Supplementary Information

Synthesis and molecular properties of donor-π-spacer-acceptor ynamides with up to 4 conjugated alkyne units

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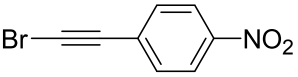
I. Experimental procedures and spectroscopic and analytical Data for all new compounds

General: All reactions were performed under an atmosphere of dry nitrogen. Commercially available reagents were used without further purification; solvents and gases were dried by standard procedures. IR spectra were recorded on a Bruker IFS 28 FTIR spectrometer, a Perkin Elmer Paragon 500 FTIR spectrometer and a JASCO 4100 FTIR spectrometer. NMR spectra were recorded using a Bruker AV 400 instrument operating at 400 MHz for ^{1}H spectra and 100 MHz for ^{13}C spectra, a Bruker ARX 400 instrument operating at 400 MHz for ^{1}H spectra and 100 MHz for ^{13}C spectra and a Bruker AC 300 instrument operating at 300 MHz for ^{1}H spectra and 75 MHz for ^{13}C spectra. Mass spectra were obtained on a Quattro-LCZ from Waters-Micromass (ESI), a MicroTof from Bruker Daltonics (ESI), a Q-Tof Ultima Apt from Waters-Micromass (ESI), a Finnigan MAT 90 (FD) and a Finnigan MAT 311 (EI). Microanalyses were recorded using a Vario Micro Cube from Elementar. Melting points were recorded on a HWS SG 2000 apparatus and are uncorrected. UV-Vis Spectra were recorded on a Shimadzu UV-2501PC spectrophotometer.

Bromoacetylenes 2a, 2b, and 11

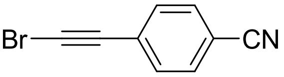
General Procedure: A solution of the corresponding terminal acetylene (1.0 equiv.), silver nitrate (5 mol%) and *N*-bromosuccinimide (1.3 equiv.) in acetone was stirred for one hour at room temperature. Thereafter the reaction mixture was poured into ice water and was extracted three times with diethyl ether. The combined organic phases were washed with brine, dried with $MgSO_4$ and concentrated in vacuo. The obtained product was purified by crystallisation from chloroform.

1-(2-Bromoethynyl)-4-nitrobenzene (2a):



2a was obtained as a yellow solid (1.33 g, 5.9 mmol, 72%).
M.p. 162–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.4 (s), 132.9 (d), 129.5 (s), 123.6 (d), 78.5 (s), 56.3 (s); IR (KBr): ν_{max}/cm^{-1} = 3106, 2838, 2361, 2343, 2195, 1927, 1591, 1508, 1404, 1374, 1345, 1310, 1285, 1262, 1177, 1107; MS (EI); m/z (%): 225 (M^+, 100), 208 (2), 195 (28), 179 (44), 167 (35), 153 (6), 129 (5), 119 (1), 100 (87), 74 (83), 62 (9), 51 (13); Anal. Calcd. for $C_8H_4BrNO_2$ (266.03 g mol^{-1}): C, 42.51; H, 1.78; N, 6.20. Found: C, 42.47; H, 1.60; N 5.97.

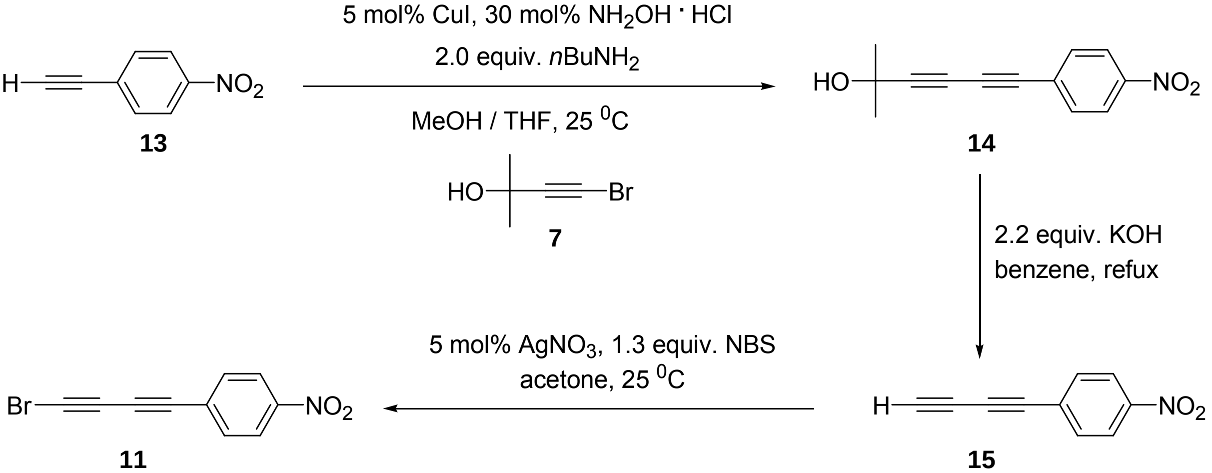
4-(2-Bromoethynyl)-benzonitrile (2b)



2b was obtained as a yellow solid (1.28 g, 6.22 mmol, 79%).
M.p. 135–137 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.6 (d), 132.1 (d), 127.5 (s), 118.3 (s), 112.1 (s), 78.6 (s), 55.4 (s); IR (KBr): ν_{max}/cm^{-1} = 3088, 2229, 2195, 1920, 1668, 1601, 1498, 1406, 1384, 1272, 1174, 1104, 1018; MS (EI); m/z (%): 205 (M^+, 100), 126 (39), 100 (22), 76 (10), 62 (16), 51 (9); Anal. Calcd. for C_9H_4BrN (206.04 g mol^{-1}): C, 52.46; H, 1.96; N, 6.80. Found: C, 52.33; H, 2.01; N 6.75.

1-(4-Bromobuta-1,3-diynyl)-4-nitrobenzene (11)

1-(4-Bromobuta-1,3-diynyl)-4-nitrobenzene **11** was synthesised along the following reaction sequence:



Diyne **14**: The reaction was carried out in methanol that was purged with argon prior to use. A 3-necked flask equipped with reflux condenser and dropping funnel was charged with CuI (94 mg, 5 mol%), hydroxylamine hydrochloride (206 mg, 30 mol%) and with methanol (30 mL) and dry THF (20 mL). *n*-Butyl amine (1.44 g, 19.72 mmol) was introduced and thereafter the 1-ethinyl-4-nitro-benzene[1] **13** (1.45g, 9.86 mmol). Thereafter, a solution of the bromoalkyne **7** (2.41 g, 14.79 mmol) in methanol (10 mL) was added drop wise at ambient temperature. The resulting reaction mixture was stirred at room temperature over night. After completion of the reaction (checked by TLC), water was added to the reaction mixture and the mixture was extracted 3 times with CH_2Cl_2 (40 mL). The combined organic layers were washed with brine, dried with $MgSO_4$ and were concentrated. Column chromatography (silica gel, petroleum ether : ethyl acetate = 1:1 (v/v) gave the diyne **14** (1.45g, 6.34 mmol) in a yield of 64% as a solid, R_f = 0.57.

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[1] J. Wettergren, A. B. E. Minidis, *Tetrahedron Lett.* 2003, **44**, 7611.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 2.25 (bs, 1H, OH), 1.57 (s, 6H).

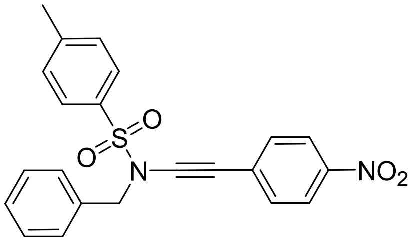
Diyne **15**: To a solution of diyne **14** (1.67 g, 7.30 mmol) in benzene (300 mL) KOH (903 mg, 16.10 mmol) was added and the resulting mixture was heated to reflux for 1h. After cooling the reaction mixture was filtered through a plug of Celite®, the filtrate was concentrated and the resulting product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 1:1 (v/v). The product **15** (1.13 g, 6.6 mmol) was obtained in 90% yield as a yellow solid, R_f = 0.71.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 2H), 2.61 (s, 1H).

1-(4-Bromobuta-1,3-diynyl)-4-nitrobenzene **11**: According to the general procedure for the synthesis of bromoacetylenes, a solution of the diyne **14** (500 mg, 2.92 mmol) in dry acetone (10 mL) was treated with $AgNO_3$ (25 mg, 5 mol%) and N-bromosuccinimide (676 mg, 3.8 mmol). The reaction mixture was stirred at ambient temperature for one hour. Thereafter the reaction mixture was poured into ice water and was extracted three times with diethyl ether. The combined organic phases were washed with brine, dried with $MgSO_4$ and concentrated in vacuo. The crude product was thereafter crystallised from chloroform to give **11** (516 mg, 2.06 mmol, 71%), as a yellow solid.
M.p. 137–139 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.7 (s), 133.6 (d), 128.0 (s), 123.6 (d), 79.0 (s), 71.6 (s), 64.8 (s), 48.0 (s); IR (KBr): ν_{max}/cm^{-1} = 3102, 2836, 2360, 2342, 2217, 2131, 1927, 1684, 1591, 1516, 1401, 1371, 1339, 1309, 1282, 1174, 1105, 1013, 854; MS (EI); m/z (%): 249 (M^+, 67), 221 (27), 193 (27), 124 (100), 98 (62); Anal. Calcd. for $C_{10}H_4BrNO_2$ (250.05 g mol^{-1}): C, 48.03; H, 1.61; N, 5.60. Found: C, 48.05; H, 1.58; N 5.62.

Ynamides 3a-e

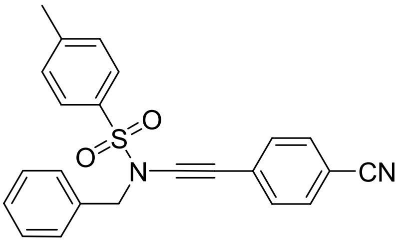
General Procedure: In a Schlenk tube with screw cap bromoacetylene **2** (1.1 equiv.) was dissolved in toluene (2 mL). Thereafter, the corresponding amide **1** (1.0 equiv.), K_2CO_3 (2.0 equiv.), 1,10-phenanthroline (20 mol%) and $CuSO_4 \cdot 5H_2O$ (10 mol%) were added and the reaction mixture was stirred at 80 °C for 24h. Thereafter, dichloromethane was added and the mixture was filtrated through a plug of Celite® and concentrated in vacuo. The obtained product was purified by column chromatography on silica gel.

N-Benzyl-2-(4-nitrophenyl)-*N*-tosylethynylamine (3a)



3a was obtained after column chromatography (silica gel, petroleum ether/diethyl ether = 1/1 (v/v)) as a yellow oil (218 mg, 0.54 mmol, 95%); R_f: 0.50.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 9.0 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.30 (m, 7H), 7.27 (d, *J* = 9.0 Hz, 2H), 4.62 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.1 (s), 145.2 (s), 134.5 (s), 133.9 (s), 130.6 (d), 130.2 (s), 130.0 (d), 128.9 (d), 128.7 (d), 128.6 (d), 127.7 (d), 123.5 (d), 88.6 (s), 71.4 (s), 55.5 (t), 21.7 (q); IR (KBr): ν_{max}/cm^{-1} = 3106, 3065, 2923, 2365, 2227, 1677, 1594, 1515, 1494, 1455, 1404, 1365, 1344, 1285, 1212, 1188, 1169, 1089, 1009, 926, 912, 864, 853; MS (ESI); m/z: 429 $[M+Na]^+$; Anal. Calcd. for $C_{22}H_{18}N_2O_4S$ (406.45 g mol^{-1}): C, 65.01; H, 4.46; N, 6.89; S, 7.89. Found: C, 64.92; H, 4.53; N 7.01; S, 8.02; ε (λ_{max} = 337.5 nm, 1,4-Dioxane) = 10663.94 l mol^{-1}cm^{-1}.

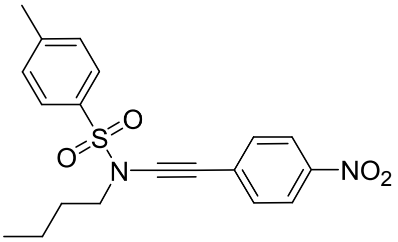
4-(2-(*N*-Benzyl-*N*-tosylamino)ethynyl)benzonitrile (3b)



3b was obtained after column chromatography (silica gel, petroleum ether/ethyl acetate = 3/1 (v/v)) as a colourless solid (212 mg, 0.55 mmol, 96%); R_f: 0.36.

M.p. 97–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.36 – 7.28 (m, 7H), 7.23 (d, J = 8.6 Hz, 2H), 4.60 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.1 (s), 134.5 (s), 133.9 (s), 131.9 (d), 130.7 (d), 129.9 (d), 128.9 (d), 128.6 (d, 2 signals), 128.1 (s), 127.7 (d), 118.6 (s), 110.4 (s), 87.4 (s), 71.2 (s), 55.5 (t), 21.7 (q); IR (KBr): ν_{max}/cm^{-1} = 3067, 3035, 2922, 2238, 2220, 1601, 1508, 1498, 1490, 1462, 1455, 1408, 1392, 1381, 1363, 1302, 1292, 1211, 1187, 1169, 1103, 1088, 1018, 995, 983, 959, 844; MS (ESI); m/z: 409 $[M+Na]^+$; Anal. Calcd. for $C_{23}H_{18}N_2O_2S$ (386.47 g mol^{-1}): C, 71.48; H, 4.69; N, 7.25; S, 8.30. Found: C, 71.45; H, 4.70; N 7.16; S, 8.42, ε (λ_{max} = 302.9 nm, 1,4-Dioxane) = 19849.93 l mol^{-1}cm^{-1}.

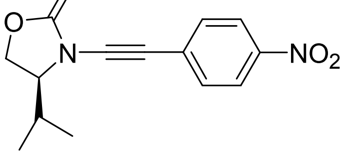
N-(2-(4-Nitrophenyl)ethynyl)-*N*-tosylbutan-1-amine (3c)



3c was obtained after column chromatography (silica gel, petroleum ether/diethyl ether = 2/1 (v/v)) as an oil (199 mg, 0.53 mmol, 93%); R_f: 0.33.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 3.45 (t, J = 7.1 Hz, 2H), 2.46 (s, 3H), 1.74 – 1.64 (m, 2H), 1.44 – 1.35 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2 (s), 145.1 (s), 134.4 (s), 130.8 (d), 130.4 (s), 129.9 (d), 127.6 (d), 123.6 (d), 88.5 (s), 70.5 (s), 51.2 (t), 30.0 (t), 21.7 (q), 19.4 (t), 13.6 (q); IR (neat): ν_{max}/cm^{-1} = 2960, 2934, 2874, 2228, 1709, 1679, 1596, 1515, 1468, 1345, 1252, 1167, 1087, 1019, 929, 854; MS (FD); m/z: 372 $[M]^+$; Anal. Calcd. for $C_{19}H_{20}N_2O_4S$ (372.44 g mol^{-1}): C, 61.27; H, 5.41; N, 7.52; S, 8.61 Found: C, 61.14; H, 5.50; N 7.57; S, 8.56; ε (λ_{max} = 336.7 nm, 1,4-Dioxane) = 14641.32 l mol^{-1}cm^{-1}.

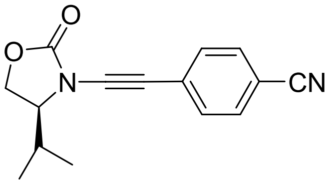
(*S*)-4-Isopropyl-3-(2-(4-nitrophenyl)ethynyl)oxazolidin-2-one (3d)



3d was obtained after column chromatography (silica gel, petroleum ether/ethyl acetate = 2/1 (v/v)) as a yellow solid (131 mg, 0.48 mmol, 83%); R_f: 0.24.

M.p. 122-124 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, J = 9.2 Hz, 2H), 7.55 (d, J = 9.2 Hz, 2H), 4.48 (t, J = 8.8 Hz, 1H), 4.25 (dd, J = 8.8 Hz, J = 5.5 Hz, 1H), 4.14 – 4.08 (m, 1H), 2.35 – 2.22 (m, 1H), 1.06 (d, J = 7.0 Hz, 2 x 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.4 (s), 146.6 (s), 131.3 (d), 129.7 (s), 123.6 (d), 84.1 (s), 71.7 (s), 65.1 (t), 62.0 (d), 29.6 (d), 17.2 (q), 15.3 (q); IR (KBr): ν_{max}/cm^{-1} = 2967, 2933, 2878, 2839, 2359, 2341, 2241, 1756, 1593, 1510, 1487, 1417, 1397, 1373, 1338, 1296, 1205, 1157, 1142, 1106, 1042, 983; MS (FD); m/z: 274 $[M]^+$; Anal. Calcd. for $C_{14}H_{14}N_2O_4$ (274.27 g mol^{-1}): C, 61.31; H, 5.14; N, 10.21. Found: C, 61.27; H, 5.04; N 10.18; ε (λ_{max} = 330.7 nm, 1,4-Dioxane) = 13750.94 l mol^{-1}cm^{-1}.

4-(2-((*S*)-4-Isopropyl-2-oxooxazolidin-3-yl)ethynyl)benzonitrile (3e)



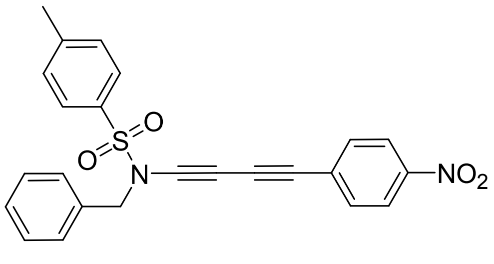
3e was obtained after column chromatography (silica gel, petroleum ether/ethyl acetate = 2/1 (v/v)) as a colourless solid (114 mg, 0.45 mmol, 78%); R$_f$: 0.34.

M.p. 93-95 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 4.47 (t, *J* = 8.8 Hz, 1H), 4.23 (dd, *J* = 9.0 Hz, *J* = 5.7 Hz, 1H), 4.12 – 4.06 (m, 1H), 2.33 – 2.23 (m, 1H), 1.05 (d, *J* = 7.4 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 155.5 (s), 132.0 (d), 131.3 (d), 127.6 (s), 118.5 (s), 111.0 (s), 83.1 (s), 71.6 (s), 65.1 (t), 62.0 (d), 29.5 (d), 17.2 (q), 15.3 (q); IR (neat): ν_{max}/cm^{-1} = 2965, 2874, 2358, 2337, 2251, 2227, 1763, 1604, 1488, 1417, 1392, 1292, 1231, 1194, 1179, 1157, 1086, 1046, 976, 834; MS (FD); m/z: 254 $[M]^+$; Anal. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.81; H, 5.40; N 10.94; ε (λ_{max} = 302.7 nm, 1,4-Dioxane) = 23955.38 l mol^{-1}cm^{-1}.

Diynamides 6a-c:

General Procedure: The reactions were carried out in methanol or in a methanol/THF solution that was purged with argon prior to use. In a Schlenk tube with screw cap were added *n*-butylamine (2.0 equiv.), CuI (5 mol%) , hydroxylamine hydrochloride (30 mol%) and methanol (5 mL) or methanol/THF (2.5 mL/2.5 mL). Thereafter, the corresponding ynamide **5** (1.0 equiv.) in 2-3 mL methanol was added. After heating to 40 °C, the bromoalkyne **2a** or **2b** (1.5 equiv.) was added in small portions over 20 minutes and the reaction mixture was stirred at 40 °C. After completion of the reaction (20 min to 1h, TLC control) dichloromethane and brine were added and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with brine, dried with MgSO$_4$, filtrated through a plug of Celite® and concentrated in vacuo. The obtained product was purified by column chromatography on silica gel.

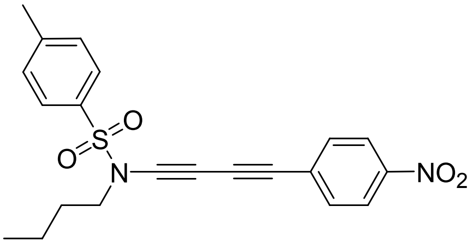
Diynamide 6a:



6a was obtained after column chromatography (silica gel, petroleum ether/diethyl ether = 1/1 (v/v)) as a yellow solid (223 mg, 0.52 mmol, 93%); R$_f$: 0.51.

M.p. 99–101 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.14 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.33 – 7.24 (m, 7H), 4.56 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 147.2 (s), 145.3 (s), 134.5 (s), 133.7 (s), 132.8 (d), 130.0 (d), 129.1 (s), 128.7 (d), 128.6 (d, 2 signals), 127.6 (d), 123.6 (d), 79.3 (s), 78.9 (s), 77.2 (s), 58.6 (s), 55.7 (t), 21.7 (q); IR (KBr): ν_{max}/cm^{-1} = 3113, 3034, 2928, 2362, 2343, 2231, 2163, 1590, 1519, 1493, 1458, 1401, 1367, 1346, 1307, 1282, 1188, 1168, 1106, 1088, 1021, 853; MS (ESI); m/z: 453 $[M+Na]^+$; Anal. Calcd. for $C_{24}H_{18}N_2O_4S$ (430.48 g mol^{-1}): C, 66.96; H, 4.21; N, 6.51; S, 7.45. Found: C, 67.08; H, 4.35; N, 6.53; S, 6.57; ε (λ_{max} = 322.7 nm, 1,4-Dioxane) = 15618.22 l $mol^{-1}cm^{-1}$.

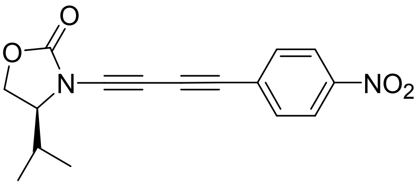
Diynamide 6b:



6b was obtained after column chromatography (silica gel, petroleum ether/diethyl ether = 4/1 (v/v)) as a yellow solid (136 mg, 0.34 mmol, 61%); R_f: 0.25.

M.p. 66–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 9.0 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 3.39 (t, J = 7.3 Hz, 2H), 2.47 (s, 3H), 1.69-1.61 (m, 2H), 1.40-1.30 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1 (s), 145.3 (s), 134.4 (s), 132.8 (d), 130.0 (d), 129.2 (s), 127.5 (d), 123.6 (d), 79.1 (s), 79.0 (s), 77.1 (s), 58.0 (s), 51.4 (t), 29.9 (t), 21.7 (q), 19.4 (t), 13.5 (q); IR (KBr): ν_{max}/cm^{-1} = 2962, 2931, 2872, 2221, 2156, 1592, 1520, 1493, 1459, 1400, 1373, 1342, 1307, 1284, 1238, 1188, 1172, 1106, 1088, 1030, 971, 883, 849; MS (FD); m/z: 396 $[M]^+$; Anal. Calcd. for $C_{21}H_{20}N_2O_4S$ (396.46 g mol^{-1}): C, 63.62; H, 5.08; N, 7.07. Found: C, 63.59; H, 5.12; N, 7.06; ε (λ_{max} = 322.3 nm, 1,4-Dioxane) = 15837.46 l $mol^{-1}cm^{-1}$.

