Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Generation of Azomethine Imine and Metal Free Formal 1,3-Dipolar Cycloaddition of Imine with PhIO: Reaction, Scope, and Synthesis

Dilip K. Maiti,* Nirbhik Chatterjee, Palash Pandit, and Sandip K. Hota

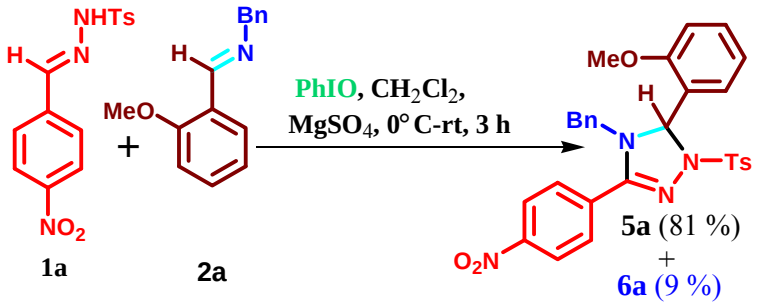
Department of Chemistry, University Colleges of Science and Technology, University of Calcutta, 92, Acharya Prafulla Chandra Road, Kolkata-700009, India

*Corresponding author. Fax: 91-33-23519755, Tel: 91-33-23501014
maitidk@yahoo.com

1. Materials and Methods

All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Commercially supplied ethyl acetate and petroleum ether were distilled before use. CH_2Cl_2 was dried by distillation over P_2O_5. Petroleum ether used in our experiments was in the boiling range of 60°-80° C. Column chromatography was performed on silica gel (60-120 mesh, 0.120 mm-0.250 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Melting points are reported uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 300 MHz spectrometers (300 MHz for ^{1}H and 75 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer as KBr pellets. Optical rotation of the chiral compounds was measured in a polarimeter using standard 10 cm quartz cell in sodium-D lamp at ambient temperature.

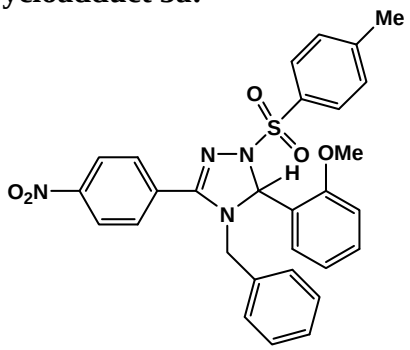
2. Synthesis of 4-Benzyl-5-(2-methoxyphenyl)-3-(4-nitrophenyl)-1-(4-methylphenylsulfonyl)-4,5-dihydro-1*H*-[1,2,4]triazole (5a)



ESI Scheme 1

The *N*-benzyl-2-methoxyphenylaldimine (**2a**, 495 mg, 2.2 mmol), *N*-(4-nitrobenzylidene)-*N'*-4-methylphenylsulfonylhydrazine (**1a**, 638 mg, 2.0 mmol), anhydrous $MgSO_4$ (0.5 g) and dichloromethane (10 mL) were taken together in a round-bottom flask (25 mL) and the content was cooled to 0° C. PhIO (880 mg, 4.0 mmol) was added under vigorous stirring and the content of the reaction mixture was allowed to attain room temperature. Progress of the reaction was monitored by TLC and the reaction was complete after 3.0 hours. The post reaction mixture was filtered and washed well with dichloromethane. The combined organic portion was washed with aqueous sodium bicarbonate solution (1 x 10 mL) and brine (3 x 10 mL) solution, dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. The crude brown oil was chromatographed on silica gel (60-120 mesh). The cycloadduct 4-benzyl-3-(2-methoxyphenyl)-2-(4-methylphenylsulfonyl)-5-(4-nitrophenyl)-3,4-dihydro-1*H*-[1,2,4]triazole (**5a)** was eluted at ethyl acetate-petroleum ether (1:13) in an isolated yield of 81% (878 mg, 1.62 mmol) and 4-benzyl-3-(2-methoxyphenyl)-5-(4-nitrophenyl)-4*H*-[1,2,4]triazole (**6a**) at (2:3) ethyl acetate-petroleum ether in an isolated yield of 9% (70 mg, 0.18 mmol).

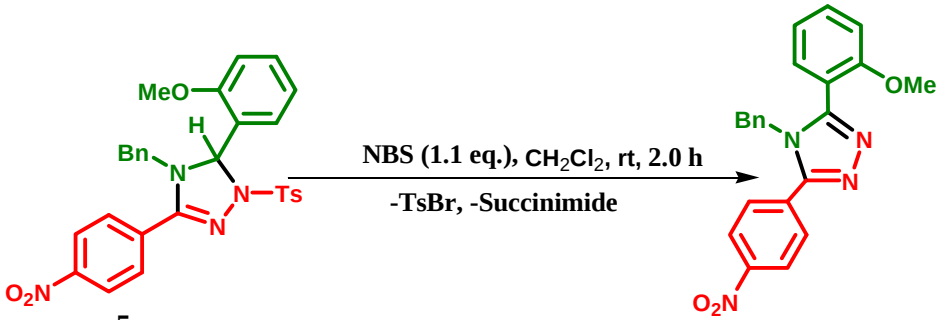
Characterization Data of Cycloadduct 5a:



5a

Yield: 81% (878 mg, 1.62 mmol).
Characteristic: Yellow solid.
Melting point: 162° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (3H, s), 3.62 (3H, s), 3.79 (1H, d, *J* = 16.5 Hz), 4.05 (1H, d, *J* = 16.5 Hz), 6.34 (1H, s), 6.46 (2H, d, *J* = 7.2 Hz), 6.81 (1H, d, *J* = 8.1 Hz), 6.93-7.05 (3H, m), 7.11-7.32 (4H, m), 7.43 (1H, dd, *J* = 1.5, 7.5 Hz), 7.54 (2H, d, *J* = 8.7 Hz), 7.70 (2H, d, *J* = 8.1 Hz), 8.17 (2H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 48.6, 55.5, 111.0, 121.3, 123.9, 125.9, 126.1, 126.7, 127.0, 127.5, 128.5, 128.7, 129.4, 129.5, 130.2, 130.8, 131.7, 133.2, 135.2, 144.1, 149.0, 157.4.
IR (KBr, cm^{-1}): 668, 1165, 1347, 1524, 1599, 2931.
HR-MS (*m*/*z*) for $C_{29}H_{26}N_4O_5S$ (M+Na) : Calculated 565.1522, found 565.1505.

3. Transformation of 4-Benzyl-5-(2-methoxyphenyl)-3-(4-nitrophenyl)-1-(4-methylphenylsulfonyl)-4,5-dihydro-1*H*-[1,2,4]triazole (5a) to 4-Benzyl-3-(2-methoxyphenyl)-5-(4-nitrophenyl)-4*H*-[1,2,4]triazole (6a) by *N*-Bromosuccinimide



5a **6a** (95 %)

ESI Scheme 2

The cycloadduct (**5a**, 108 mg, 0.2 mmol) and dichloromethane (5 mL) were taken together in a round-bottom flask (10 mL) and stirred magnetically. *N*-Bromo succinimide (40 mg, 0.22 mmol) was added and the content of the reaction mixture was stirred at room temperature for 2 hours to complete the elimination of C_3-*H* and N_2-*Ts* to afford the end product **6a**. The reaction was monitored by TLC comparing with the authentic sample. The post reaction mixture was washed well with aqueous sodium bicarbonate solution (1 x 5 mL) and brine (3 x 5 mL) solution, dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. The crude yellow solid was collected as pure product (95%, 73 mg, 0.19 mmol) without further purification.

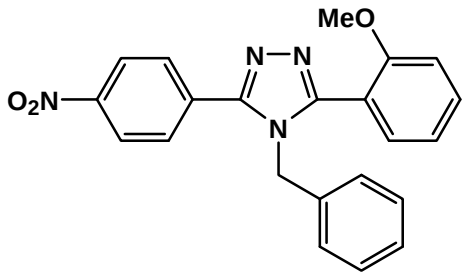
Characterization Data of Compound 6a:
Yield: 95% (73 mg, 0.19 mmol).
Characteristic: Pale yellow solid.
Melting point: 168° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.70 (3H, s), 5.12 (2H, s), 6.67 (1H, dd, *J* = 4.2, 7.5 Hz), 6.92 (1H, d, *J* = 8.7 Hz), 6.98 (1H, d, *J* = 7.5 Hz), 7.07-7.10 (4H, m), 7.39 (2H, d, *J* = 7.5 Hz), 7.53 (2H, d, *J* = 8.7 Hz), 8.17 (2H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.5, 55.5, 111.1, 115.5, 121.1, 123.7, 126.2, 128.0, 128.7, 129.6, 130.1, 132.4, 133.5, 134.9, 148.4, 153.1, 154.8, 157.2.
IR (KBr, cm^{-1}): 725, 857, 1254, 1344, 1467, 1520, 1602.
HR-MS (*m*/*z*) for $C_{22}H_{19}N_4O_3$ (M+H): Calculated 387.1457, found 387.1469.

4. General Procedure for Synthesis of the 3,4,5-Trisubstituted-1,2,4-triazoles (6) by the Three Component One Pot Strategy

The aldehyde **3** (2.2 mmol), amine **4** (2.2 mmol), anhydrous $MgSO_4$ (0.5 g) and dichloromethane (10 mL) were taken together in a round-bottom flask (25 mL) and the content was stirred at room temperature for 6.5 hours. The *N*-tosylaldohydrazone **1** (2.0 mmol) was added into the reaction mixture at 0° C. Iodosobenzene (880 mg, 4.0 mmol) was added and the content of the reaction mixture was allowed to attain the room temperature. Progress of the reaction was monitored by TLC and the reaction was complete after 2.5-3.0 hours depending on the substrates used. Finally *N*-bromo succinimide (392 mg, 2.2 mmol) was added and the content was stirred at room temperature for another 1.5-2.0 hours to complete the conversion of the cycloadduct **5** into the end product **6**. The post reaction mixture was filtered and washed well with dichloromethane. The combined organic portion was washed with aqueous sodium bicarbonate solution (1 x 10 mL) and brine (3 x 10 mL) solution, dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. After standing for sometime at ambient temperature the crude product became solid and it was triturated with minimum volume of ethyl acetate, and filtered. The solid compound was washed with minimum volume of ethyl acetate. Thus, the reaction with p-anisaldehyde (**3b**, 300 mg, 2.2 mmol), benzyl amine (**4a**, 235 mg, 2.2 mmol) and *N*-naphthalen-2-yl-methylene-*N'*-4-methylphenylsulfonylhydrazine (**1b**, 648 mg, 2 mmol) afforded 4-benzyl-3-(4-methoxyphenyl)-5-naphthalen-2-yl-4*H*-[1,2,4]triazole (**6b**) after processing in an isolated yield of 88% (688 mg, 1.76 mmol). Asymmetric syntheses of the chiral triazoles (**6o**-**q**) and sugar-based triazoles (**6r**,**s**) were also synthesized following the same general procedure. The compound **6b** and other end products (**6a-l** and **6o**-**s**) were characterized by ^{1}H and ^{13}C NMR (NDC & DEPT), FT-IR, HR-MS and also measuring the melting points of the solid compounds. The structure of the 3,4,5-trisubstituted-1,2,4-triazoles was determined by comparing the melting point of the known compound **6j** synthesized in this methodology and also by single crystal X-ray diffraction analyses of the compound **6i**.

5. Characterization Data of the 3,4,5-Trisubstituted-1,2,4-triazoles (6a-l and 6o-s)

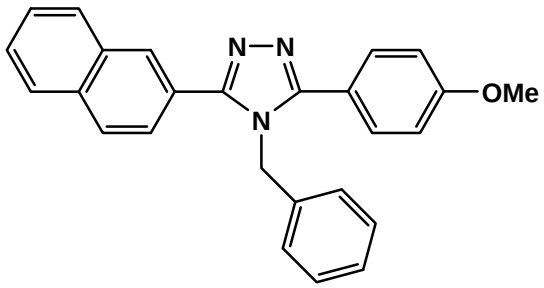
5.1. 4-Benzyl-3-(2-methoxyphenyl)-5-(4-nitrophenyl)-4*H*-[1,2,4]triazole (6a):



6a

Yield: 84% (648 mg, 1.68 mmol).
Characteristic: Pale yellow solid.
Melting point: 168° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.70 (3H, s), 5.12 (2H, s), 6.67 (1H, dd, *J* = 4.2, 7.5 Hz), 6.92 (1H, d, *J* = 8.7 Hz), 6.98 (1H, d, *J* = 7.5 Hz), 7.07-7.10 (4H, m), 7.39 (2H, d, *J* = 7.5 Hz), 7.53 (2H, d, *J* = 8.7 Hz), 8.17 (2H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.5, 55.5, 111.1, 115.5, 121.1, 123.7, 126.2, 128.0, 128.7, 129.6, 130.1, 132.4, 133.5, 134.9, 148.4, 153.1, 154.8, 157.2.
IR (KBr, cm^{-1}): 725, 857, 1254, 1344, 1467, 1520, 1603.
HR-MS (*m*/*z*) for $C_{22}H_{19}N_4O_3$ (M+H): Calculated 387.1457, found 387.1467.

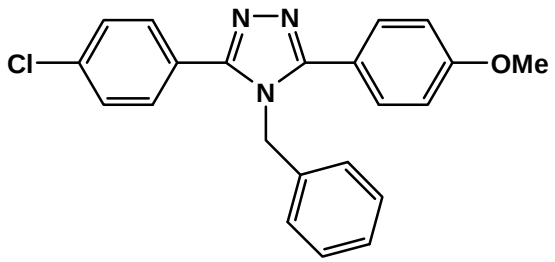
5.2. 4-Benzyl-3-(4-methoxyphenyl)-5-naphthalen-2-yl-4*H*-[1,2,4]triazole (6b):



6b

Yield: 88% (689 mg, 1.76 mmol).
Characteristic: Colorless solid.
Melting point: 196° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81 (3H, s), 5.42 (2H, s), 6.87-6.93 (5H, m), 7.26-7.28 (2H, m), 7.46-7.57 (2H, m), 7.63 (2H, d, *J* = 8.7 Hz), 7.73 (2H, d, *J* = 8.1 Hz), 7.85 (2H, t, *J* = 8.7 Hz), 8.09 (1H,s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.9, 55.3, 114.4, 117.9, 123.4, 125.5, 125.9, 126.7, 127.4, 127.6, 128.1, 128.5, 128.7, 129.1, 130.5, 132.6, 133.7, 135.6, 155.4, 155.5, 161.3.
IR (KBr, cm^{-1}): 718, 821, 1025, 1175, 1256, 1451, 1611, 2927.
HR-MS (*m*/*z*) for $C_{26}H_{22}N_3O$ (M+H): Calculated 392.1763, found 392.1782.

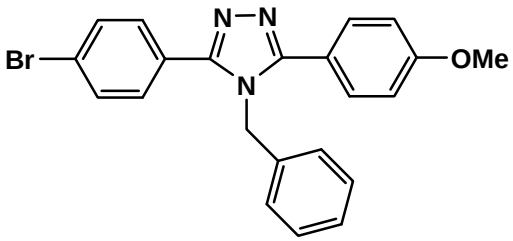
5.3. 4-Benzyl-3-(4-chlorophenyl)-5-(4-methoxyphenyl)-4*H*-[1,2,4]triazole (6c):



6c

Yield: 82% (615 mg, 1.64 mmol)
Characteristic: Pale yellow solid.
Melting point: 166° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.79 (3H, s), 5.27 (2H, s), 6.84-6.91 (4H, m), 7.25-7.37 (5H, m), 7.45-7.53 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.4, 55.3, 114.3, 125.2, 125.8, 128.1, 128.2, 129.1, 129.2, 130.0, 130.1, 130.3, 133.7, 135.5, 136.4, 161.2.
IR (KBr, cm^{-1}): 708, 831, 1174, 1249, 1468, 1608, 2925.
HR-MS (*m*/*z*) for $C_{22}H_{19}ClN_3O$ (M+H): Calculated 376.1217, found 376.1197 (one of the peaks).

