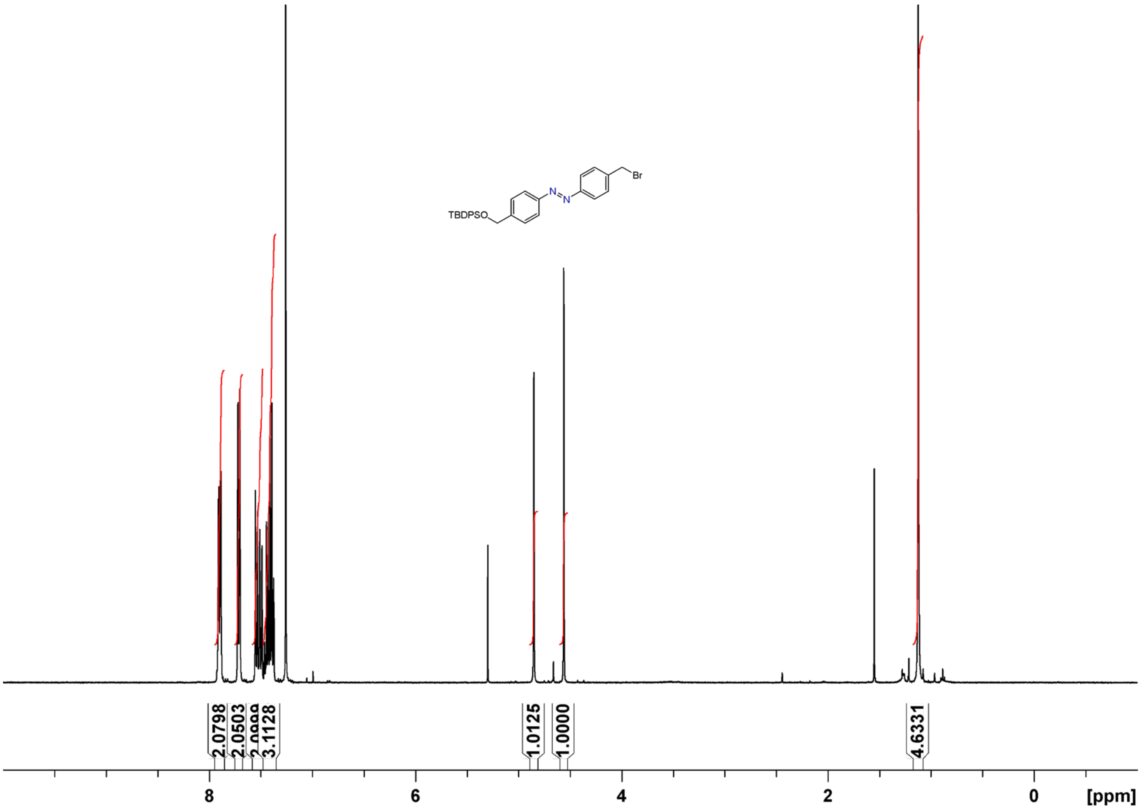


Figure S3. ^{1}H NMR spectrum of azobenzene **8** (400 MHz, $CDCl_3$).

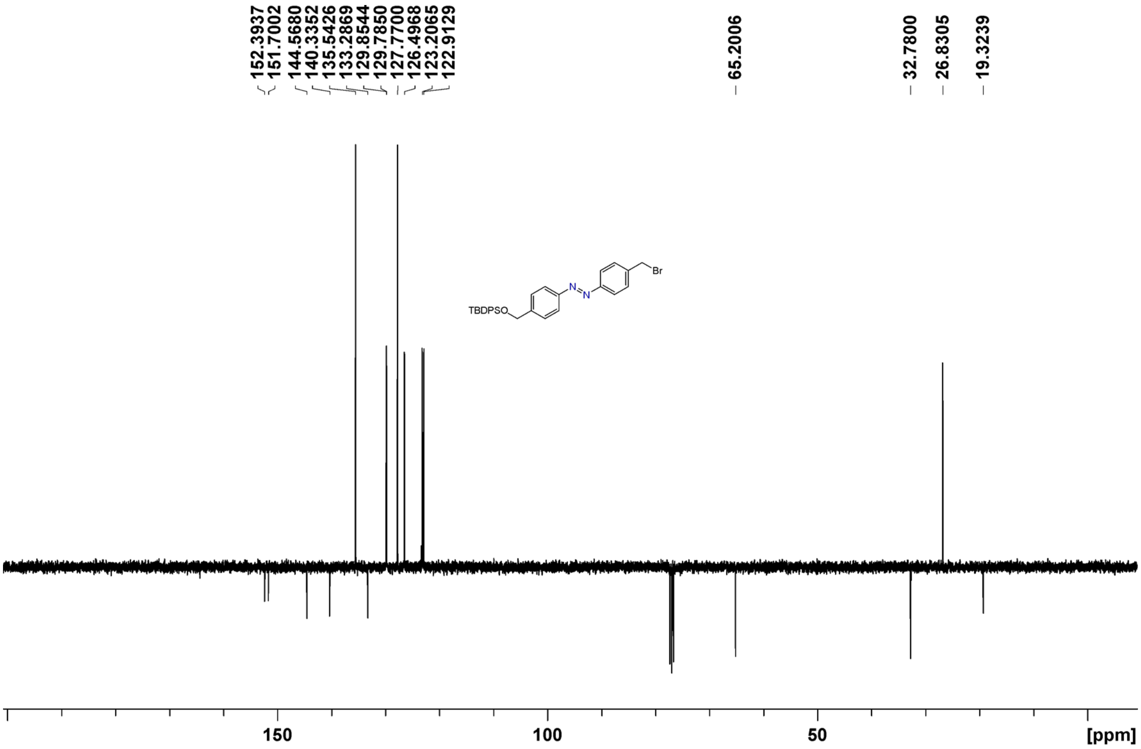


Figure S4. ^{13}C NMR spectrum (APT) of azobenzene **8** (100 MHz, $CDCl_3$).

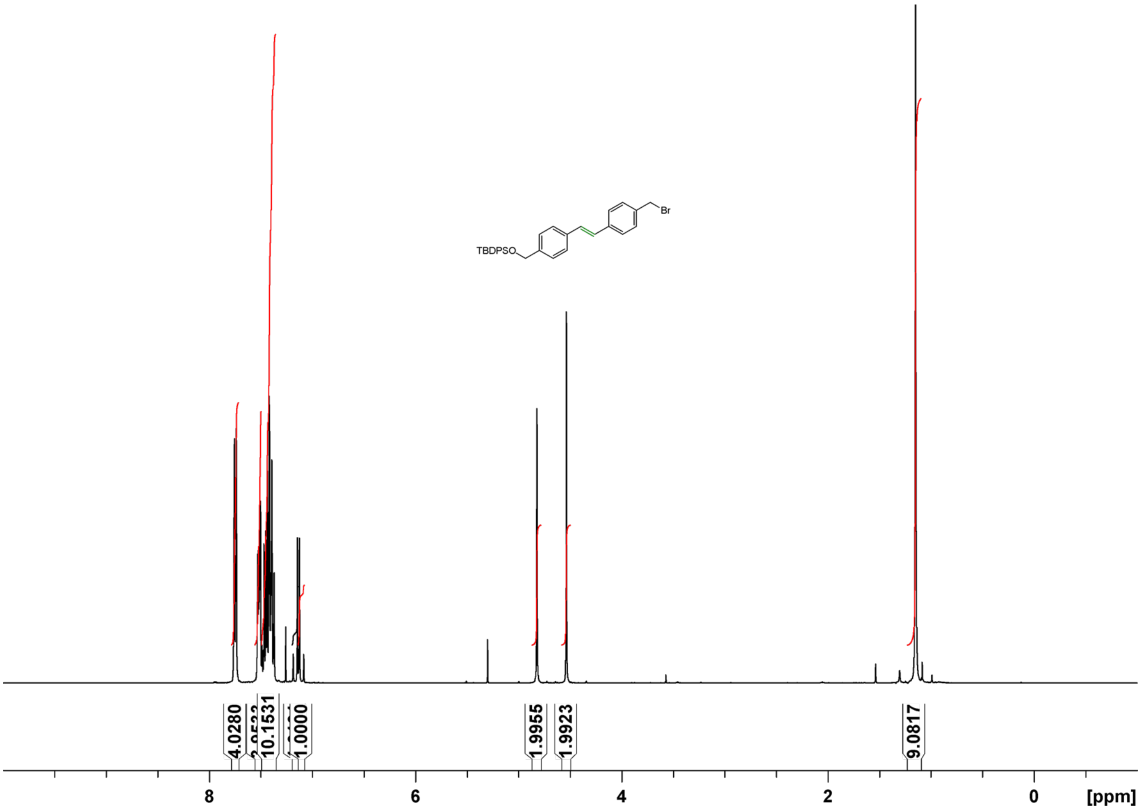


Figure S5. ^{1}H NMR spectrum of stilbene **9** (400 MHz, $CDCl_3$).

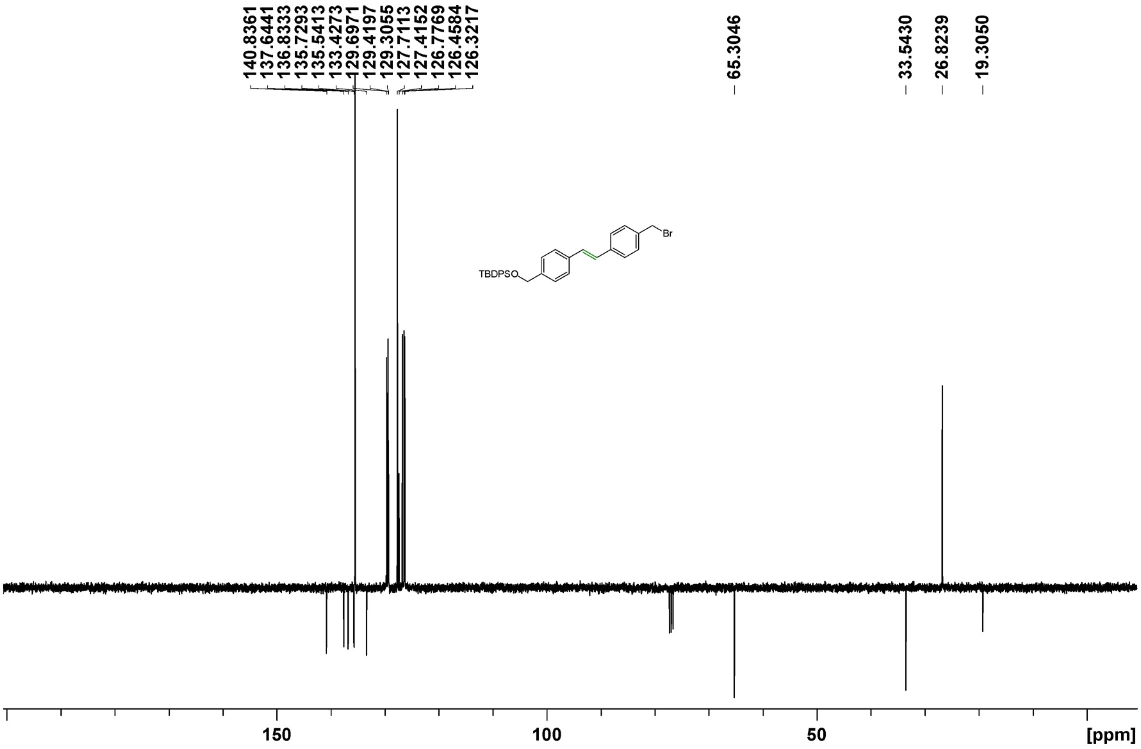


Figure S6. ^{13}C NMR spectrum (APT) of stilbene **9** (100 MHz, $CDCl_3$).

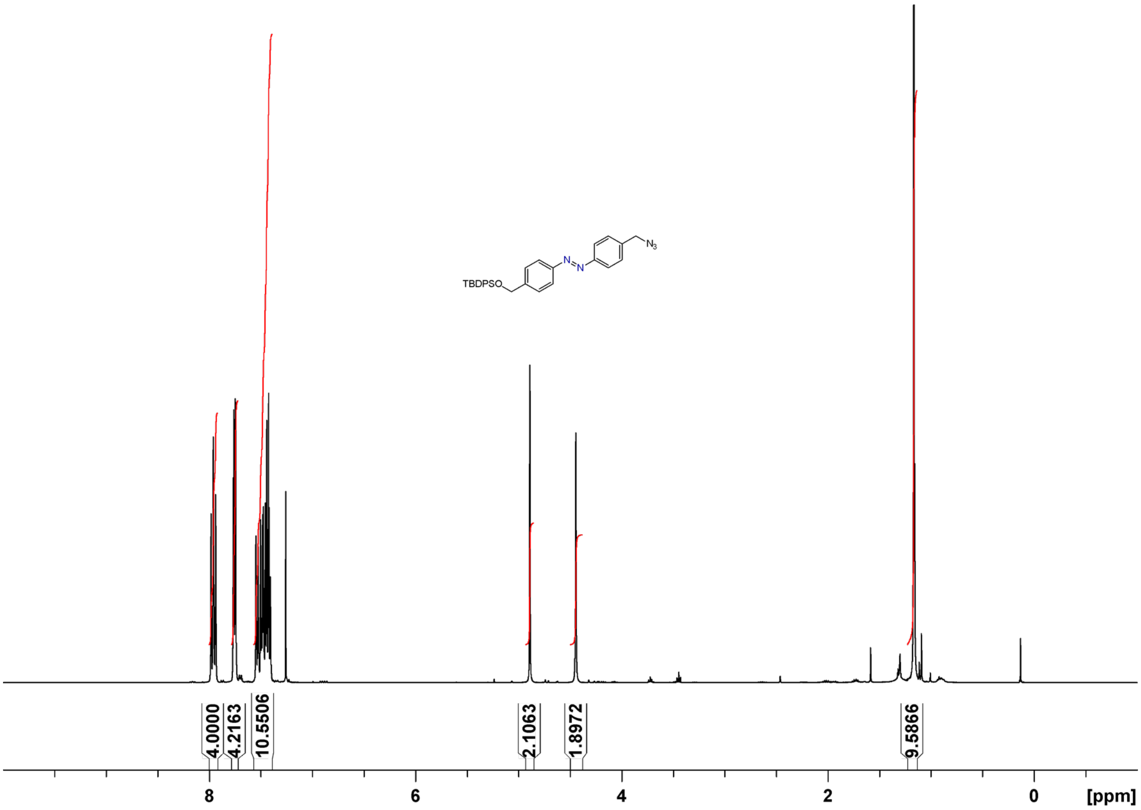


Figure S7. ^{1}H NMR spectrum of azobenzene **10** (400 MHz, $CDCl_3$).