Diynamide 6c:

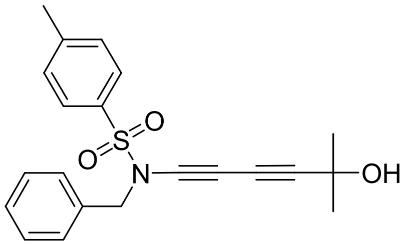


6c was obtained after column chromatography (silica gel, *n*-pentane/ethyl acetate = 1/1 (v/v)) as a yellow solid (133 mg, 0.45 mmol, 76%); R_f: 0.49.

M.p. 148–151 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, J = 9.1 Hz, 2H), 7.61 (d, J = 9.1 Hz, 2H), 4.45 (t, J = 8.9 Hz, 1H), 4.22 (dd, J = 9.0 Hz, J = 5.6 Hz, 1H), 4.11-4.05 (m, 1H), 2.32-2.19 (m, 1H), 1.04 (d, J = 7.0 Hz, 3H), 1.03 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.5 (s), 147.5 (s), 133.0 (d), 128.9 (s), 123.7 (d), 79.4 (s), 78.3 (s), 73.0 (s), 65.3 (t), 62.1 (d), 59.3 (s), 29.6 (d), 17.3 (q), 15.3 (q); IR (neat): ν_{max}/cm^{-1} = 3443, 2951, 2934, 2874, 2361, 2240, 2162, 1784, 1768, 1593, 1511, 1495, 1428, 1384, 1340, 1235, 1177, 1105, 1044; MS (ESI); m/z: 321 $[M+Na]^+$; HRMS (ESI): found 321.0850, $C_{16}H_{14}N_2O_4Na$ requires 321.0846; ε (λ_{max} = 318.5 nm, 1,4-Dioxane) = 16348.71 l $mol^{-1}cm^{-1}$.

Synthesis of triynamide 10:

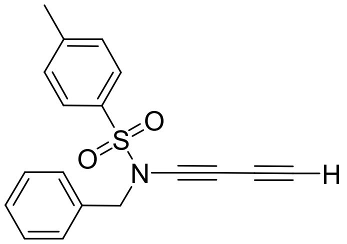
a) Diynamide 8:



The reaction was carried out in methanol that was purged with argon prior to use. A 3-necked flask equipped with reflux condenser and dropping funnel was charged with CuI (33 mg, 0.17 mmol), hydroxylamine hydrochloride (73 mg, 1.40 mmol) and with methanol (20 mL). *n*-Butyl amine (512 mg, 0.7 mL, 7.00 mmol) was introduced and thereafter the ynamide **5** (1.000 g, 3.51 mmol) in methanol (20 mL) was added. The reaction mixture was heated to 40 °C and bromoalkyne **7** (856 mg, 5.25 mmol) in methanol (20 mL) was added to the reaction mixture during 20 min. The reaction was followed by TLC and after completion (approx. 1h) CH_2Cl_2 (20 mL) and brine (50 mL) were added. The product was extracted with CH_2Cl_2 (3 times 20 mL) and the combined organic layers were washed with brine, dried with $MgSO_4$ and were concentrated. Column chromatography (silica gel, *n*-pentane/ethyl acetate = 1/1 (v/v)) yielded the diynamide **8** (1.250 g, 3.40 mmol, 97%) as a colourless solid, $R_f = 0.58$.

M.p. 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.66 (m, 2H), 7.28-7.19 (m, 7H), 4.48 (s, 2H), 2.40 (s, 3H), 1.87 (bs, 1H, OH), 1.47 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.9 (s), 134.6 (s), 133.9 (s), 129.7 (d), 128.5 (d), 128.4 (d), 128.3 (d), 127.5 (d), 86.3 (s), 71.5 (s), 66.6 (s), 65.6 (s), 58.0 (s), 55.5 (t), 31.0 (q), 21.5 (q). IR (film): ν_{max}/cm^{-1} = 3377, 3034, 2983, 2933, 2245, 2164, 1597, 1496, 1456, 1369, 1209, 1169; MS (ESI); m/z: 390 $[M+Na]^+$; Anal. Calcd. for $C_{21}H_{21}NO_3S$ (367.5 g mol^{-1}): C, 68.64; H, 5.76; N, 3.81. Found: C, 68.48; H, 5.38; N, 3.58.

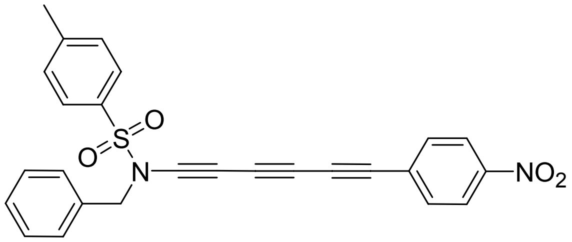
b) Diynamide 9



To a solution of diyne **8** (1.000 g, 2.72 mmol) in benzene (120 mL) KOH (336 mg, 5.99 mmol) was added and the resulting mixture was heated to reflux for 1h. After cooling the reaction mixture was filtered through a plug of Celite®, the filtrate was concentrated and the resulting product purified by column chromatography (silica gel, petrol ether/ethyl acetate = 1:1 (v/v/)) to give the diyne **9** (755 mg, 2.44 mmol, 90%) as a colourless solid, R_f = 0.65.

M.p. 61-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 7.4 Hz, 2H), 7.30-7.28 (m, 5H), 7.24-7.22 (m, 2H), 4.50 (s, 2H), 2.42 (s, 3H), 2.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2 (s), 134.5 (s), 133.8 (s), 129.9 (d), 128.7 (d), 128.7 (d), 128.6 (d), 127.6 (d), 71.4 (d), 68.1 (s), 67.7 (s), 58.8 (s), 55.5 (t), 21.7 (q). IR (KBr): ν_{max}/cm^{-1} = 3269, 3032, 2361, 2343, 2228, 2068, 1595, 1496, 1456, 1442, 1360, 1294, 1276, 1245, 1188, 1174, 1088, 1041, 1028; MS (ESI); m/z: 332 $[M+Na]^+$; Anal. Calcd. for $C_{18}H_{15}NO_2S$ (309.4 g mol^{-1}): C, 69.88; H, 4.89; N, 4.53;. Found: C, 69.85; H, 4.87; N, 4.61.

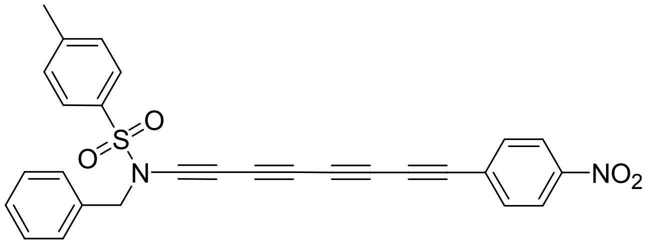
c) Triynamide 10:



The reaction was carried out in a methanol/THF solution that was purged with argon prior to use. In a Schlenk tube with screw cap were added *n*-butylamine (22 mg, 30 μL, 0.30 mmol), CuI (1 mg, 0.005 mmol, 4 mol%) , hydroxylamine hydrochloride (3 mg, 30 mol%) and methanol (1.5 mL). Thereafter ynamide **9** (46 mg, 0.15 mmol) methanol (1 mL) and THF (1.25 mL) were added. The bromoalkyne **2a** (51 mg, 0.23 mmol) was added in small portions over 20 minutes and the reaction mixture was stirred for 2h at room temperature. After completion of the reaction dichloromethane and brine were added and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with brine, dried with $MgSO_4$, filtrated through a plug of Celite® and concentrated in vacuo. The obtained product was purified by column chromatography (silica gel, petroleum ether/diethyl ether = 4/5 (v/v)) to give **10** as a yellow solid (49 mg, 0.11 mmol, 73 %); R_f: 0.57.

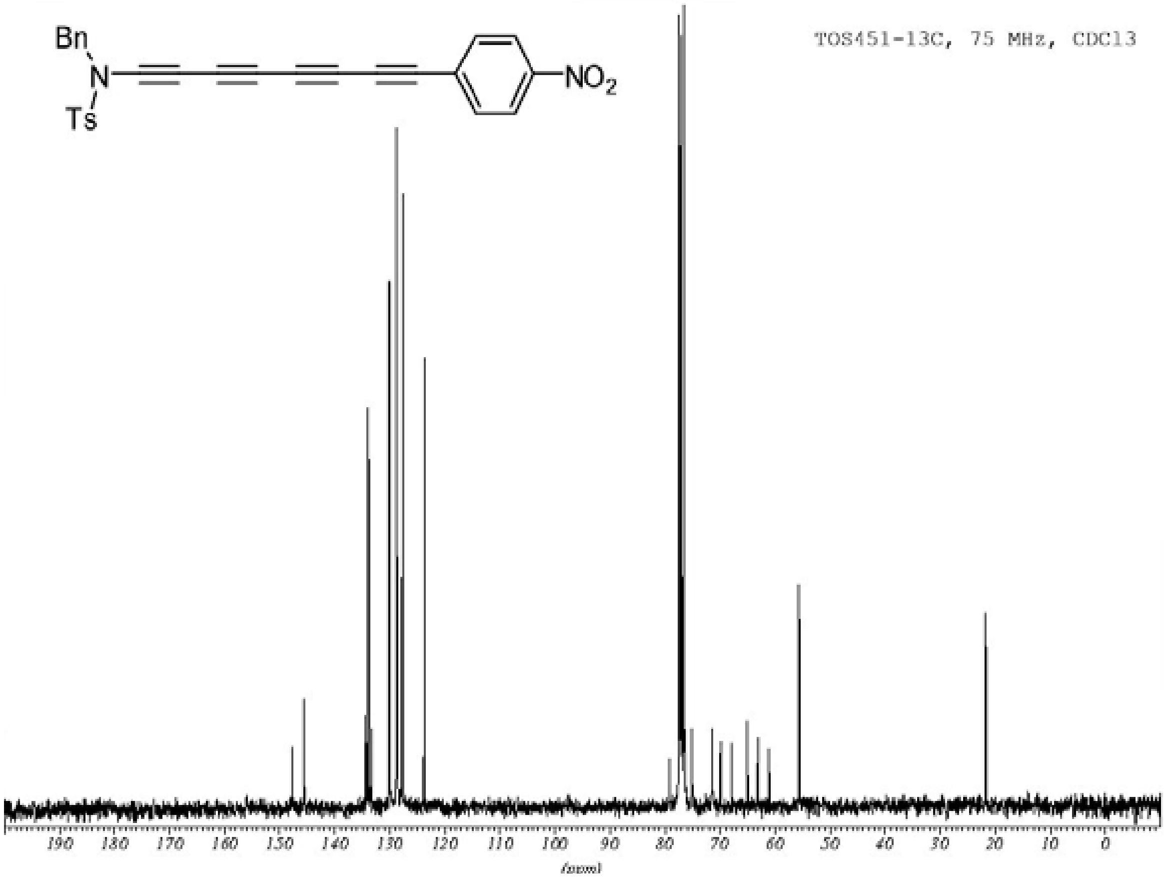
M.p. 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 9.0 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.35 – 7.30 (m, 5H), 7.27 – 7.24 (m, 2H), 4.56 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.5 (s), 145.5 (s), 134.4 (s), 133.5 (d), 133.4 (s), 130.0 (d), 128.8 (d, 3 signals), 128.2 (s), 127.7 (d), 123.7 (d), 79.4 (s), 76.2 (s), 73.0 (s), 69.0 (s), 66.3 (s), 60.5 (s), 55.7 (t), 21.7 (q); IR (KBr): ν_{max}/cm^{-1} = 3103, 3066, 3032, 2925, 2853, 2210, 2174, 2108, 1684, 1592, 1518, 1496, 1455, 1420, 1368, 1342, 1286, 1226, 1188, 1168, 1152, 1107, 1085, 1011, 854; MS (ESI); m/z: 477 [M+Na]$^+$; Anal. Calcd. for $C_{26}H_{18}N_2O_4S$ (454.50 g mol^{-1}): C, 68.71; H, 3.99; N, 6.16; S, 7.06. Found: C, 68.69; H, 4.05; N, 6.15; S, 6.98; ε (λ_{max} = 339.4 nm, 1,4-Dioxane) = 22324.05 l mol^{-1}cm^{-1}.

Tetraynamide 12:

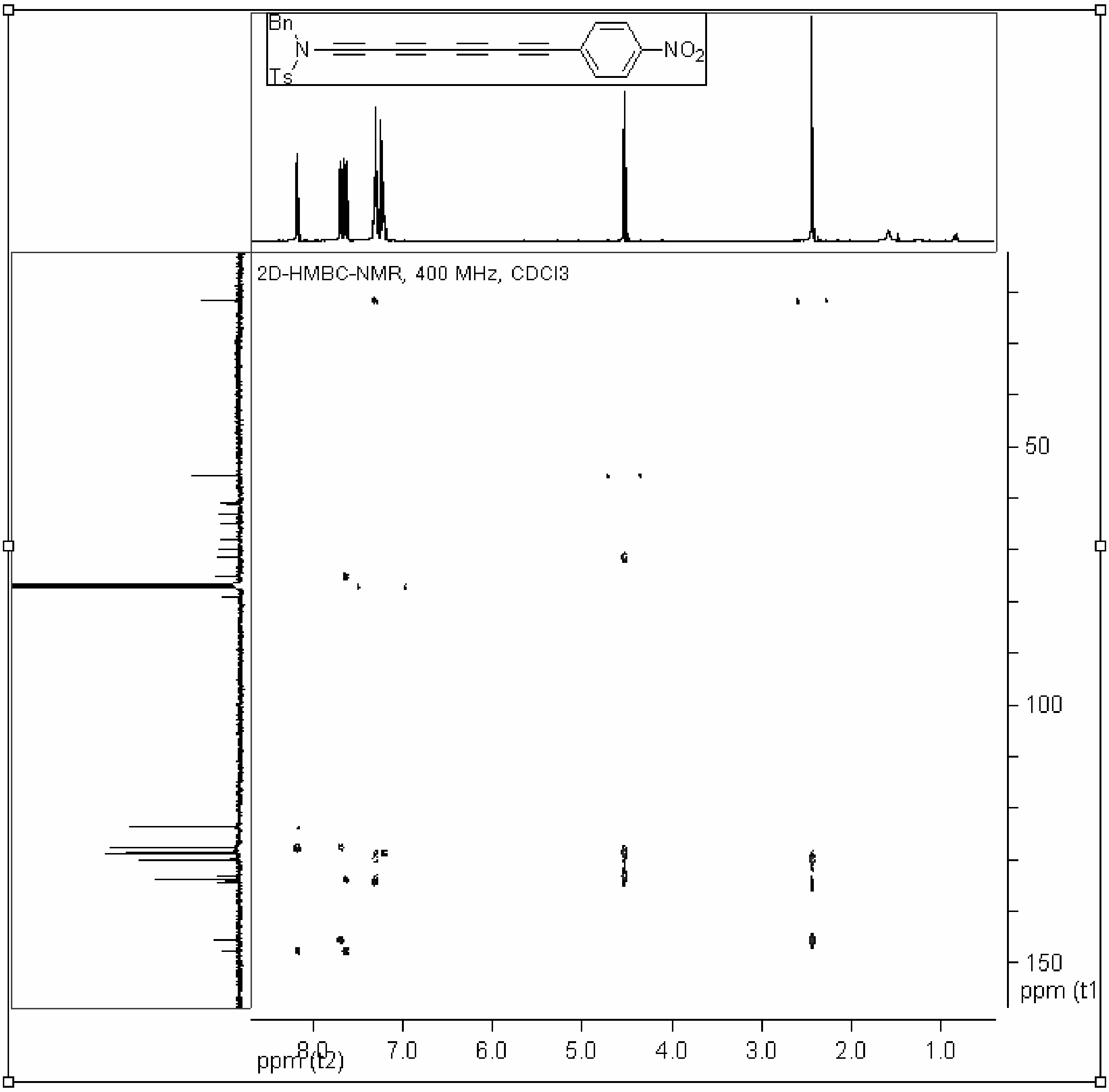


The reaction was carried out in a methanol/THF solution that was purged with argon prior to use. In a Schlenk tube with screw cap were added *n*-butylamine (22 mg, 30 μL, 0.30 mmol), CuI (1 mg, 0.005 mmol, 4 mol%) , hydroxylamine hydrochloride (3 mg, 30 mol%) and methanol (1.5 mL). Thereafter ynamide **9** (46 mg, 0.15 mmol) methanol (1 mL) and THF (1.25 mL) were added. The bromoalkyne **2a** (56 mg, 0.23 mmol) was added in small portions over 20 minutes and the reaction mixture was stirred for 2h at room temperature. After completion of the reaction dichloromethane and brine were added and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with brine, dried with $MgSO_4$, filtrated through a plug of Celite® and concentrated in vacuo. The obtained product was purified by column chromatography (silica gel, petroleum ether/diethyl ether = 4/5 (v/v)) to give **12** as a yellow oil (34 mg, 0.07 mmol, 47 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 9.0 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 9.0 Hz, 2H), 7.35-7.30 (m, 5H), 7.25-7.22 (m, 2H), 4.56 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.7 (s), 145.6 (s), 134.3 (s), 133.8 (d), 133.3 (s), 130.0 (d), 128.8 (d, 2 signals), 128.7 (d), 127.6 (d), 127.6 (s), 123.7 (d), 79.2 (s), 75.1 (s), 71.4 (s), 69.9 (s), 67.9 (s), 65.0 (s), 63.1 (s), 61.1 (s), 55.6 (t), 21.7 (q); IR (film): ν_{max}/cm^{-1} = 3033, 2983, 2958, 2921, 2851, 2366, 2358, 2339, 2209, 2195, 2182, 2127, 1596, 1521, 1495, 1445, 1343, 1188, 1175. MS (FD); m/z: 478 $[M]^+$.



^{13}C NMR spectra (75 MHz) of tetraynamide **12** in $CDCl_3$.



2D-HMBC-NMR spectra (400 MHz (^{1}H)-75 MHz (^{13}C)) of tetraynamide **12** in $CDCl_3$.

II. UV/Vis-spectra of compounds **3**, **6** and **10**:

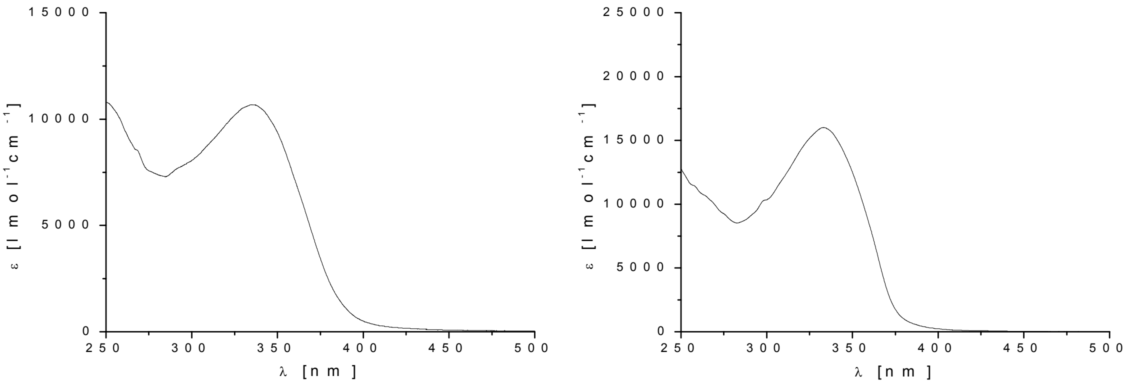


Figure 1: Absorption Spectra of compound **3a** in 1,4-dioxane (left) and cyclohexane (right).

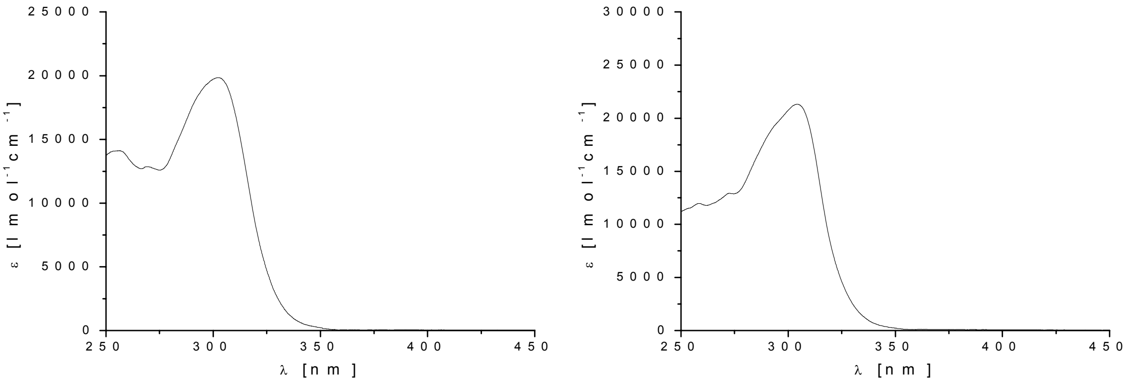


Figure 2: Absorption spectra of compound **3b** in 1,4-dioxane (left) and cyclohexane (right).

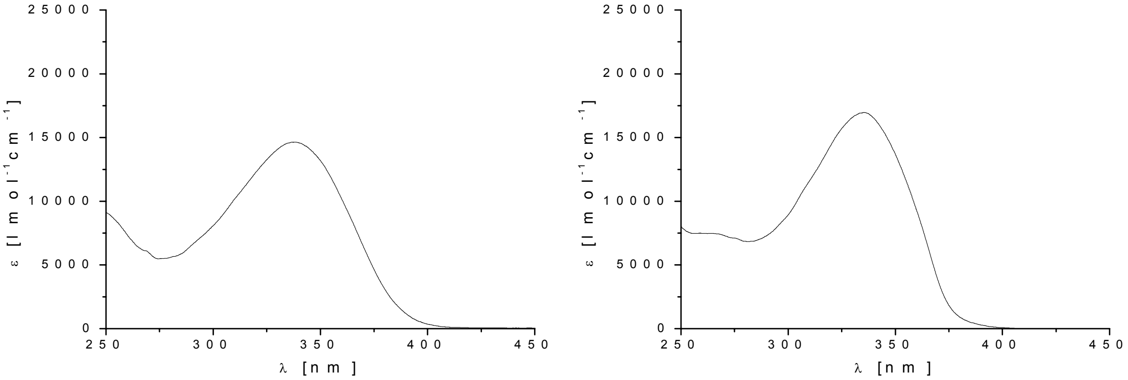


Figure 3: Absorption spectra of compound **3c** in 1,4-dioxane (left) and cyclohexane (right).