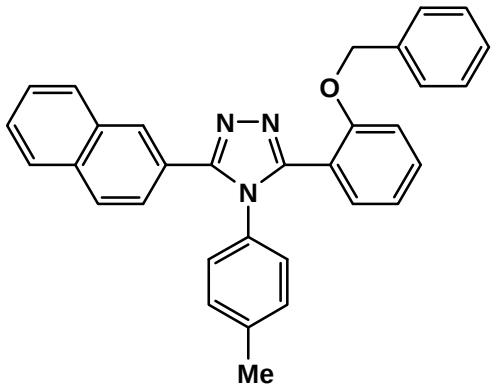
5.4. 4-Benzyl-3-(4-bromophenyl)-5-(4-methoxyphenyl)-4*H*-[1,2,4]triazole (6d):



6d

Yield: 81% (678 mg, 1.62 mmol).
Characteristic**:** Pale yellow solid.
Melting point: 176° C
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (3H, s), 5.23 (2H, s), 6.77-6.85 (4H, m), 7.19-7.25 (3H, m), 7.38-7.50 (6H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.6, 55.3, 114.4, 125.0, 125.7, 125.8, 128.2, 129.2, 129.3, 130.2, 130.3, 130.4, 132.1, 135.4, 155.6, 161.4.
IR (KBr, cm^{-1}): 730, 833, 1018, 1177, 1253, 1471, 1608, 2931.
HR-MS (*m*/*z*) for $C_{22}H_{19}BrN_3O$ (M+H): Calculated 420.0711, found 420.0729 (one of the peaks).

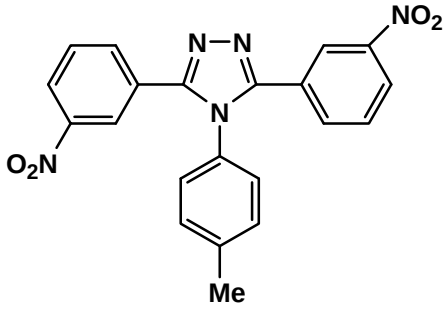
5.5. 3-(2-Benzyloxyphenyl)-5-naphthalen-2-yl-(4-methylphenyl)-4*H*-[1,2,4]triazole (6e):



6e

Yield: 80% (747 mg, 1.60 mmol).
Characteristic: Brown solid.
Melting point: 82° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (3H, s), 4.72 (2H, s), 6.68 (2H, d, *J* = 8.4 Hz), 6.74 (2H, d, *J* = 8.4 Hz), 6.88-7.03 (6H, m), 7.10-7.39 (5H, m), 7.50 (1H, dd, *J* = 1.2, 7.5 Hz), 7.64 (2H, d, *J* = 8.4 Hz), 7.70 (1H, d, *J* = 7.5 Hz), 7.94 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 70.1, 112.5, 116.5, 120.9, 123.8, 125.3, 126.4, 126.7, 126.8, 127.5, 127.7, 128.0, 128.1, 128.3, 128.5, 129.6, 129.7, 131.9, 132.2, 132.4, 132.6, 133.4, 136.3, 138.9, 153.5, 154.0, 156.5.
IR (KBr, cm^{-1}): 749, 818, 1013, 1234, 1455, 1512, 1599, 2923.
HR-MS (*m*/*z*) for $C_{32}H_{26}N_3O$ (M+H): Calculated 468.2076, found 468.2049.

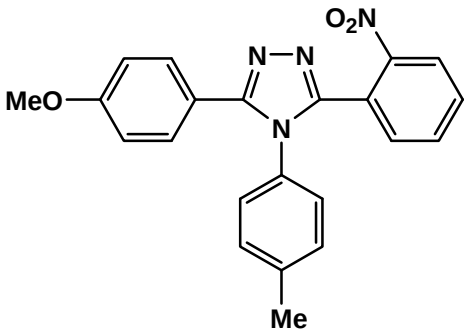
5.6. 3,5-Bis-(3-nitrophenyl)-4-(4-methylphenyl)-4*H*-[1,2,4]triazole (6f):



6f

Yield: 85% (681 mg, 1.70 mmol).
Characteristic: Pale brown solid.
Melting point: 222° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.46 (3H, s), 7.18 (2H, d, *J* = 8.1 Hz), 7.35 (2H, d, *J* = 8.1 Hz), 7.31-7.60 (2H, m), 7.55 (2H, dd, *J* = 3.9, 8.1 Hz), 8.22 (4H, dd, *J* = 1.8, 3.9 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 123.2, 124.5, 127.2, 128.1, 129.7, 131.2, 131.4, 134.2, 141.5, 148.0, 153.2.
IR (KBr, cm^{-1}): 721, 821, 1087, 1346, 1516, 3084.
HR-MS (*m*/*z*) for $C_{21}H_{16}N_5O_4$ (M+H): Calculated 402.1202, found 402.1219.

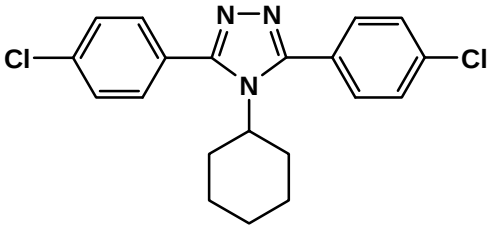
5.7. 5-(4-Methoxyphenyl)-3-(2-nitrophenyl)-4-(4-methylphenyl)-4*H*-[1,2,4]triazole (6g):



6g

Yield: 81% (625 mg, 1.62 mmol).
Characteristic: Yellow solid.
Melting point: 142° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (3H, s), 3.79 (3H, s), 6.82 (2H, d, *J* = 8.7 Hz), 6.92 (2H, d, *J* = 8.7 Hz), 7.07 (2H, d, *J* = 8.1 Hz), 7.41 (2H, d, *J* = 8.7 Hz), 7.59-7.72 (3H, m), 8.02 (1H, dd, *J* = 0.9, 8.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 55.2, 113.9, 118.9, 123.1, 124.7, 127.0, 130.0, 130.2, 131.0, 131.4, 133.3, 139.5, 148.2, 152.0, 154.4, 160.6.
IR (KBr, cm^{-1}): 595, 835, 1018, 1254, 1465, 1529, 1610, 2925.
HR-MS (*m*/*z*) for $C_{22}H_{19}N_4O_3$ (M+H): Calculated 387.1457, found 387.1452.

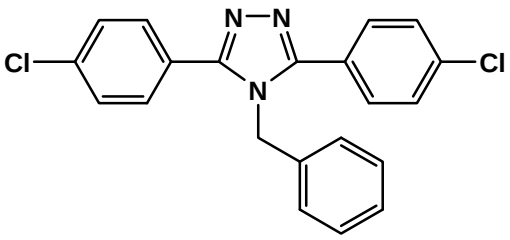
5.8. 3,5-Bis-(4-chlorophenyl)-4-cyclohexyl-4*H*-[1,2,4]triazole (6h):



6h

Yield: 88% (654 mg, 1.76 mmol).
Characteristic: Colorless solid.
Melting point: Above 300° C
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (1H, t, *J* = 12.9 Hz), 1.00-1.13 (2H, m), 1.37-1.53 (3H, m), 1.70 (2H, d, *J* = 12.9 Hz), 2.20 (2H, d, *J* = 11.1 Hz), 4.03 (1H, t, *J* = 12.0 Hz), 7.49 (4H, d, *J* = 8.1 Hz), 7.79 (4H, d, *J* = 8.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 24.5, 25.6, 32.8, 60.7, 129.4, 130.8, 132.2, 138.7, 152.4.
IR (KBr, cm^{-1}): 744, 828, 963, 1014, 1091, 1481, 1604, 1697, 2588, 2933.
HR-MS (*m*/*z*) for $C_{20}H_{19}Cl_2N_3$ (M+H): Calculated 372.1034, found 372.1016

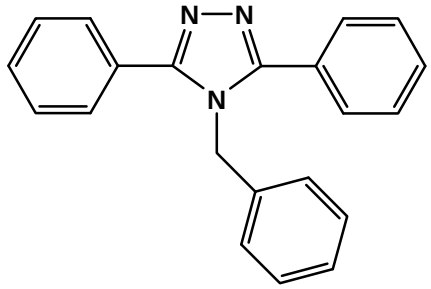
5.9. 4-Benzyl-3,5-bis-(4-chlorophenyl)-4*H*-[1,2,4]triazole (6i):



6i

Yield: 82% (623 mg, 1.64 mmol).
Characteristic: White solid.
Melting point: 202° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.22 (2H, s), 6.77 (2H, dd, *J* = 2.1, 5.7 Hz), 7.17-7.23 (3H, m), 7.32 (4H, d, *J* = 8.4 Hz), 7.48 (4H, d, *J* = 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.7, 124.5, 125.7, 128.4, 129.2, 130.2, 135.0, 136.9, 154.8.
IR (KBr, cm^{-1}): 727, 833, 1092, 1465, 1701, 3068.
HR-MS (*m*/*z*) for $C_{21}H_{16}Cl_2N_3$ (M+H): Calculated 380.0721, found 380.0702 (one of the peaks).

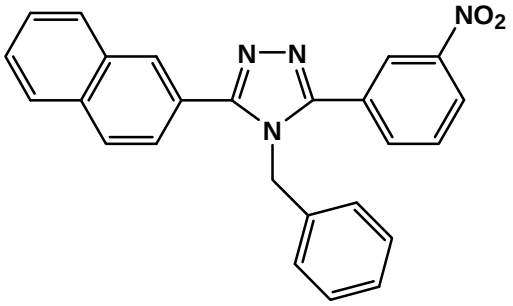
5.10. 4-Benzyl-3,5-diphenyl-4*H*-[1,2,4]triazole (6j):



6j

Yield: 89% (554 mg, 1.78 mmol).
Characteristic: White solid.
Melting point: 205° C [reported[20] 210° C].
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.28 (2H, s), 6.85-6.88 (2H, m), 7.25-7.27 (3H, m), 7.37-7.45 (6H, m), 7.57-7.59 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.2, 125.8, 127.2, 128.0, 128.8, 128.8, 129.0, 130.0, 135.9, 155.9.
IR (KBr, cm^{-1}): 689, 727, 783, 1365, 1405, 1465, 3067.
HR-MS (*m*/*z*) for $C_{21}H_{18}N_3$ (M+H): Calculated 312.1501, found 312.1488.

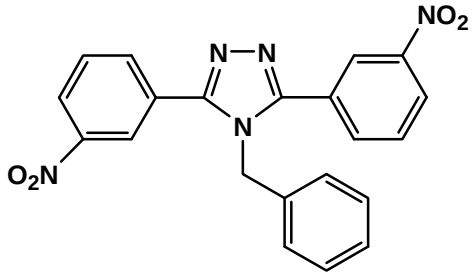
5.11. 4-Benzyl-(3-naphthalen-2-yl)-5-(3-nitrophenyl)-4*H*-[1,2,4]triazole (6k):



6k

Yield: 82% (665 mg, 1.64 mmol).
Characteristic: Pale yellow solid.
Melting point: 180° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.27 (2H, s), 6.87 (2H, dd, *J* = 1.8, 7.5 Hz), 7.22-7.28 (3H, m), 7.42-7.53 (3H, m), 7.69 (2H, d, *J* = 7.8 Hz), 7.79 (1H, d, *J* = 7.5 Hz), 7.84 (1H, d, *J* = 8.7 Hz), 7.96 (1H, d, *J* = 7.8 Hz), 8.06 (1H, s), 8.20 (1H, dd, *J* = 1.8, 7.8 Hz), 8.37 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.2, 123.4, 124.7, 125.4, 125.7, 126.9, 127.6, 127.7, 128.5, 128.7, 128.9, 129.1, 129.4, 130.0, 132.7, 133.8, 134.7, 135.1, 148.2, 153.7, 156.7.
IR (KBr, cm^{-1}): 743, 819,1344,1452,1529, 2924.
HR-MS (*m*/*z*) for $C_{25}H_{19}N_4O_2$ (M+H): Calculated 407.1508, found 407.1532.

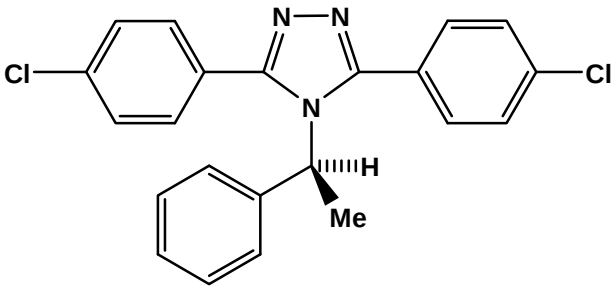
5.12. 4-Benzyl-3,5-bis-(3-nitrophenyl)-4*H*-[1,2,4]triazole (6l):



6l

Yield: 88% (706 mg, 1.76 mmol)**.**
Characteristic: White solid.
Melting point: 188° C
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.36 (2H, s), 6.82-6.84 (2H, m), 7.21-7.23 (3H, m), 7.62 (2H, t, *J* = 8.1 Hz), 7.94 (2H, d, *J* = 8.1 Hz), 8.26 (2H, dd, *J* = 1.2, 8.1 Hz), 8.43 (2H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 48.2, 123.0, 124.3, 125.0, 127.6, 127.9, 128.7, 129.7, 133.9, 147.5, 153.7.
IR (KBr, cm^{-1}): 691, 732, 1350, 1516, 3083.
HRMS (*m*/*z*) for $C_{21}H_{16}N_5O_4$ (M+H): Calculated 402.1202, found 402.1177.

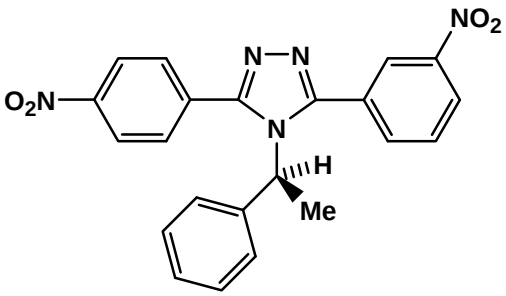
5.13. (S)-(-)-3,5-Bis-(4-chlorophenyl)-4-(1-phenylethyl)-4*H*-[1,2,4]triazole (6o):



6o

Yield: 86% (676 mg, 1.72 mmol).
Characteristic: White solid.
Melting point: 162° C.
$[\alpha]_D^{20}$ –1.76° (*c* 1.25, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (3H, d, *J* = 7.2 Hz), 5.19 (1H, q, *J* = 7.2, 14.4 Hz), 6.93-6.97 (2H, m), 7.26-7.34 (11H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 19.2, 54.1, 125.9, 126.3, 128.2, 128.8, 128.9,130.9, 136.3, 139.5, 154.7.
IR (KBr, cm^{-1}): 702, 836, 1011, 1090, 1405, 1459, 1595.
HR-MS (*m*/*z*) for $C_{22}H_{18}Cl_2N_3$ (M+H): Calculated 394.0878, found 394.0867 (one of the peaks).

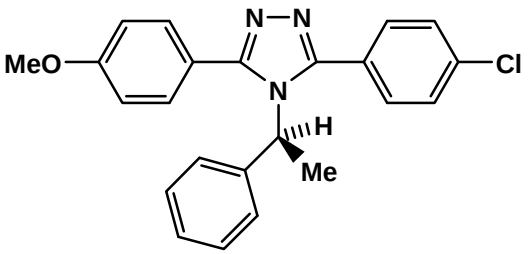
5.14. (S)-(-)-3-(4-Nitrophenyl)-5-(3-nitrophenyl)-4-(1-phenylethyl)-4*H*-[1,2,4]triazole (6p):



6p

Yield: 80% (664mg, 1.60 mmol).
Characteristic: Yellow semisolid.
$[\alpha]_D^{20}$ –27.50° (*c* 0.60, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (3H, d, *J* =7.2 Hz), 5.60 (1H, q, *J* = 7.2, 14.1 Hz), 6.90-6.93 (2H, m), 7.24-7.29 (3H, m), 7.49-7.59 (3H, m), 7.67 (1H, dd, *J* = 1.2, 7.8 Hz), 8.07-8.08 (1H, m), 8.19-8.23 (3H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 19.5, 54.7, 123.8, 124.7, 124.9, 125.8, 128.9,129.3, 129.8, 130.6, 133.7, 135.4, 138.6, 148.0, 148.8.
IR (KBr, cm^{-1}): 689, 728, 860, 1348, 1452, 1519, 1721, 2927.
HR-MS (*m*/*z*) for $C_{22}H_{18}N_5O_4$ (M+H): Calculated 416.1359, found 416.1345.