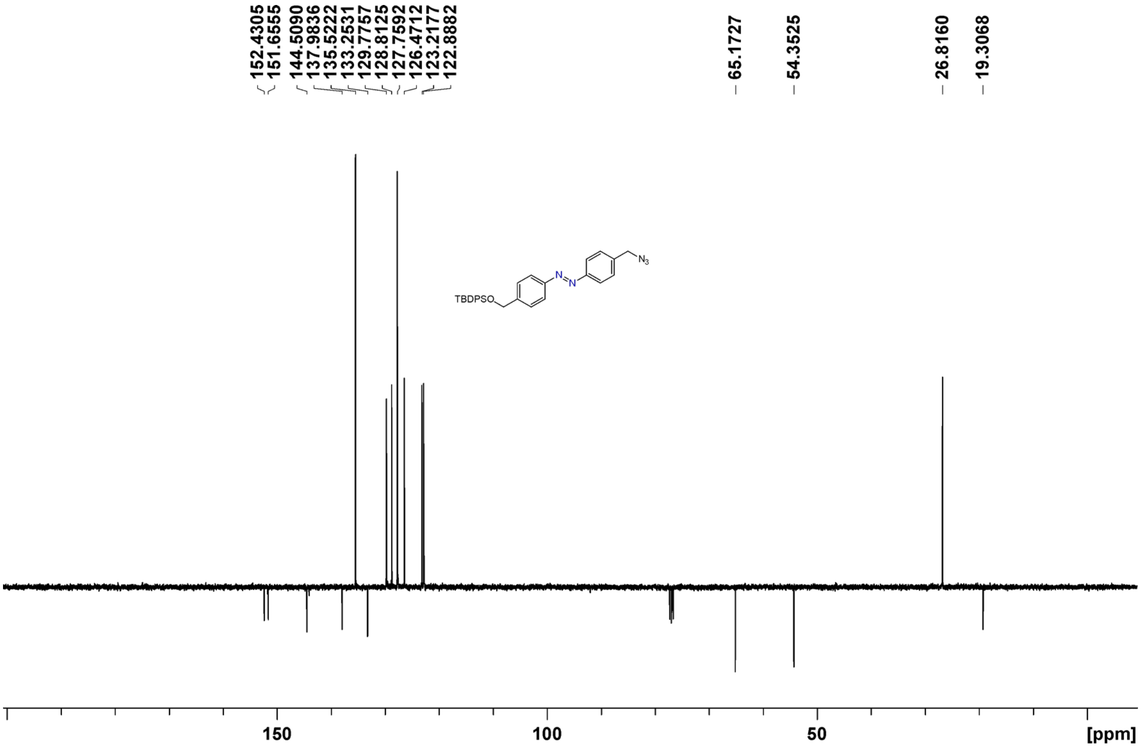


Figure S8. ^{13}C NMR spectrum (APT) of azobenzene **10** (100 MHz, $CDCl_3$).

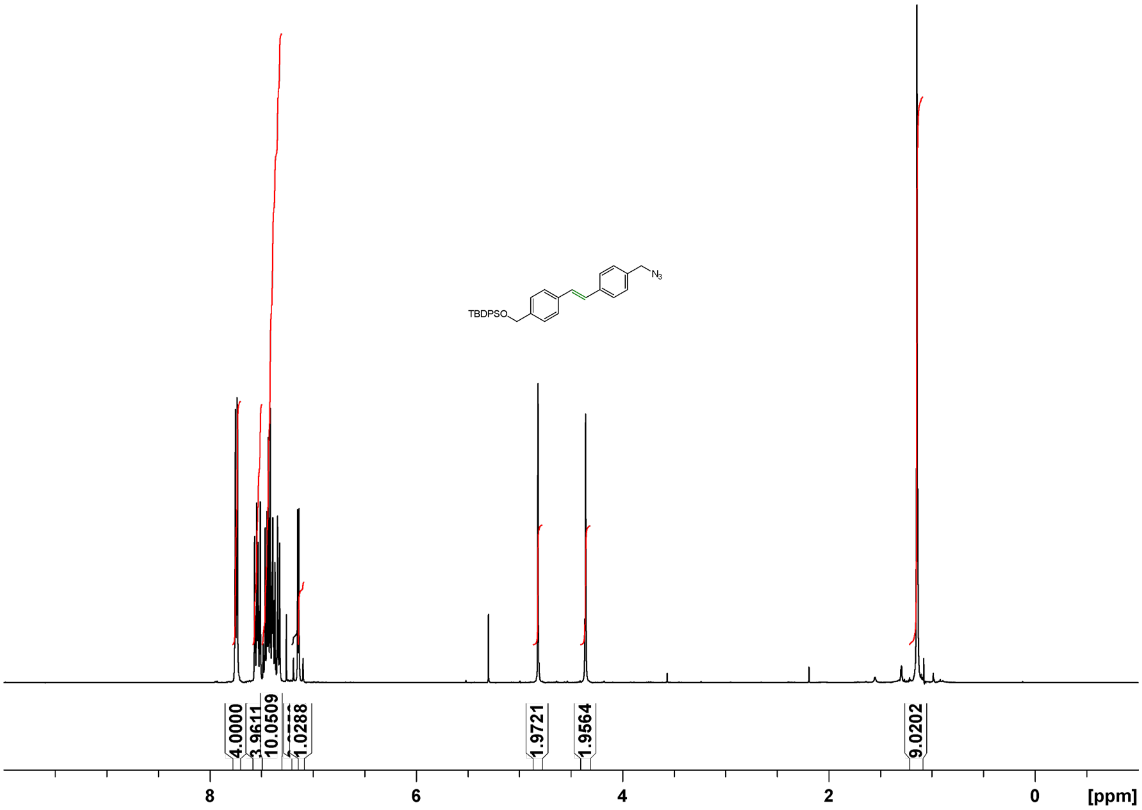


Figure S9. ^{1}H NMR spectrum of stilbene **11** (400 MHz, CDCl$_3$).

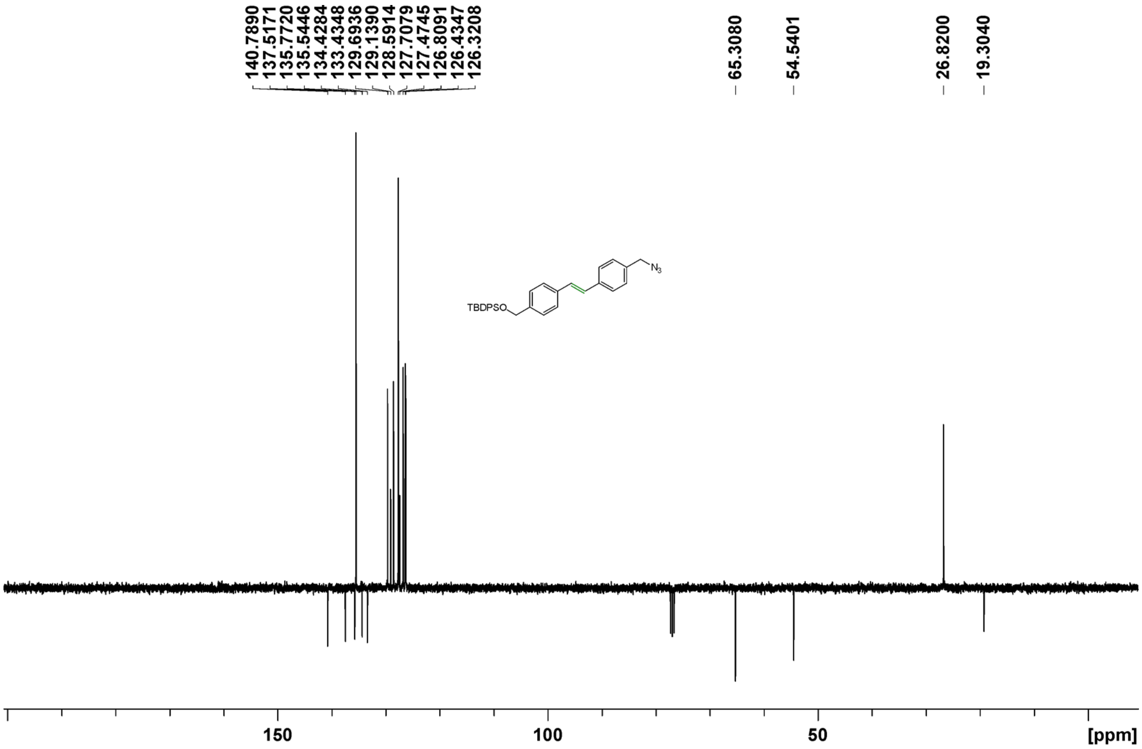


Figure S10. ^{13}C NMR spectrum (APT) of stilbene **11** (100 MHz, CDCl$_3$).

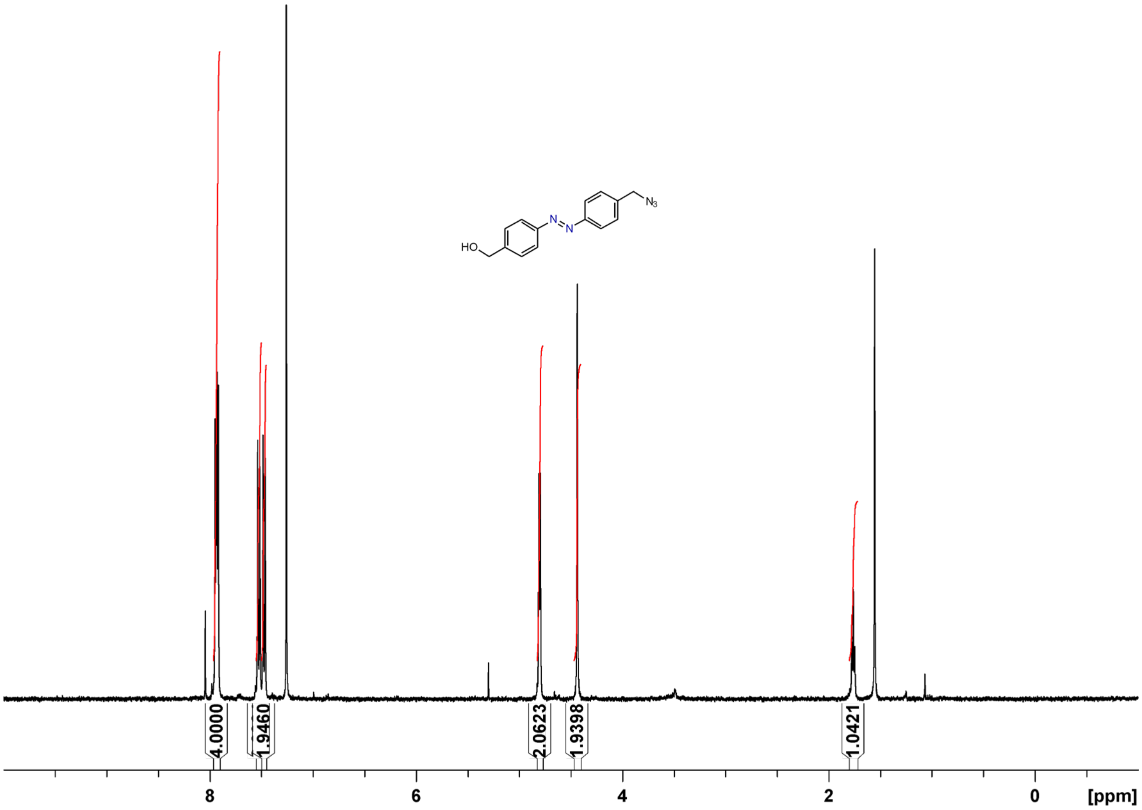


Figure S11. ^{1}H NMR spectrum of azobenzene **12** (400 MHz, CDCl$_3$).

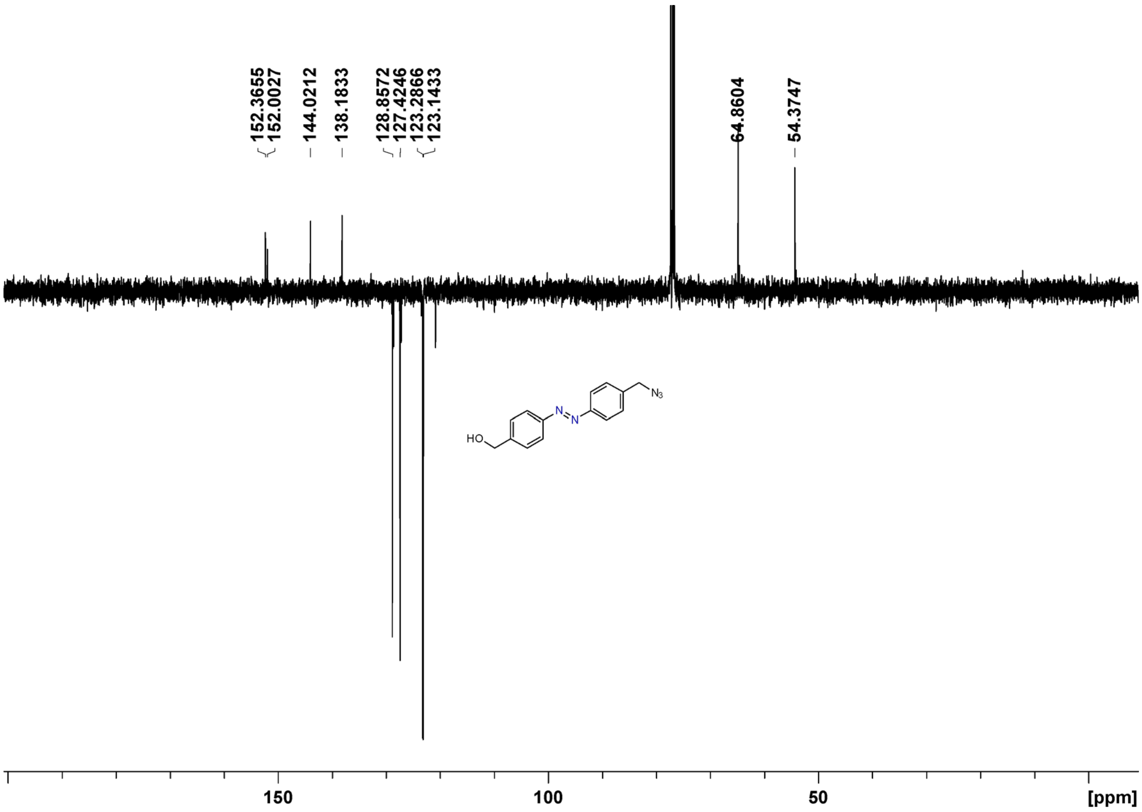


Figure S12. ^{13}C NMR spectrum (APT) of azobenzene **12** (100 MHz, CDCl$_3$).