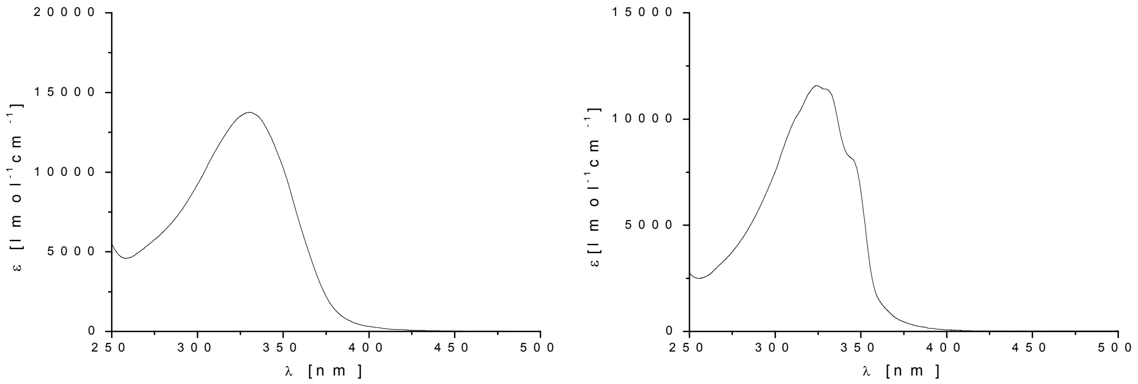


Figure 4: Absorption spectra of compound **3d** in 1,4-dioxane (left) and cyclohexane (right).

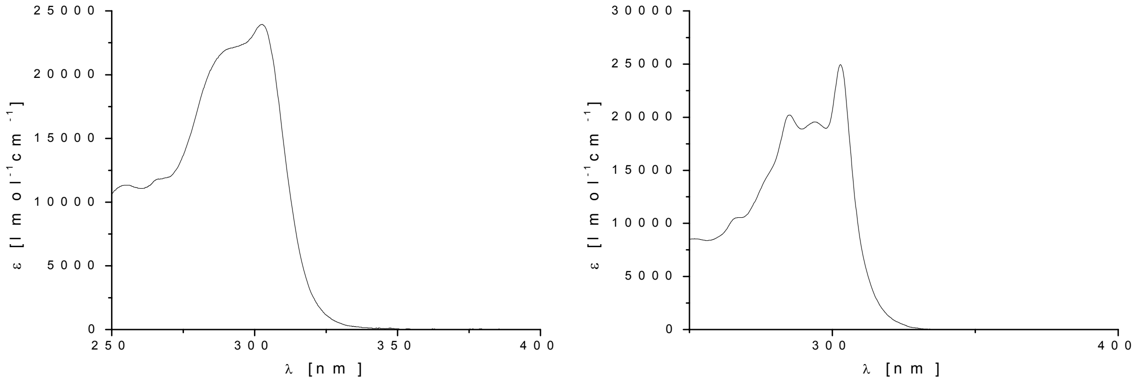


Figure 5: Absorption spectra of compound **3e** in 1,4-dioxane (left) and cyclohexane (right).

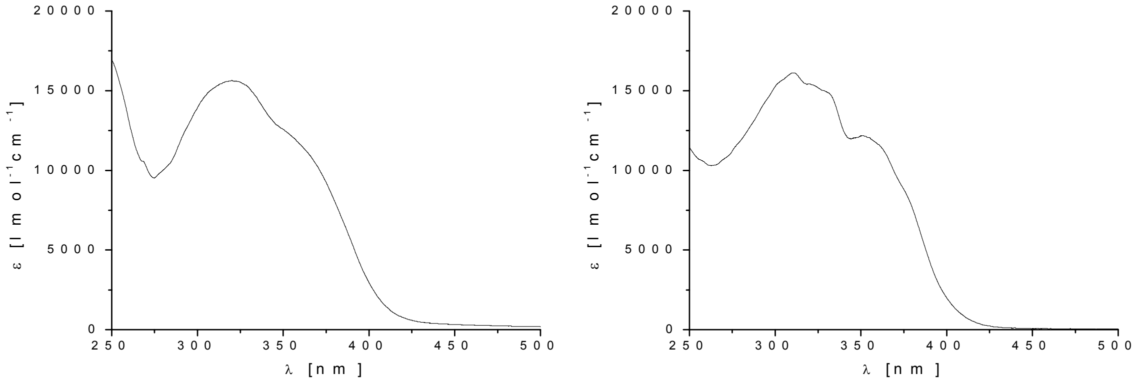


Figure 6: Absorption spectra of compound **6a** in 1,4-dioxane (left) and cyclohexane (right).

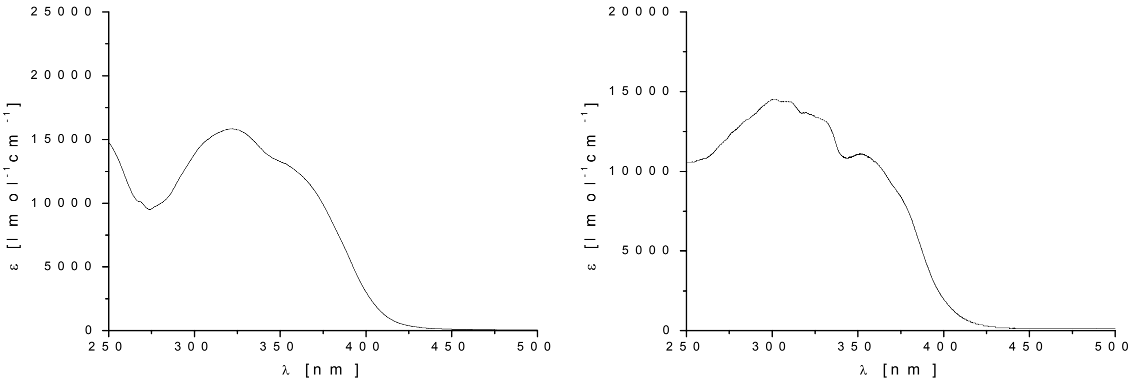


Figure 7: Absorption spectra of compound **6b** in 1,4-dioxane (left) and cyclohexane (right).

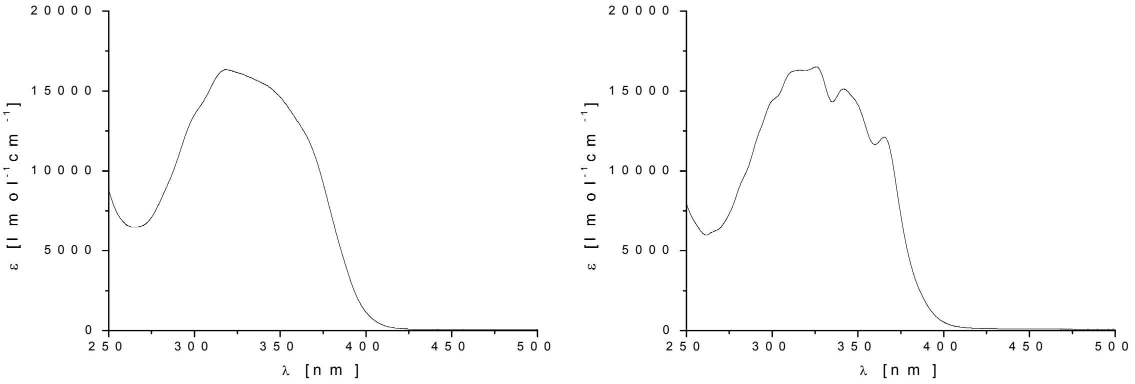


Figure 8: Absorption spectra of compound **6c** in 1,4-dioxane (left) and cyclohexane (right).

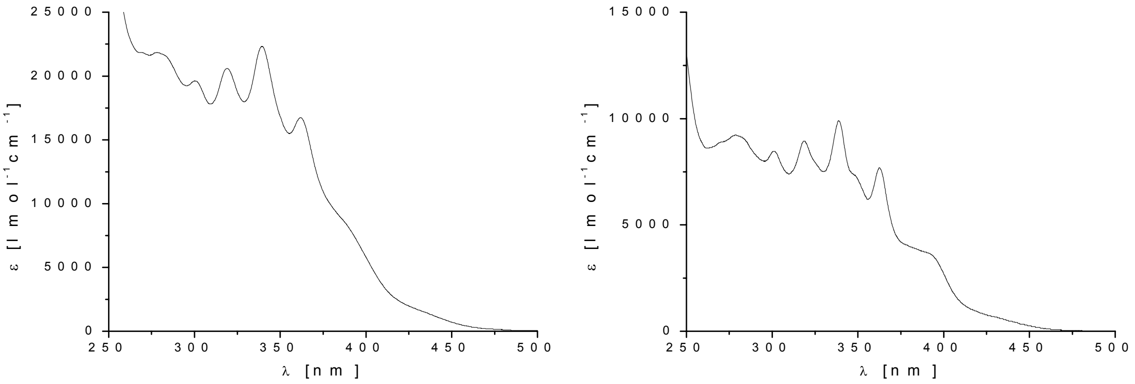


Figure 9: Absorption spectra of compound **10** in 1,4-dioxane (left) and cyclohexane (right).

III Description of the EOAM measurements

To determine the ground- and exited state dipole moments the electro-optical absorption method (EOAM) was used. Experimental and theoretical details on the electro-optical methods have been reviewed extensively.[2] In the EOAM measurements one determines the effect of an external electric field on the absorption of linearly polarised light by a dilute solution of an organic dye. Following Liptay's formalism[1a] the effect on an external electric field E_f on the molar absorption coefficient $\kappa\ (\tilde{\nu})$ can be described by a quantity L, which is defined by:

$$L = L\ (\tilde{\nu}, \chi) = [\kappa^E\ (\tilde{\nu}, \chi) - \kappa(\tilde{\nu})/[\ \kappa(\tilde{\nu}/E^2{}_\mathrm{f}] \qquad (1)$$

$\kappa^E\ (\tilde{\nu}, \chi)$ is the molar absorption coefficient in the presence of an applied electric field, κ is the molar absorption coefficient without applied electrical field, χ is the angle between the direction of E_f and the electrical field vector of the incident light and $\tilde{\nu}$ is the wavenumber. For a homogeneously broadened absorption band L can be given by the following equation:

$$L = Dr + [1/6]Es + Frt + Gst + Hru + Isu \qquad (2)$$

The parameters r and s are determined by the angle χ. The quantities t and u can be calculated from the first and second derivatives of the absorption spectrum $(\kappa/\tilde{\nu})$, with h being Planck's constant and c_0 the speed of light in vacuum.

$$r = (2 - \cos^2\chi)/5 \qquad (3)$$

$$s = (3\cos^2\chi - 1)/5 \qquad (4)$$

$$t = (1/hc_0)\ (\kappa/\tilde{\nu})^{-1}\ \mathrm{d}(\kappa/\tilde{\nu})/\mathrm{d}\tilde{\nu} \qquad (5)$$

$$u = (1/2h^2c_0{}^2)\ (\kappa/\tilde{\nu})^{-1}\ \mathrm{d}^2(\kappa/\tilde{\nu})/\mathrm{d}\tilde{\nu}^2 \qquad (6)$$

For molecules with large ground state dipoles and large dipole changes upon electronic excitation explicit polarisability terms and second order-contributions of the field dependence of the transition dipoles can be neglected. The expressions for the electro-optical coefficients D, E, F, G, H, and I may then be written as follows:[3]

$$\mathrm{D} = (f_\mathrm{e}{}^2/kT)\ \mathbf{R}^{(1)}\mu_\mathrm{g} \qquad (7)$$

$$\mathrm{E} = (f_\mathrm{e}/kT)^2\ [3(\mathbf{m}_\mathrm{a}\mu_\mathrm{g})^2 - \mu_\mathrm{g}{}^2] + (f_\mathrm{e}{}^2/kT)\ (3\mathbf{R}^{(2)} - 2\mathbf{R}^{(1)})\ \mu_\mathrm{g} \qquad (8)$$

$$\mathrm{F} = (f_\mathrm{e}{}^2/kT)\ (\mu_\mathrm{g}\,\Delta^\mathrm{a}\mu) + f_\mathrm{e}{}^2\ \mathbf{R}^{(1)}\ \Delta^\mathrm{a}\mu \qquad (9)$$

$$\mathrm{G} = (f_\mathrm{e}{}^2/kT)\ (\mathbf{m}_\mathrm{a}\mu_\mathrm{g})\ (\mathbf{m}_\mathrm{a}\Delta^\mathrm{a}\mu) + (f_\mathrm{e}{}^2/2)\ \mathbf{R}^{(2)}\ \Delta^\mathrm{a}\mu \qquad (10)$$

$$\mathrm{H} = f_\mathrm{e}{}^2\ (\Delta^\mathrm{a}\mu)^2 \qquad (11)$$

$$\mathrm{I} = f_\mathrm{e}{}^2\ (\mathbf{m}_\mathrm{a}\Delta^\mathrm{a}\mu)^2 \qquad (12)$$

Where k is the Boltzman constant, T is the temperature, $\mathbf{m}_\mathrm{a}$ is the unit vector in the direction of the transition moment for absorption, μ_g is the equilibrated ground state dipole moment vector, $\Delta^\mathrm{a}\mu$ is the change of the dipole moment vector upon excitation to the corresponding Franck-Condon excited state. The vectors $\mathbf{R}^{(1)}$ and $\mathbf{R}^{(2)}$ are related to the transition polarisability of the considered transition and describe the effects due to the electric field

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[2] a) W. Liptay, in Excited states, Vol. 1. *Dipole moments and polarizabilities of molecules in excited electronic states*, ed. E. C. Lim, Academic Press, New York, 1974, pp. 120-229; b) R. Wortmann, K. Elich, S. Lebus, W. Lipray, P. Borowicz and A. Grabowska, *J. Phys. Chem.* 1992, **96**, 9724; c) W. Baumann, in *Physical Methods of Chemistry*, eds. B. W. Rossiter and J.F. Hamitton, Wiley, New York, 1989, Vol. 3b, pp.45-131; d) W. Rettig, W. Baumann, in *Progress in Photochemistry and Photophysics*, ed. J. F. Ralek, CRC Press, Boca Raton, vol. 6, pp. 79-134; e) N. A. Nemkovich, W. Baumann, V. G. Pivovarenko, *J. Photochem. Photobiol. A: Chemistry,* 2002, **153**, 19.

[3] W. Liptay, R. Wortmann, H. Schaffrin, O. Burkhard, W. Reitinger and N. Detzer, *Chem. Phys.,* 1988*,* **120**, 429.

dependence of the transition moment. The field correction is done by the cavity field factor f_e which is solvent dependent.[4]

The quantity $L(\tilde{\nu}, \chi)$ in the present work was determined for two values of the angle χ ($\chi = 0$ and $\chi = \pi/2$) and for a set of wave numbers within the first absorption band. Then the EOAM coefficients and their standard deviations were obtained from fitting of the experimental L values by the program SYSTAT Vers. 7.0 according to Eq. (2).

From our measurements, it follows that for all probes investigated here, the coefficient F equals G and the coefficient H equals I, within the experimental errors. This means that the transition dipole moment, the dipole moment of the ground state, as well as the change of the dipole moment vector upon excitation to the corresponding Franck-Condon excited state are parallel ($\mathbf{m_a} \| \mu_g \| \Delta^a\mu$).

Using the symmetry condition $\mathbf{m_a} \| \mu_g \| \Delta^a\mu$ the values of the dipole moments μ_g and $\Delta^a\mu$ were calculated from Eq. (13) and (14).

$$\mu_g = (kT/f_e)\sqrt{\frac{E - 6D}{2}} \qquad (13)$$

$$\Delta^a\mu = (kT/f_e^2)\,(F+G)/2\,\mu_g \qquad (14)$$

The dipole moment in the excited Franck-Condon state μ_e^{FC} was determined by Eq. (15), which is sufficiently valid for low-polar solvents.

$$\Delta^a\mu = (\mu_e^{FC} - \mu_g) \qquad (15)$$

Electro-optical absorption measurements were performed by a set-up, which is a modern modification of the laboratory's apparatus described by Baumann,[5] and the principal set-up which was used is shown in Figure 10.

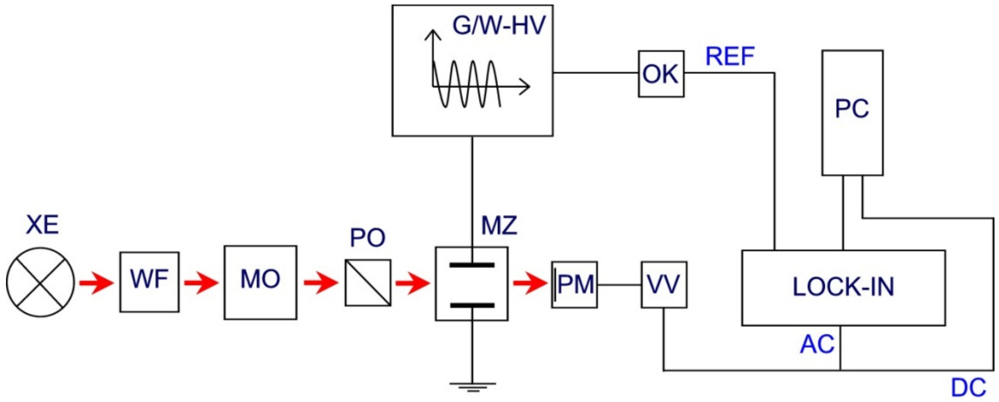

Figure 10:

XE: Xenon Lamp (450 W); **WF**: Thermal Filter; **MO**: Monochromator; **PO**: Polarisator; **MZ**: Measure Cell; **PM**: Photomultiplier; **VV**: Pre-Amplifier; **G/W-HV**: High Voltage Generator; **OK**: Opto Coupler; **REF**: Reference Signal; **LOCK-IN**: Lock-In Amplifier; **AC**:AC Voltage Signal; **DC**: DC Voltage Signal; **PC**: Personal Computer

For all measurements dry 1,4-dioxane with a water content of < 50 ppm, that was purchased from Acros Organics, was used. For calibration measurements, p-amino-p'-nitrobiphenyl was used. All measurements were performed at 298 K within a thermostated measure cell. The used AC and DC current was set to $U_{DC} = U_{Ac} = 18000$ V. The quantity $L(\tilde{\nu}, \chi)$ in the present work was determined for two values of the angle χ ($\chi = 0$ and $\chi = 90^o$) and for a set of wave numbers within the first absorption band. Then the EOAM coefficients and their

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[4] L. Onsager, *J. Am. Chem. Soc.*, 1936, **58**, 1486

[5] a) W. Baumann, in *Physical methods of chemistry*; Eds. B. W. Rossiter, J. F. Hamilton; John Wiley and Sons, 1989, Vol. 3b; b) W. Baumann, *Ber. Bunsenges. Physik. Chem.,*1976, **80**, 231.

standard deviations were obtained from fitting of the experimental L values by multi-linear regression analysis with the program SYSTAT Vers. 7.0

IV. EOAM measurements of compounds **3**, **6** and **10**:

Compound **3a**:

Electro-optical coefficients and data for dipole moments in 1,4-dioxane at T = 298 K, data collection at λ = 395-365 nm.

D [10^{-20} $V^{-2}m^2$]	~0
E [10^{-20} $V^{-2}m^2$]	1573.11
F [10^{-40} $CV^{-1}m^2$]	2611.71
G [10^{-40} $CV^{-1}m^2$]	3039.09
μ_g [10^{-30} Cm]	9.7 $\pm$ 0.3
$\Delta^a\mu$ [10^{-30} Cm]	74.6 $\pm$ 3
μ_a^{FC} [10^{-30} Cm]	84.3 $\pm$ 3

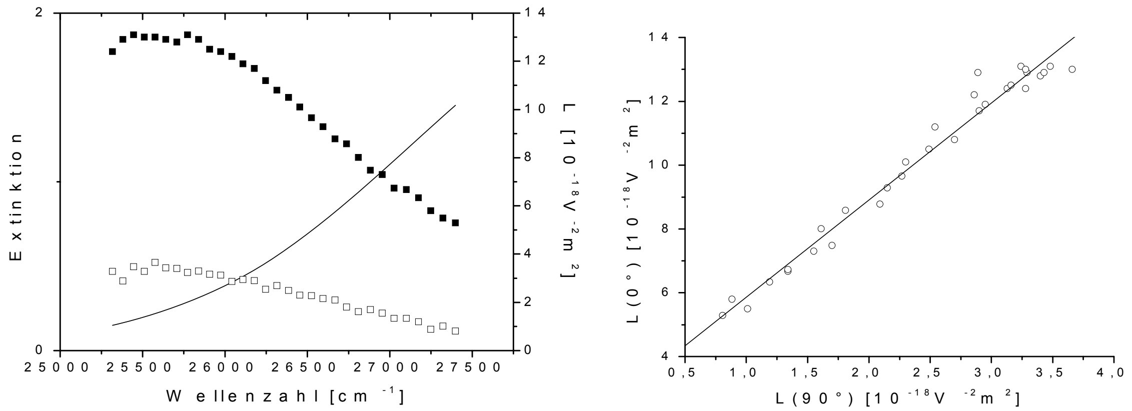


Figure 11: Electro-optical absorption measurement of compound **3a** in 1,4-dioxane. Left picture: Absorption (solid curve) and electro-optical absorption (■- χ = 0°, ○- χ = 90°) spectra of the compounds at T = 298 K. Right picture: Plot of $L(\chi = 0°)$ versus $L(\chi = 90°)$. The points show the experimental data and the line is their approximation by a linear fit.

Compound **3b**:

Electro-optical coefficients and data for dipole moments in 1,4-dioxane at T = 298 K, data collection at λ = 340-300 nm.