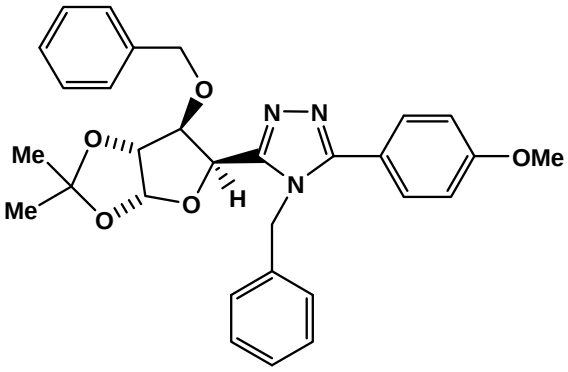
5.15. (S)-(-)-3-(4-Chlorophenyl)-5-(4-methoxyphenyl)-4-(1-phenylethyl)-4*H*-[1,2,4]triazole (6q):



6q

Yield: 83% (645mg, 1.66 mmol).
Characteristic: Yellow semisolid.
$[\alpha]_D^{20}$ –3.28° (*c* 1.40, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (3H, d, *J* =7.2 Hz), 3.74 (3H, s), 5.54 (1H, q, *J* = 7.2, 14.1 Hz), 6.81 (2H, d, *J* =8.4 Hz), 6.88-6.91 (2H, m), 7.13 (2H, d, *J* =8.4 Hz), 7.19-7.35 (7H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 19.1, 54.0, 55.2, 114.0, 119.7, 125.9, 126.6, 128.0,128.6, 128.8, 130.9, 136.1, 139.7, 160.9.
IR (KBr, cm^{-1}): 698, 838, 1204, 1176, 1256, 1472, 1610, 1715, 2928.
HR-MS (*m*/*z*) for $C_{23}H_{21}ClN_3O$ (M+H): Calculated 390.1373, found 390.1364 (one of the peaks).

5.16. (3aR,5R,6S,6aR)-(-)-4-Benzyl-3-(6-benzyloxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-5-(4-methoxyphenyl)-4*H*-[1,2,4]triazole (6r):

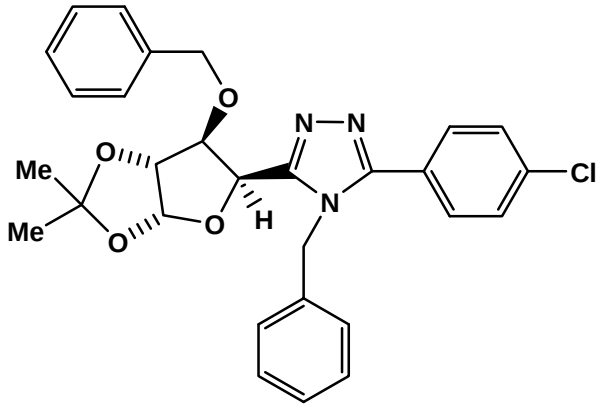


6r

Yield: 70% (718 mg, 1.40 mmol).
Characteristic: Brown semisolid.
$[\alpha]_D^{20}$ –4.67° (*c* 0.75, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (3H, s), 1.42 (3H, s), 3.73 (3H, s), 4.21-4.30 (2H, m), 4.50 (1H, d, *J* = 11.4 Hz), 4.63 (1H, d, *J* = 3.9 Hz), 4.73 (1H, d, *J* = 16.2 Hz), 5.54 (1H, d, *J* = 16.2 Hz), 5.66 (1H, d, *J* = 3.3 Hz), 5.85 (1H, d, *J* = 3.3 Hz), 6.76-6.78 (3H, m), 7.01-7.22 (11H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 26.7, 48.7, 55.2, 72.9, 76.8, 82.5, 84.6, 104.9, 112.3, 114.0, 119.3, 126.3, 127.3, 127.6, 128.0, 128.4, 128.5, 130.4, 136.5, 136.9, 150.3, 156.4, 160.8.

IR (KBr, cm^{-1}): 731, 1025, 1079, 1254, 1464, 1615.
HR-MS (*m*/*z*) for $C_{30}H_{32}N_3O_5$ (M+H): Calculated 514.2342, found 514.2319

5.17. (3aR,5R,6S,6aR)-(-)-4-Benzyl-3-(6-benzyloxy-2,2-dimethyltetrahydrofuro-[2,3-*d*][1,3]dioxol-5-yl)-5-(4-chlorophenyl)-4*H*-[1,2,4]triazole (6s):



6s

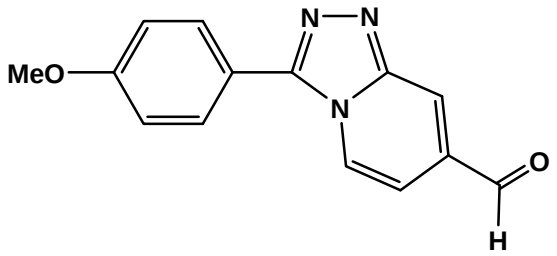
Yield: 75% (777 mg, 1.50 mmol).
Characteristic: Yellow semisolid.
$[\alpha]_D^{20}$ –29.00° (*c* 1.10, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (3H, s), 1.42 (3H, s), 2.43-2.81 (2H, m), 4.51 (1H, d, *J* = 11.4 Hz), 4.61-4.66 (2H, m), 5.56 (1H, d, *J* = 16.5 Hz), 5.70 (1H, d, *J* = 3.3 Hz), 5.85 (1H, d, *J* = 3.3 Hz), 6.72-6.75 (2H, m), 6.91-7.34 (12H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 26.7, 48.9, 72.9, 76.8, 82.3, 84.6, 105.0, 112.5, 125.5, 126.3, 127.2, 127.5, 128.1, 128.5, 128.8, 129.2, 130.3, 136.1, 136.3, 136.8, 150.7, 155.5.
IR (KBr, cm^{-1}): 734, 843, 1024, 1080, 1393, 1457, 1595, 1716.
HR-MS (*m*/*z*) for $C_{29}H_{29}ClN_3O_4$ (M+H): Calculated 518.1847, found 518.1831 (one of the peaks).

6. General Procedure for Synthesis of the Fused 1,2,4-triazolo[3,4-*a*]pyridines and Quinolines by the One Step Strategy

The aromatic *N*-heterocycle **7** (2.2 mmol), *N*-tosylaldohydrazone **1** (2.0 mmol), anhydrous $MgSO_4$ (0.5 g) and dichloromethane (10 mL) were taken together in a round-bottom flask (25 mL) and stirred at 0° C. Iodosobenzene (880 mg, 4.0 mmol) was added and the content of the reaction mixture was allowed to attain the room temperature. Progress of the reaction was monitored by TLC and the reaction was complete after 2.0-2.5 hours. The post reaction mixture was filtered and washed well with dichloromethane. The combined organic portion was washed with aqueous sodium bicarbonate solution (1 x 10 mL) and brine (3 x 10 mL) solution, dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. The crude brown oil was chromatographed on silica gel (60-120 mesh). Thus, the reaction with pyridine-4-aldehyde (**7a**, 235 mg, 2.2 mmol), *N*-(4-methoxybenzylidene)-*N'*-4-methylphenylsulfonylhydrazine (**1f**, 608 mg, 2 mmol) afforded 3-(4-Methoxyphenyl)-[1,2,4]triazolo[4,3-*a*]pyridine-7-carbaldehyde (**8a**) after processing in an isolated yield of 81% (409 mg, 1.62 mmol). Asymmetric syntheses of the fused sugar-based 1,2,4-triazoles (**8g-i**) are also synthesized following the same general procedure. The compound **8a** and others (**8b-f** and **8g-i**) were characterized by ^1H and ^{13}C NMR (NDC & DEPT), FT-IR, HR-MS, and measuring optical rotation and also the melting points of the solid products.

7. Characterization Data of the Functionalized Fused 1,2,4-Triazolo[3,4-*a*]pyridines and quinolines (8a-8i):

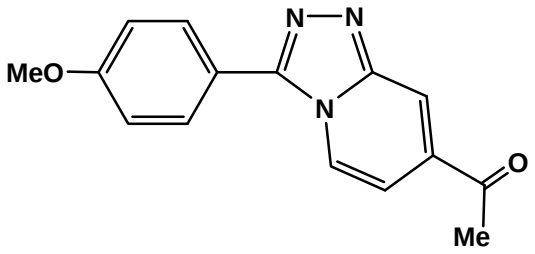
7.1. 3-(4-Methoxyphenyl)-[1,2,4]triazolo[4,3-*a*]pyridine-7-carbaldehyde (8a):



8a

Yield: 81% (409 mg, 1.62 mmol).
Characteristic: Yellow solid.
Melting point: 218° C.
^1H NMR (300 MHz, $CDCl_3$): δ 3.91 (3H, s), 7.13 (2H, d, J = 8.7 Hz), 7.35 (1H, dd, J = 1.5, 7.2 Hz), 7.79 (2H, dd, J = 2.1, 7.2 Hz), 8.28 (1H, s), 8.31 (1H, s), 10.04 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 109.8, 114.9, 117.9, 123.4, 123.8, 129.8, 134.5, 149.8.9, 161.5, 189.1.
IR (KBr, cm^{-1}): 609, 784, 831, 1167, 1261, 1468, 1615, 1690.
HR-MS (*m*/*z*) for $C_{14}H_{12}N_3O_2$ (M+H): Calculated 254.0930, found 254.0909.

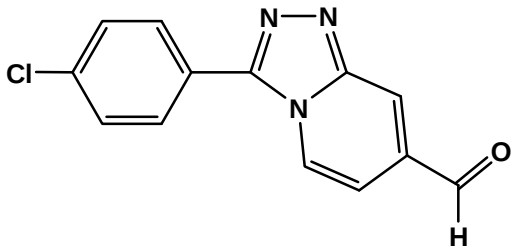
7.2. 1-[3-(4-Methoxyphenyl)-[1,2,4]triazolo[4,3-*a*]pyridine-7-yl]-ethanone (8b):



8b

Yield: 79% (421 mg, 1.58 mmol).
Characteristic: Yellow solid.
Melting point: 222° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.68 (3H, s), 3.89 (3H, s), 7.08-7.13 (2H, m), 7.42 (1H, dd, *J* = 1.5, 7.5 Hz), 7.74-7.79 (2H, m), 8.25 (1H, d, *J* = 7.5 Hz), 8.39 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.9, 55.4, 111.6, 114.9, 118.1, 119.0, 122.6, 129.7, 134.9, 161.4, 195.2.
IR (KBr, cm^{-1}): 837, 1026, 1174, 1253, 1463, 1612, 1670.
HR-MS (*m*/*z*) for $C_{15}H_{14}N_3O_2$ (M+H): Calculated 268.1086, found 268.1115.

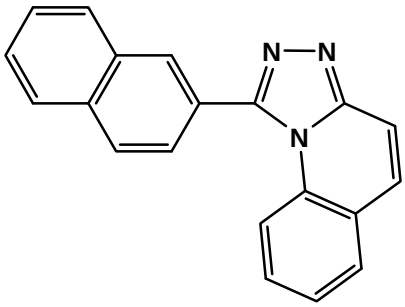
8.3. 3-(4-Chlorophenyl)-[1,2,4]triazolo[4,3-*a*]pyridine-7-carbaldehyde (8c):



8c

Yield: 78% (400 mg, 1.56 mmol).
Characteristic: Yellow solid.
Melting point: 225° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (1H, dd, *J* = 1.5, 7.2 Hz), 7.53 (2H, dd, *J* = 1.8, 6.6 Hz), 7.73 (2H, dd, *J* = 1.8, 6.6 Hz), 8.22 (1H, d, *J* = 7.2 Hz), 8.27 (1H, s), 9.98 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 110.4, 123.3, 123.6, 124.1, 129.5, 129.8, 134.8, 137.1, 147.1, 150.1, 188.9.
IR (KBr, cm^{-1}): 824, 1092, 1157, 1457, 1692.
HR-MS (*m*/*z*) for $C_{13}H_9ClN_3O$ (M+H): Calculated 258.0434, found 258.0422 (one of the peaks).

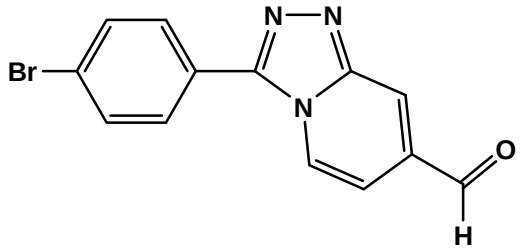
8.4. 1-Naphthalen-2-yl-[1,2,4]triazolo[4,3-*a*]quinoline (8d):



8d

Yield: 80% (472 mg, 1.60 mmol).
Characteristic: Pale yellow semisolid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14-7.31 (1H, m), 7.32-7.41 (1H, m), 7.42-7.72 (7H, m), 7.82-7.90 (2H, m), 7.95 (1H, d, *J* = 8.4 Hz), 8.18 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 114.9, 116.7, 124.5, 126.1, 126.2, 126.4, 127.0, 127.5, 127.8, 128.5, 128.7, 128.9, 129.2, 129.8, 130.1, 131.7, 133.0, 133.8, 149.0, 149.8.
IR (KBr, cm^{-1}): 753, 814, 1143, 1279, 1399, 1612, 1723.
HR-MS (*m*/*z*) for $C_{20}H_{14}N_3$ (M+H): Calculated 296.1188, found 296.1167.

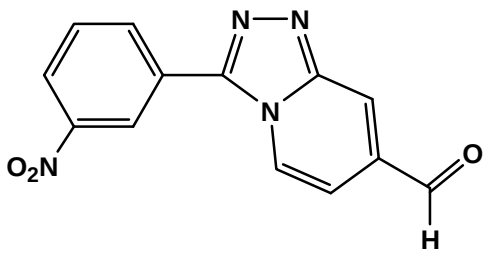
8.5. 3-(4-Bromophenyl)-[1,2,4]triazolo[4,3-*a*]pyridine-7-carbaldehyde (8e):



8e

Yield: 79% (474 mg, 1.58 mmol).
Characteristic: Yellow solid.
Melting point: 223° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21 (1H, dd, *J* = 1.2, 7.2 Hz), 7.51-7.60 (4H, m), 8.11 (1H, d, *J* = 7.2 Hz) , 8.17 (1H, s), 9.87 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 110.5, 123.3, 123.7, 124.6, 125.4, 129.7, 132.8, 134.9, 150.1, 188.9.
IR (KBr, cm^{-1}): 817, 910, 1452, 1691, 1915.
HR-MS (*m*/*z*) for $C_{13}H_9BrN_3O$ (M+H): Calculated 301.9929, found 301.9948 (one of the peaks).

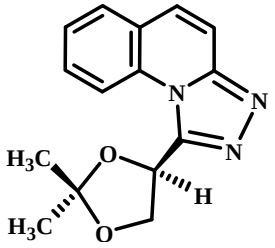
8.6. 3-(3-Nitrophenyl)-[1,2,4]triazolo[4,3-*a*]pyridine-7-carbaldehyde (8f):



8f

Yield: 74% (396 mg, 1.48 mmol).
Characteristic: Pale yellow solid.
Melting point: 228° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (1H, dd, *J* = 1.2, 7.2 Hz), 7.79 (1H, t, *J* = 8.1 Hz), 8.22 (1H, d, *J* = 7.2 Hz) , 8.30-8.34 (2H, m), 8.41 (1H, dd, *J* =1.2, 7.2 Hz), 8.67-8.69 (1H, m), 10.02 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 111.6, 122.7, 123.0, 123.6, 125.4, 127.6, 130.9, 134.2, 135.1, 188.7.
IR (KBr, cm^{-1}): 737, 1075, 1283, 1355, 1527, 1705.
HR-MS (*m*/*z*) for $C_{13}H_9N_4O_3$ (M+H): Calculated 269.0675, found 269.0691.