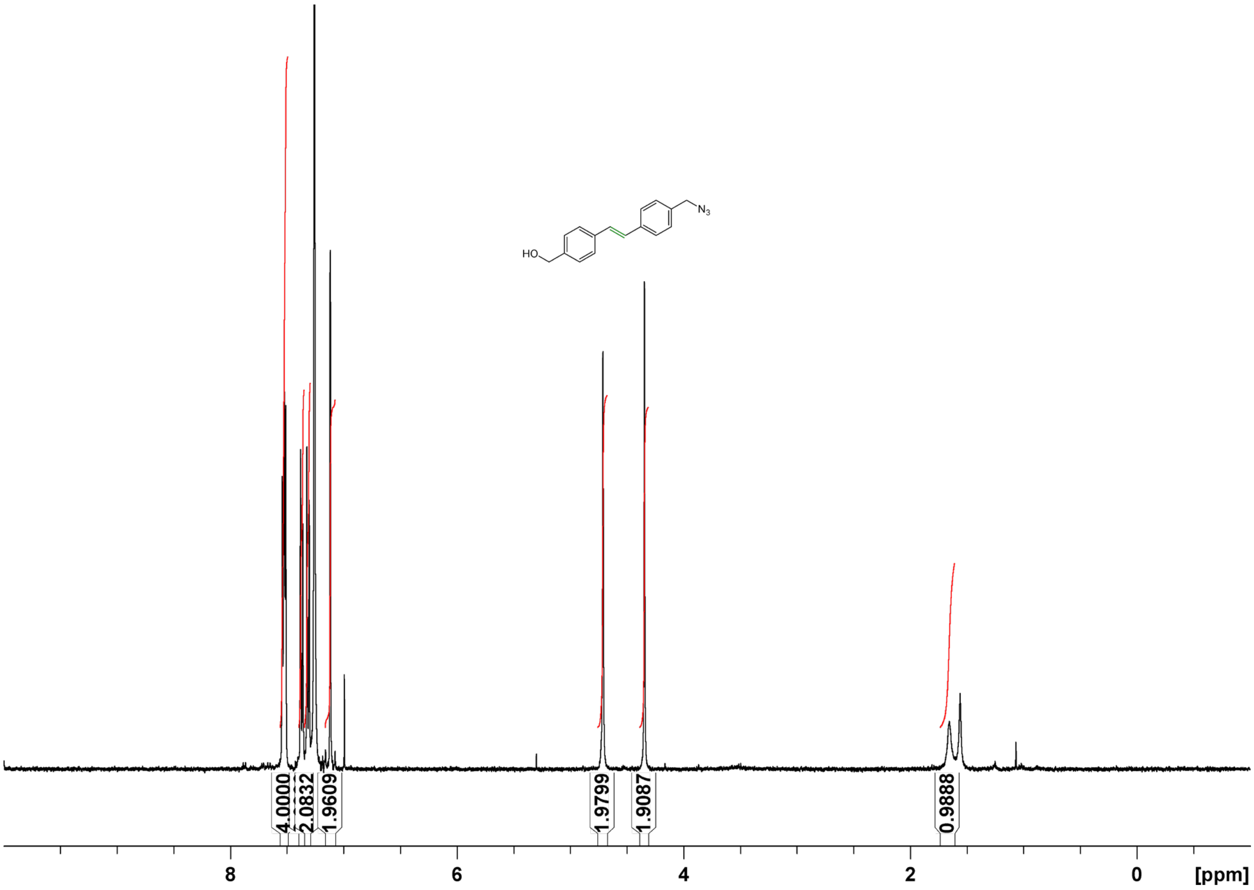


Figure S13. ^{1}H NMR spectrum of stilbene **13** (400 MHz, $CDCl_3$).

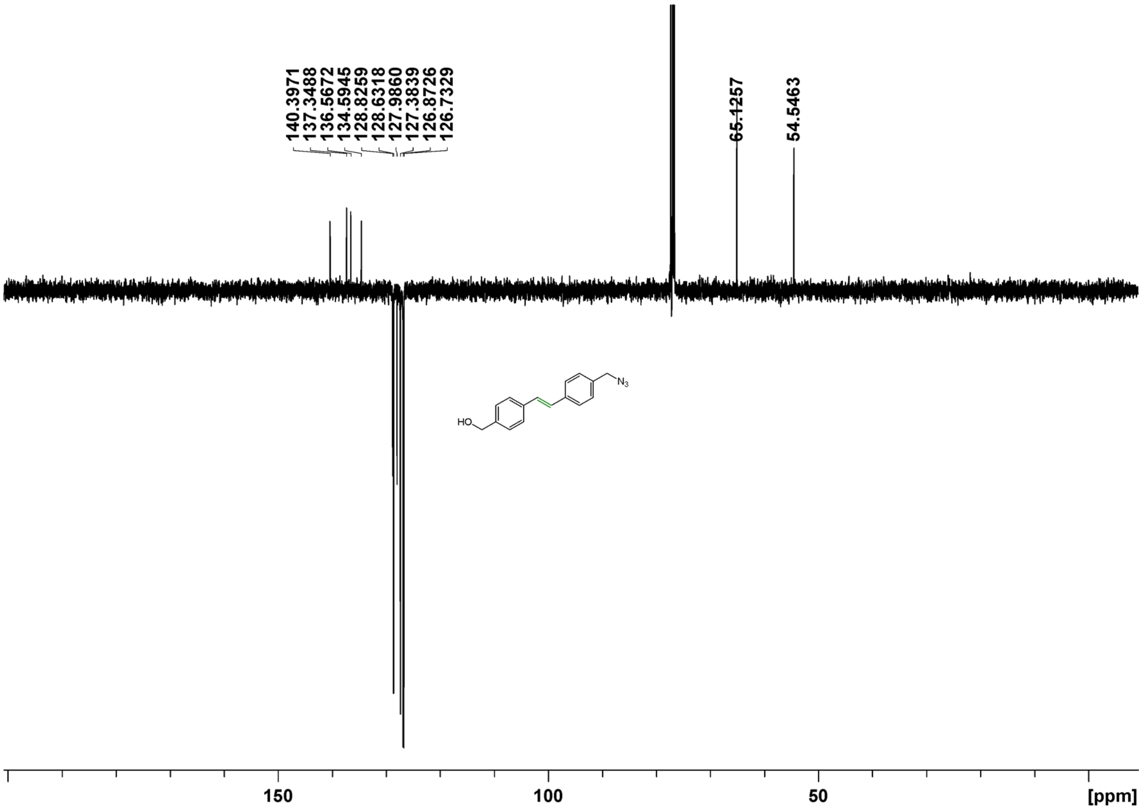


Figure S14. ^{13}C NMR spectrum (APT) of stilbene **13** (100 MHz, $CDCl_3$).

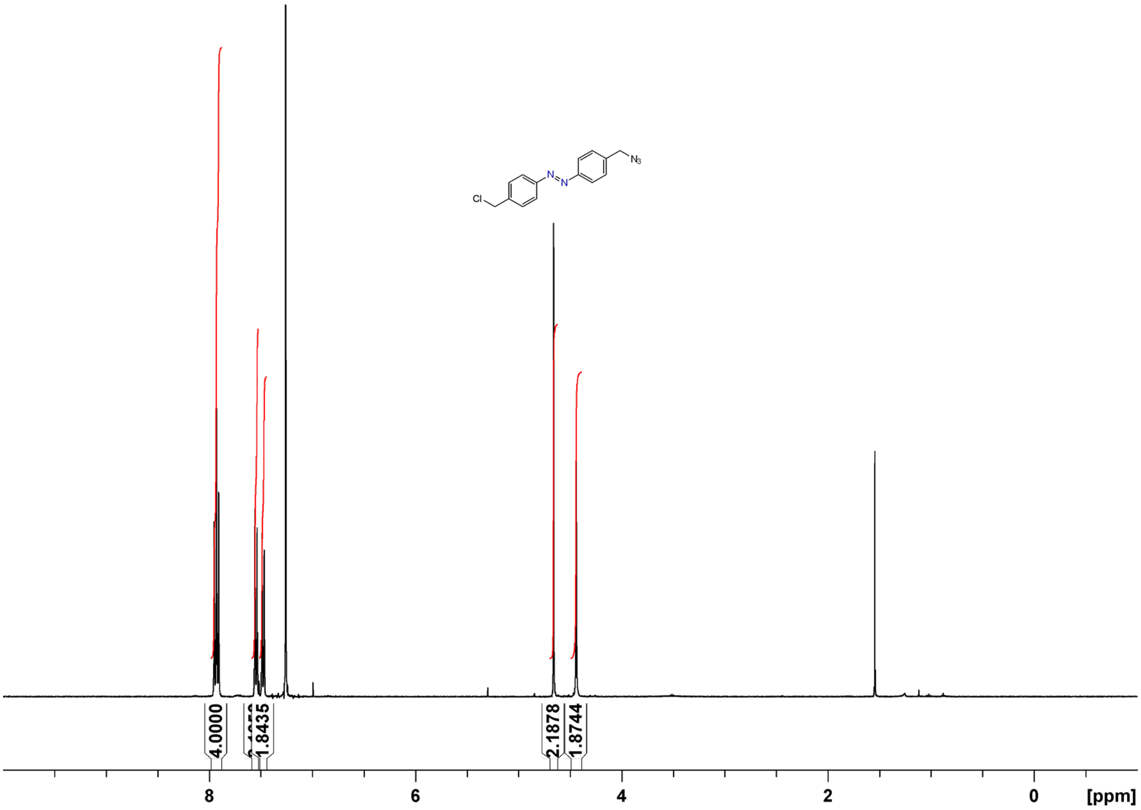


Figure S15. ^{1}H NMR spectrum of azobenzene **14** (400 MHz, $CDCl_3$).

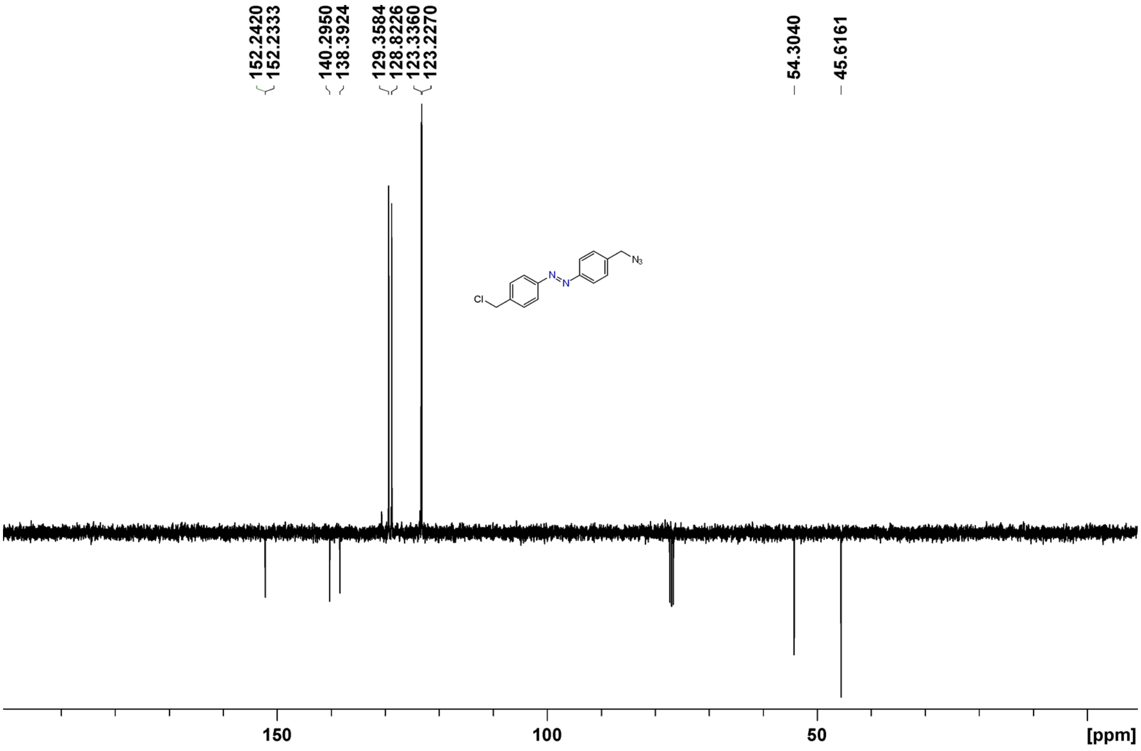


Figure S16. ^{13}C NMR spectrum (APT) of azobenzene **14** (100 MHz, $CDCl_3$).

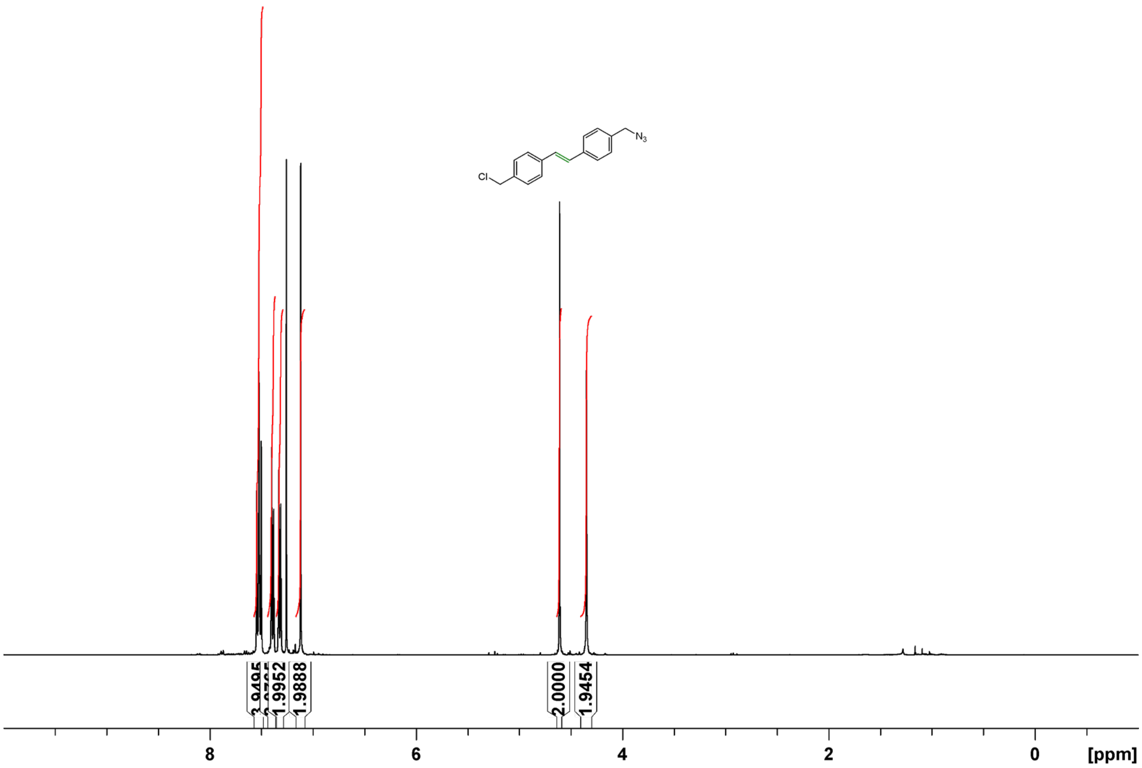


Figure S17. ^{1}H NMR spectrum of stilbene **15** (400 MHz, CDCl$_3$).

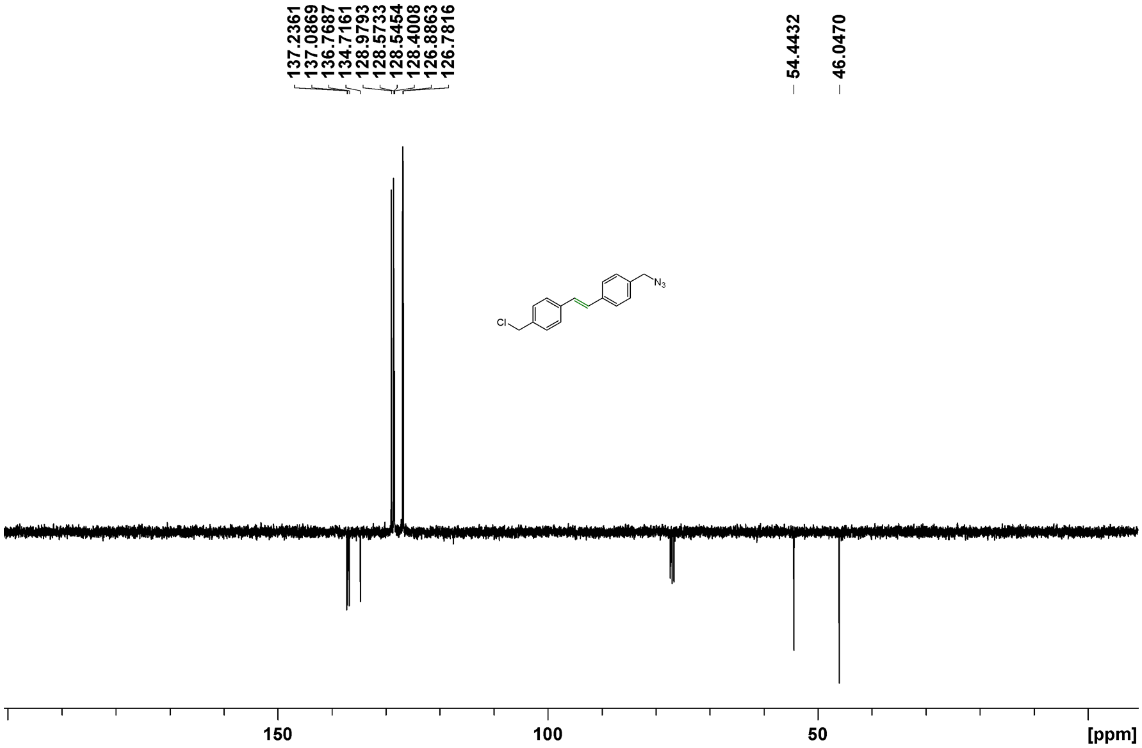


Figure S18. ^{13}C NMR spectrum (APT) of stilbene **15** (100 MHz, CDCl$_3$).