D [10^{-20} $V^{-2}m^2$]	27.84
E [10^{-20} $V^{-2}m^2$]	1540.80
F [10^{-40} $CV^{-1}m^2$]	1401.58
G [10^{-40} $CV^{-1}m^2$]	1765.81
μ_g [10^{-30} Cm]	10.3 $\pm$ 0.1
$\Delta^a\mu$ [10^{-30} Cm]	40.6 $\pm$ 0.4

μ_a^{FC} [10^{-30} Cm]	50.9 $\pm$ 0.4

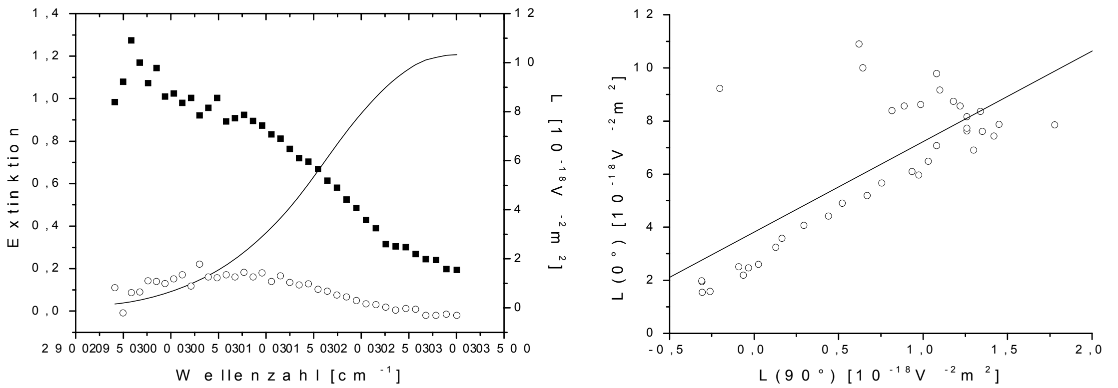


Figure 12: Electro-optical absorption measurement of compound **3b** in 1,4-dioxane. Left picture: Absorption (solid curve) and electro-optical absorption (■- $\chi = 0°$, ○- $\chi = 90°$) spectra of the compounds at $T = 298$ K. Right picture: Plot of $L(\chi = 0°)$ versus $L(\chi = 90°)$. The points show the experimental data and the line is their approximation by a linear fit.

Compound **3c**:
Electro-optical coefficients and data for dipole moments in 1,4-dioxane at T = 298 K, data collection at λ = 390-330 nm.

D [10^{-20} V^{-2}m^2]	10.01
E [10^{-20} V^{-2}m^2]	1782.78
F [10^{-40} CV^{-1}m^2]	2340.56
G [10^{-40} CV^{-1}m^2]	2607.06
μ_g [10^{-30} Cm]	10.1 $\pm$ 0.2
$\Delta^a\mu$ [10^{-30} Cm]	68.8 $\pm$ 3
μ_a^{FC} [10^{-30} Cm]	78.9 $\pm$ 3

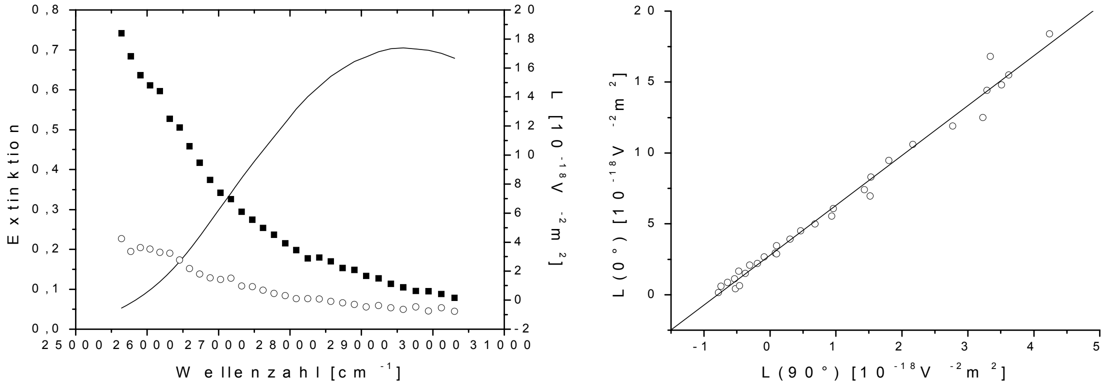


Figure 13: Electro-optical absorption measurement of compound **3c** in 1,4-dioxane. Left picture: Absorption (solid curve) and electro-optical absorption (■- $\chi = 0°$, ○- $\chi = 90°$) spectra of the compounds at $T = 298$ K. Right picture: Plot of $L(\chi = 0°)$ versus $L(\chi = 90°)$. The points show the experimental data and the line is their approximation by a linear fit.

Compound **3d**:
Electro-optical coefficients and data for dipole moments in 1,4-dioxane at T = 298 K, data collection at λ = 376-320 nm.

$D\ [10^{-20}\ \mathrm{V^{-2}m^2}]$	7.32
$E\ [10^{-20}\ \mathrm{V^{-2}m^2}]$	2605.59
$F\ [10^{-40}\ \mathrm{CV^{-1}m^2}]$	3128.03
$G\ [10^{-40}\ \mathrm{CV^{-1}m^2}]$	3341.53
$\mu_g\ [10^{-30}\ \mathrm{Cm}]$	12.2 ± 0.1
$\Delta^a\mu\ [10^{-30}\ \mathrm{Cm}]$	72.2 ± 1
$\mu_a^{FC}\ [10^{-30}\ \mathrm{Cm}]$	84.4 ± 1

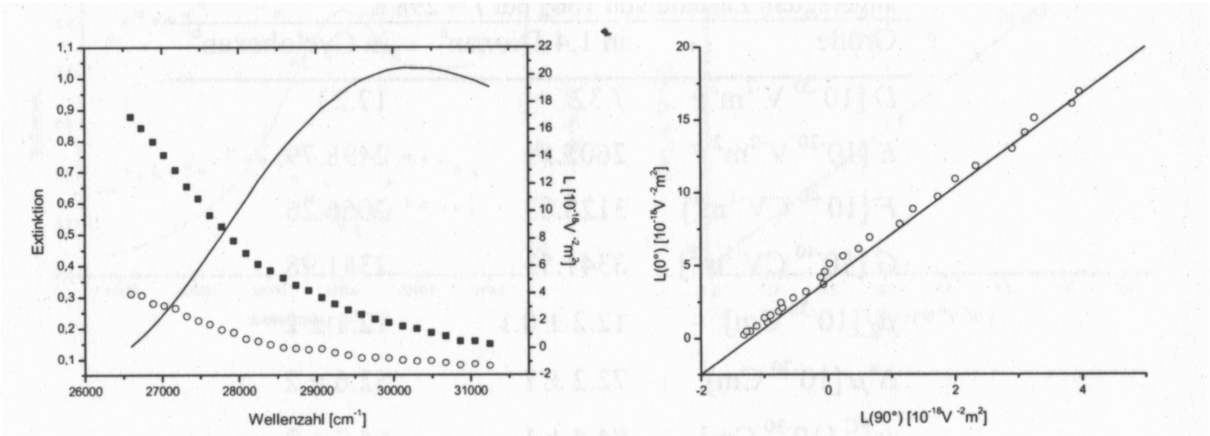


Figure 14: Electro-optical absorption measurement of compound **3d** in 1,4-dioxane. Left picture: Absorption (solid curve) and electro-optical absorption (■- $\chi = 0°$, ○- $\chi = 90°$) spectra of the compounds at $T = 298$ K. Right picture: Plot of $L(\chi = 0°)$ versus $L(\chi = 90°)$. The points show the experimental data and the line is their approximation by a linear fit.

Compound **3e**:

Electro-optical coefficients and data for dipole moments in 1,4-dioxane at T = 298 K, data collection at λ = 320-300 nm.

D [10^{-20} $V^{-2}m^2$]	24.00
E [10^{-20} $V^{-2}m^2$]	2892.00
F [10^{-40} $CV^{-1}m^2$]	1692.76
G [10^{-40} $CV^{-1}m^2$]	1666.23
μ_g [10^{-30} Cm]	11.4 ± 2
$\Delta^a\mu$ [10^{-30} Cm]	38.6 ± 5
μ_a^{FC} [10^{-30} Cm]	50.0 ± 5

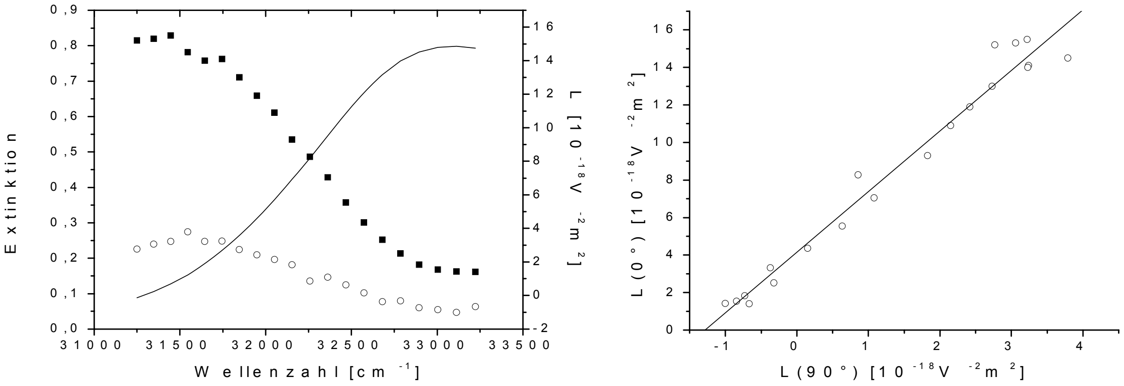


Figure 15: Electro-optical absorption measurement of compound **3e** in 1,4-dioxane. Left picture: Absorption (solid curve) and electro-optical absorption (■- $\chi = 0°$, ○- $\chi = 90°$) spectra of the compounds at $T = 298$ K. Right picture: Plot of $L(\chi = 0°)$ versus $L(\chi = 90°)$. The points show the experimental data and the line is their approximation by a linear fit.

Compound **6a**:

Electro-optical coefficients and data for dipole moments in 1,4-dioxane at T = 298 K, data collection at λ = 400-320 nm.

D [10^{-20} $V^{-2}m^2$]	~0
E [10^{-20} $V^{-2}m^2$]	1481.25
F [10^{-40} $CV^{-1}m^2$]	3089.89
G [10^{-40} $CV^{-1}m^2$]	3222.30
μ_g [10^{-30} Cm]	9.5 ± 0.2
$\Delta^a\mu$ [10^{-30} Cm]	92.3 ± 5
μ_a^{FC} [10^{-30} Cm]	101.8 ± 5

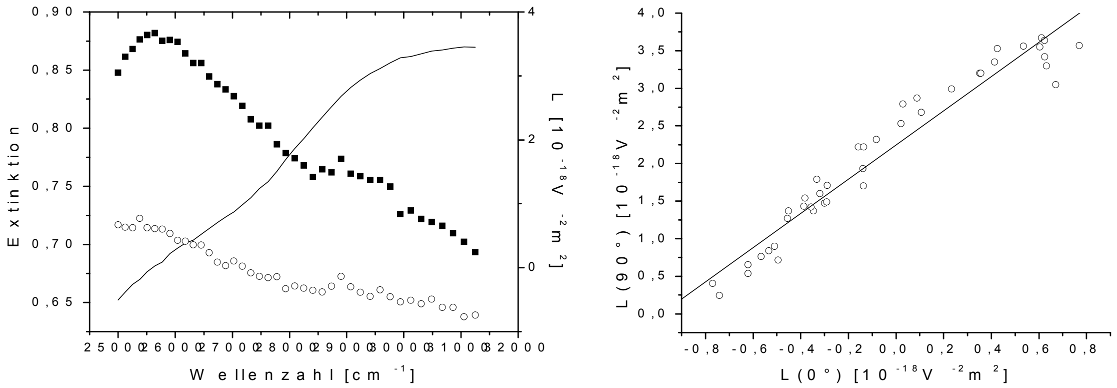


Figure 16: Electro-optical absorption measurement of compound **6a** in 1,4-dioxane. Left picture: Absorption (solid curve) and electro-optical absorption (■- $\chi = 0°$, ○- $\chi = 90°$) spectra of the compounds at $T = 298$ K. Right picture: Plot of $L(\chi = 0°)$ versus $L(\chi = 90°)$. The points show the experimental data and the line is their approximation by a linear fit.

Compound **6b**:

Electro-optical coefficients and data for dipole moments in 1,4-dioxane at T = 298 K, data collection at λ = 340-300 nm.

D [10^{-20} V^{-2}m^{2}]	~0
E [10^{-20} V^{-2}m^{2}]	1505.94
F [10^{-40} CV^{-1}m^{2}]	3080.00
G [10^{-40} CV^{-1}m^{2}]	3273.92
μ_g [10^{-30} Cm]	9.7 ± 0.1
$\Delta^a\mu$ [10^{-30} Cm]	91.1 ± 5
μ_a^{FC} [10^{-30} Cm]	100.8 ± 5

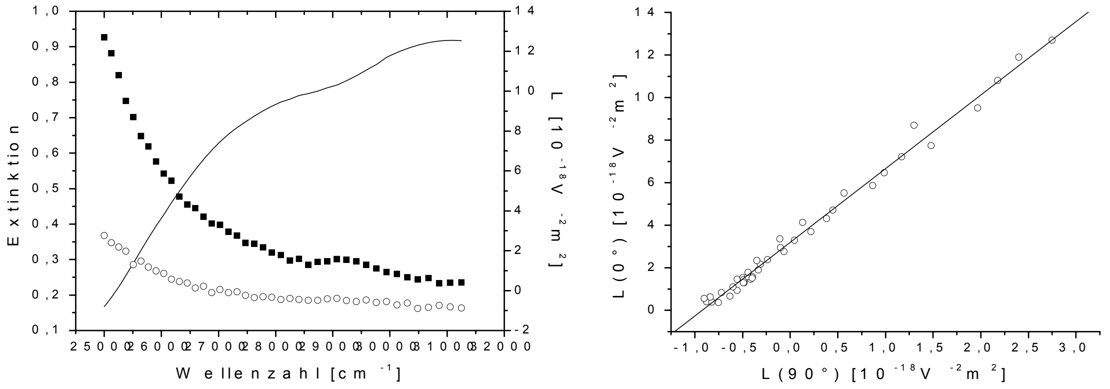


Figure 17: Electro-optical absorption measurement of compound **6b** in 1,4-dioxane. Left picture: Absorption (solid curve) and electro-optical absorption (■- $\chi = 0°$, ○- $\chi = 90°$) spectra of the compounds at $T = 298$ K. Right picture: Plot of $L(\chi = 0°)$ versus $L(\chi = 90°)$. The points show the experimental data and the line is their approximation by a linear fit.

Compound **6c**:
Electro-optical coefficients and data for dipole moments in 1,4-dioxane at T = 298 K, data collection at λ = 394-320 nm.

D [10^{-20} $V^{-2}m^{2}$]	~0
E [10^{-20} $V^{-2}m^{2}$]	2288.85
F [10^{-40} $CV^{-1}m^{2}$]	2819.48
G [10^{-40} $CV^{-1}m^{2}$]	3163.43
μ_g [10^{-30} Cm]	11.8 $\pm$ 0.1
$\Delta^a\mu$ [10^{-30} Cm]	69.7 $\pm$ 2
μ_a^{FC} [10^{-30} Cm]	81.5 $\pm$ 2

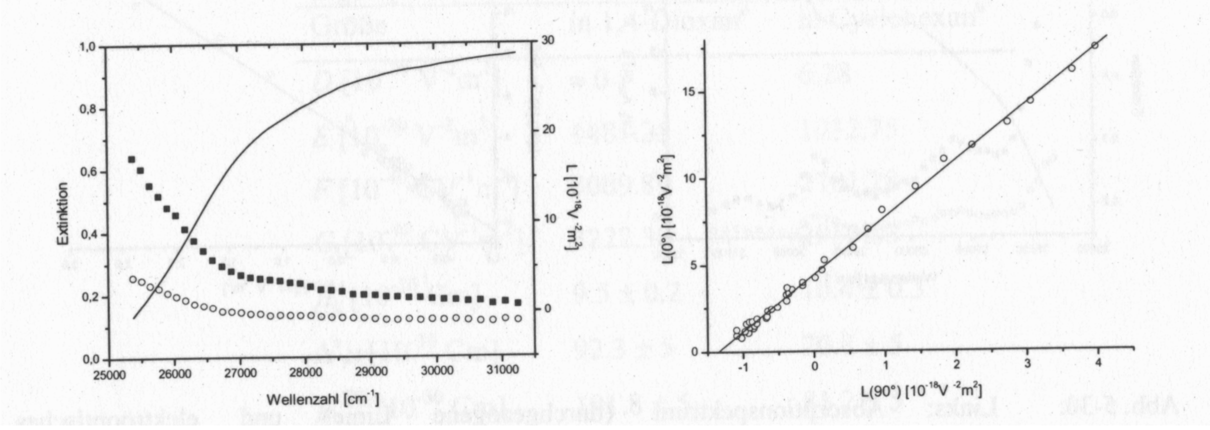


Figure 18: Electro-optical absorption measurement of compound **6c** in 1,4-dioxane. Left picture: Absorption (solid curve) and electro-optical absorption (■- χ = 0°, ○- χ = 90°) spectra of the compounds at T = 298 K. Right picture: Plot of $L(\chi = 0°)$ versus $L(\chi = 90°)$. The points show the experimental data and the line is their approximation by a linear fit.

Compound **10**:
Electro-optical coefficients and data for dipole moments in 1,4-dioxane at T = 298 K, data collection at λ = 340-300 nm.

D [10^{-20} $V^{-2}m^{2}$]	47.97
E [10^{-20} $V^{-2}m^{2}$]	1641.06
F [10^{-40} $CV^{-1}m^{2}$]	1544.82
G [10^{-40} $CV^{-1}m^{2}$]	2421.31
μ_g [10^{-30} Cm]	10.9 $\pm$ 0.2
$\Delta^a\mu$ [10^{-30} Cm]	30.8 $\pm$ 0.8
μ_a^{FC} [10^{-30} Cm]	41.7 $\pm$ 0.8

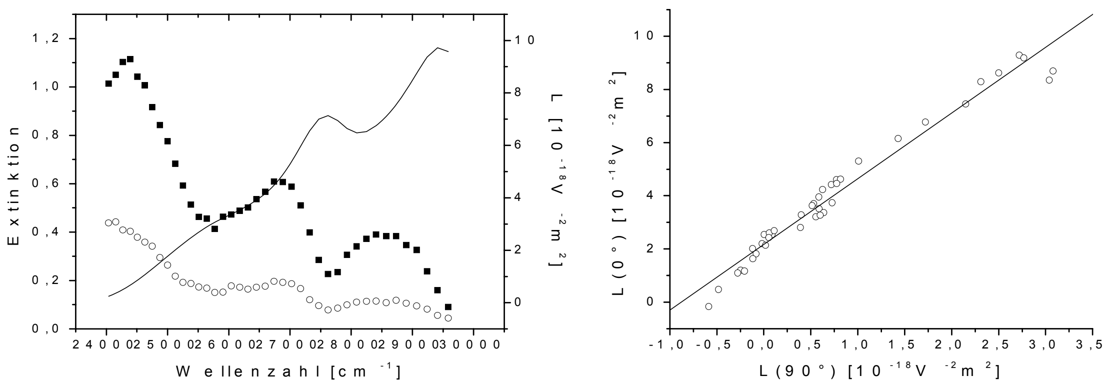


Figure 19: Electro-optical absorption measurement of compound **10** in 1,4-dioxane. Left picture: Absorption (solid curve) and electro-optical absorption (■- $\chi = 0°$, ○- $\chi = 90°$) spectra of the compounds at $T = 298$ K. Right picture: Plot of $L(\chi = 0°)$ versus $L(\chi = 90°)$. The points show the experimental data and the line is their approximation by a linear fit.