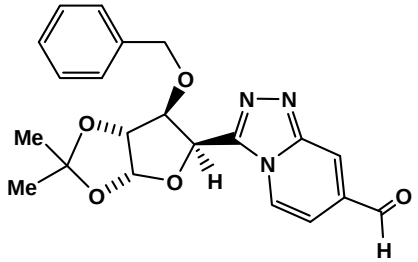
8.7. (S)-(-)-1-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-[1,2,4]triazolo[4,3-*a*]quinoline (8g):



8g

Yield: 76% (408 mg, 1.52 mmol).
Characteristic: Yellow semisolid.
$[\alpha]_D^{20}$ -107.20° (*c* 0.50, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36 (3H, s), 1.55 (3H, s), 4.54 (1H, dd, *J* = 6.3, 8.7 Hz), 5.22-5.27 (1H, m), 5.59-5.64 (1H, m), 7.48-7.58 (2H, m), 7.61-7.69 (2H, m), 7.77 (1H, d, *J* =7.8 Hz), 8.55 (1H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 26.3, 67.0, 69.7, 111.1, 114.9, 117.8, 124.5, 126.3, 129.1, 129.8, 130.0, 131.8, 146.6.
IR (KBr, cm^{-1}): 747, 806, 1058, 1219, 1347, 1612.
HR-MS (*m*/*z*) for $C_{15}H_{16}N_3O_2$ (M+H): Calculated 270.1243, found 270.1229.

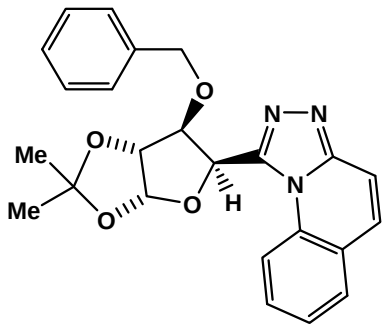
8.8. (3aR,5R,6S,6aR)-(+)-3-(6-Benzyloxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-[1,2,4]triazolo[4,3-*a*]pyridine-7-carbaldehyde (8h):



8h

Yield: 72% (568 mg, 1.44 mmol).
Characteristic: Yellow semisolid.
$[\alpha]_D^{20}$ +50.0° (*c* 0.90, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (3H, s), 1.50 (3H, s), 3.98-4.06 (1H, m), 4.28-4.33 (2H, m), 4.70 (1H, d, *J* = 3.6 Hz), 5.92 (1H, d, *J* = 3.0 Hz), 6.11 (1H, d, *J* = 3.6 Hz), 6.61 (2H, d, *J* = 6.9 Hz), 6.96-7.09 (4H, m), 8.16 (1H, s), 8.38 (1H, d, *J* = 6.9 Hz), 9.91 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 26.7, 60.3, 72.7, 77.1, 82.3, 85.1, 105.1, 108.2, 112.7, 122.3, 127.3, 128.0, 135.1, 136.0, 143.8, 150.4, 175.2, 189.3.
IR (KBr, cm^{-1}): 785, 8611026, 1079, 1390, 1453, 1700.
HR-MS (*m*/*z*) for $C_{21}H_{22}N_3O_5$ (M+H): Calculated 396.1559, found 396.1553.

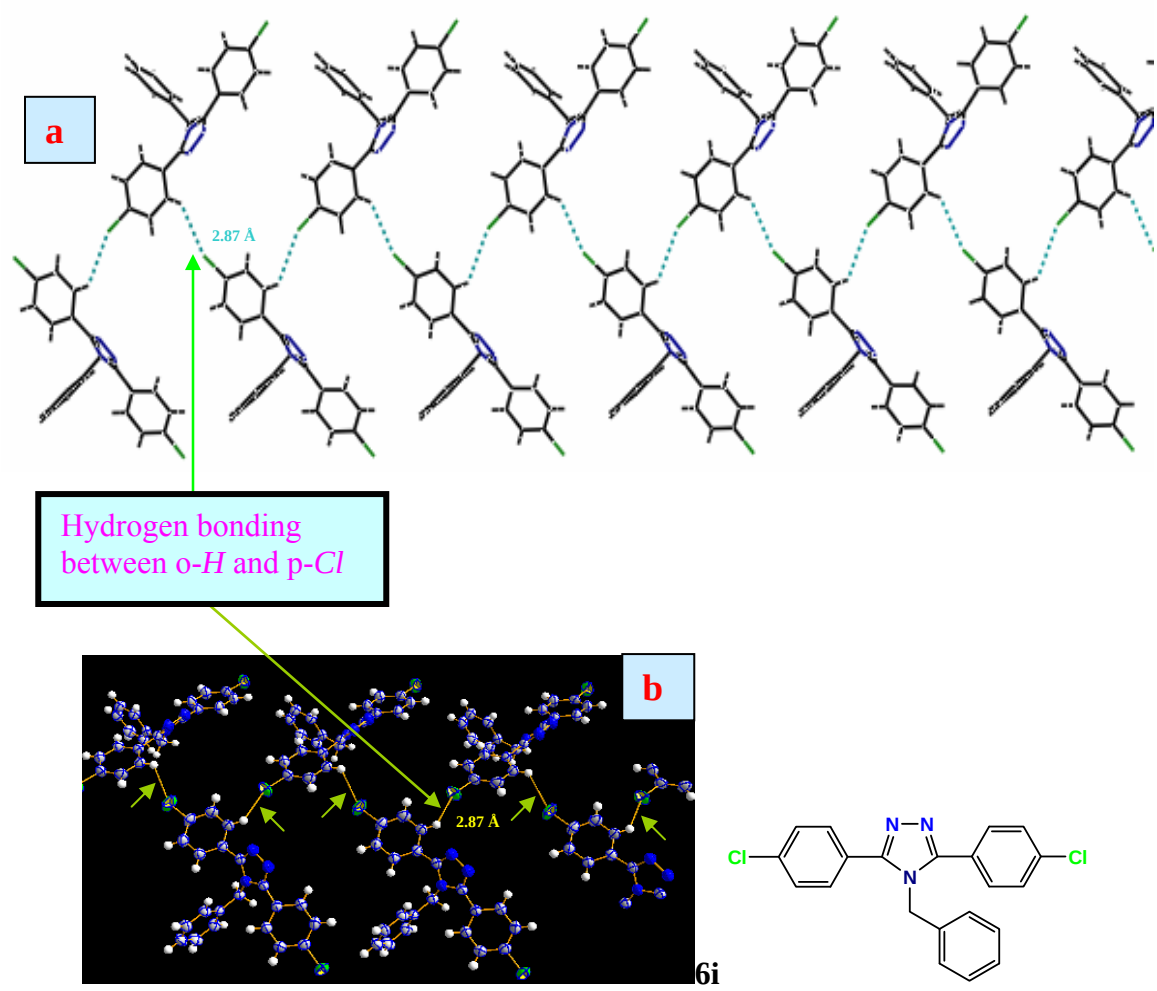
8.9. (3aR,5R,6S,6aR)-(+)-1-(6-Benzyloxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-[1,2,4]triazolo[4,3-*a*]quinoline (8i):



8i

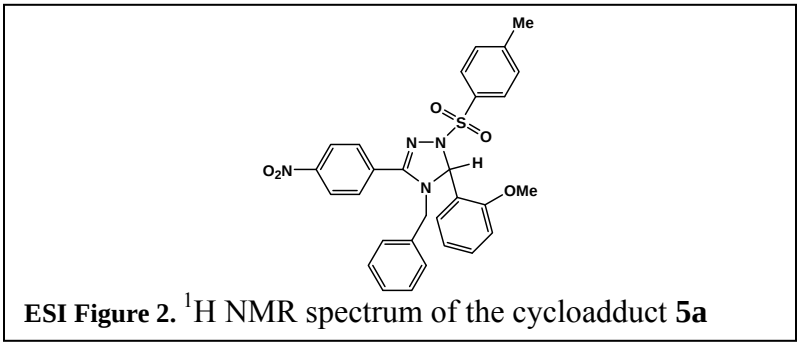
Yield: 75% (625 mg, 1.50 mmol).
Characteristic: yellow semisolid.
$[\alpha]_D^{20}$ +9.90° (*c* 0.70, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, s), 1.63 (3H, s), 4.45-4.56 (3H, m), 4.81 (1H, d, *J* = 3.6 Hz), 6.02 (1H, d, *J* = 3.0 Hz), 6.34 (1H, d, *J* = 3.6 Hz), 6.85-6.88 (2H, m), 6.99-7.06 (3H, m), 7.44-7.67 (3H, m), 7.70-7.75 (2H, m) 8.46 (1H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 26.3, 26.8, 72.8, 76.0, 82.8, 83.5, 105.2, 112.5, 114.7, 119.3, 124.5, 126.1, 127.6, 127.6, 128.0, 128.8, 129.1, 130.1, 131.8, 136.6, 145.3, 150.5.
IR (KBr, cm^{-1}): 749, 1022, 1078, 1255, 1380, 1716.
HR-MS (*m*/*z*) for $C_{24}H_{24}N_3O_4$ (M+H): Calculated 418.1767, found 418.1738.

8. Crystal Engineering Projection of the Crystal Lattice (6i) and Preliminary Observations on Self-Aggregation Property

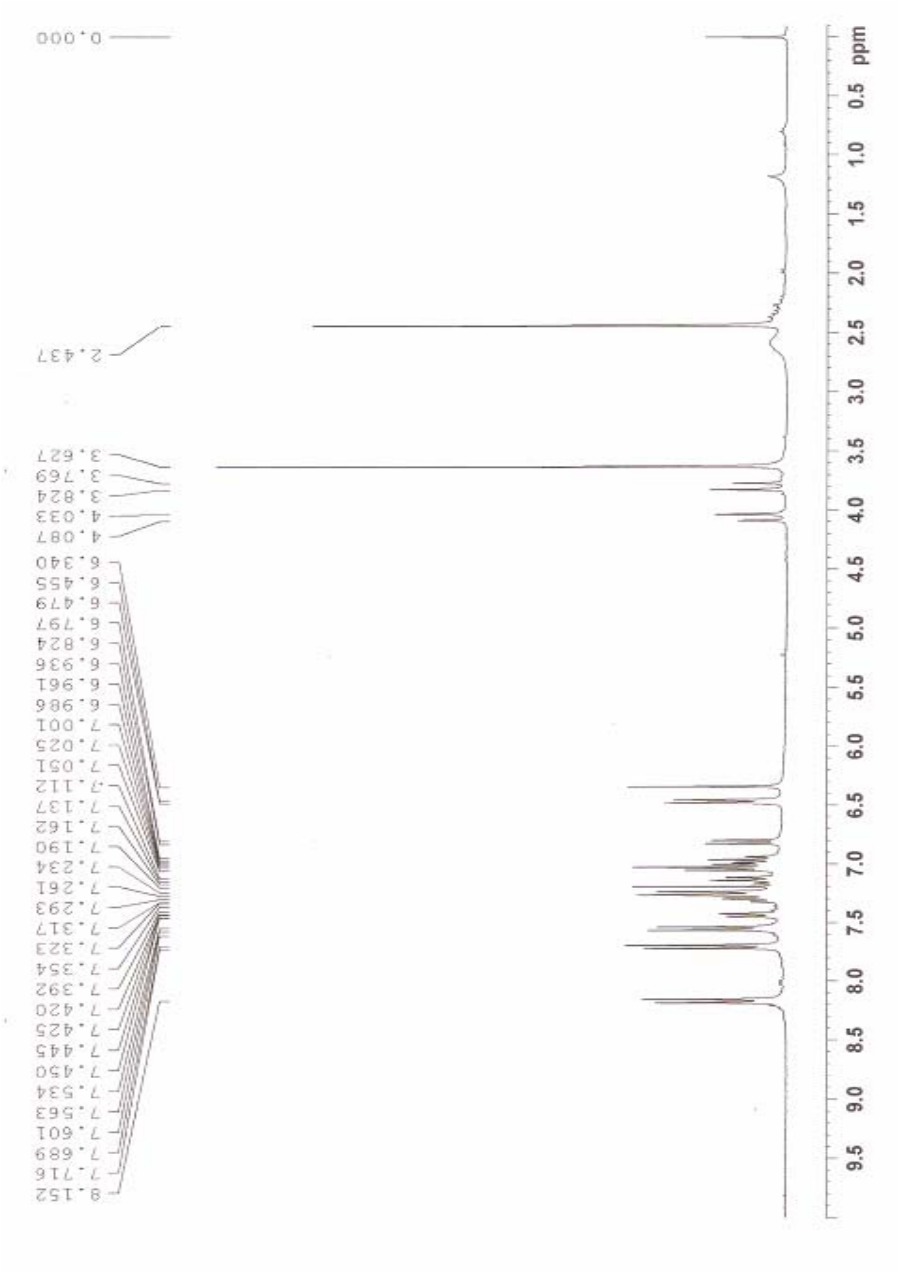


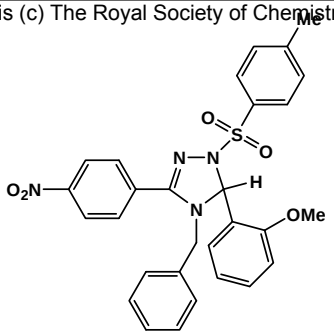
ESI Figure 1. **a**,**b** - Crystal engineering projection of the crystal lattice of 1,2,4-triazole **6i** reveals strong hydrogen bonding between the potential nanoscale building blocks; **c**,**d** – Scanning electron microscope (SEM) imaging morphology of the solid compound **6c** and **6l** has shown generation of ultralong rod-like self-aggregated materials of diameter 500-900 nm.