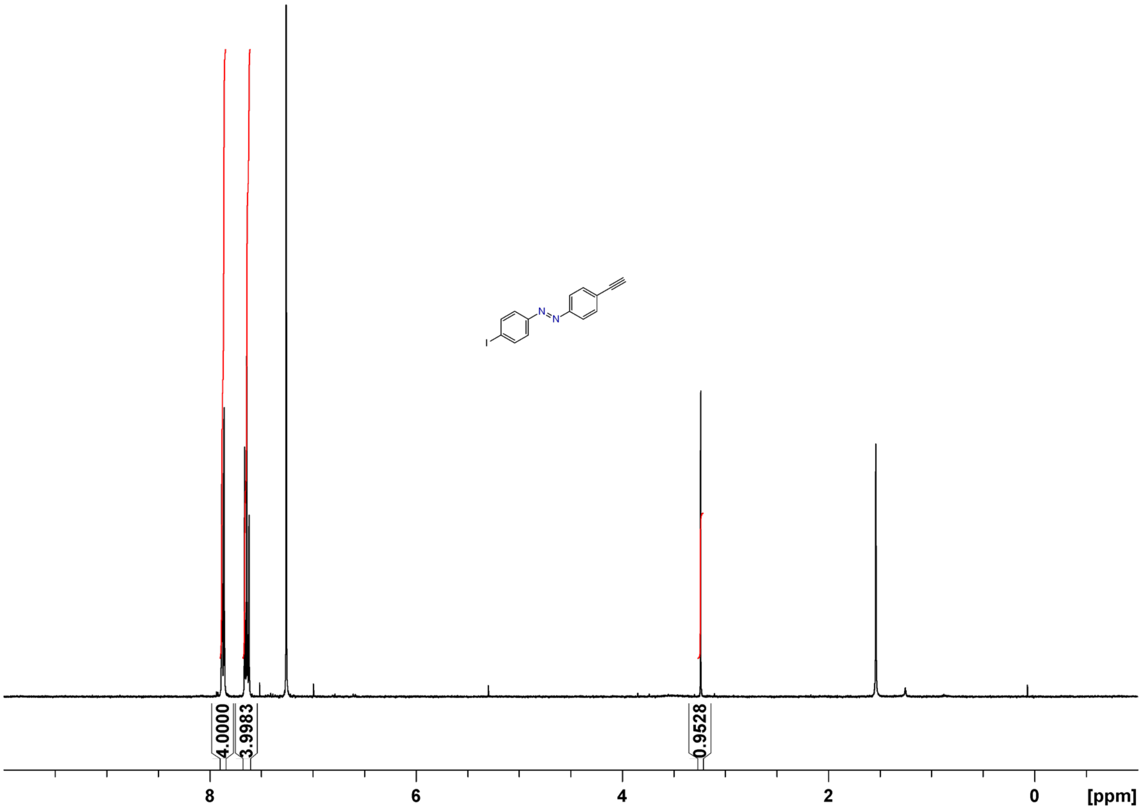


Figure S19. ^{1}H NMR spectrum of azobenzene **19** (400 MHz, $CDCl_3$).

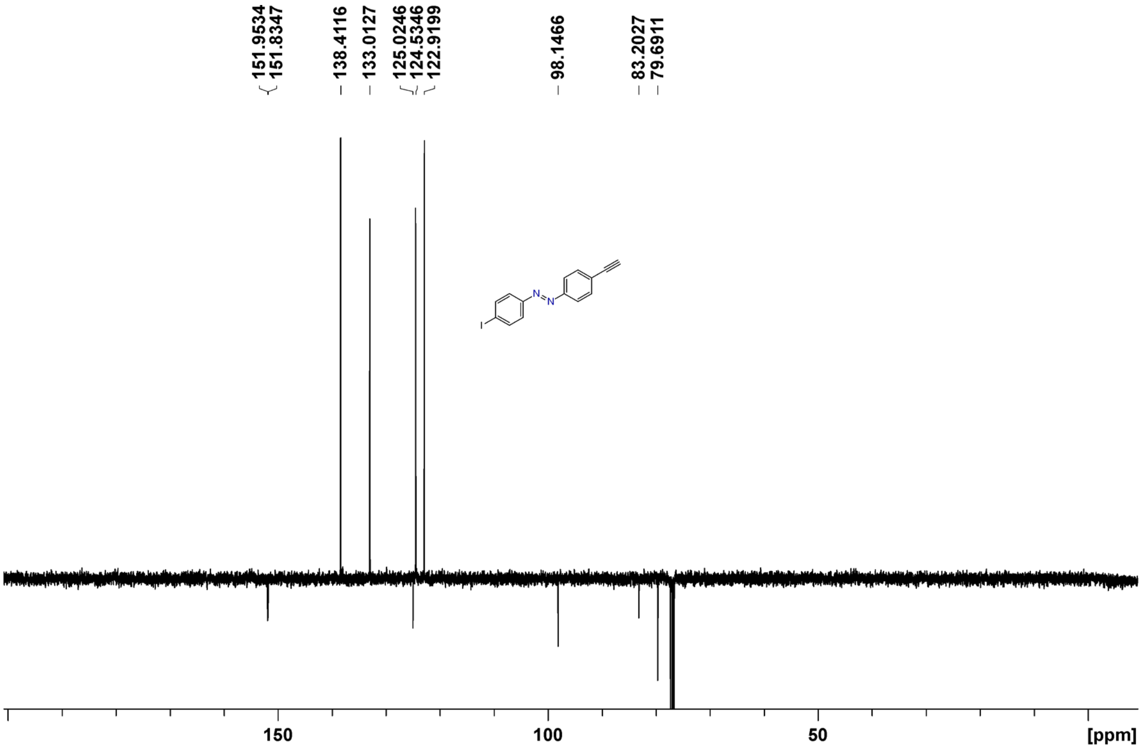


Figure S20. ^{13}C NMR spectrum (APT) of azobenzene **19** (100 MHz, $CDCl_3$).

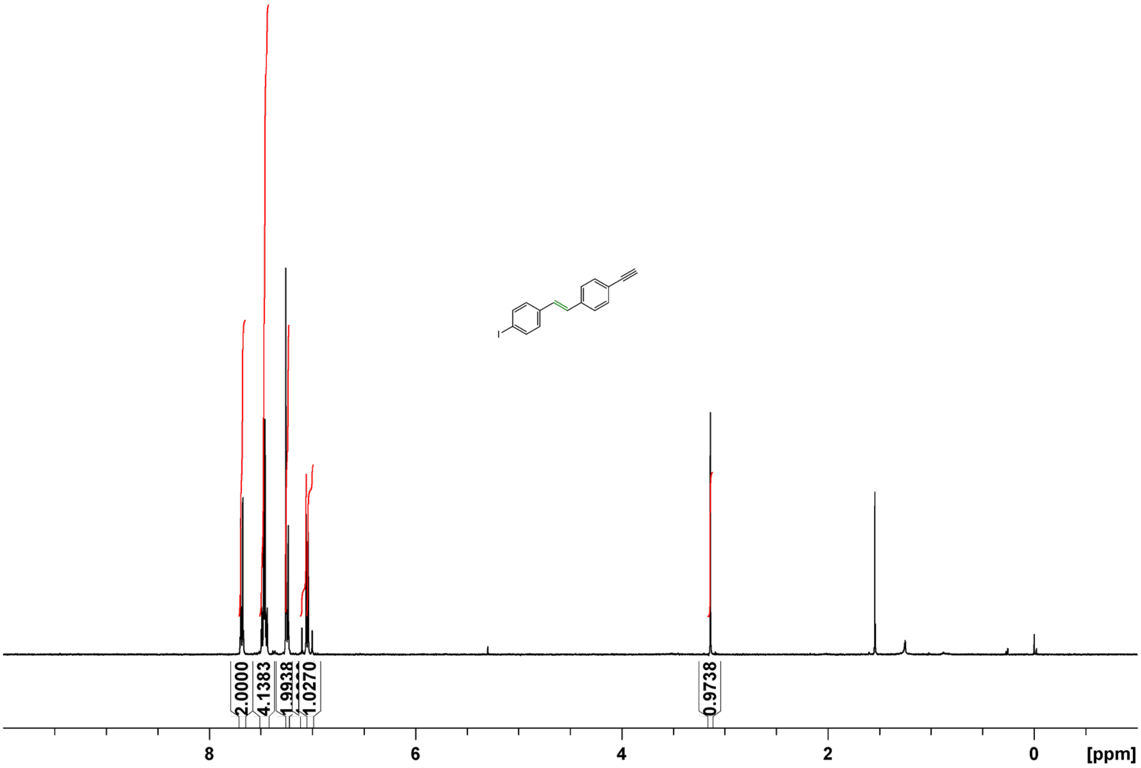


Figure S21. ^{1}H NMR spectrum of stilbene **23** (400 MHz, $CDCl_3$).

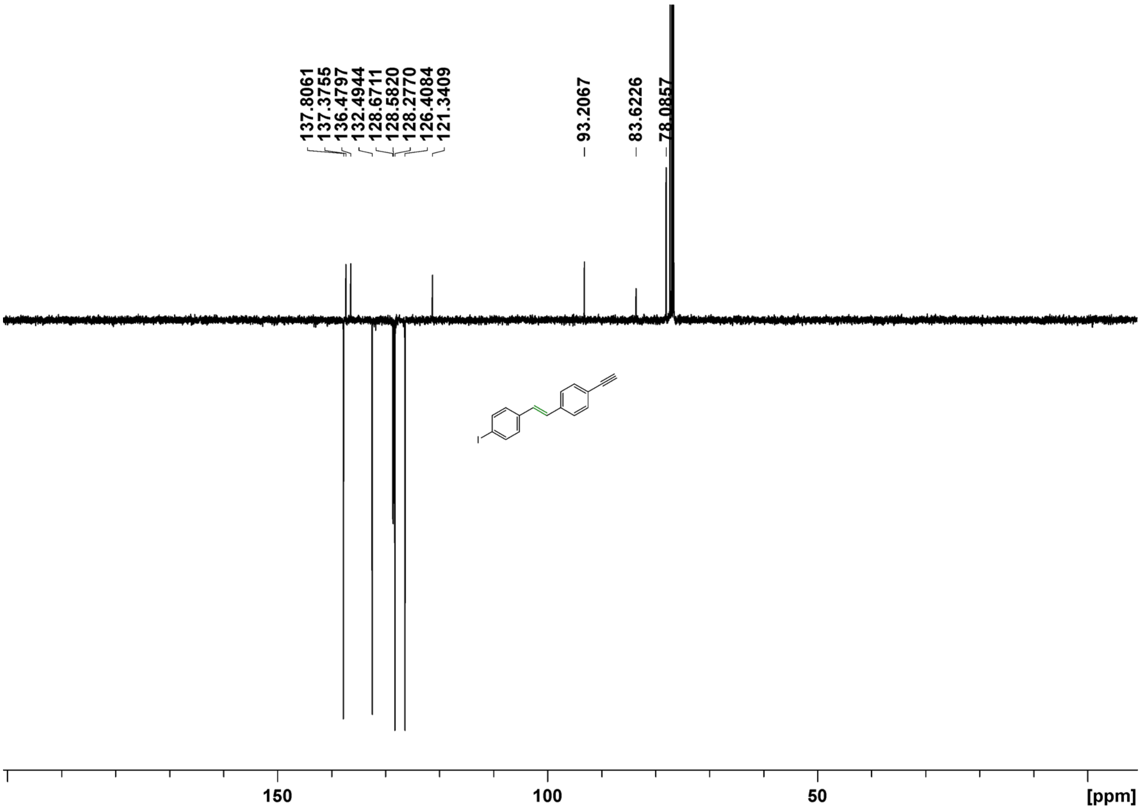


Figure S22. ^{13}C NMR spectrum (APT) of stilbene **23** (100 MHz, $CDCl_3$).

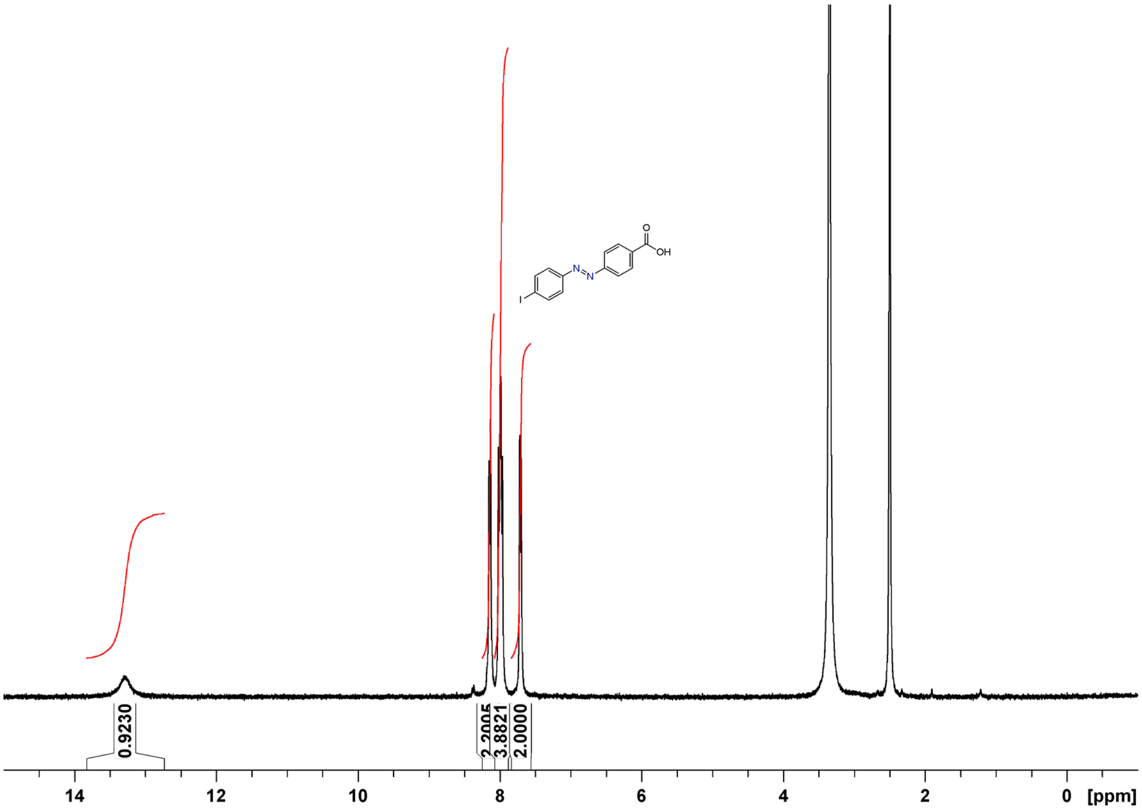


Figure S23. ^{1}H NMR spectrum of azobenzene **25** (400 MHz, DMSO-d$_6$).