V. X-ray crystallographic structure of compound **10**

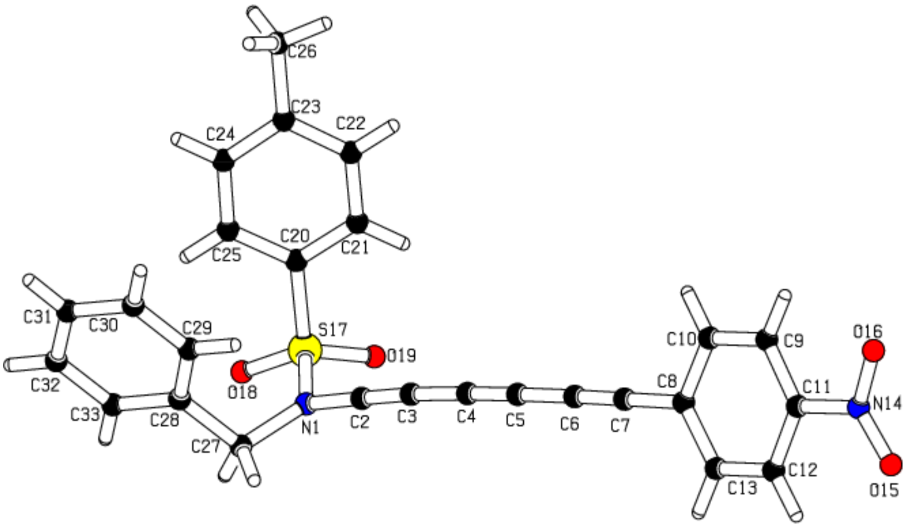
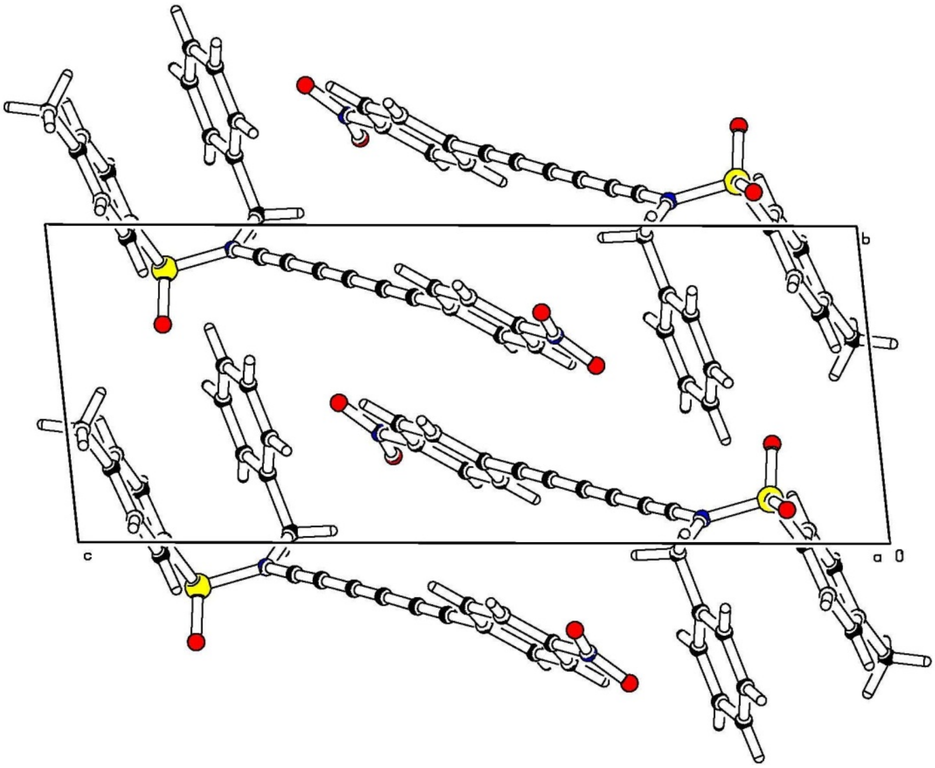


Figure 20:



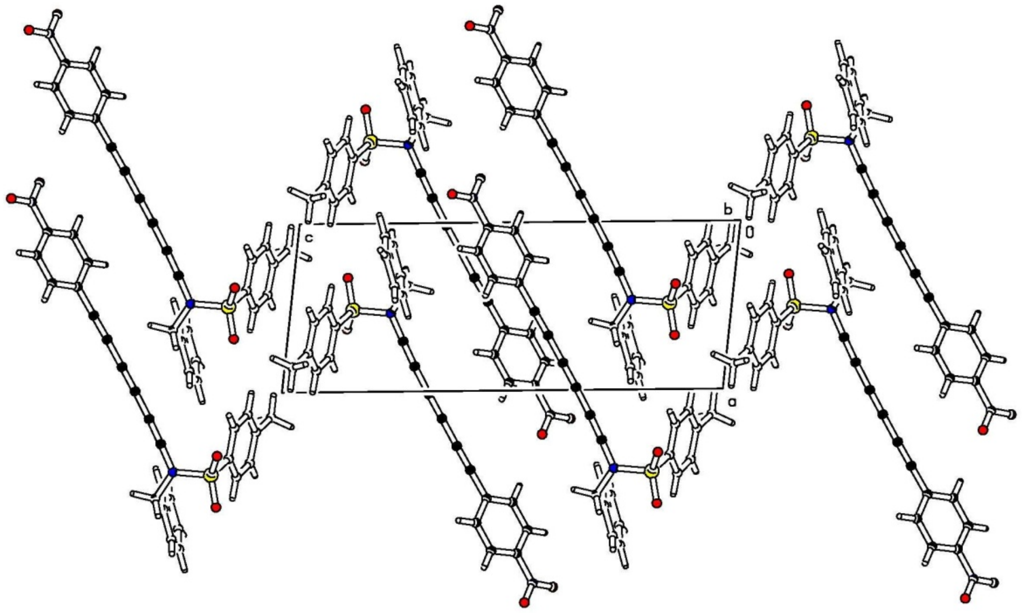


Table 1. Bond lengths [A] and angles [deg] for **10**.

N(1)-C(2)	1.340(3)
N(1)-C(27)	1.495(3)
N(1)-S(17)	1.6832(18)
C(2)-C(3)	1.207(3)
C(3)-C(4)	1.363(3)
C(4)-C(5)	1.211(3)
C(5)-C(6)	1.371(3)
C(6)-C(7)	1.202(3)
C(7)-C(8)	1.438(3)
C(8)-C(13)	1.390(3)
C(8)-C(9)	1.398(3)
C(9)-C(10)	1.381(3)
C(10)-C(11)	1.377(3)
C(11)-C(12)	1.372(3)
C(11)-N(14)	1.476(3)
C(12)-C(13)	1.383(3)
N(14)-O(15)	1.219(3)
N(14)-O(16)	1.224(3)
S(17)-O(18)	1.4241(15)
S(17)-O(19)	1.4272(14)
S(17)-C(20)	1.756(2)
C(20)-C(21)	1.379(3)
C(20)-C(25)	1.399(3)
C(21)-C(22)	1.383(3)
C(22)-C(23)	1.394(3)
C(23)-C(24)	1.390(3)

C(23)-C(26)	1.509(3)
C(24)-C(25)	1.373(3)
C(27)-C(28)	1.511(3)
C(28)-C(33)	1.384(3)
C(28)-C(29)	1.389(3)
C(29)-C(30)	1.376(3)
C(30)-C(31)	1.368(4)
C(31)-C(32)	1.374(4)
C(32)-C(33)	1.396(3)

C(2)-N(1)-C(27)	120.03(18)
C(2)-N(1)-S(17)	118.28(15)
C(27)-N(1)-S(17)	120.67(13)
C(3)-C(2)-N(1)	178.6(2)
C(2)-C(3)-C(4)	176.8(2)
C(5)-C(4)-C(3)	178.6(2)
C(4)-C(5)-C(6)	179.1(2)
C(7)-C(6)-C(5)	178.9(2)
C(6)-C(7)-C(8)	179.6(3)
C(13)-C(8)-C(9)	119.3(2)
C(13)-C(8)-C(7)	121.3(2)
C(9)-C(8)-C(7)	119.4(2)
C(10)-C(9)-C(8)	120.3(2)
C(11)-C(10)-C(9)	118.6(2)
C(12)-C(11)-C(10)	122.6(2)
C(12)-C(11)-N(14)	119.3(2)
C(10)-C(11)-N(14)	118.2(2)
C(11)-C(12)-C(13)	118.6(2)
C(12)-C(13)-C(8)	120.6(2)
O(15)-N(14)-O(16)	124.1(2)
O(15)-N(14)-C(11)	118.3(2)
O(16)-N(14)-C(11)	117.6(2)
O(18)-S(17)-O(19)	121.43(9)
O(18)-S(17)-N(1)	103.92(9)
O(19)-S(17)-N(1)	106.06(9)
O(18)-S(17)-C(20)	110.77(9)
O(19)-S(17)-C(20)	107.97(9)
N(1)-S(17)-C(20)	105.39(9)
C(21)-C(20)-C(25)	121.04(19)
C(21)-C(20)-S(17)	118.73(14)
C(25)-C(20)-S(17)	120.22(16)
C(20)-C(21)-C(22)	119.12(18)
C(21)-C(22)-C(23)	121.2(2)
C(24)-C(23)-C(22)	118.22(19)
C(24)-C(23)-C(26)	120.93(19)
C(22)-C(23)-C(26)	120.9(2)
C(25)-C(24)-C(23)	121.84(18)
C(24)-C(25)-C(20)	118.6(2)
N(1)-C(27)-C(28)	113.84(16)
C(33)-C(28)-C(29)	118.92(19)
C(33)-C(28)-C(27)	120.41(19)
C(29)-C(28)-C(27)	120.66(18)
C(30)-C(29)-C(28)	120.6(2)
C(31)-C(30)-C(29)	120.2(2)
C(30)-C(31)-C(32)	120.6(2)
C(31)-C(32)-C(33)	119.5(2)
C(28)-C(33)-C(32)	120.2(2)

Torsion angles [deg] for **10**.

C(27)-N(1)-C(2)-C(3)	-2(10)
S(17)-N(1)-C(2)-C(3)	167(10)
N(1)-C(2)-C(3)-C(4)	73(11)
C(2)-C(3)-C(4)-C(5)	-17(14)
C(3)-C(4)-C(5)-C(6)	46(24)
C(4)-C(5)-C(6)-C(7)	-76(23)
C(5)-C(6)-C(7)-C(8)	-71(40)
C(6)-C(7)-C(8)-C(13)	109(35)
C(6)-C(7)-C(8)-C(9)	-72(35)
C(13)-C(8)-C(9)-C(10)	0.3(3)
C(7)-C(8)-C(9)-C(10)	-179.3(2)
C(8)-C(9)-C(10)-C(11)	-0.5(4)
C(9)-C(10)-C(11)-C(12)	0.8(4)
C(9)-C(10)-C(11)-N(14)	180.0(2)
C(10)-C(11)-C(12)-C(13)	-1.0(3)
N(14)-C(11)-C(12)-C(13)	179.90(19)
C(11)-C(12)-C(13)-C(8)	0.8(3)
C(9)-C(8)-C(13)-C(12)	-0.5(3)
C(7)-C(8)-C(13)-C(12)	179.1(2)
C(12)-C(11)-N(14)-O(15)	7.7(3)
C(10)-C(11)-N(14)-O(15)	-171.5(2)
C(12)-C(11)-N(14)-O(16)	-172.2(2)
C(10)-C(11)-N(14)-O(16)	8.7(3)
C(2)-N(1)-S(17)-O(18)	177.27(14)
C(27)-N(1)-S(17)-O(18)	-14.31(16)
C(2)-N(1)-S(17)-O(19)	48.19(16)
C(27)-N(1)-S(17)-O(19)	-143.39(14)
C(2)-N(1)-S(17)-C(20)	-66.17(15)
C(27)-N(1)-S(17)-C(20)	102.26(15)
O(18)-S(17)-C(20)-C(21)	-160.51(16)
O(19)-S(17)-C(20)-C(21)	-25.32(19)
N(1)-S(17)-C(20)-C(21)	87.70(18)
O(18)-S(17)-C(20)-C(25)	21.0(2)
O(19)-S(17)-C(20)-C(25)	156.17(16)
N(1)-S(17)-C(20)-C(25)	-90.81(17)
C(25)-C(20)-C(21)-C(22)	0.2(3)
S(17)-C(20)-C(21)-C(22)	-178.32(16)
C(20)-C(21)-C(22)-C(23)	-0.7(3)
C(21)-C(22)-C(23)-C(24)	0.9(3)
C(21)-C(22)-C(23)-C(26)	-178.5(2)
C(22)-C(23)-C(24)-C(25)	-0.7(3)
C(26)-C(23)-C(24)-C(25)	178.8(2)
C(23)-C(24)-C(25)-C(20)	0.1(3)
C(21)-C(20)-C(25)-C(24)	0.1(3)
S(17)-C(20)-C(25)-C(24)	178.59(16)
C(2)-N(1)-C(27)-C(28)	100.7(2)
S(17)-N(1)-C(27)-C(28)	-67.5(2)
N(1)-C(27)-C(28)-C(33)	125.3(2)
N(1)-C(27)-C(28)-C(29)	-55.4(3)
C(33)-C(28)-C(29)-C(30)	-1.3(3)
C(27)-C(28)-C(29)-C(30)	179.3(2)
C(28)-C(29)-C(30)-C(31)	0.6(4)
C(29)-C(30)-C(31)-C(32)	0.6(4)
C(30)-C(31)-C(32)-C(33)	-1.1(4)
C(29)-C(28)-C(33)-C(32)	0.9(3)
C(27)-C(28)-C(33)-C(32)	-179.8(2)
C(31)-C(32)-C(33)-C(28)	0.3(4)

Endkoordinaten und äquivalente Auslenkungsparameter ($Å^2$)

$$U_{äq} = (1/3)*\sum\sum_{ij} a_i^{*} a_j^{*} \mathbf{a}_i \mathbf{a}_j$$

Atom	X	Y	Z	$U_{äq}$
N1	0.4657(2)	0.0777(2)	0.22824(9)	0.0354(6)
C2	0.2984(3)	0.1002(3)	0.2628(1)	0.0377(8)
C3	0.1492(3)	0.1183(3)	0.2951(1)	0.0414(8)
C4	-0.0165(3)	0.1448(3)	0.3338(1)	0.0428(8)
C5	-0.1622(3)	0.1696(3)	0.3693(1)	0.0431(8)
C6	-0.3268(3)	0.2003(3)	0.4096(1)	0.0436(8)
C7	-0.4696(3)	0.2267(3)	0.4459(1)	0.0444(9)
C8	-0.6402(3)	0.2570(3)	0.4895(1)	0.0393(8)
C9	-0.7852(3)	0.1981(3)	0.4718(1)	0.0491(9)
C10	-0.9509(3)	0.2277(3)	0.5126(1)	0.0503(9)
C11	-0.9692(3)	0.3147(3)	0.5709(1)	0.0406(8)
C12	-0.8301(3)	0.3751(3)	0.5896(1)	0.0432(8)
C13	-0.6644(3)	0.3448(3)	0.5487(1)	0.0418(8)
N14	-1.1468(3)	0.3456(3)	0.6141(1)	0.0552(8)
O15	-1.1702(3)	0.4404(3)	0.6609(1)	0.0835(10)
O16	-1.2616(2)	0.2736(3)	0.6006(1)	0.0753(9)
S17	0.48656(7)	0.13972(6)	0.14182(3)	0.0352(2)
O18	0.6777(2)	0.1065(2)	0.12251(8)	0.0440(6)
O19	0.3741(2)	0.3139(2)	0.13225(8)	0.0471(6)
C20	0.3905(3)	-0.0043(2)	0.1051(1)	0.0321(7)
C21	0.2065(3)	0.0407(3)	0.0998(1)	0.0387(8)
C22	0.1289(3)	-0.0742(3)	0.0726(1)	0.0411(8)
C23	0.2335(3)	-0.2329(3)	0.0500(1)	0.0384(8)
C24	0.4183(3)	-0.2745(3)	0.0563(1)	0.0399(8)
C25	0.4989(3)	-0.1634(3)	0.0833(1)	0.0381(7)
C26	0.1484(3)	-0.3554(3)	0.0188(1)	0.0488(9)
C27	0.6249(3)	-0.0308(3)	0.2630(1)	0.0401(8)
C28	0.6886(3)	-0.2170(3)	0.2421(1)	0.0335(7)
C29	0.5693(3)	-0.3290(3)	0.2494(1)	0.0434(8)
C30	0.6272(4)	-0.4979(3)	0.2297(1)	0.058(1)
C31	0.8039(4)	-0.5578(3)	0.2032(2)	0.066(1)
C32	0.9260(4)	-0.4512(4)	0.1965(1)	0.066(1)
C33	0.8677(3)	-0.2793(3)	0.2160(1)	0.0481(9)

Kristalldaten für **10**

Summenformel	$C_{26}H_{18}N_2O_4S$		
Molgewicht	454.48gmol^{-1}		
Absorption	$\mu = 0.18$ mm^{-1} Korrektur mit MULABS		
Transmission	$T_{min} = 0.7$, $T_{max} = 1.3$		
Kristallgröße	0.1 x 0.72 x 0.95 mm^3 gelbliche Platte		
Raumgruppe	P -1 (triklin)		
Gitterkonstanten	a = 7.637(1)Å	α = 82.132(9)°	
(berechnet aus	b = 7.813(1)Å	ß = 81.809(9)°	
2829 Reflexen mit	c = 19.483(3)Å	γ = 76.056(9)°	
2.7° < Θ < 27.4°)	V = 1110.4(3)Å^3	z = 2	F(000) = 472
Temperatur	-80°C		
Dichte	$d_{rön} = 1.359$ gcm^{-3}		

Datensammlung

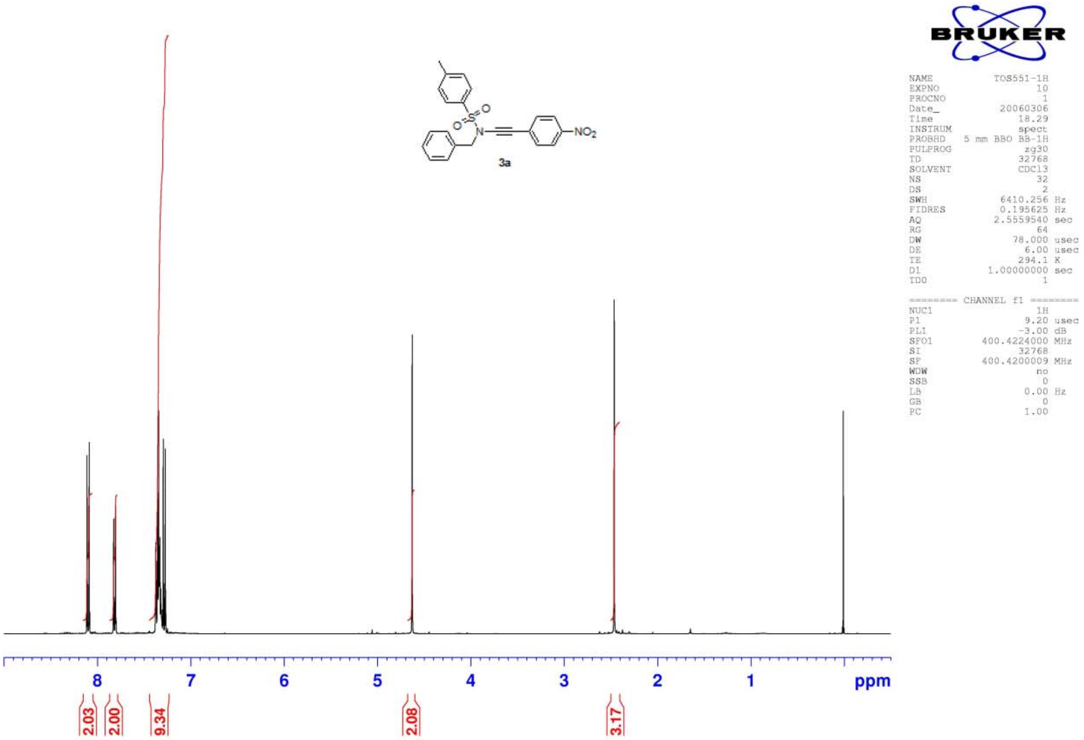
Diffraktometer	SMART CCD
Strahlung	Mo-K_α Graphitmonochromator
Scan – Typ	CCD scan

Scan – Breite	0.3°
Meßbereich	$2° \leq \theta < 28.3°$ $-10 \leq h \leq 10$ $-10 \leq k \leq 6$ $-25 \leq l \leq 25$
Reflexzahl:	
gemessen	12989
unabhängige	5423 ($R_\sigma = 0.0814$)
beobachtete	3181 ($\lvert F\rvert/\sigma(F) > 4.0$)

Datenkorrektur, Strukturlösung und -verfeinerung

Korrekturen	Lorentz- und Polarisationskorrektur.
Lösung	Programm: SIR-97 (Direkte Methoden)
Verfeinerung	Programm: SHELXL-97 (Vollmatrixverfahren). 313 verfeinerte Parameter, gewichtete Verfeinerung: $w=1/[\sigma2(F_o^2) + (0.0648*P)^2]$ wobei $P=(Max(F_o^2,0)+2*F_o^2)/3$. Wasserstoffatome geometrisch eingefügt und reitend isotrop verfeinert, Nichtwasserstoffatome anisotrop verfeinert.
Diskrepanzfaktor	wR2 = 0.1342 (R1=0.0538 für beobachtete Reflexe, 0.0943 für alle Reflexe)
Fitgüte	S = 0.891
maximale Änderung der Parameter	0.001 * e.s.d

VI Selected ^{1}H & ^{13}C NMR spectra



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PROCNO                1
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Time              18.29
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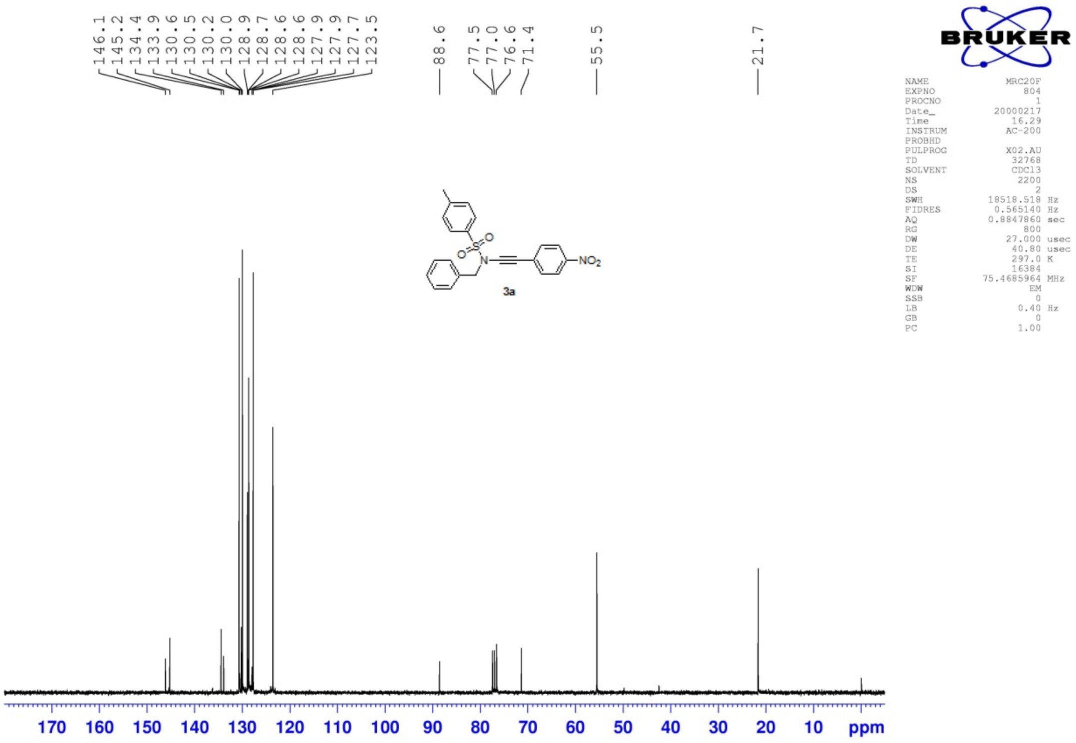
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    2
SWH            6410.256 Hz
FIDRES         0.195625 Hz
AQ            2.5559540 sec
RG                   64
DW               78.000 usec
DE                 6.00 usec
TE                294.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.20 usec
PL1               -3.00 dB
SFO1        400.4224000 MHz
SI                32768
SF          400.4200009 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

Figure 21a: ^{1}H NMR (400 MHz, $CDCl_3$) of ynamide **3a**.



```
NAME             MRC20F
EXPNO               804
PROCNO                1
Date_          20000217
Time              16.29
INSTRUM          AC-200
PROBHD
PULPROG          X02.AU
TD                32768
SOLVENT           CDCl3
NS                 2200
DS                    2
SWH           18518.518 Hz
FIDRES         0.565140 Hz
AQ            0.8847860 sec
RG                  800
DW               27.000 usec
DE                40.80 usec
TE                297.0 K
SI                16384
SF           75.4685964 MHz
WDW                  EM
SSB                   0
LB                 0.40 Hz
GB                    0
PC                 1.00
```

Figure 21b: ^{13}C NMR (75 MHz, CDCl$_3$) of ynamide **3a**.