9. ^{1}H and ^{13}C NMR Spectra of the New Heterocycles Synthesized by the Novel Approach (5a, 6a-l, 6o-s, & 8a-i):

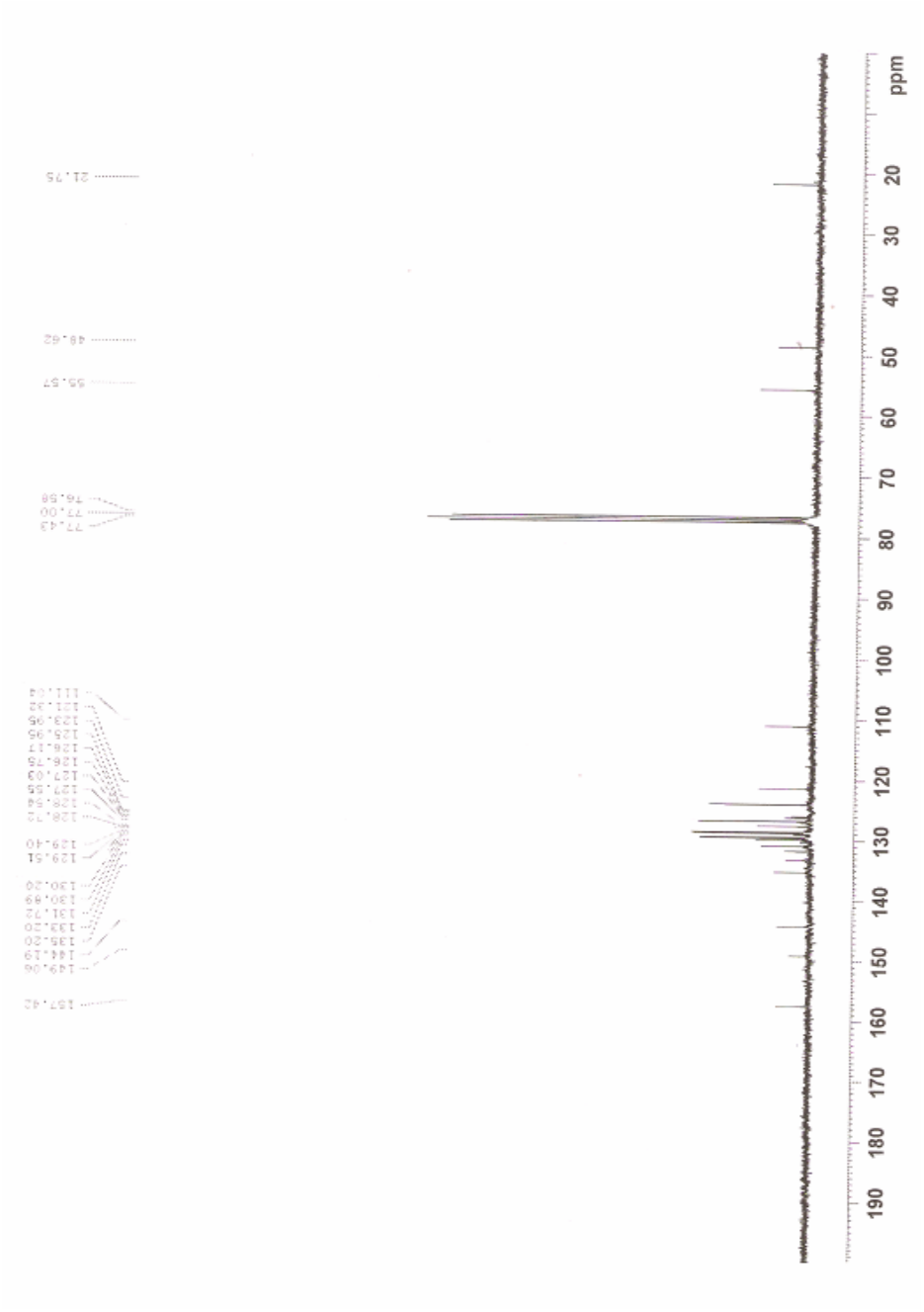


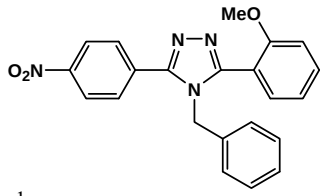
ESI Figure 2. ^{1}H NMR spectrum of the cycloadduct **5a**



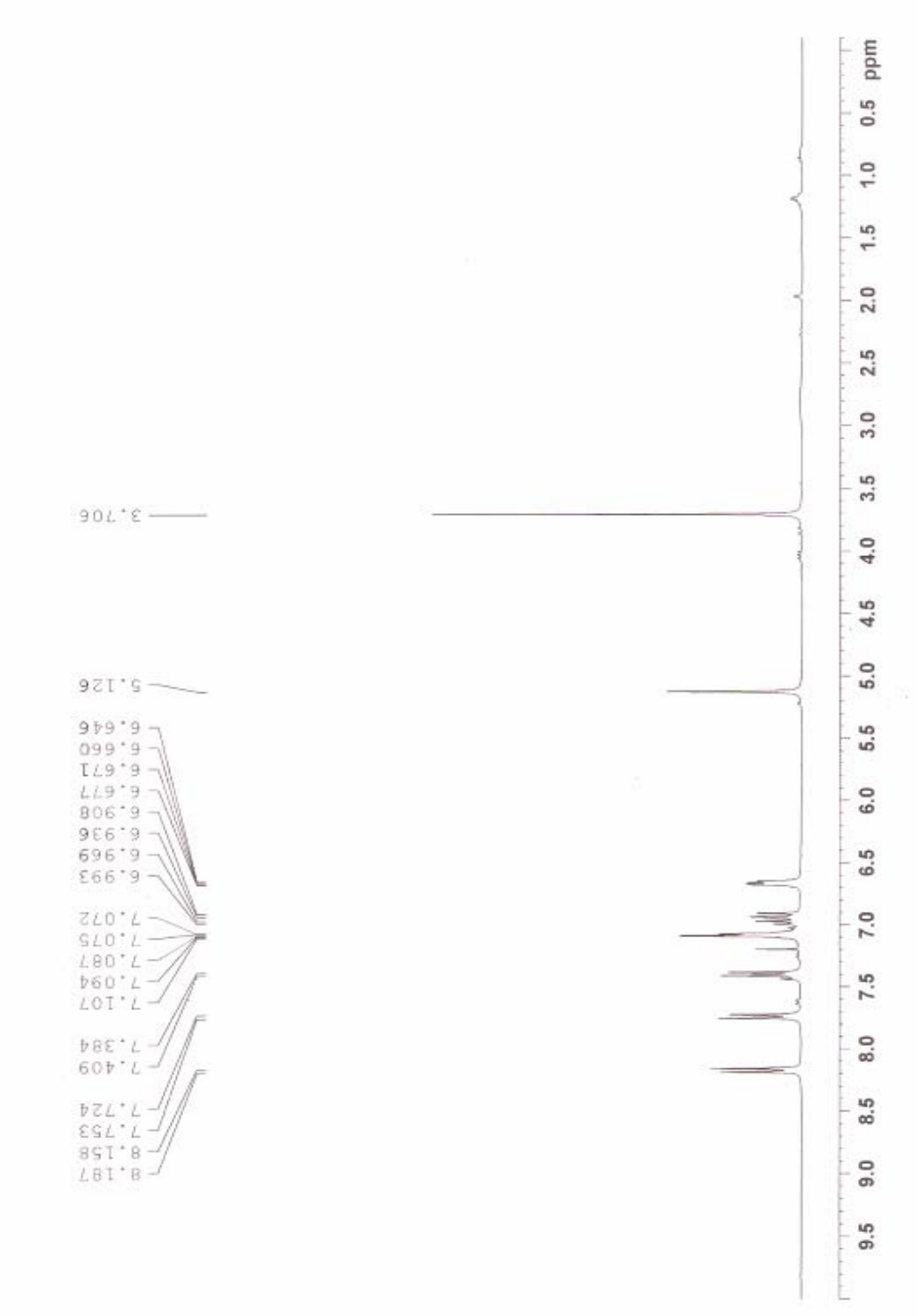


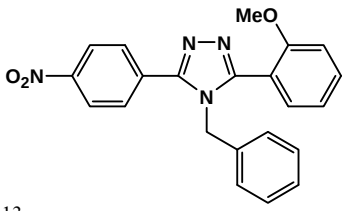
ESI Figure 3. ^{13}C NMR spectrum of the cycloadduct **5a**



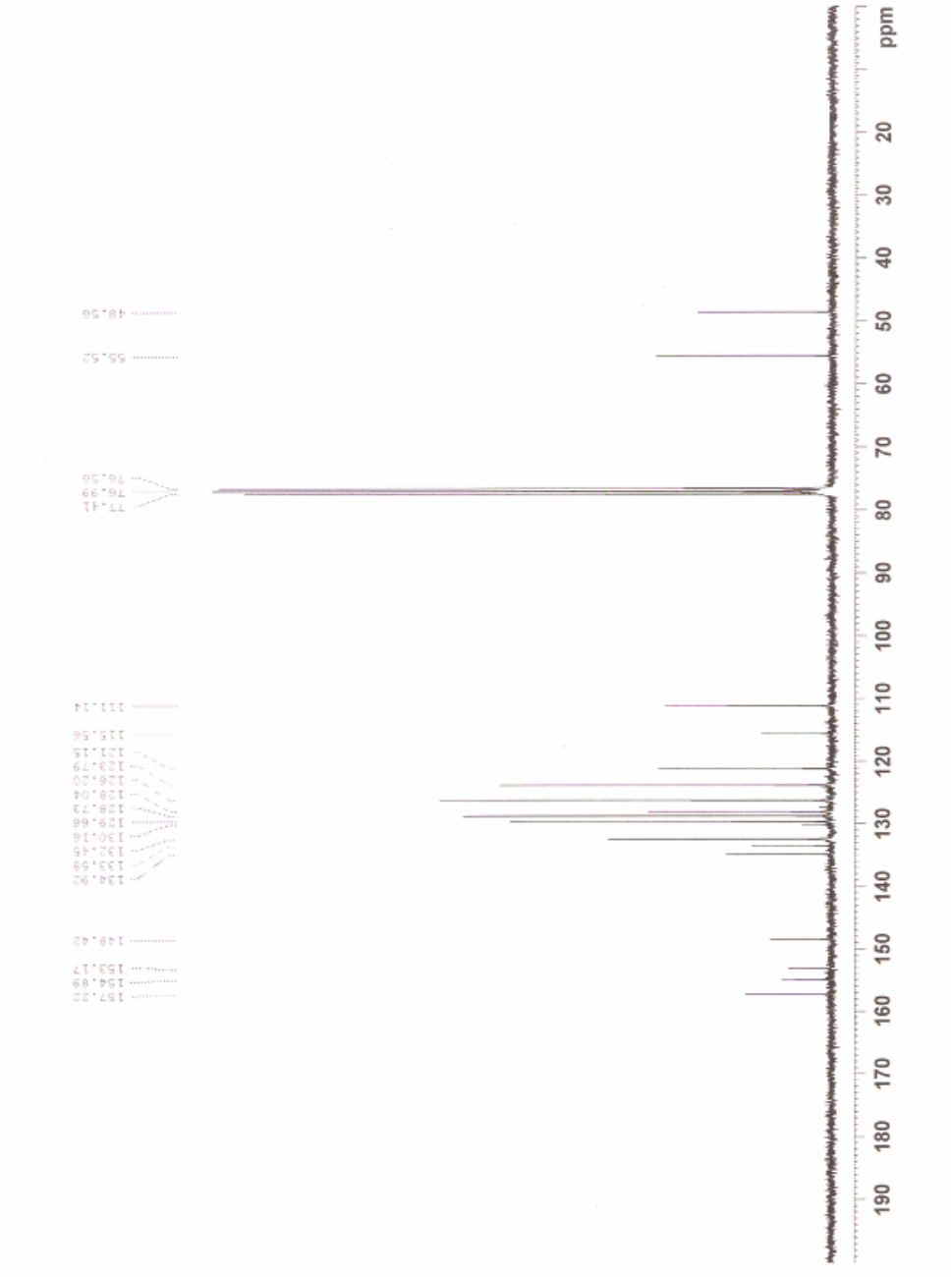


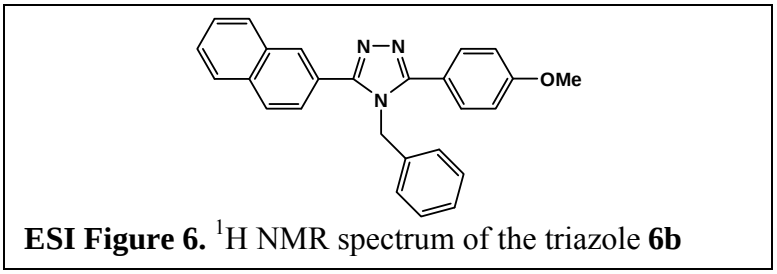
ESI Figure 4. ^{1}H NMR spectrum of the triazole **6a**



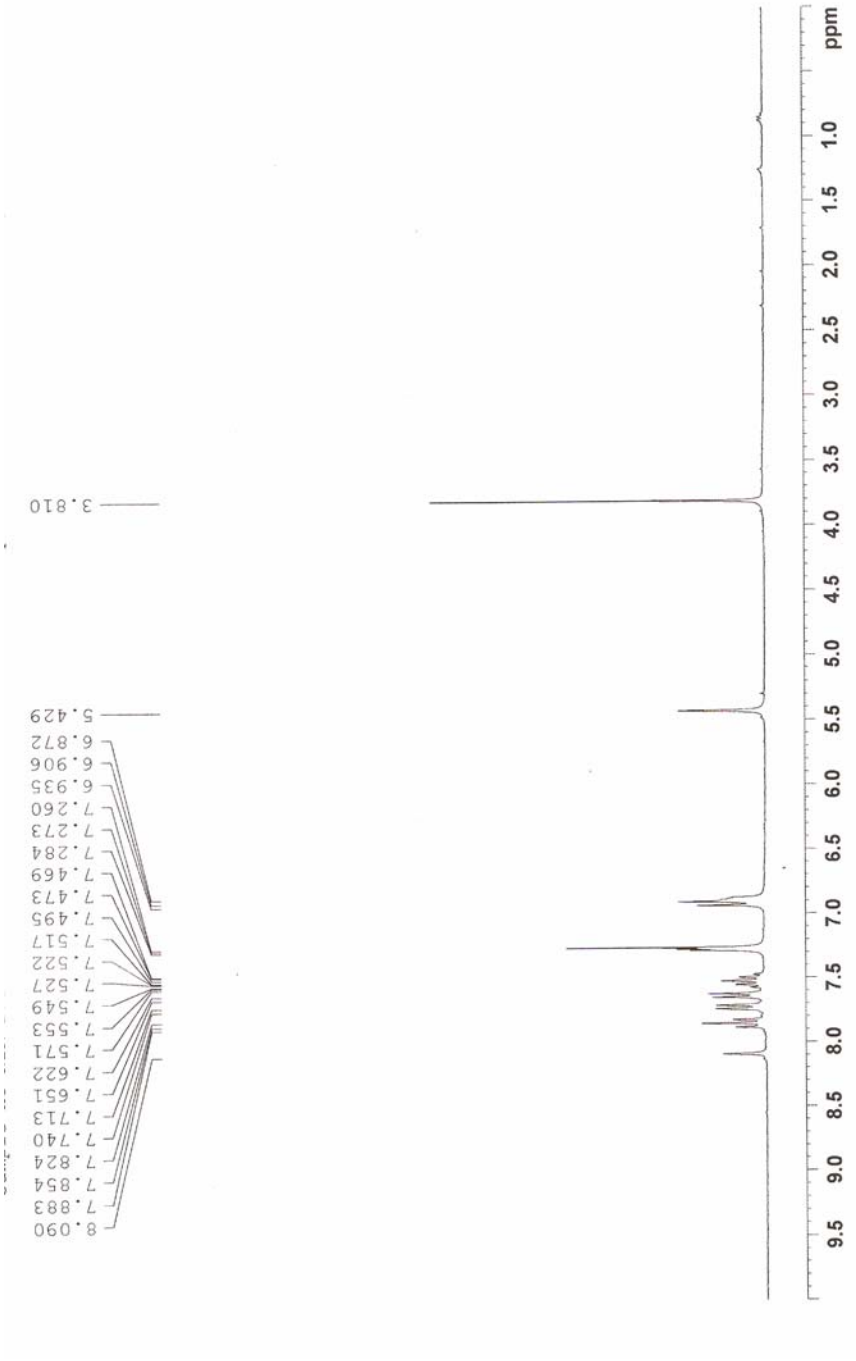


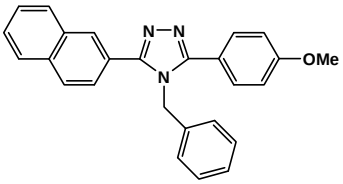
ESI Figure 5. ^{13}C NMR spectrum of the triazole **6a**