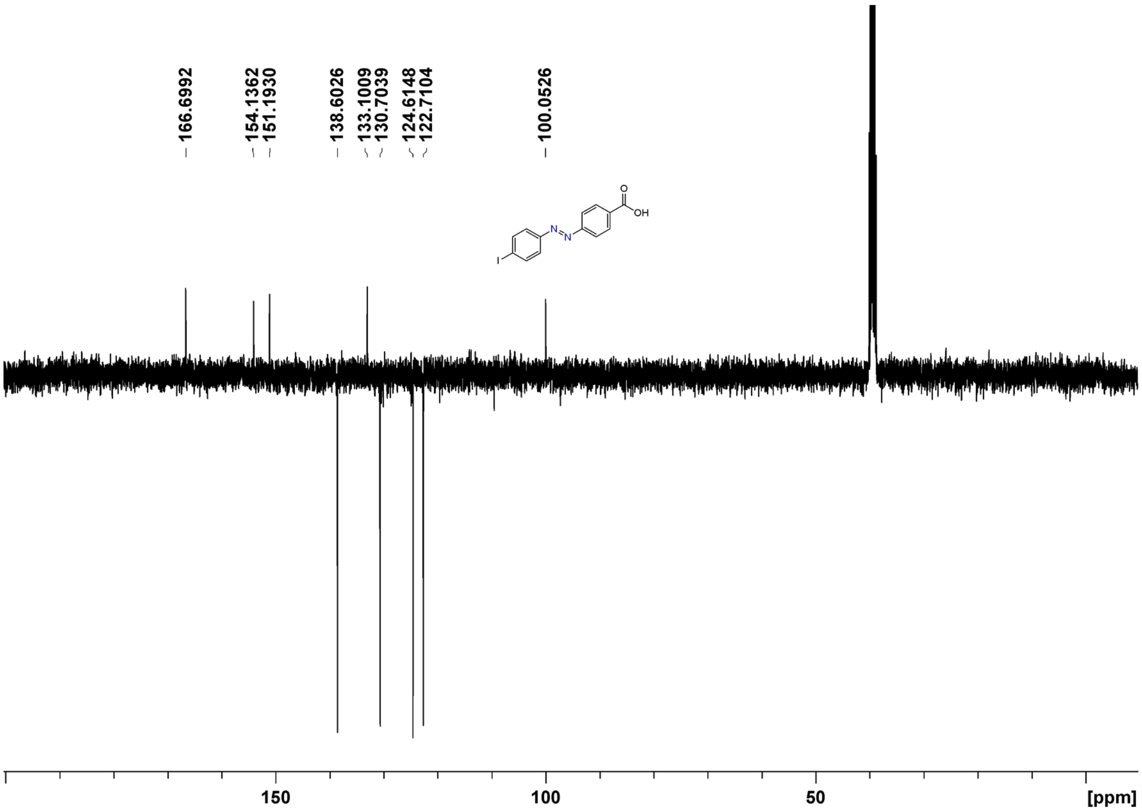


Figure S24. ^{13}C NMR spectrum (APT) of azobenzene **25** (100 MHz, DMSO-d$_6$).

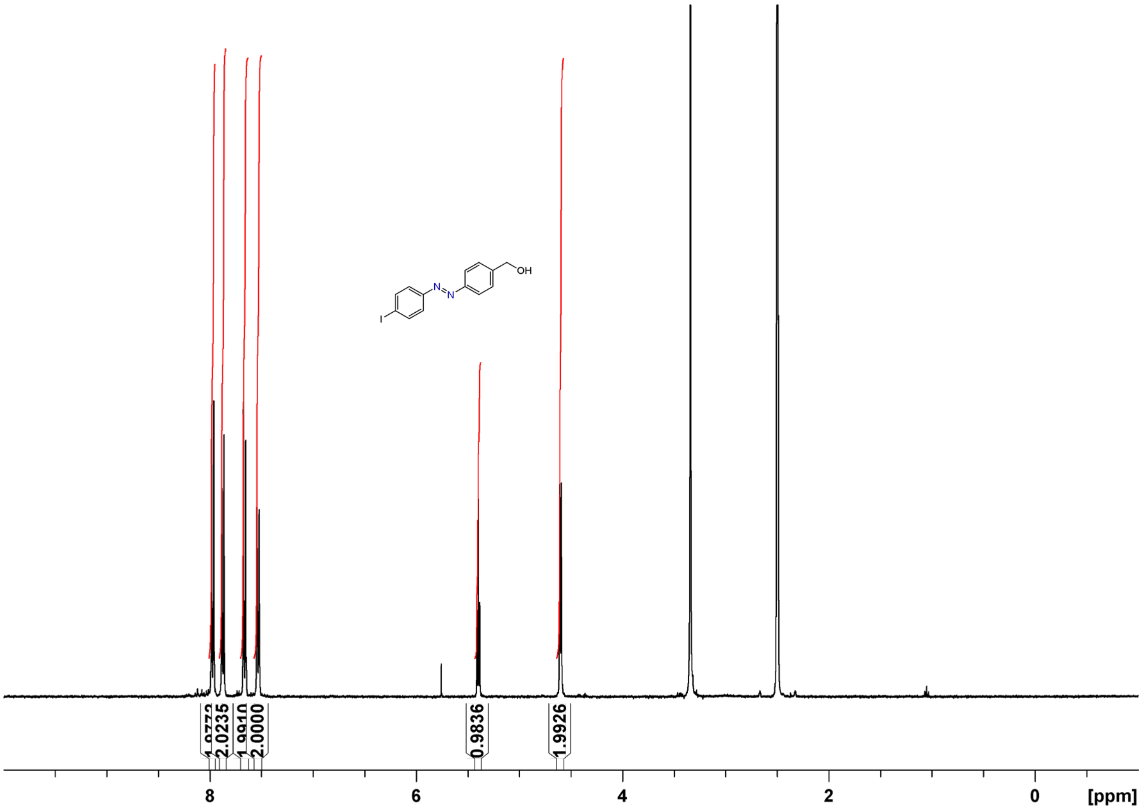


Figure S25. ^{1}H NMR spectrum of azobenzene **26** (400 MHz, DMSO-d$_6$).

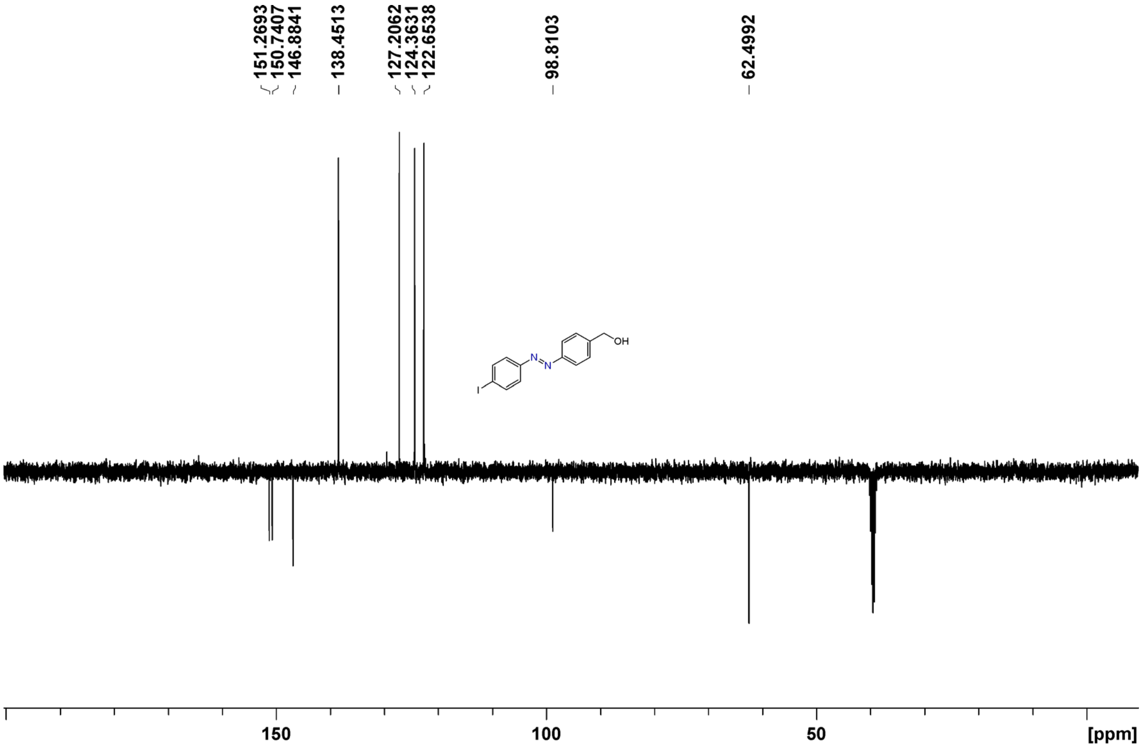


Figure S26. ^{13}C NMR spectrum (APT) of azobenzene **26** (100 MHz, CDCl$_3$).

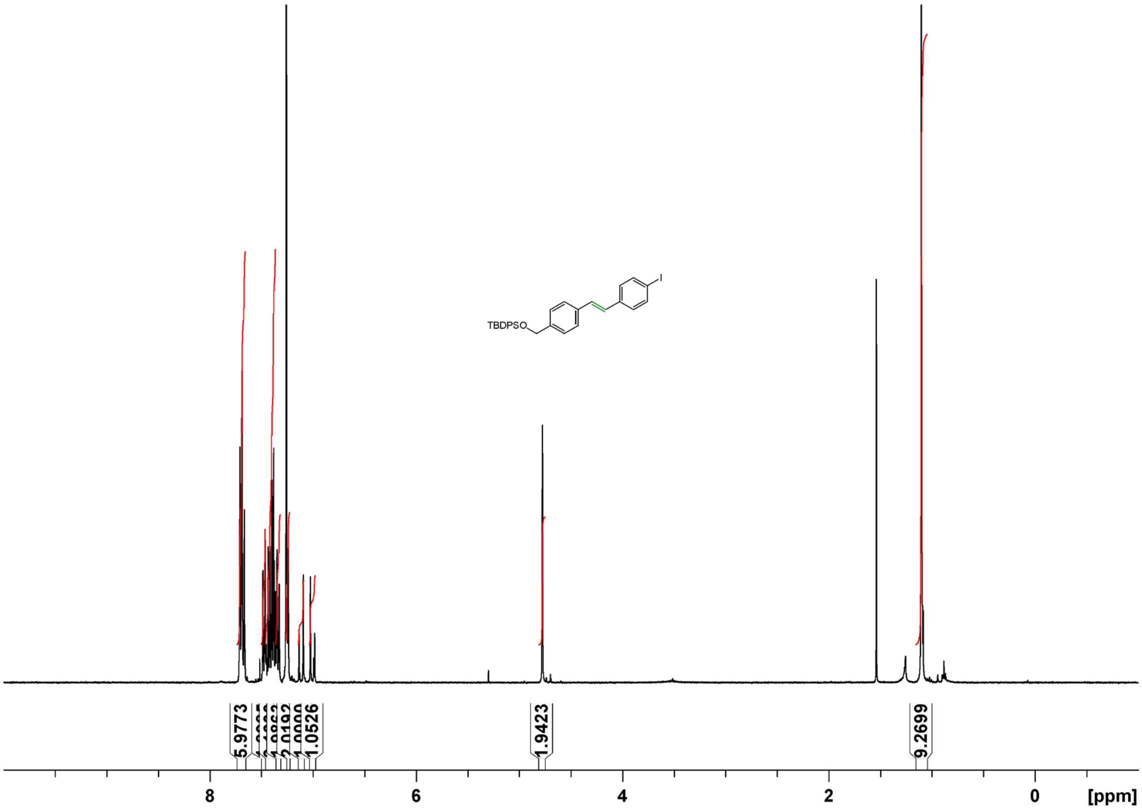


Figure S27. ^{1}H NMR spectrum of stilbene **37** (400 MHz, $CDCl_3$).

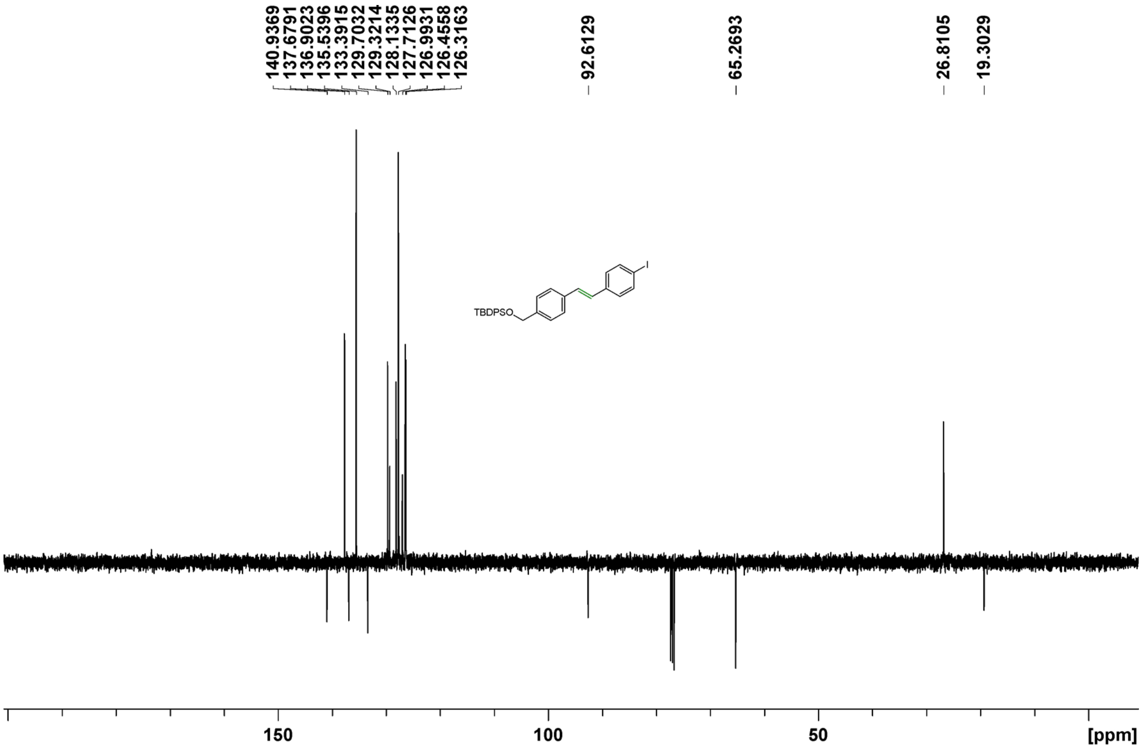


Figure S28. ^{13}C NMR spectrum (APT) of stilbene **37** (100 MHz, $CDCl_3$).