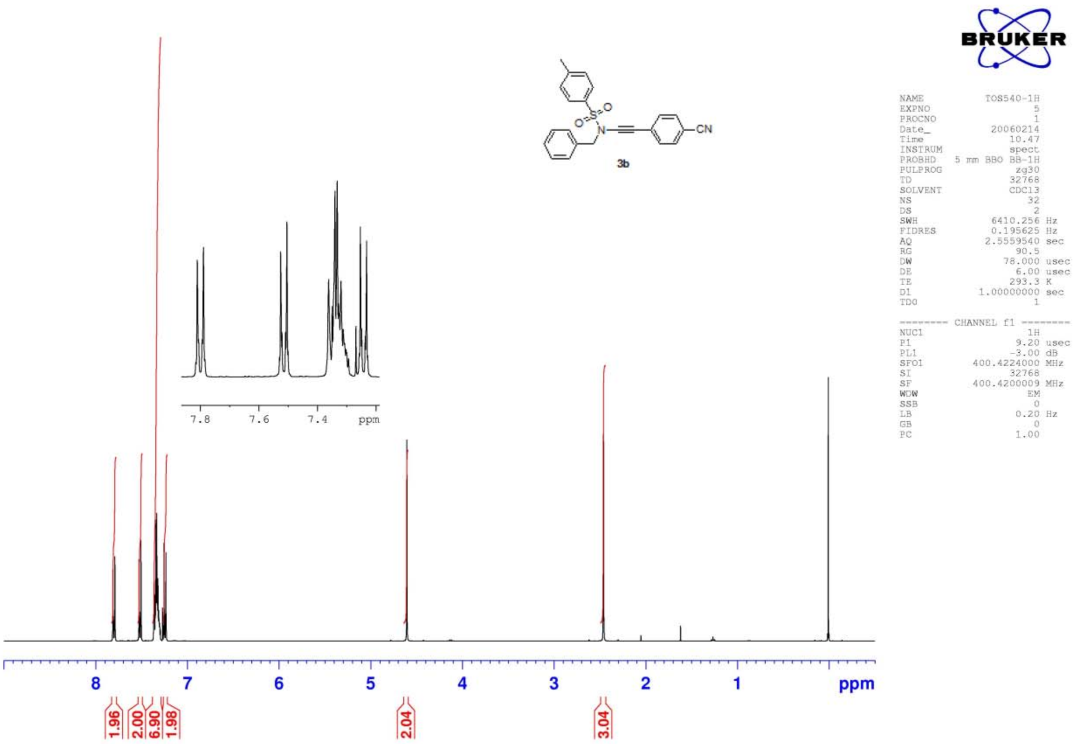


Figure 22a: ^{1}H NMR (400 MHz, CDCl$_3$) of ynamide **3b**.

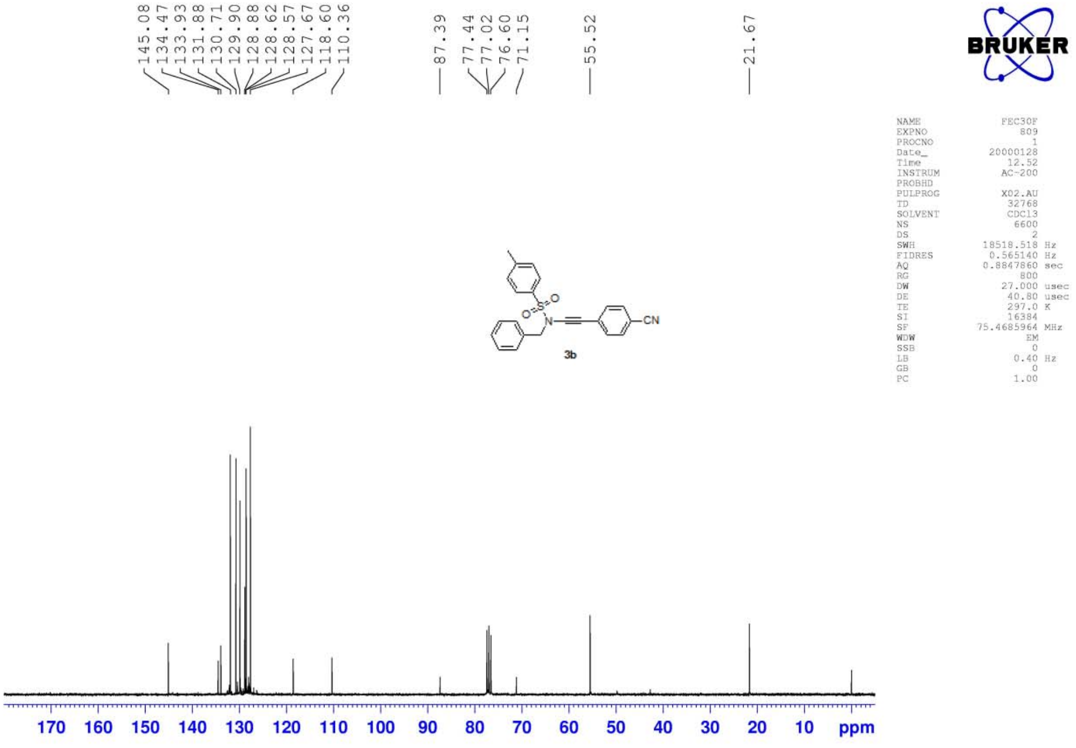
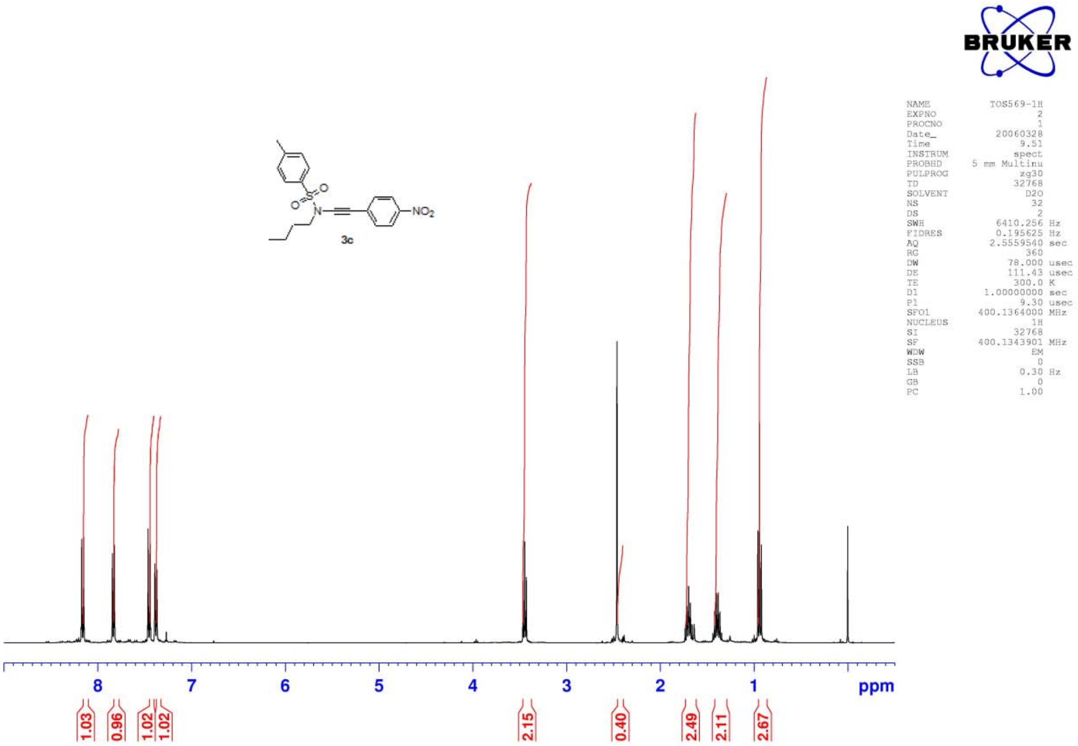
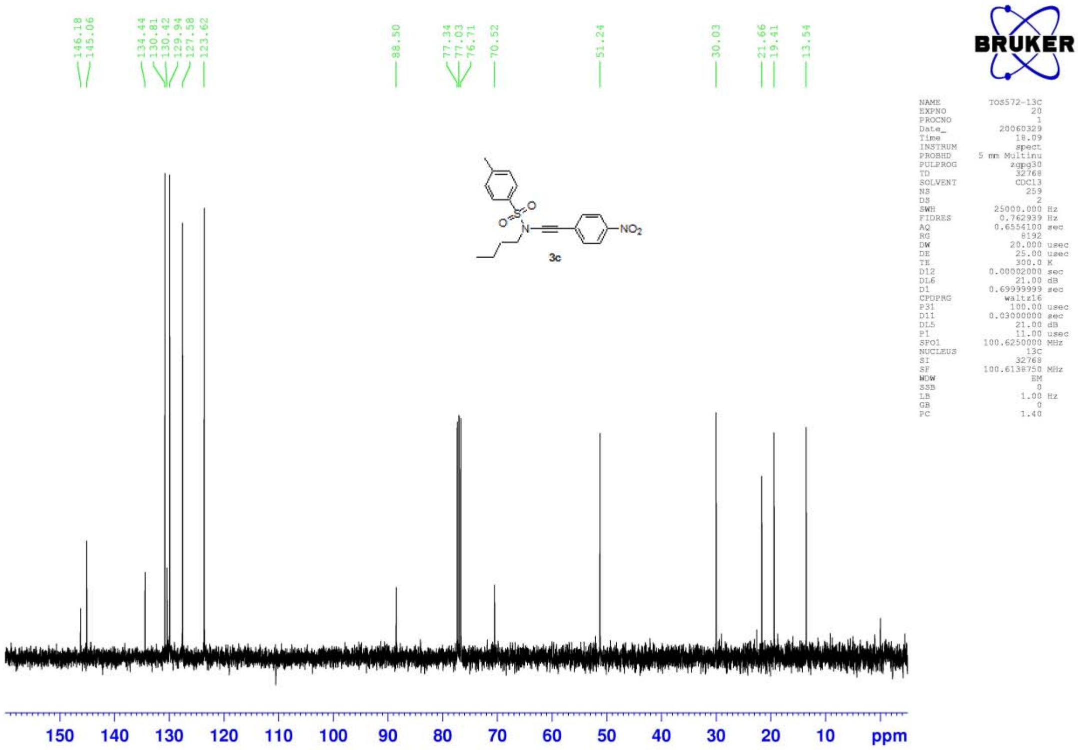


Figure 22b: ^{13}C NMR (75 MHz, CDCl$_3$) of ynamide **3b**.



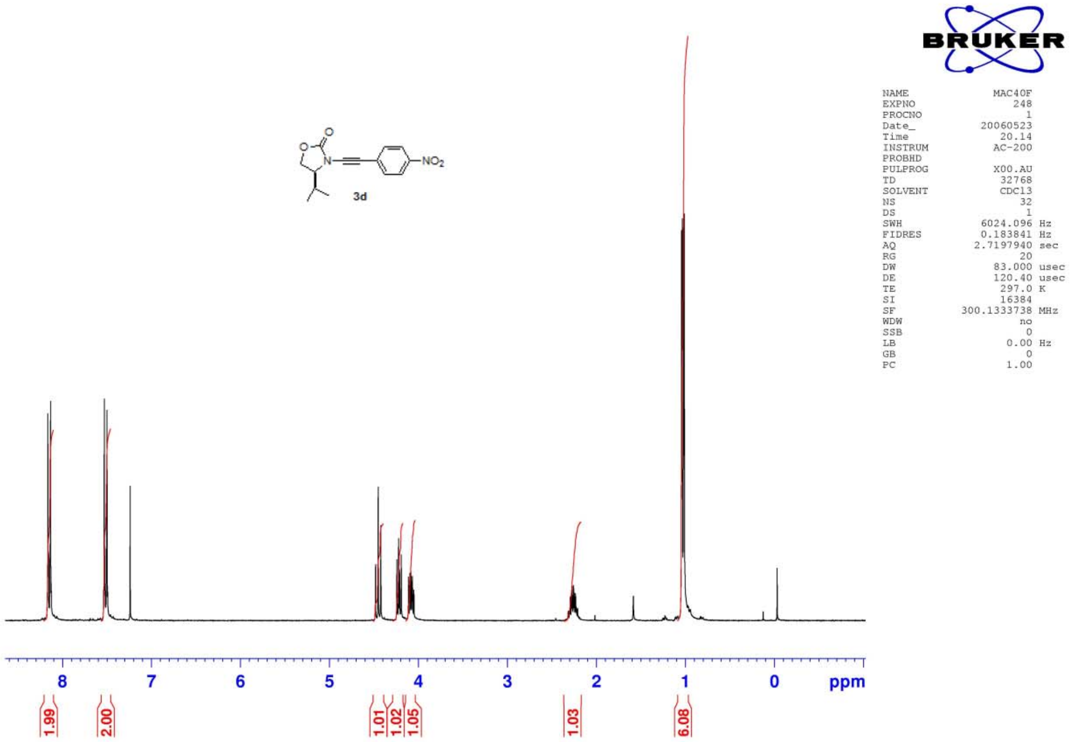
```
NAME          TOS569-1H
EXPNO                 2
PROCNO                1
Date_          20060328
Time               9.51
INSTRUM           spect
PROBHD   5 mm Multinu
PULPROG            zg30
TD                32768
SOLVENT             D2O
NS                   32
DS                    2
SWH            6410.256 Hz
FIDRES         0.195625 Hz
AQ            2.5559540 sec
RG                  360
DW               78.000 usec
DE               111.43 usec
TE                300.0 K
D1           1.00000000 sec
P1                 9.30 usec
SFO1        400.1364000 MHz
NUCLEUS              1H
SI                32768
SF          400.1343901 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Figure 23a: ^{1}H NMR (400 MHz, CDCl$_3$) of ynamide **3c**.



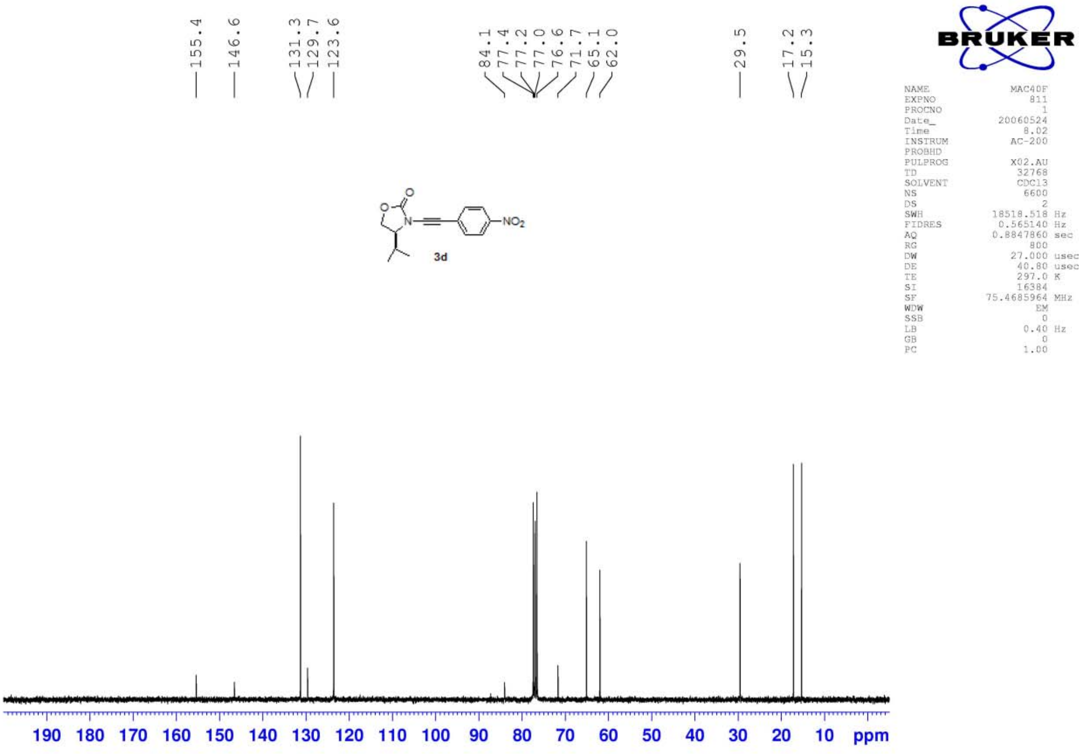
```
NAME          TOS572-13C
EXPNO                 20
PROCNO                 1
Date_           20060329
Time               18.09
INSTRUM            spect
PROBHD    5 mm Multinu
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   259
DS                     2
SWH            25000.000 Hz
FIDRES          0.762939 Hz
AQ             0.6554100 sec
RG                  8192
DW                20.000 usec
DE                 25.00 usec
TE                 300.0 K
D12           0.00002000 sec
DL6                21.00 dB
D1            0.69999999 sec
CPDPRG           waltz16
P31               100.00 usec
D11           0.03000000 sec
DL5                21.00 dB
P1                 11.00 usec
SFO1         100.6250000 MHz
NUCLEUS              13C
SI                 32768
SF           100.6138750 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure 23b: ^{13}C NMR (100 MHz, CDCl$_3$) of ynamide **3c**.



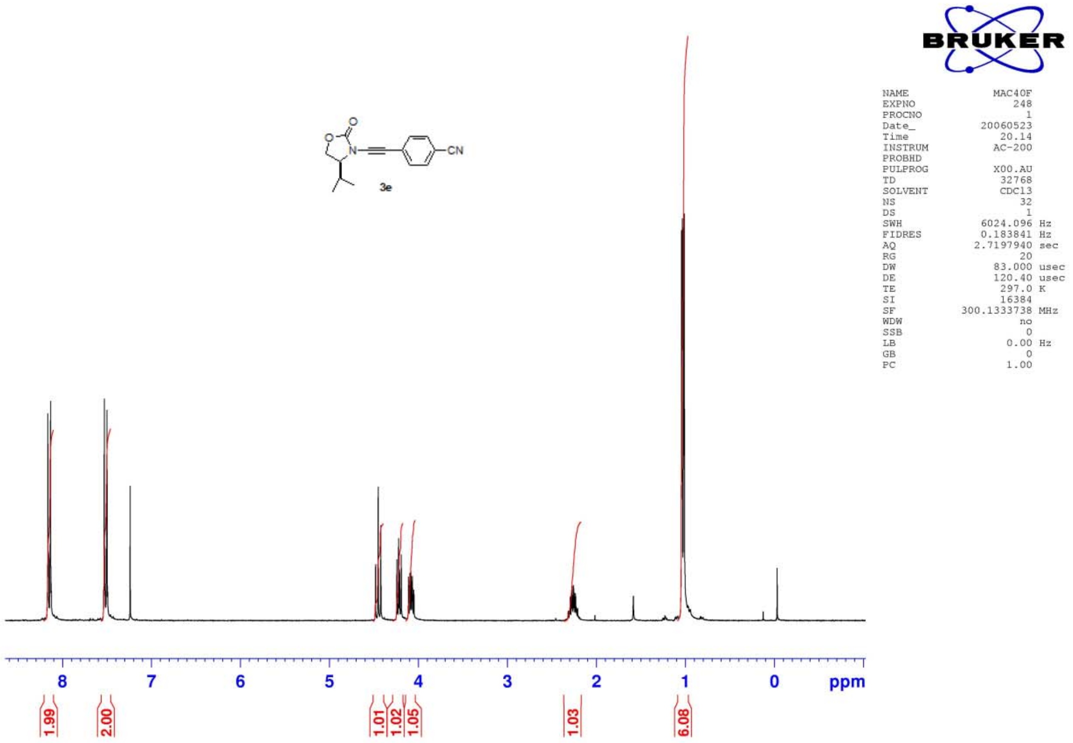
```
NAME              MAC40F
EXPNO                248
PROCNO                 1
Date_           20060523
Time               20.14
INSTRUM           AC-200
PROBHD
PULPROG           X00.AU
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     1
SWH             6024.096 Hz
FIDRES          0.183841 Hz
AQ             2.7197940 sec
RG                    20
DW                83.000 usec
DE                120.40 usec
TE                 297.0 K
SI                 16384
SF           300.1333738 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

Figure 24a: ^{1}H NMR (300 MHz, $CDCl_3$) of ynamide **3d**.



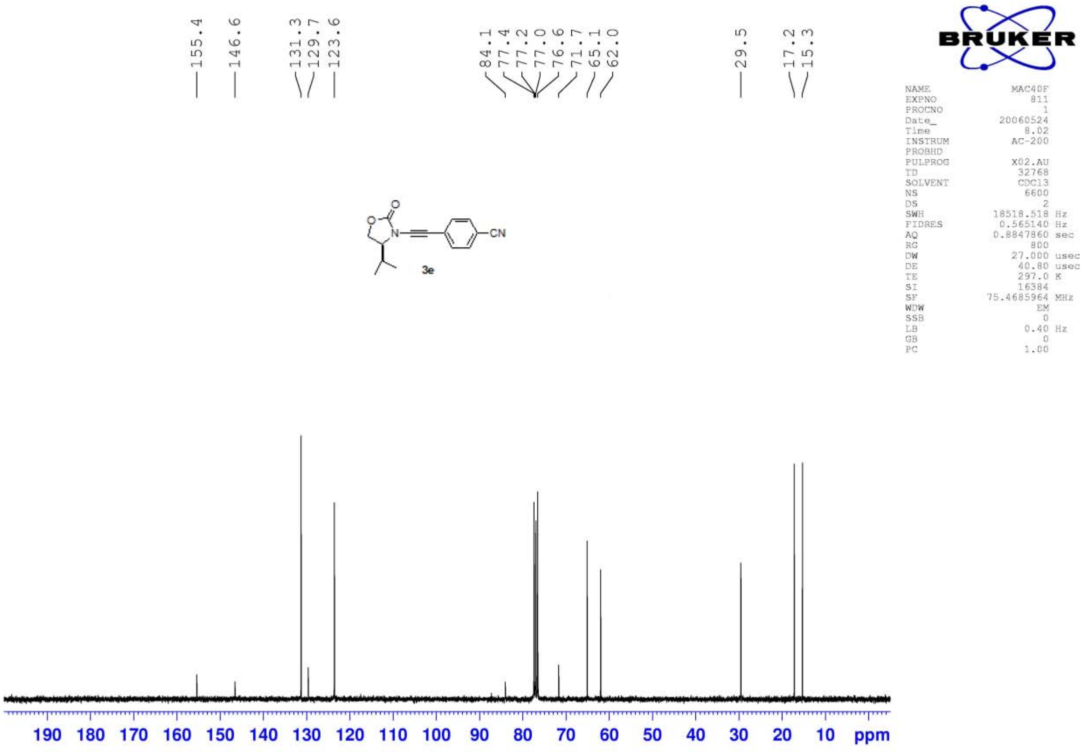
```
NAME              MAC40F
EXPNO                811
PROCNO                 1
Date_           20060524
Time                8.02
INSTRUM           AC-200
PROBHD
PULPROG           X02.AU
TD                 32768
SOLVENT            CDCl3
NS                  6600
DS                     2
SWH            18518.518 Hz
FIDRES          0.565140 Hz
AQ             0.8847860 sec
RG                   800
DW                27.000 usec
DE                 40.80 usec
TE                 297.0 K
SI                 16384
SF            75.4685964 MHz
WDW                   EM
SSB                    0
LB                  0.40 Hz
GB                     0
PC                  1.00
```

Figure 24b: ^{13}C NMR (75 MHz, $CDCl_3$) of ynamide **3d**.