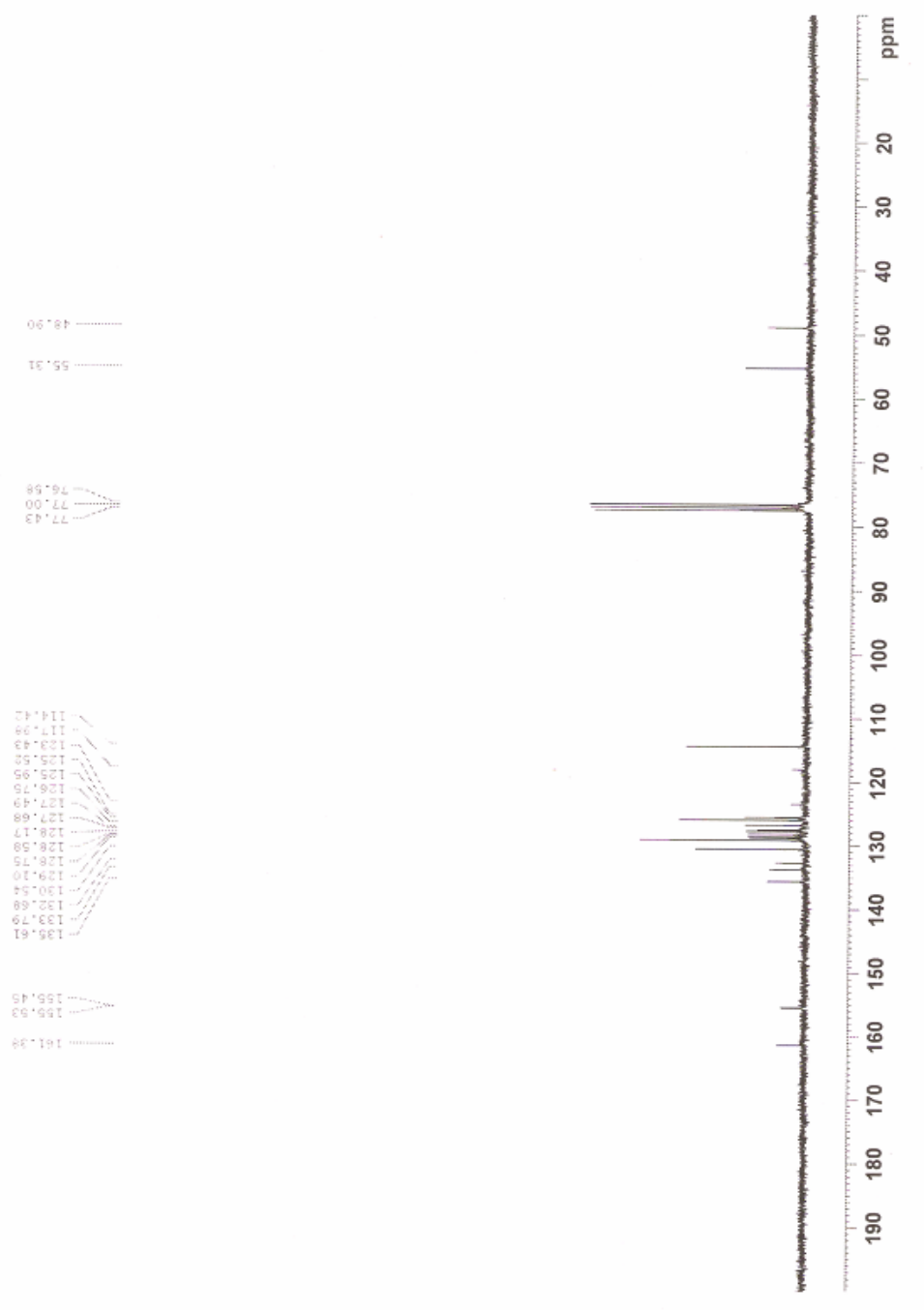


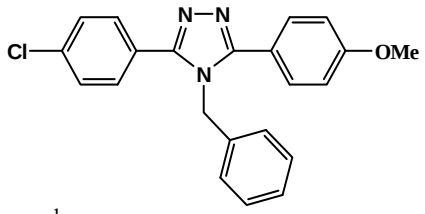
ESI Figure 6. ^{1}H NMR spectrum of the triazole **6b**



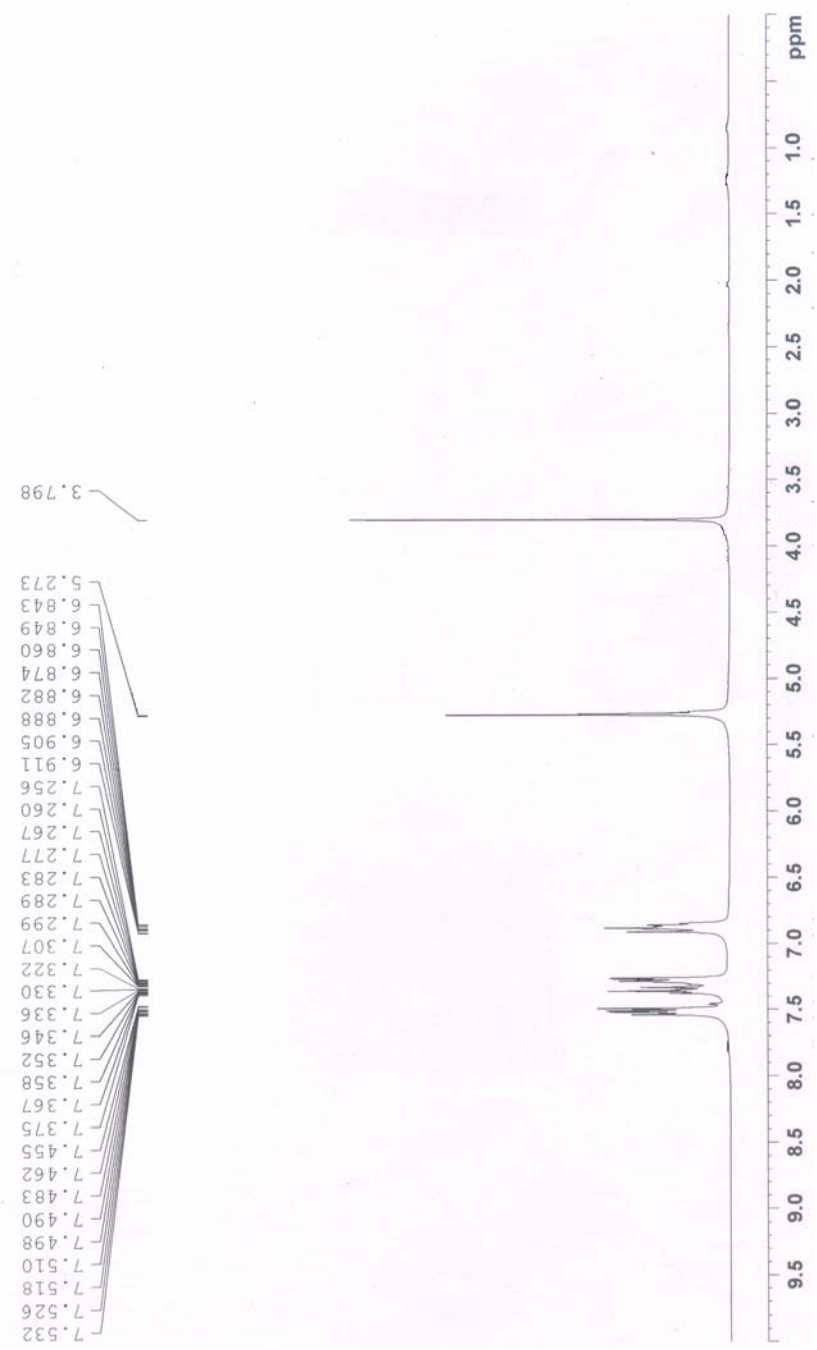


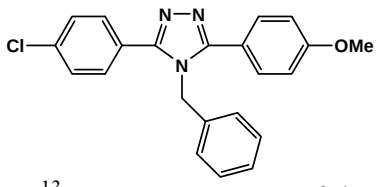
ESI Figure 7. ^{13}C NMR spectrum of the triazole **6b**



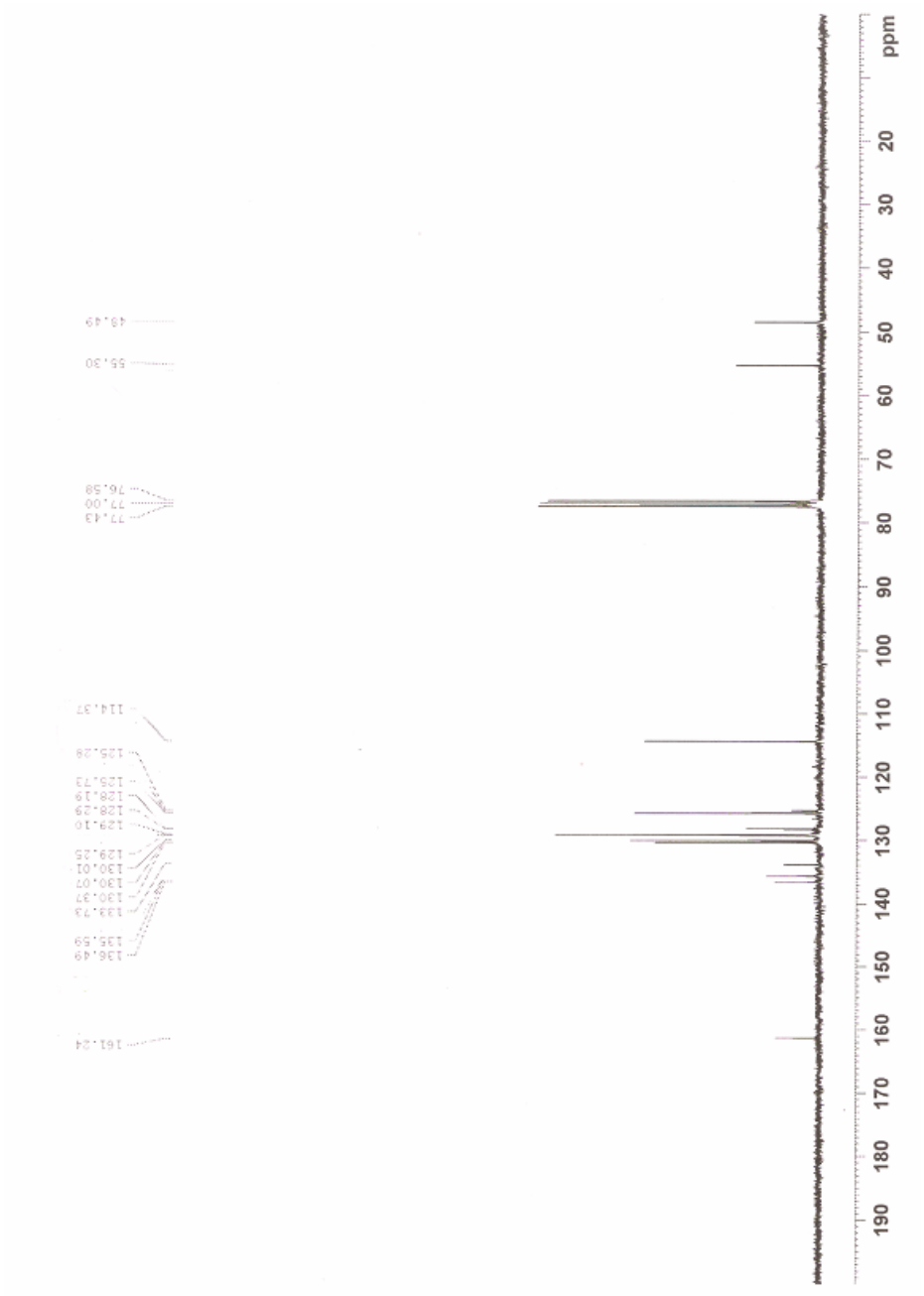


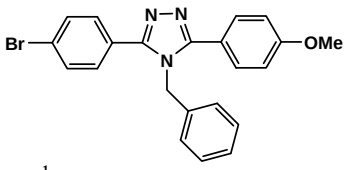
ESI Figure 8. ^{1}H NMR spectrum of the triazole **6c**



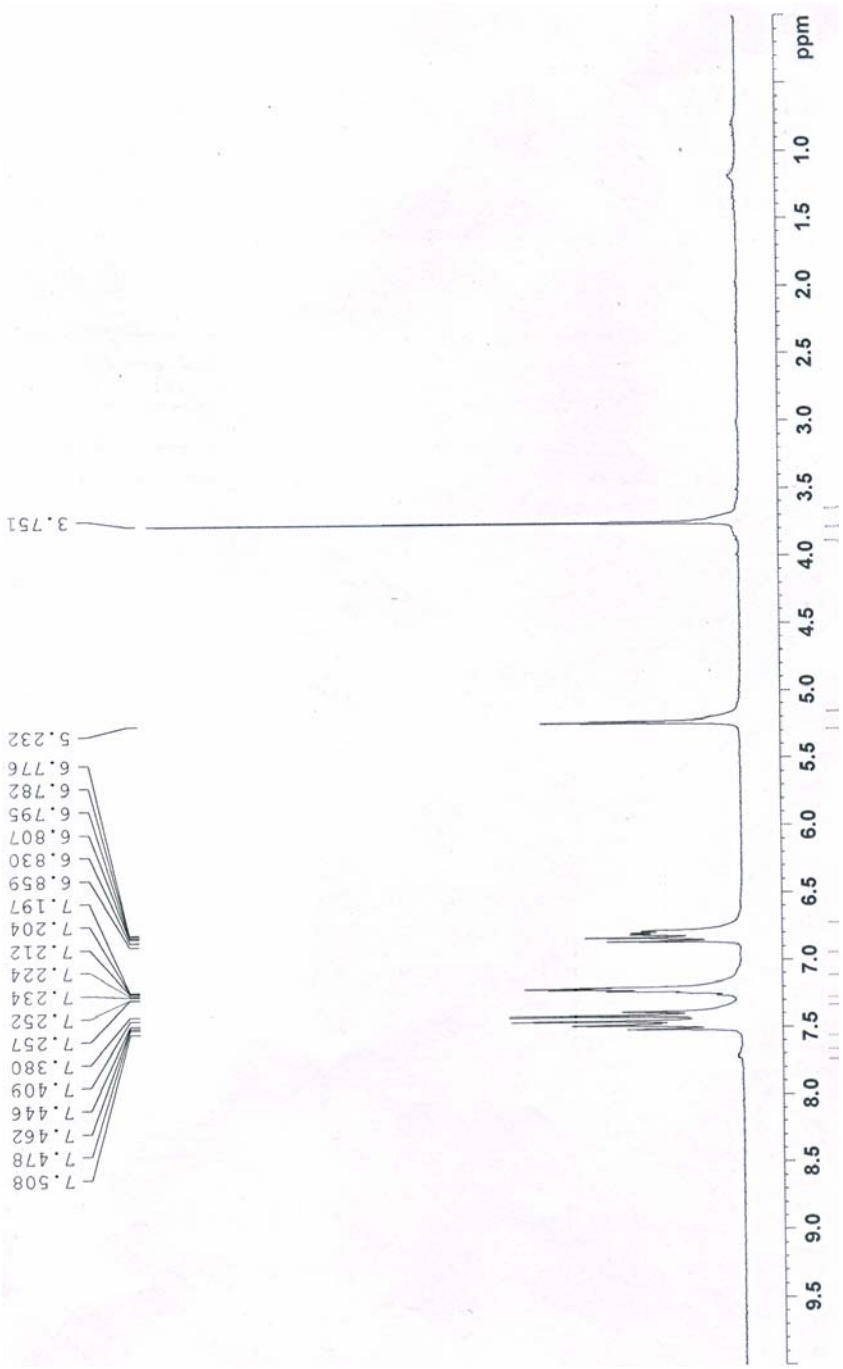


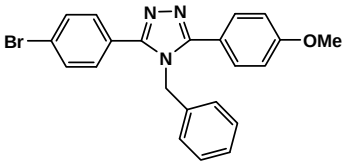
ESI Figure 9. ^{13}C NMR spectrum of the triazole **6c**