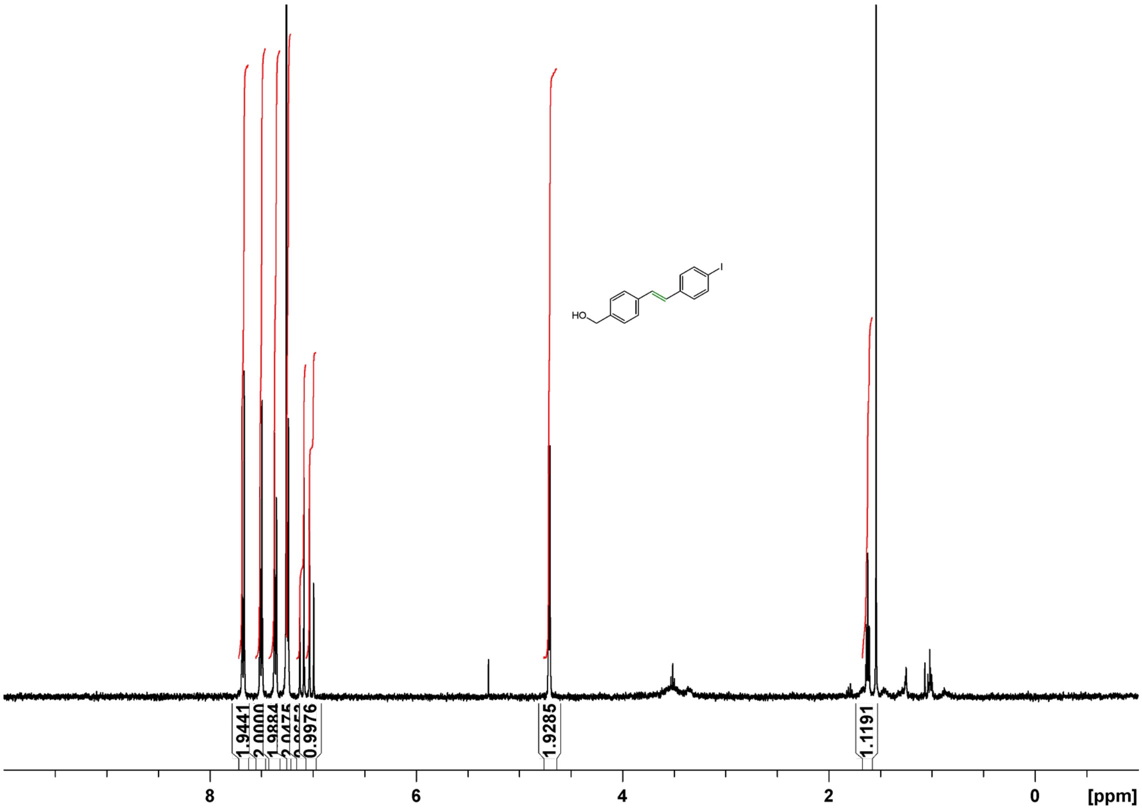


Figure S29. ^{1}H NMR spectrum of stilbene **38** (400 MHz, CDCl$_3$).

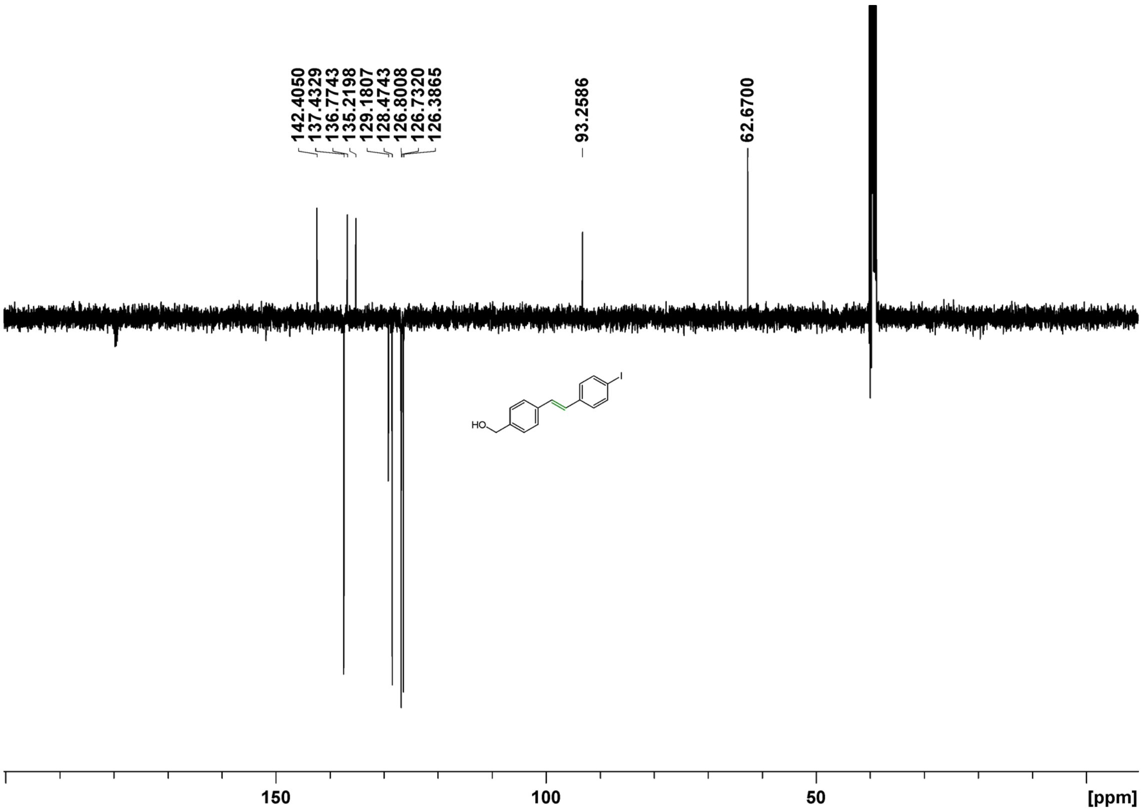


Figure S30. ^{13}C NMR spectrum (APT) of stilbene **38** (100 MHz, CDCl$_3$).

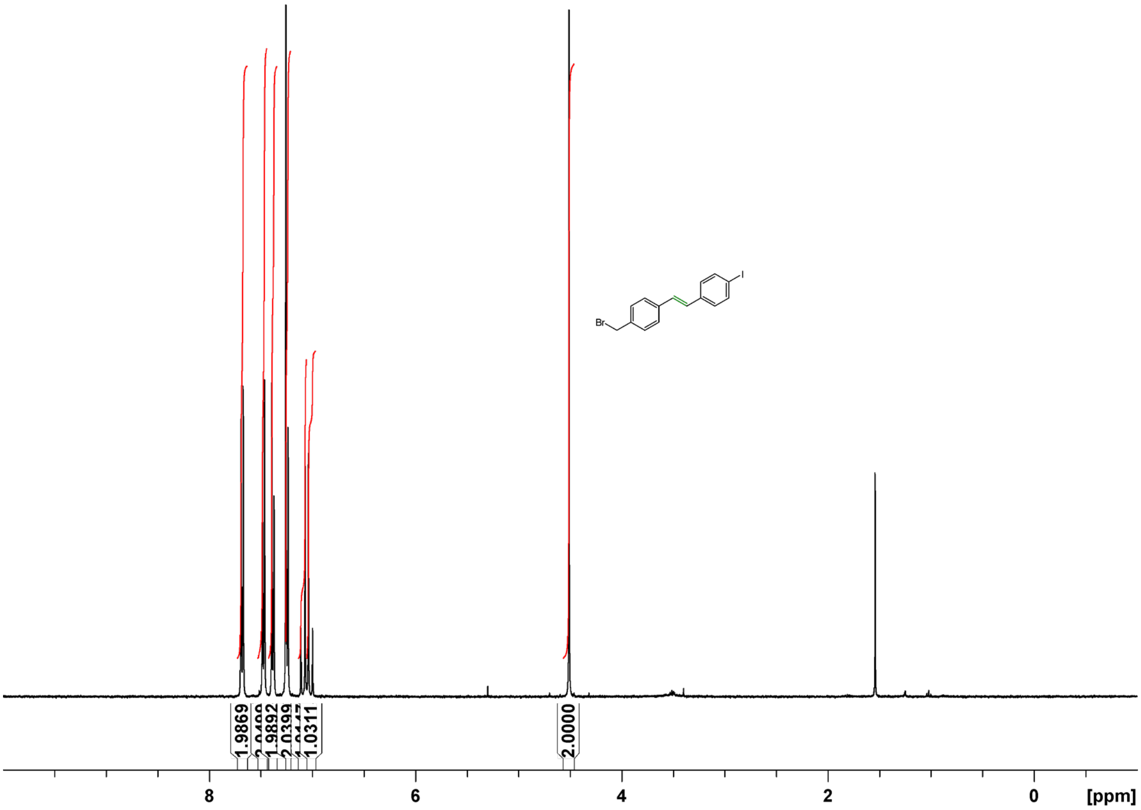


Figure S31. ^{1}H NMR spectrum of stilbene **40** (400 MHz, $CDCl_3$).

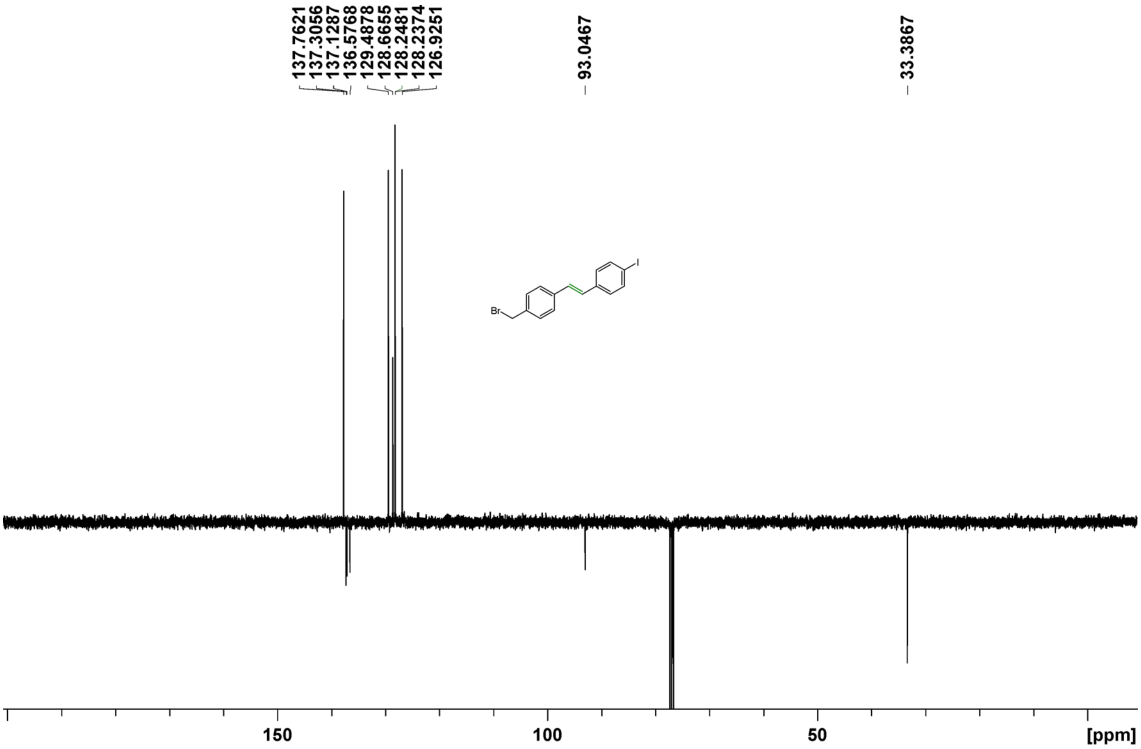


Figure S32. ^{13}C NMR spectrum (APT) of stilbene **40** (100 MHz, $CDCl_3$).

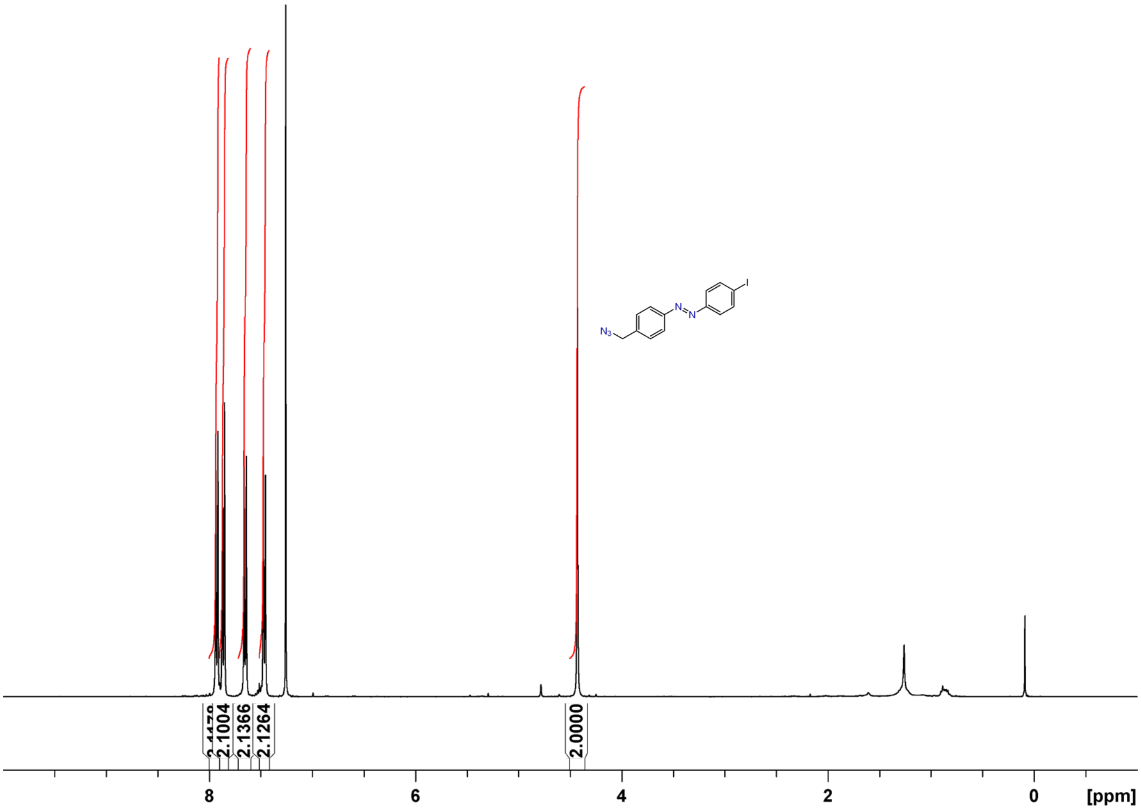


Figure S33. ^{1}H NMR spectrum of azobenzene **41** (400 MHz, $CDCl_3$).