```
NAME        MAC40F
EXPNO          248
PROCNO           1
Date_     20060523
Time         20.14
INSTRUM     AC-200
PROBHD
PULPROG     X00.AU
TD           32768
SOLVENT      CDCl3
NS              32
DS               1
SWH       6024.096 Hz
FIDRES    0.183841 Hz
AQ       2.7197940 sec
RG              20
DW          83.000 usec
DE          120.40 usec
TE           297.0 K
SI           16384
SF     300.1333738 MHz
WDW             no
SSB              0
LB            0.00 Hz
GB               0
PC            1.00
```

Figure 25a: ^{1}H NMR (300 MHz, CDCl$_3$) of ynamide **3e**.



```
NAME        MAC40F
EXPNO          811
PROCNO           1
Date_     20060524
Time          8.02
INSTRUM     AC-200
PROBHD
PULPROG     X02.AU
TD           32768
SOLVENT      CDCl3
NS            6600
DS               2
SWH      18518.518 Hz
FIDRES    0.565140 Hz
AQ       0.8847860 sec
RG             800
DW          27.000 usec
DE           40.80 usec
TE           297.0 K
SI           16384
SF      75.4685964 MHz
WDW             EM
SSB              0
LB            0.40 Hz
GB               0
PC            1.00
```

Figure 25b: ^{13}C NMR (75 MHz, CDCl$_3$) of ynamide **3e**.

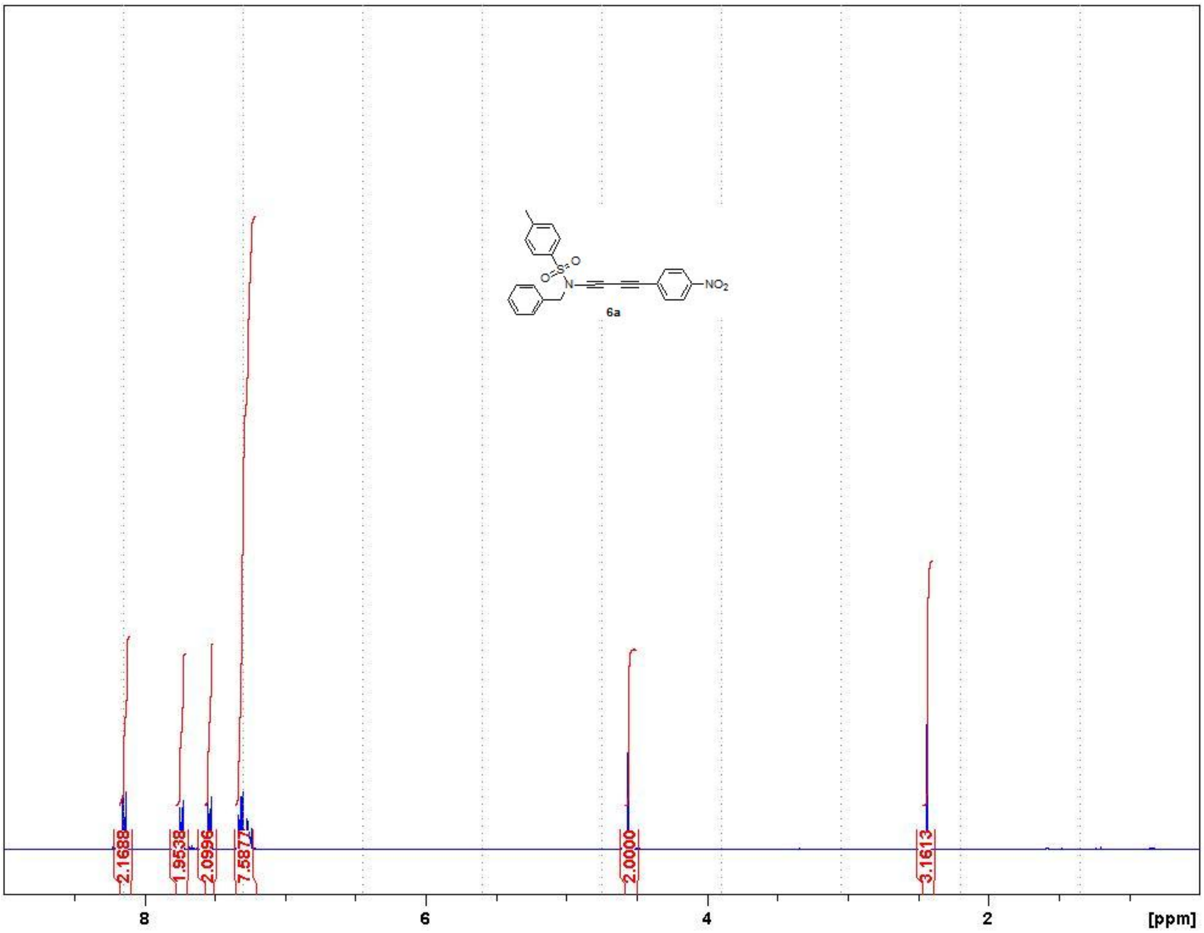


Figure 26a: ^{1}H NMR (300 MHz, CDCl$_3$) of diynamide **6a**.

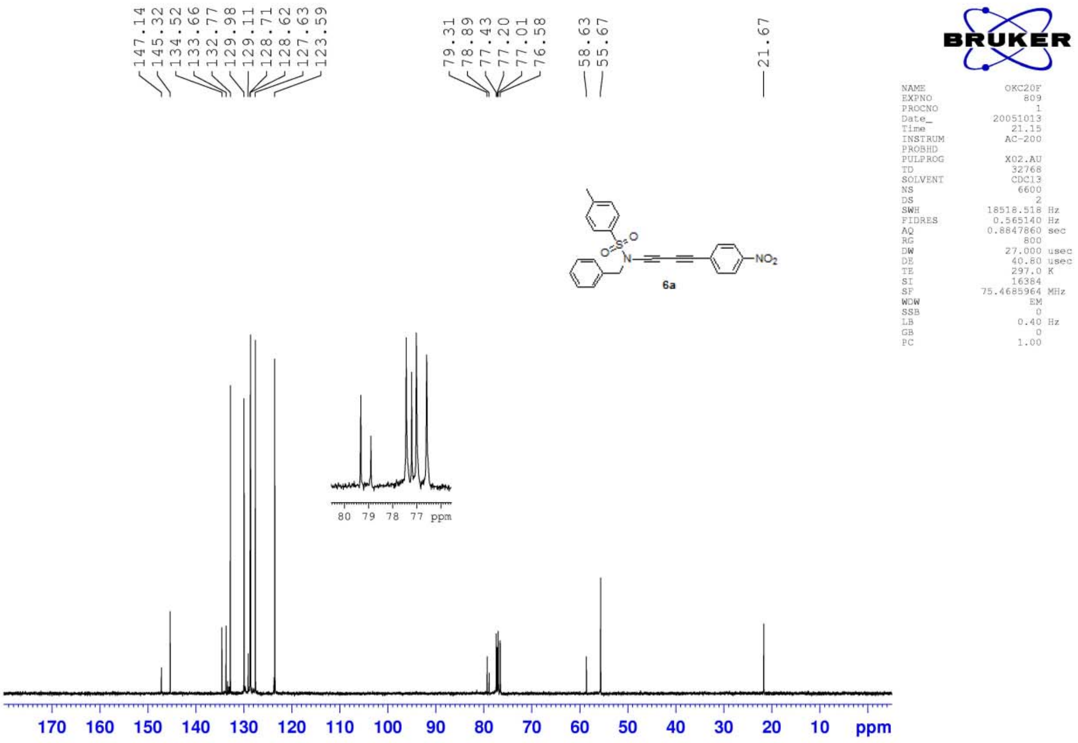
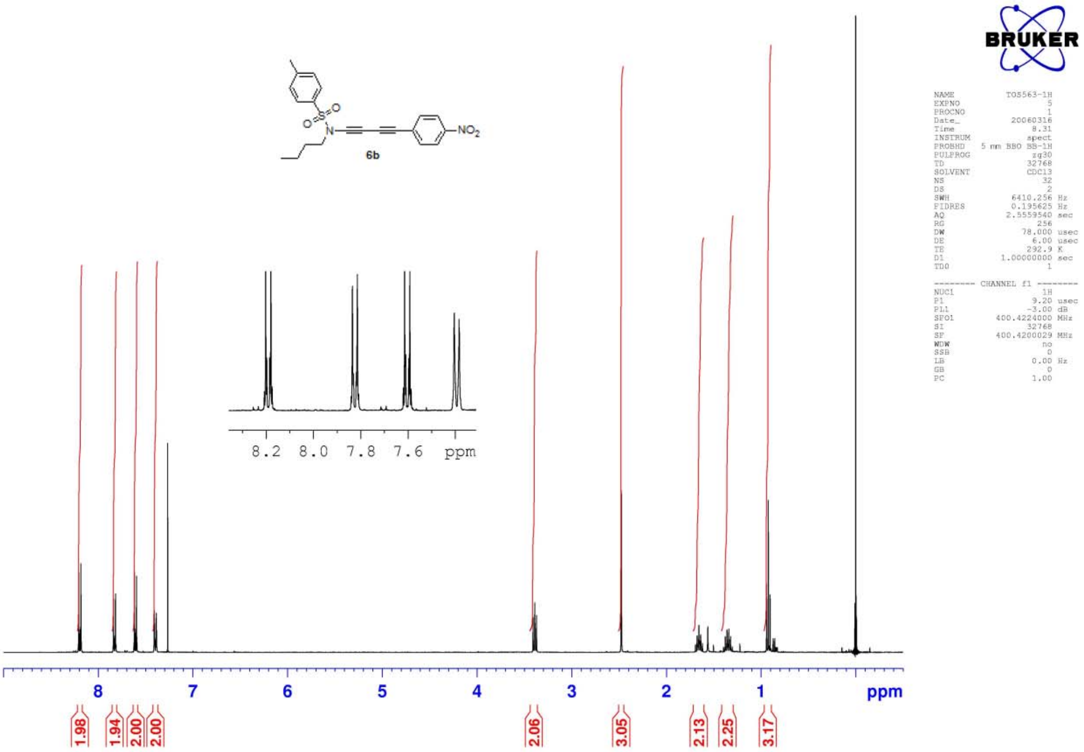


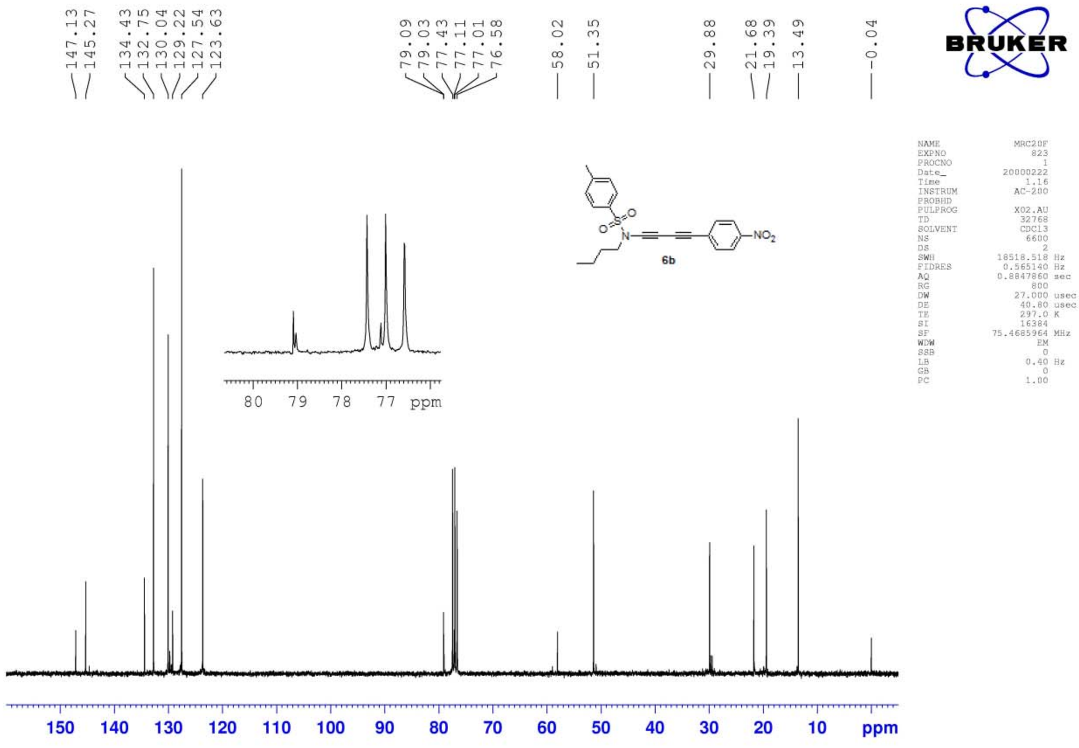
Figure 26b: ^{13}C NMR (75 MHz, $CDCl_3$) of diynamide **6a**.



```
NAME          TOS563-1H
EXPNO                 5
PROCNO                1
Date_          20060316
Time               8.31
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    2
SWH            6410.256 Hz
FIDRES         0.195625 Hz
AQ            2.5559540 sec
RG                  256
DW               78.000 usec
DE                 6.00 usec
TE                292.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.20 usec
PL1               -3.00 dB
SFO1        400.4224000 MHz
SI                32768
SF          400.4200029 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

Figure 27a: ^{1}H NMR (400 MHz, $CDCl_3$) of diynamide **6b**.



```
NAME            MRC20F
EXPNO              823
PROCNO               1
Date_         20000222
Time              1.16
INSTRUM         AC-200
PROBHD
PULPROG         X02.AU
TD               32768
SOLVENT          CDCl3
NS                6600
DS                   2
SWH          18518.518 Hz
FIDRES        0.565140 Hz
AQ           0.8847860 sec
RG                 800
DW              27.000 usec
DE               40.80 usec
TE               297.0 K
SI               16384
SF          75.4685964 MHz
WDW                 EM
SSB                  0
LB                0.40 Hz
GB                   0
PC                1.00
```

Figure 27b: ^{13}C NMR (75 MHz, $CDCl_3$) of diynamide **6b**.

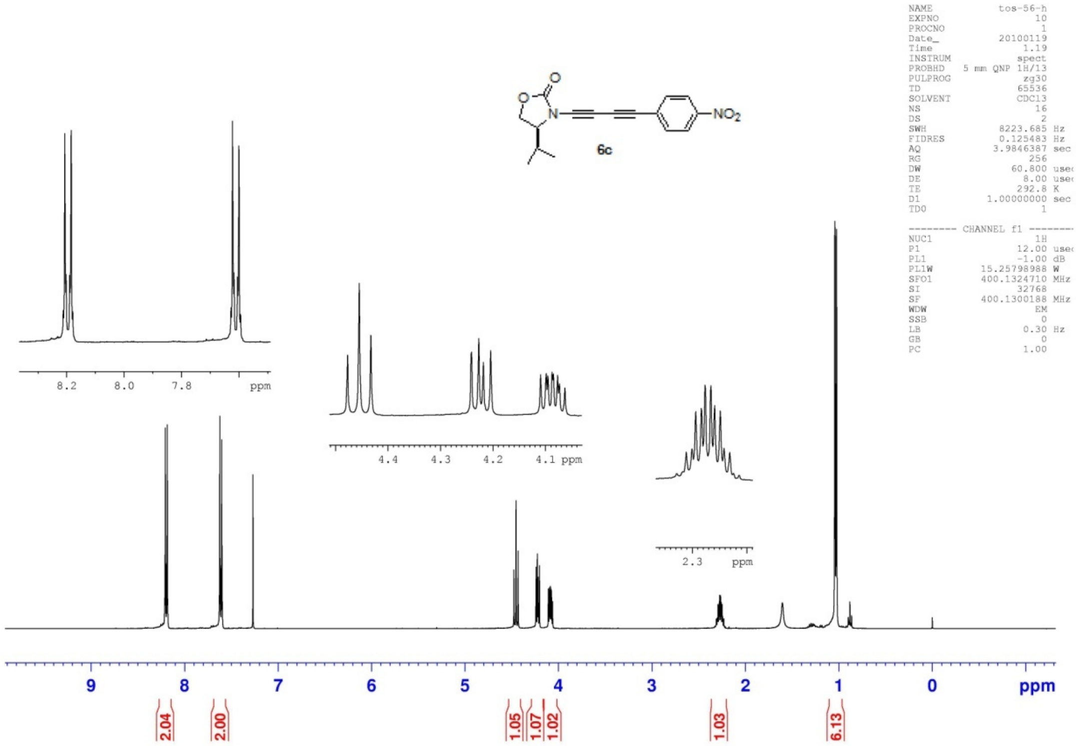


Figure 28a: ^{1}H NMR (300 MHz, CDCl$_3$) of diynamide **6c**.

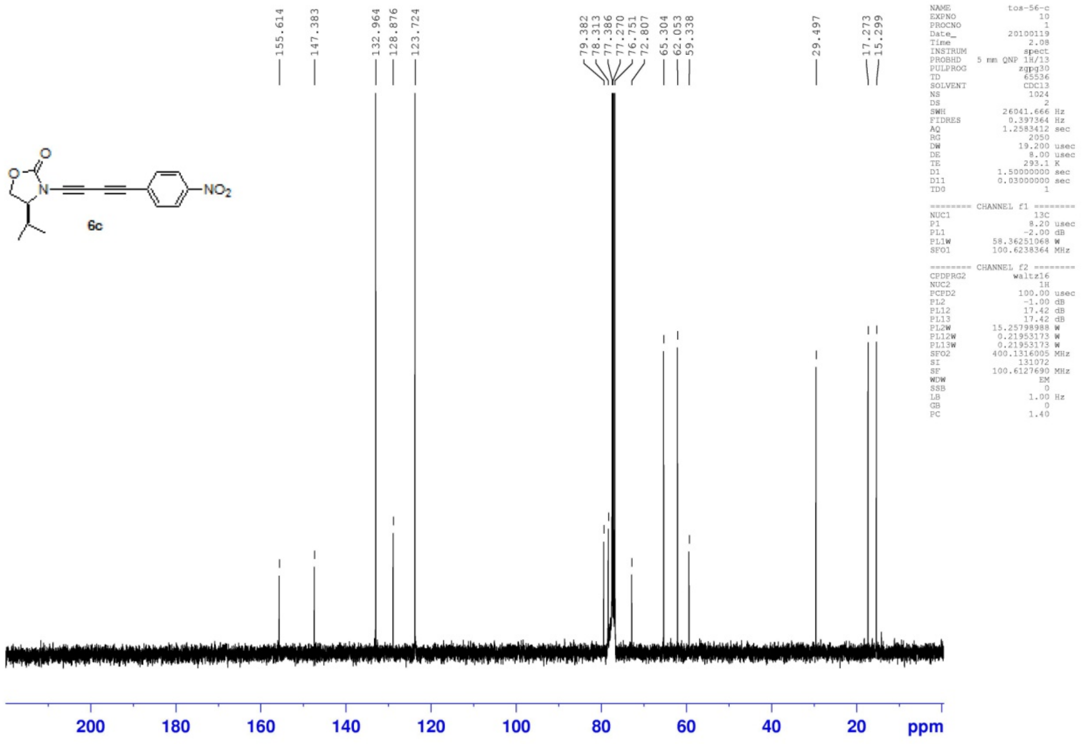


Figure 28b: ^{13}C NMR (75 MHz, CDCl$_3$) of diynamide **6c**.

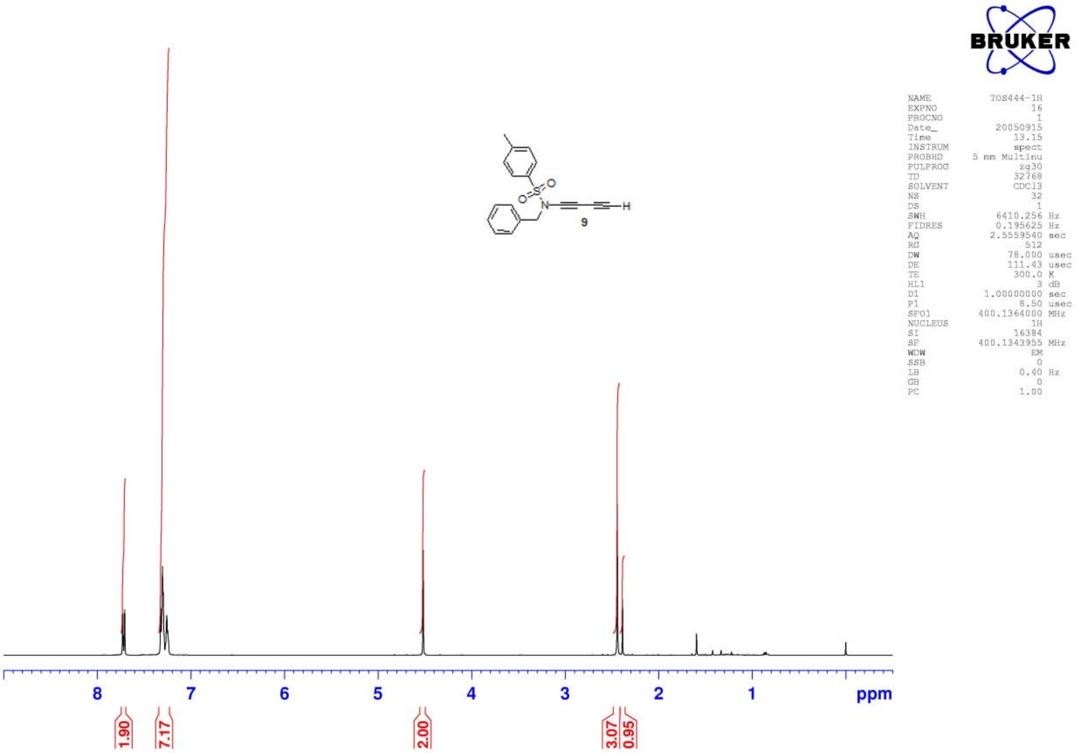


Figure 29a: ^{1}H NMR (400 MHz, CDCl$_3$) of diynamide **9**.