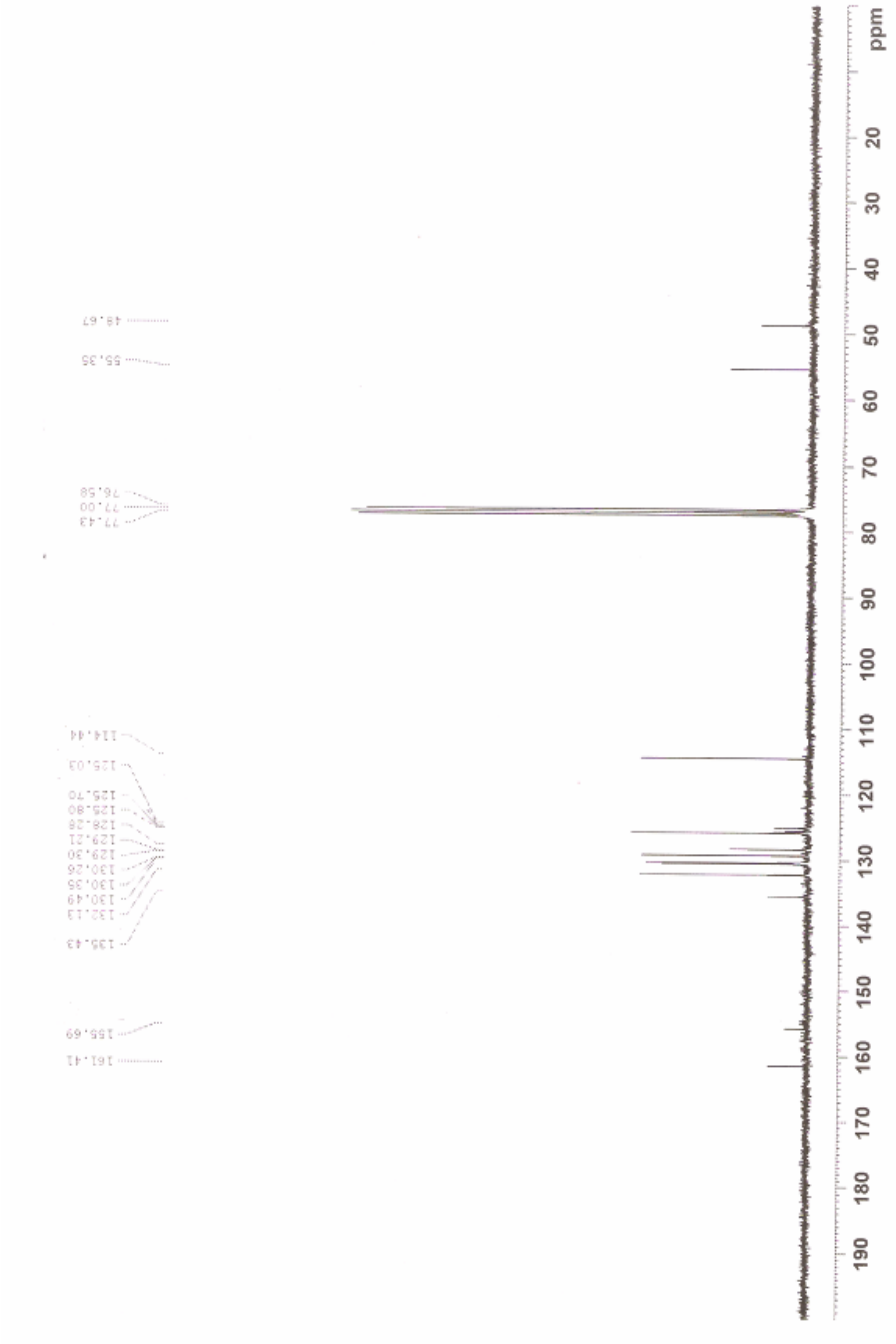


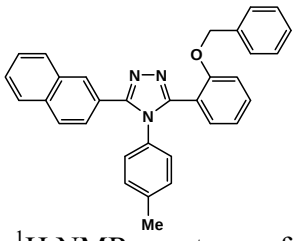
ESI Figure 10. ^{1}H NMR spectrum of the triazole **6d**



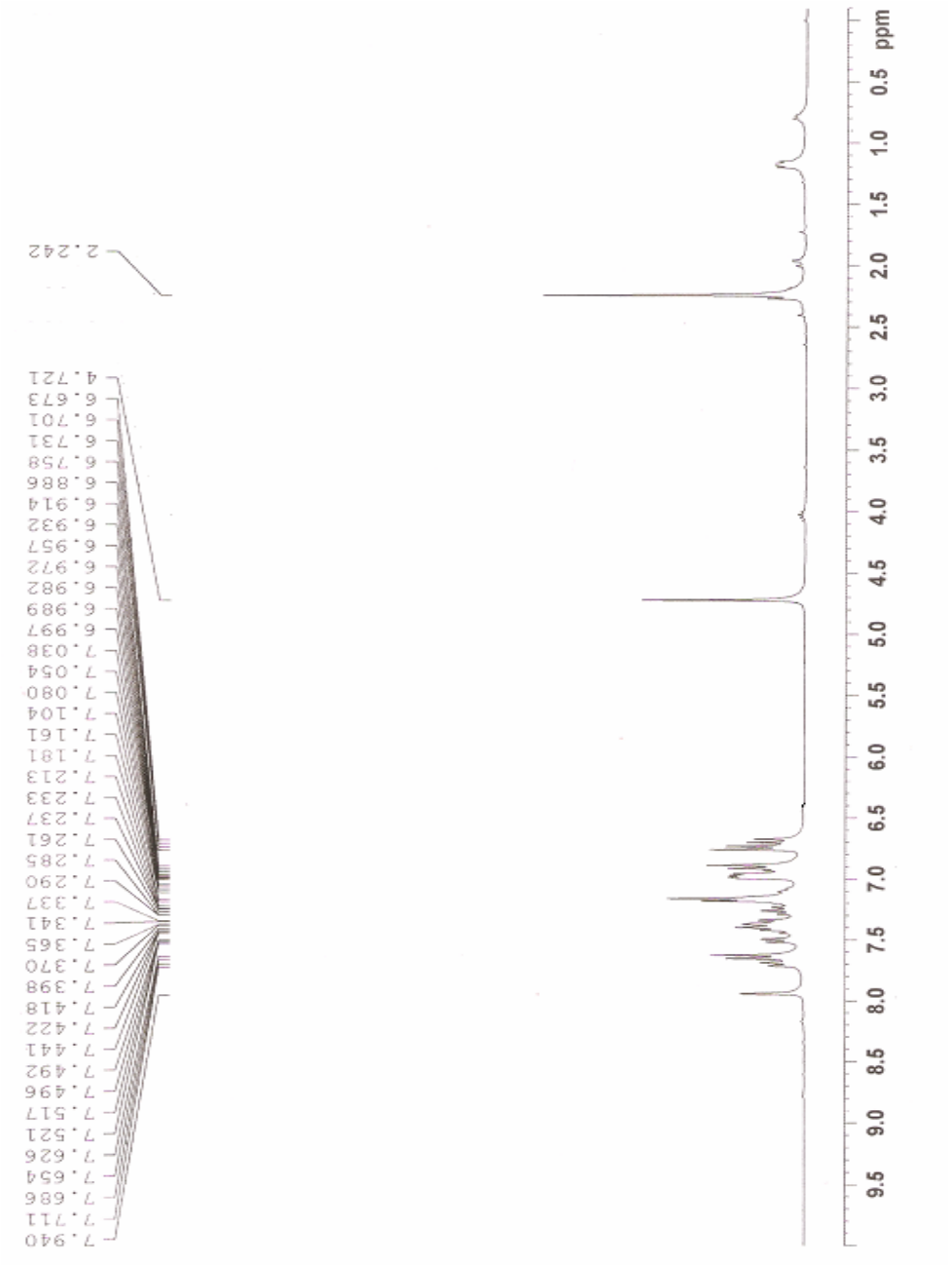


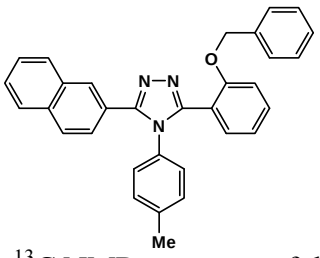
ESI Figure 11. ^{13}C NMR spectrum of the triazole **6d**



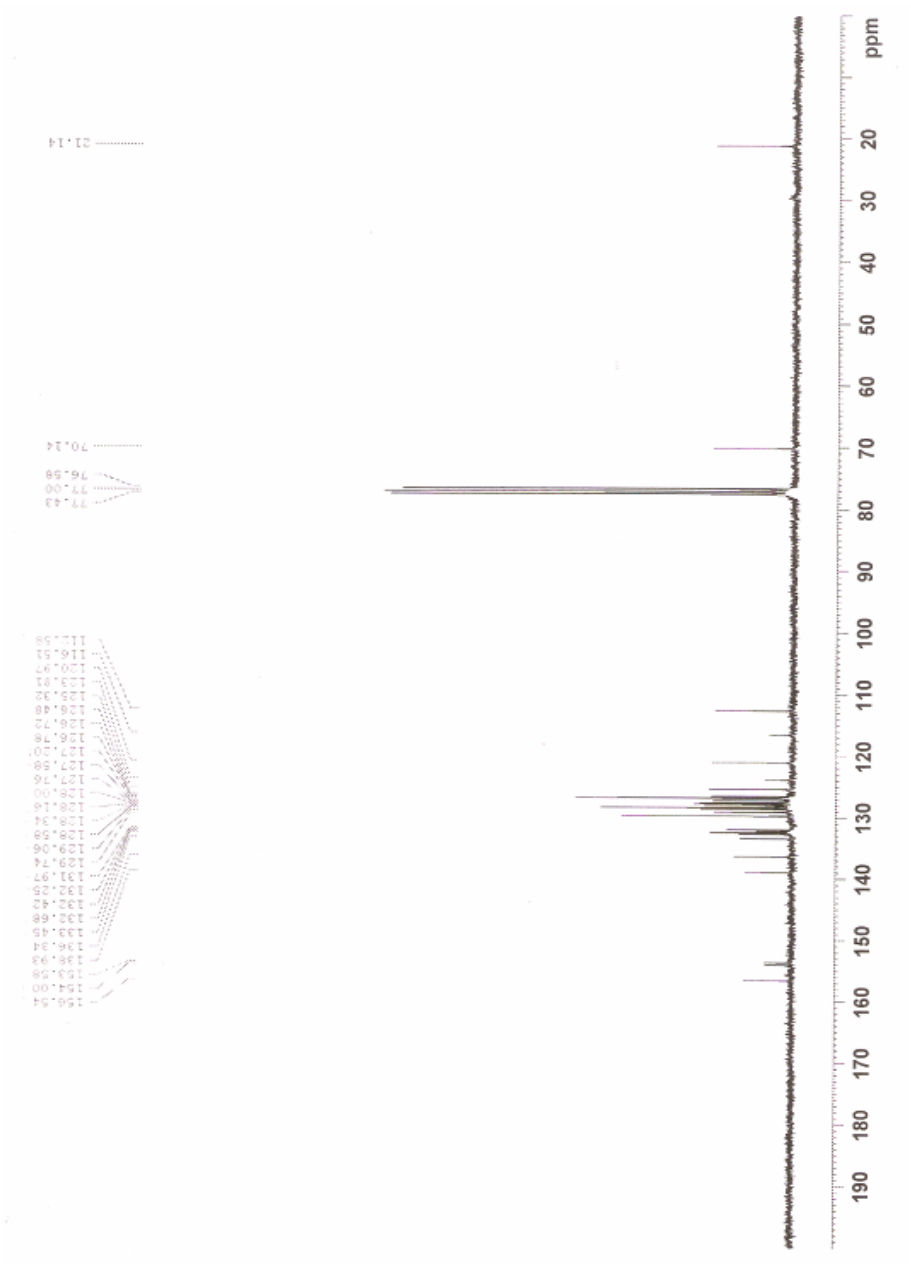


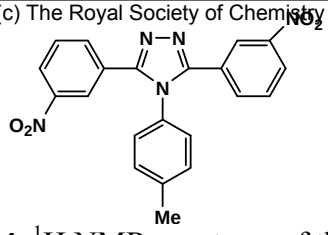
ESI Figure 12. ^{1}H NMR spectrum of the triazole **6e**



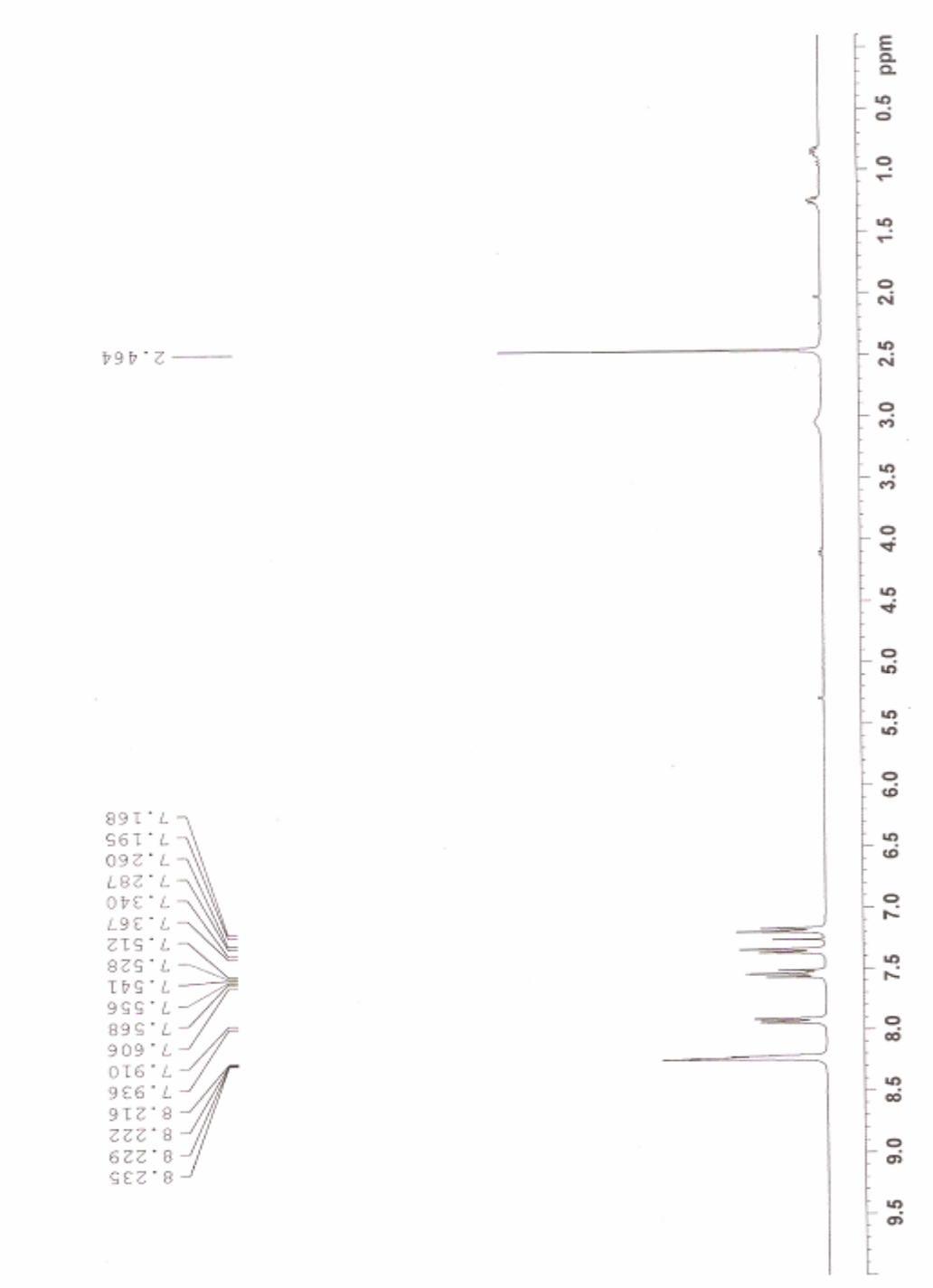


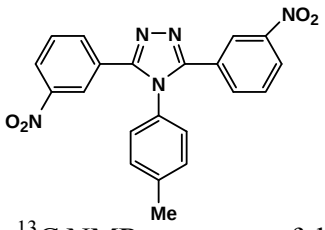
ESI Figure 13. ^{13}C NMR spectrum of the triazole **6e**