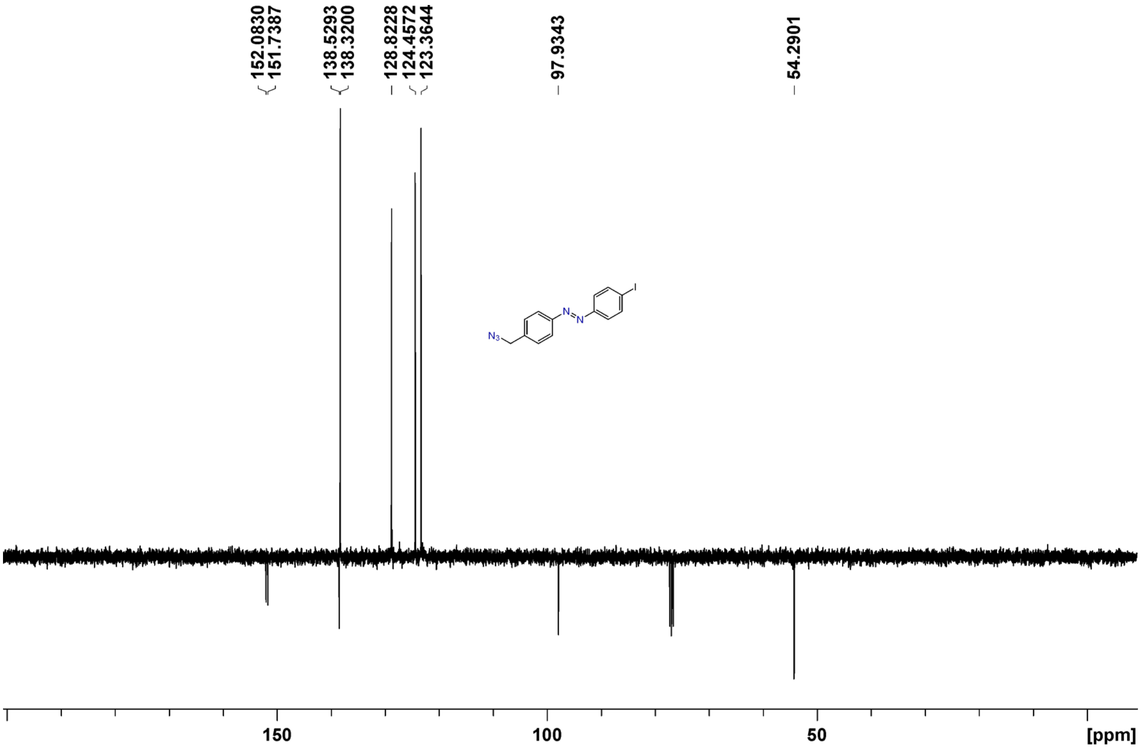


Figure S34. ^{13}C NMR spectrum (APT) of azobenzene **41** (100 MHz, $CDCl_3$).

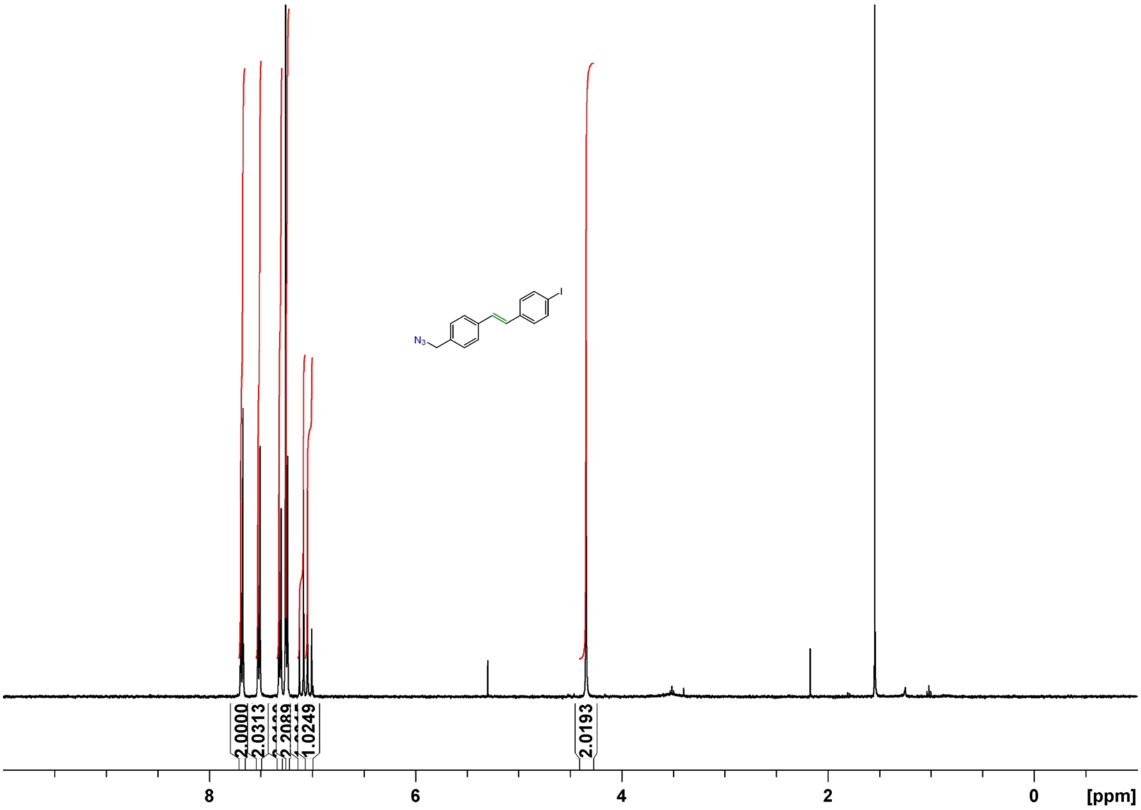


Figure S35. ^{1}H NMR spectrum of stilbene **42** (400 MHz, $CDCl_3$).

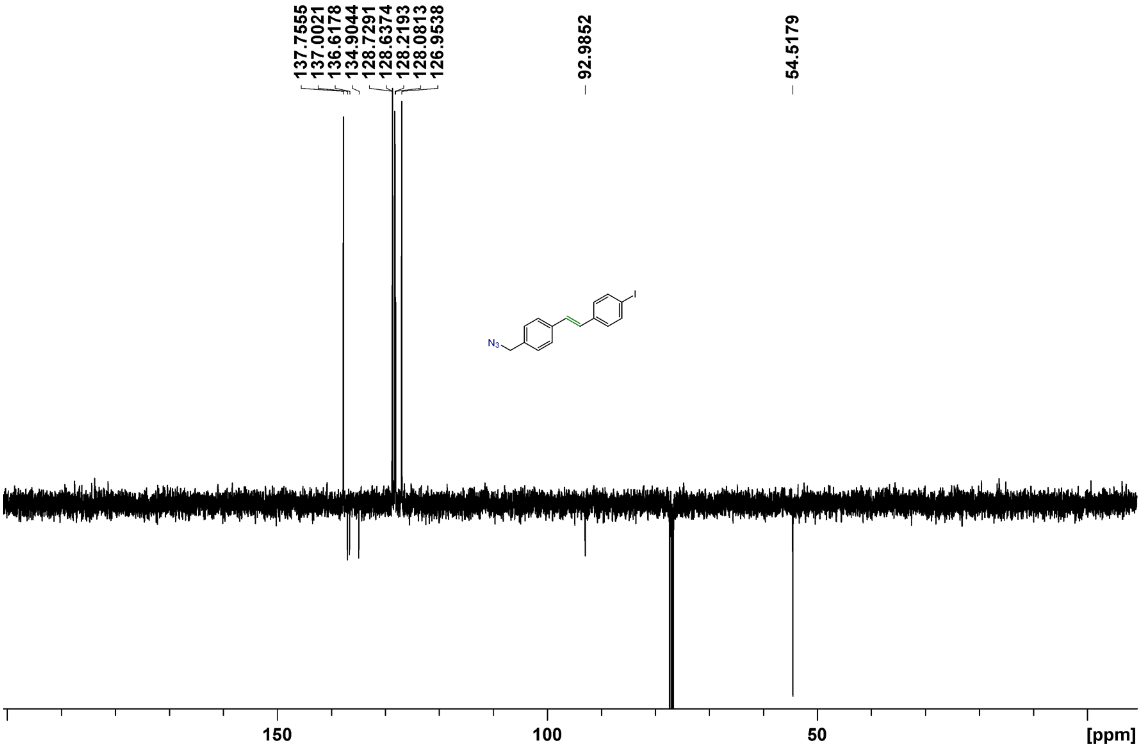


Figure S36. ^{13}C NMR spectrum (APT) of stilbene **42** (100 MHz, $CDCl_3$).

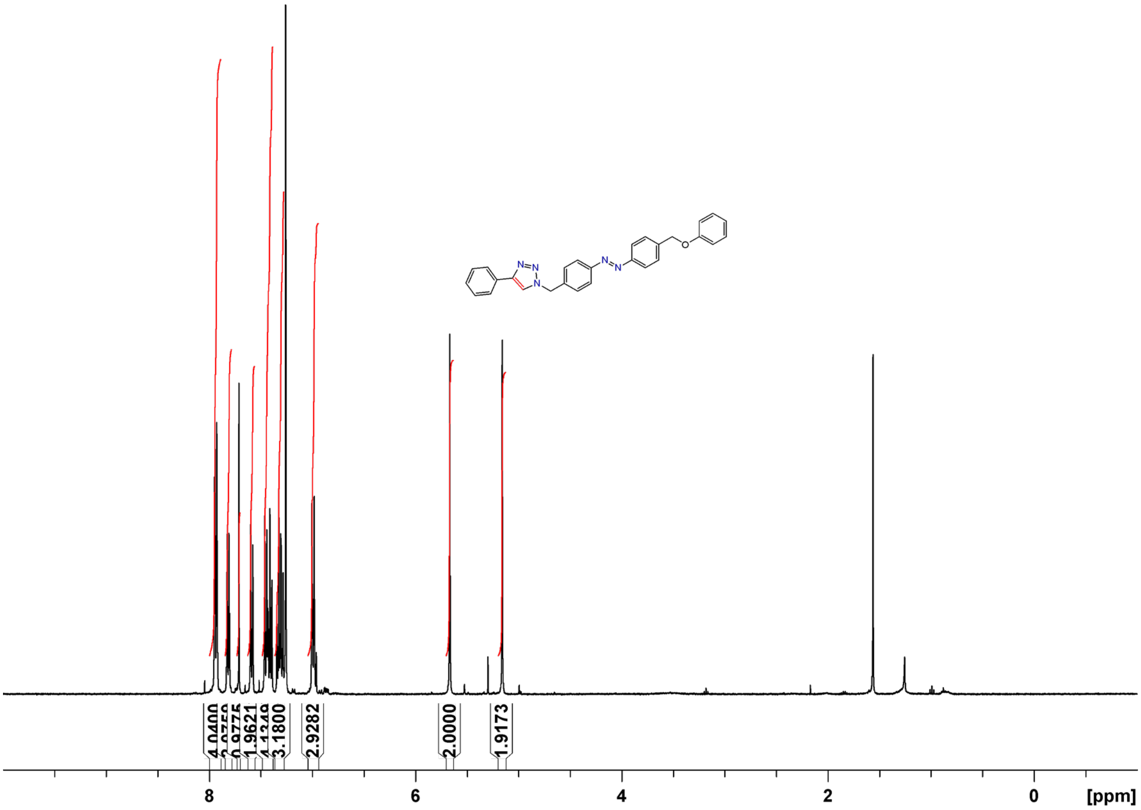


Figure S37. ^{1}H NMR spectrum of azobenzene **43** (400 MHz, CDCl$_3$).

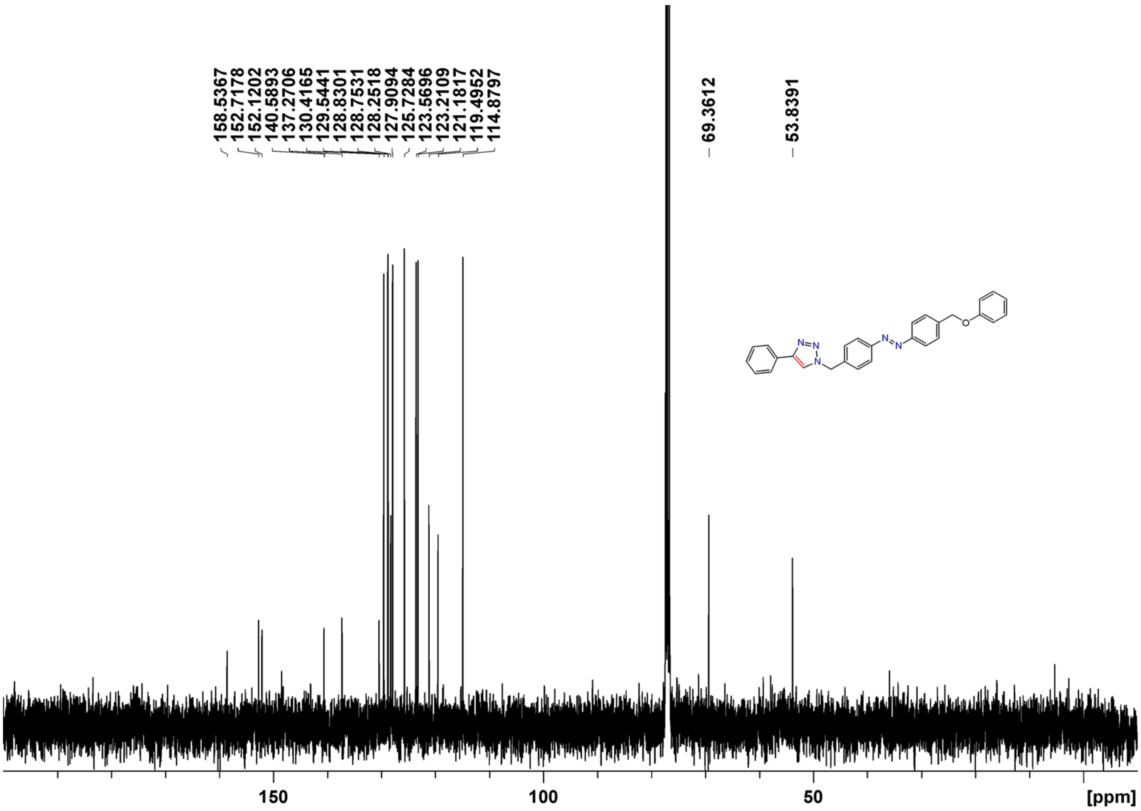


Figure S38. ^{13}C NMR spectrum of azobenzene **43** (100 MHz, CDCl$_3$).

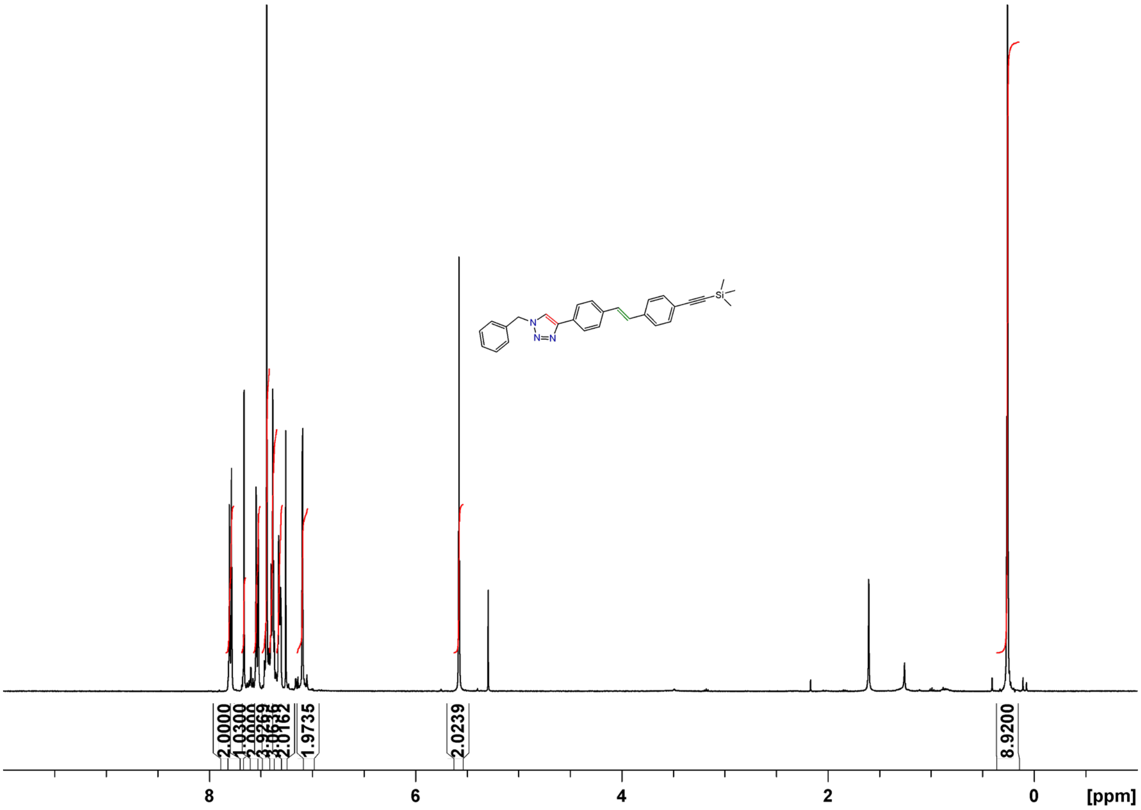


Figure S39. ^{1}H NMR spectrum of stilbene **44** (400 MHz, $CDCl_3$).