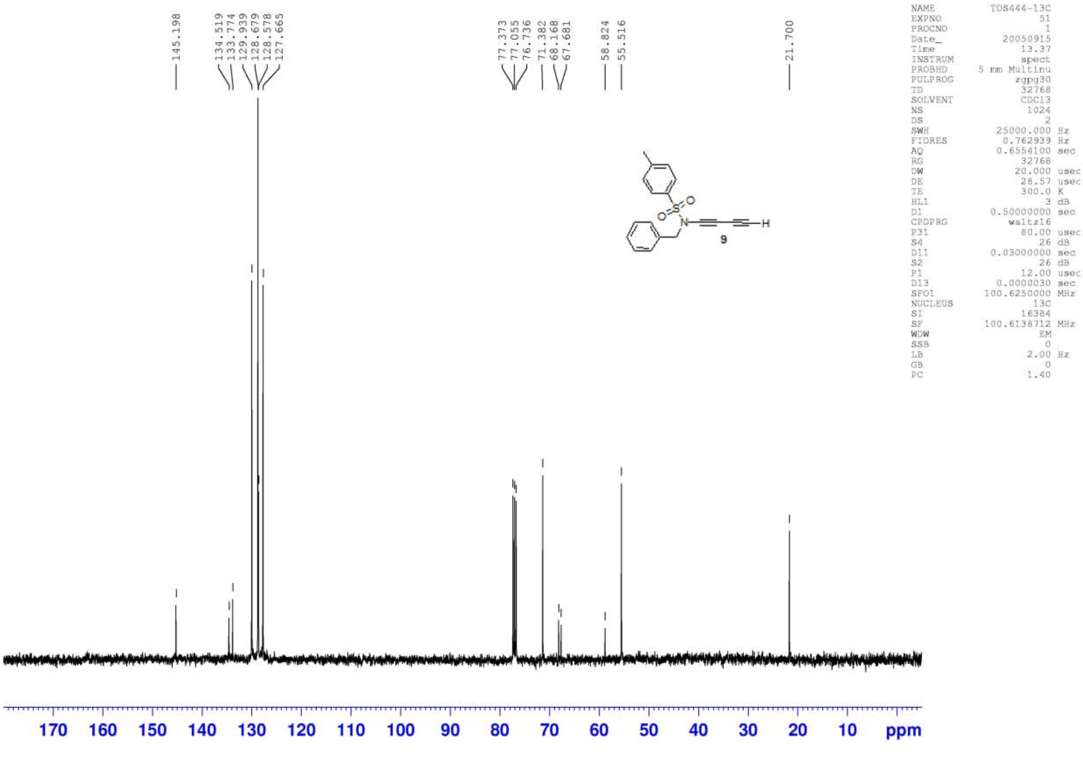
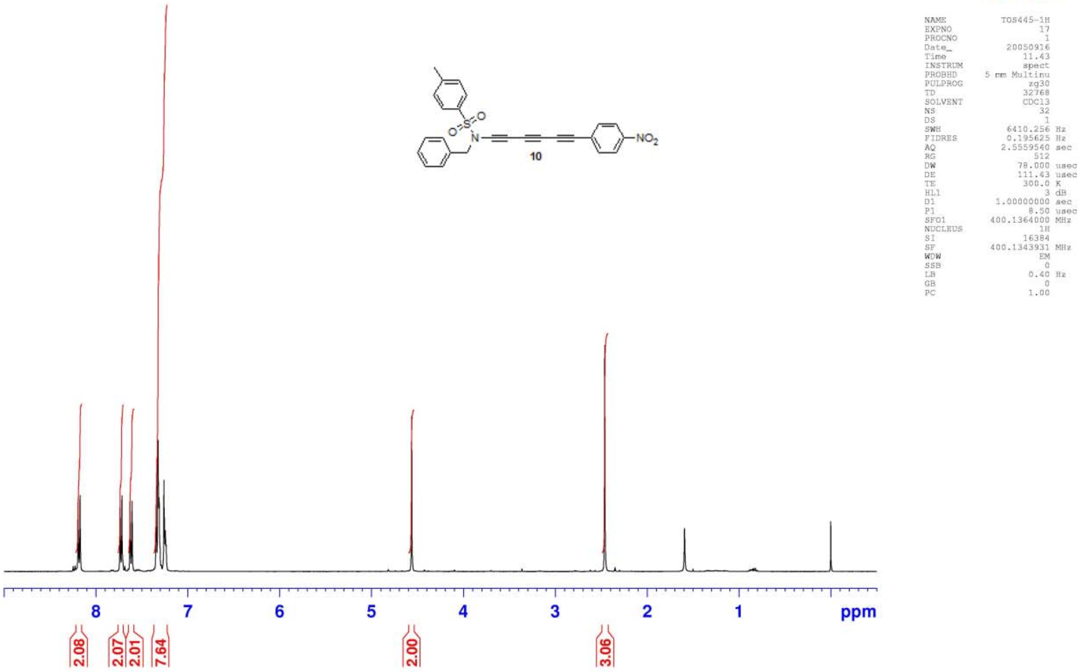
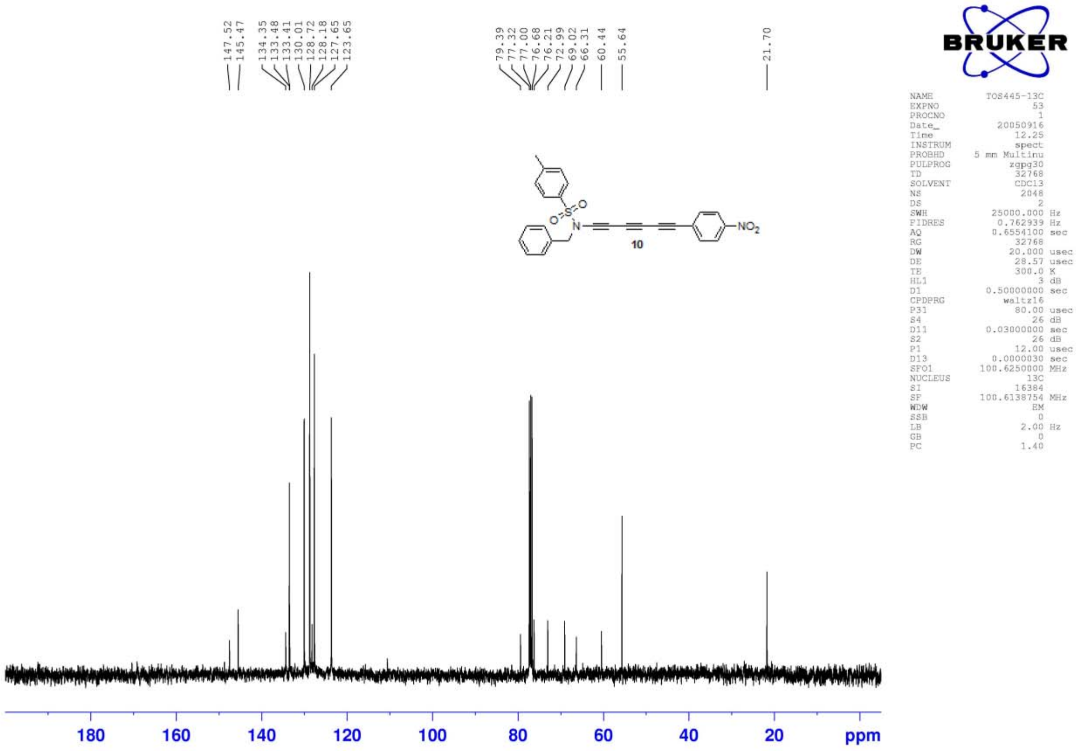


Figure 29b: ^{13}C NMR (100 MHz, CDCl$_3$) of diynamide **9**.



```
NAME          TOS445-1H
EXPNO                17
PROCNO                1
Date_          20050916
Time              11.43
INSTRUM           spect
PROBHD   5 mm Multinu
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    1
SWH            6410.256 Hz
FIDRES         0.195625 Hz
AQ            2.5559540 sec
RG                  512
DW               78.000 usec
DE               111.43 usec
TE                300.0 K
HL1                   3 dB
D1           1.00000000 sec
P1                 8.50 usec
SFO1        400.1364000 MHz
NUCLEUS              1H
SI                16384
SF          400.1343931 MHz
WDW                  EM
SSB                   0
LB                 0.40 Hz
GB                    0
PC                 1.00
```

Figure 30a: ^{1}H NMR (300 MHz, CDCl$_3$) of diynamide **10**.



```
NAME          TOS445-13C
EXPNO                 53
PROCNO                 1
Date_           20050916
Time               12.25
INSTRUM            spect
PROBHD    5 mm Multinu
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                  2048
DS                     2
SWH            25000.000 Hz
FIDRES          0.762939 Hz
AQ             0.6554100 sec
RG                 32768
DW                20.000 usec
DE                 28.57 usec
TE                 300.0 K
HL1                    3 dB
D1            0.50000000 sec
CPDPRG           waltz16
P31                80.00 usec
S4                    26 dB
D11           0.03000000 sec
S2                    26 dB
P1                 12.00 usec
D13            0.0000030 sec
SFO1         100.6250000 MHz
NUCLEUS              13C
SI                 16384
SF           100.6138754 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.40
```

Figure 30b: ^{13}C NMR (100 MHz, CDCl$_3$) of diynamide **10**.

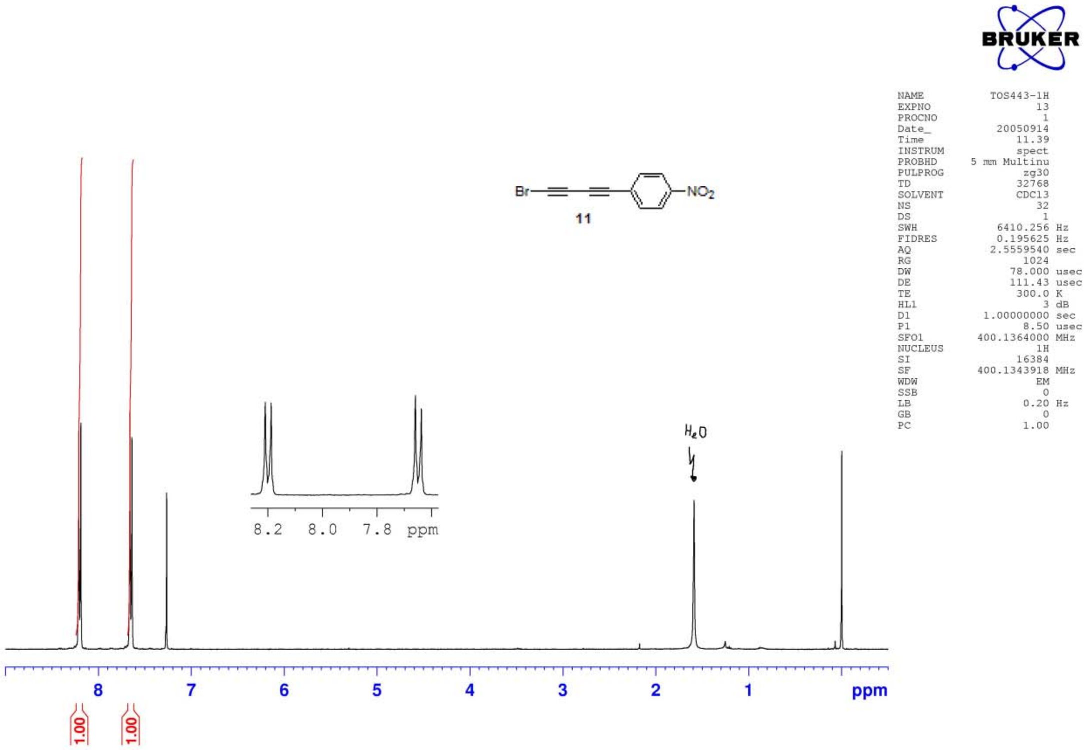


Figure 31a: ^{1}H NMR (400 MHz, CDCl$_3$) of 1-(4-bromobuta-1,3-diynyl)-4-nitrobenzene **11**.

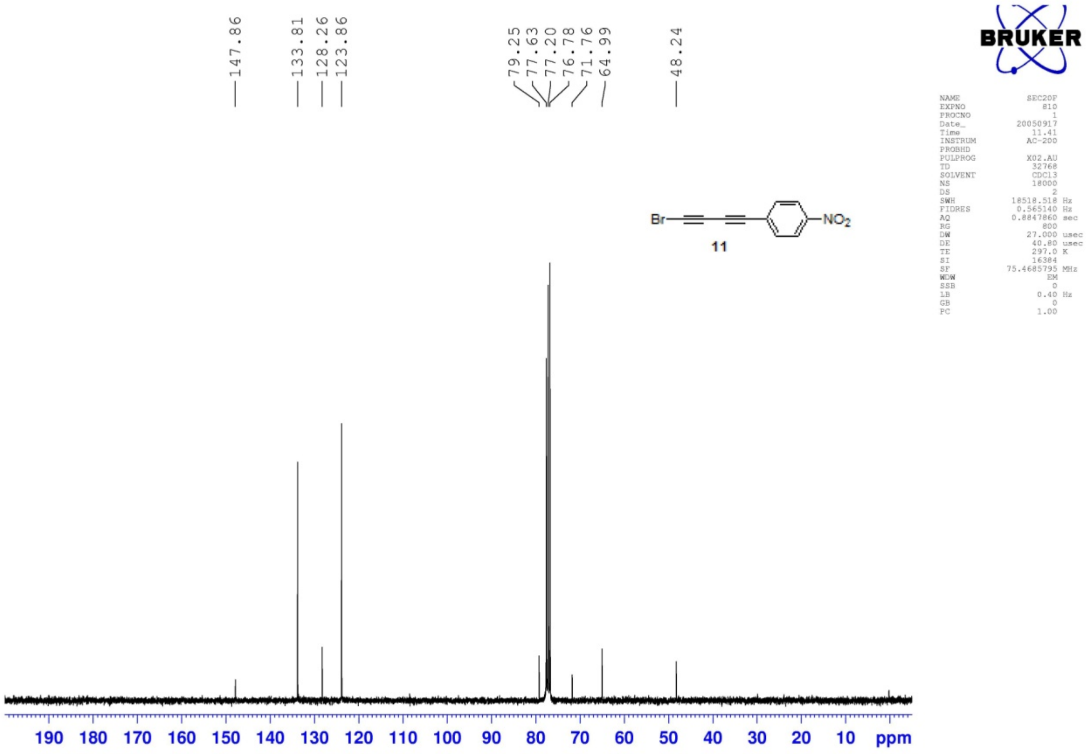
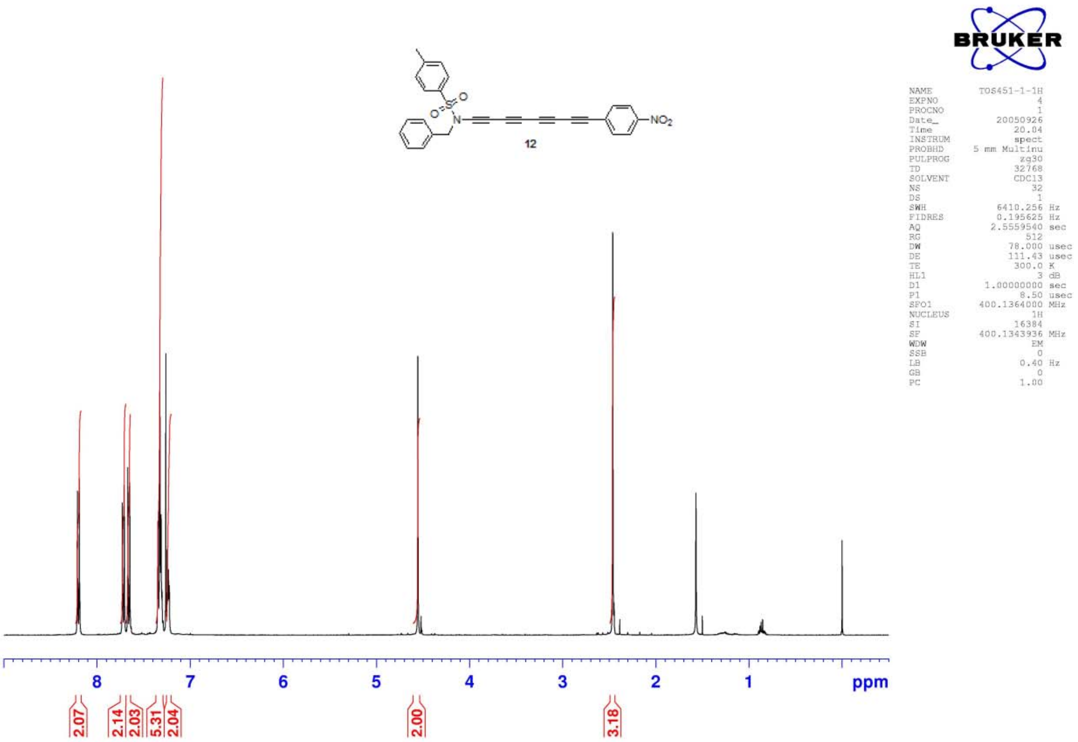
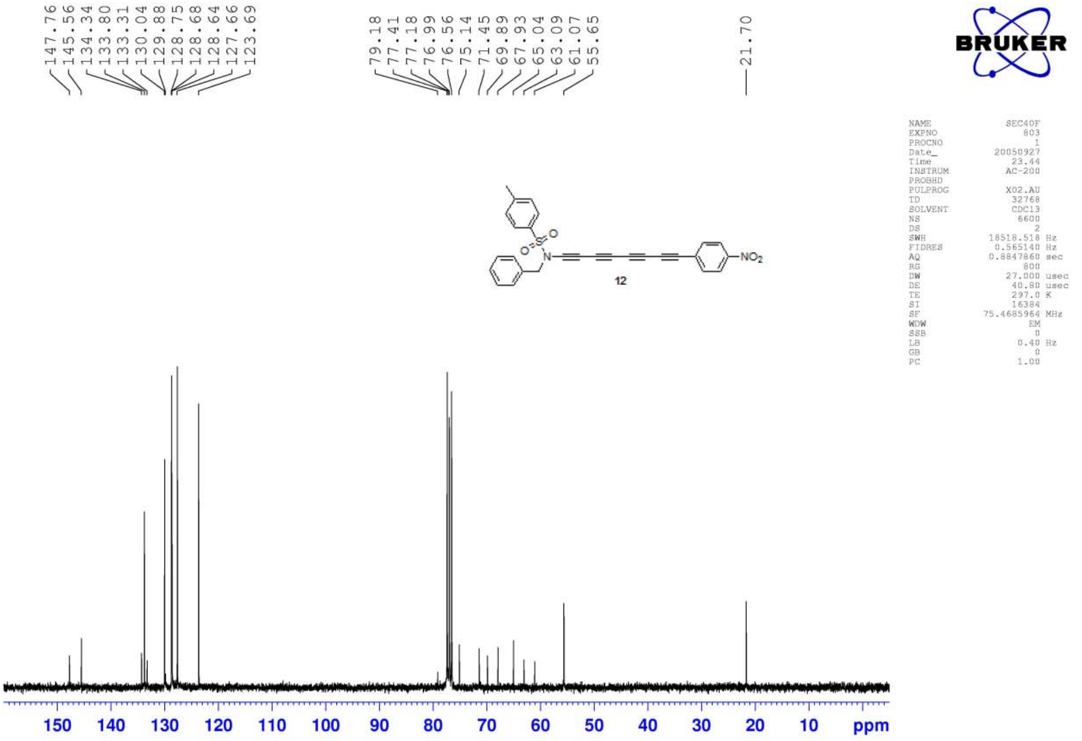


Figure 31b: ^{13}C NMR (75 MHz, CDCl$_3$) of 1-(4-bromobuta-1,3-diynyl)-4-nitrobenzene **11**.



NAME	TOS451-1-1H	
EXPNO	4	
PROCNO	1	
Date_	20050926	
Time	20.04	
INSTRUM	spect	
PROBHD	5 mm Multinu	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	32	
DS	1	
SWH	6410.256	Hz
FIDRES	0.195625	Hz
AQ	2.5559540	sec
RG	512	
DW	78.000	usec
DE	111.43	usec
TE	300.0	K
HL1	3	dB
D1	1.00000000	sec
P1	8.50	usec
SFO1	400.1364000	MHz
NUCLEUS	1H	
SI	16384	
SF	400.1343936	MHz
WDW	EM	
SSB	0	
LB	0.40	Hz
GB	0	
PC	1.00	

Figure 32a: ^{1}H NMR (400 MHz, $CDCl_3$) of tetraynamide **12**.



NAME	SEC40F	
EXPNO	803	
PROCNO	1	
Date_	20050927	
Time	23.44	
INSTRUM	AC-200	
PROBHD		
PULPROG	X02.AU	
TD	32768	
SOLVENT	CDCl3	
NS	6600	
DS	2	
SWH	18518.518	Hz
FIDRES	0.565140	Hz
AQ	0.8847860	sec
RG	800	
DW	27.000	usec
DE	40.80	usec
TE	297.0	K
SI	16384	
SF	75.4685964	MHz
WDW	EM	
SSB	0	
LB	0.40	Hz
GB	0	
PC	1.00	

Figure 32b: ^{13}C NMR (75 MHz, $CDCl_3$) of tetraynamide **12**.