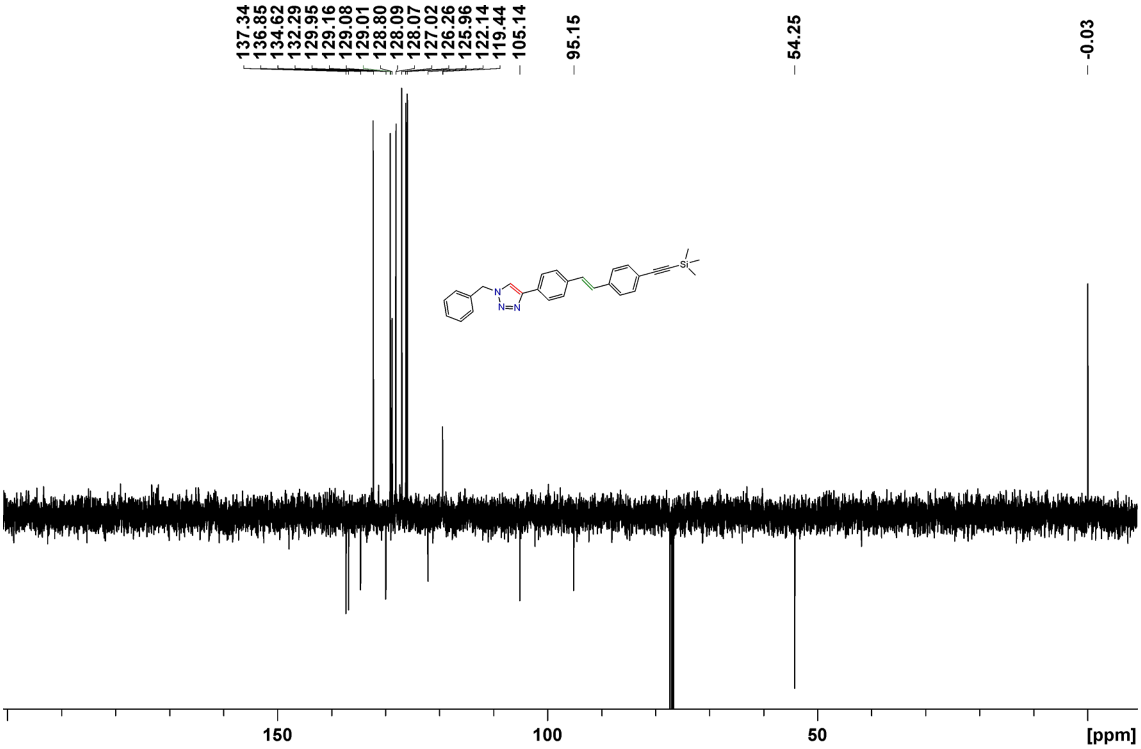


Figure S40. ^{13}C NMR spectrum (APT) of stilbene **44** (100 MHz, $CDCl_3$).

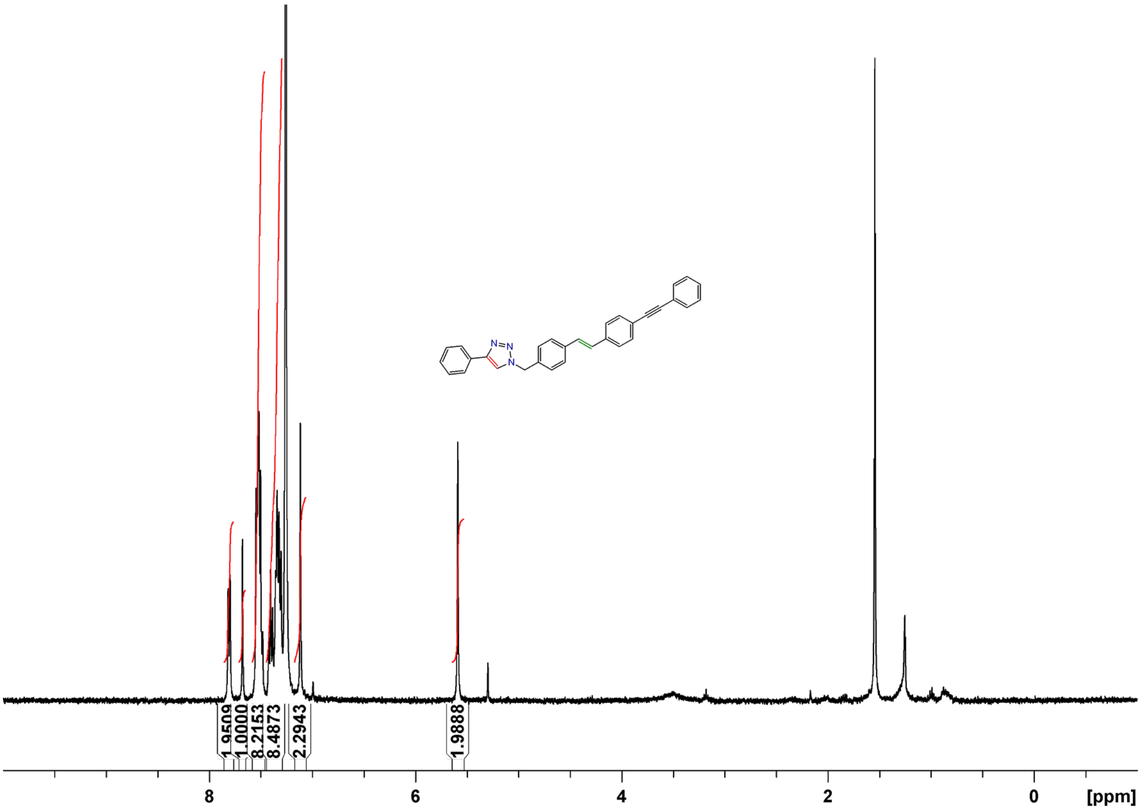


Figure S41. ^{1}H NMR spectrum of stilbene **45** (400 MHz, $CDCl_3$).

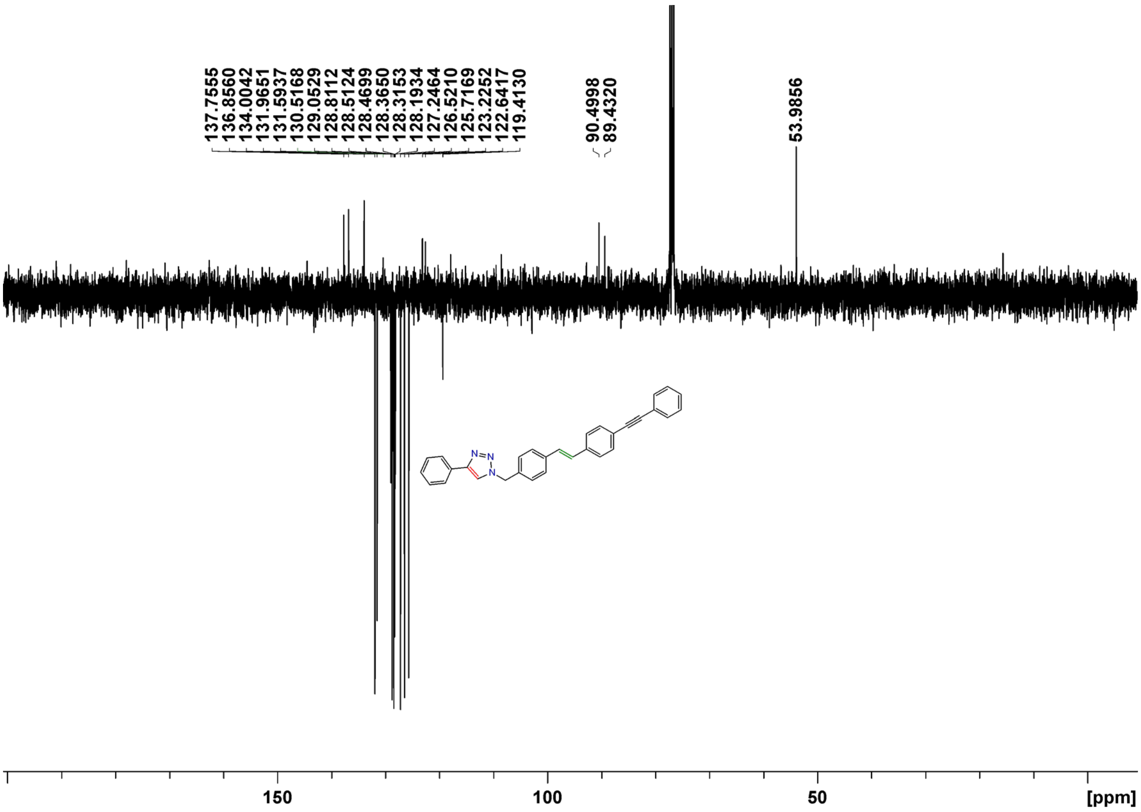


Figure S42. ^{13}C NMR spectrum (APT) of stilbene **45** (100 MHz, $CDCl_3$).

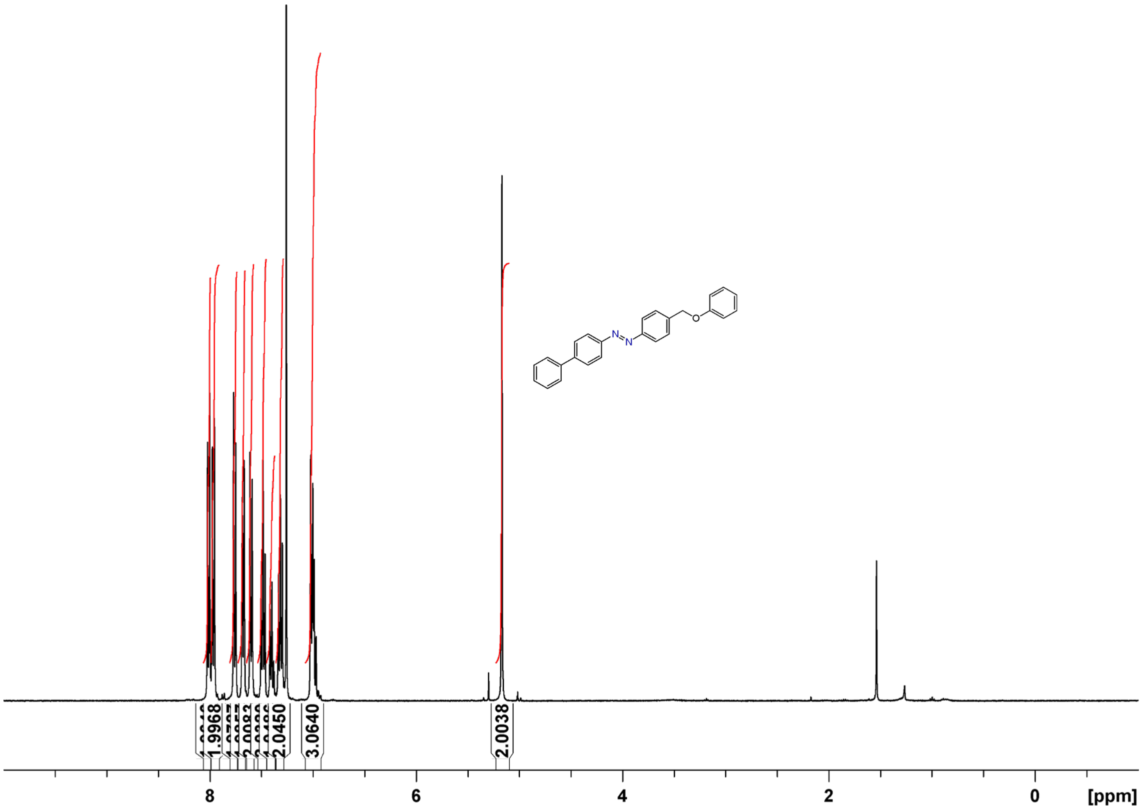


Figure S43. ^{1}H NMR spectrum of azobenzene **46** (400 MHz, $CDCl_3$).

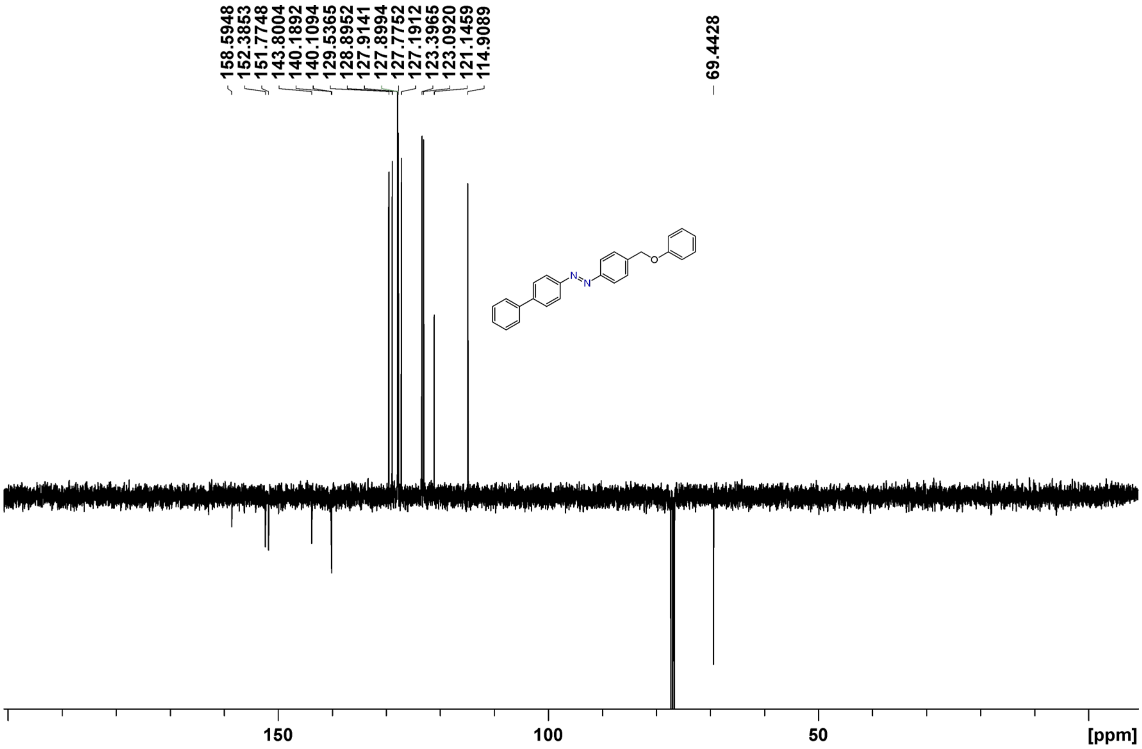


Figure S44. ^{13}C NMR spectrum (APT) of azobenzene **46** (100 MHz, $CDCl_3$).

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