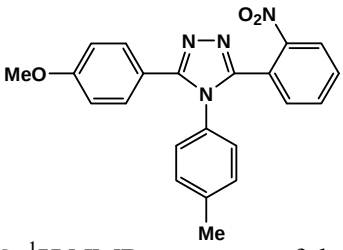


ESI Figure 14. ^{1}H NMR spectrum of the triazole **6f**

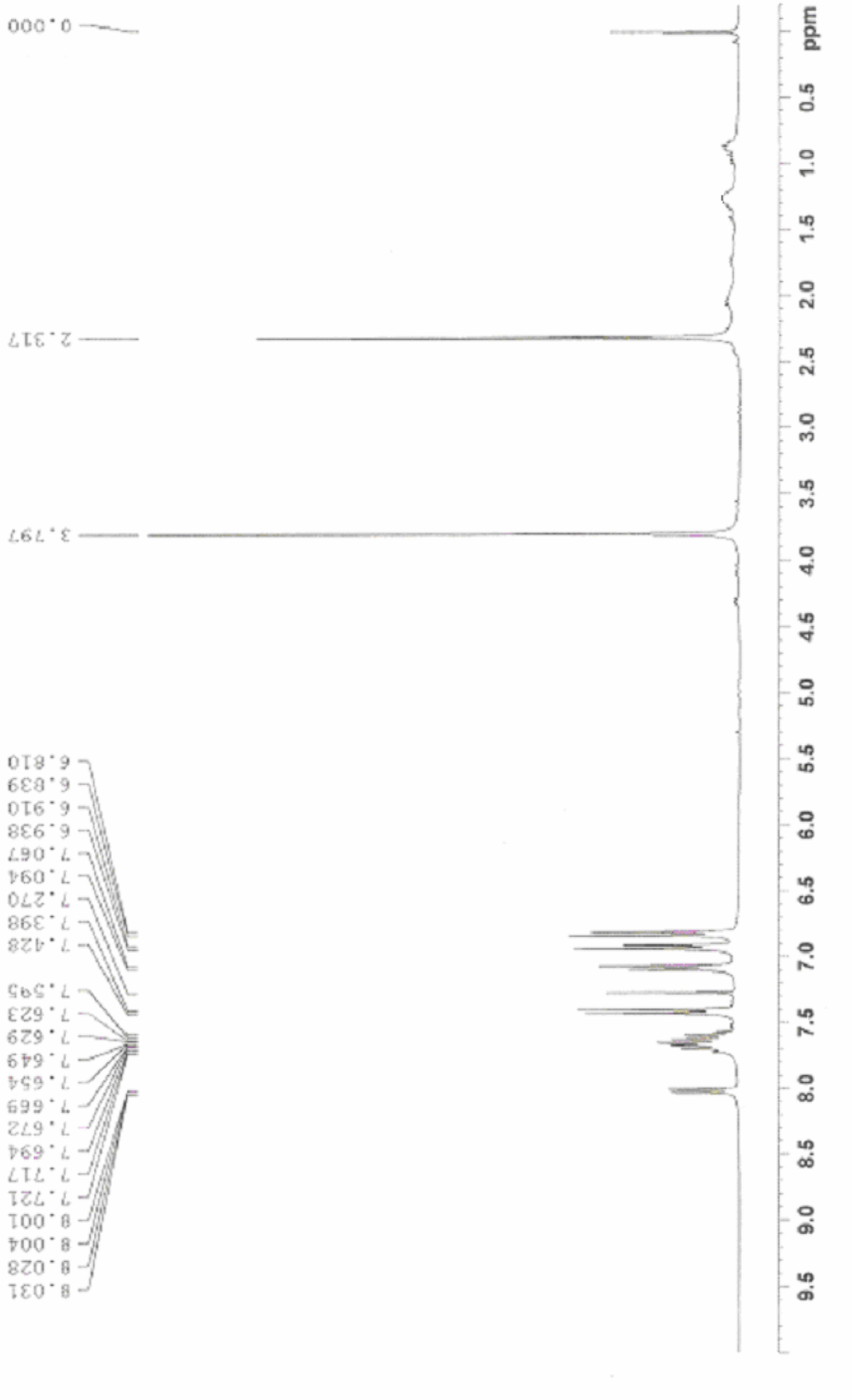


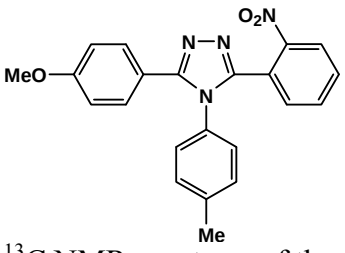


ESI Figure 15. ^{13}C NMR spectrum of the triazole **6f**

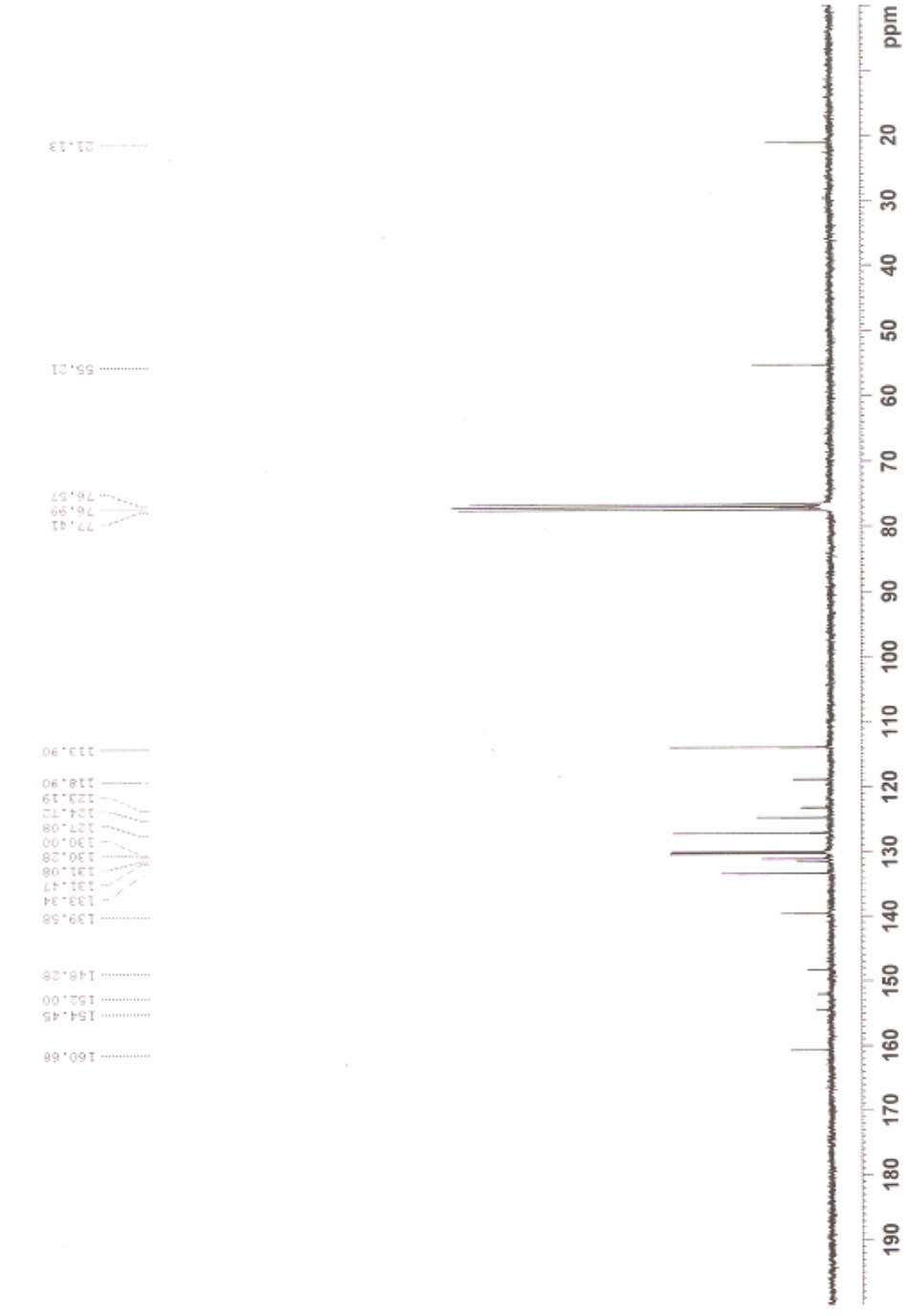


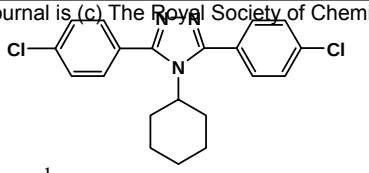
ESI Figure 16. ^{1}H NMR spectrum of the triazole **6g**



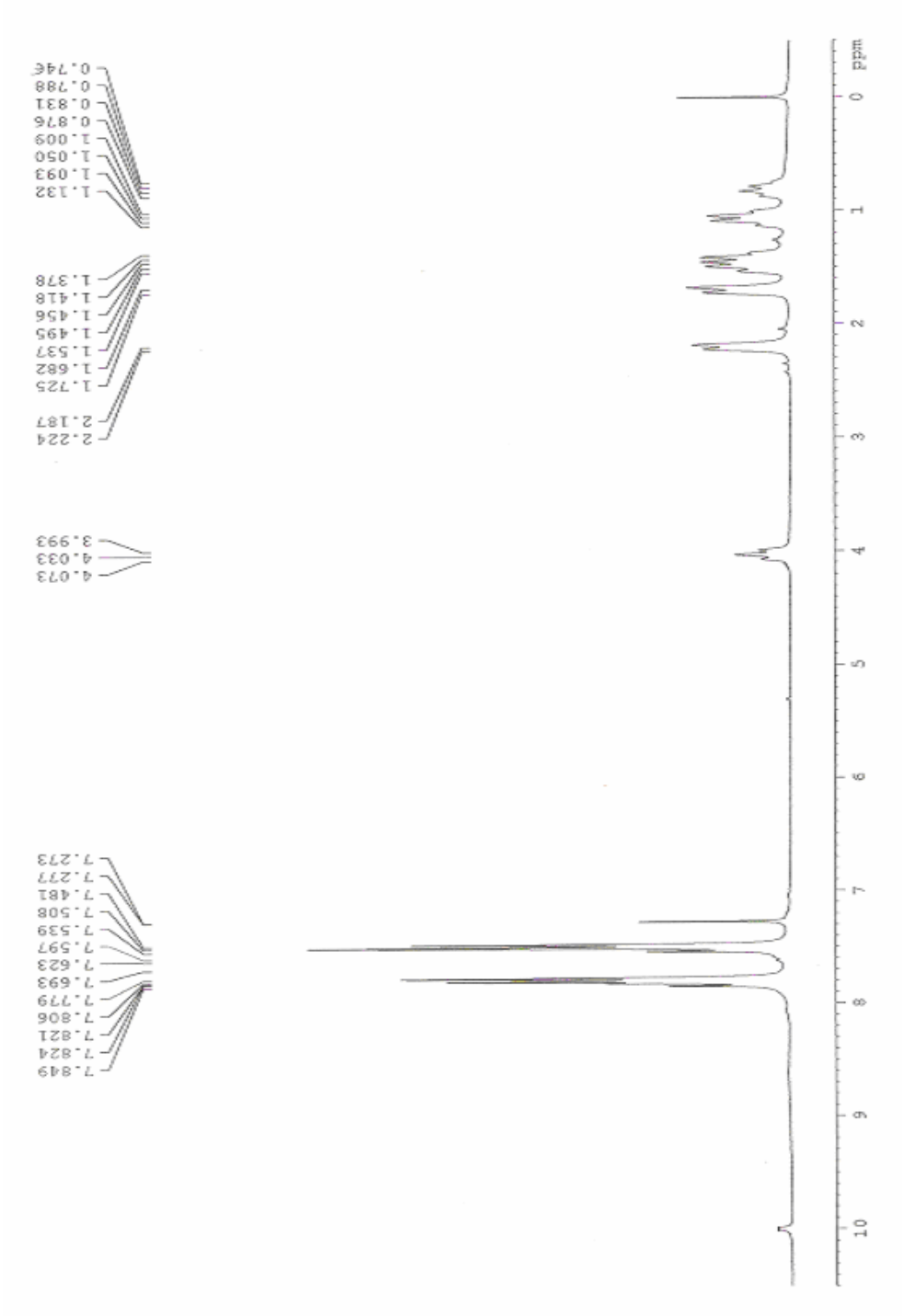


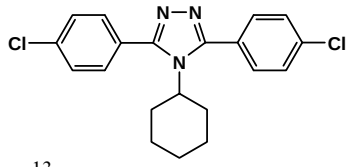
ESI Figure 17. ^{13}C NMR spectrum of the triazole **6g**



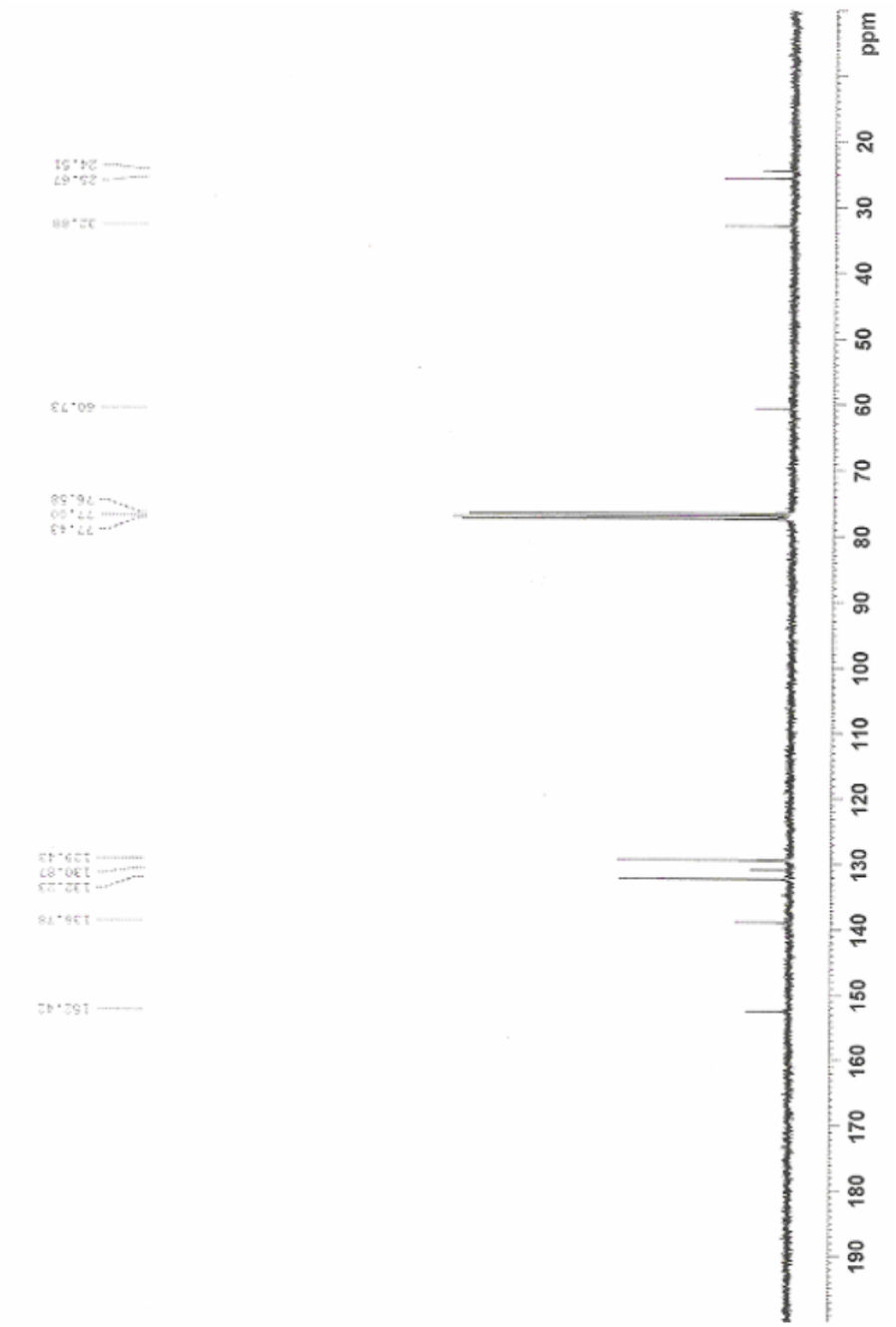


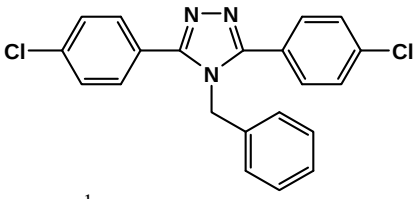
ESI Figure 18. ^{1}H NMR spectrum of the triazole **6h**



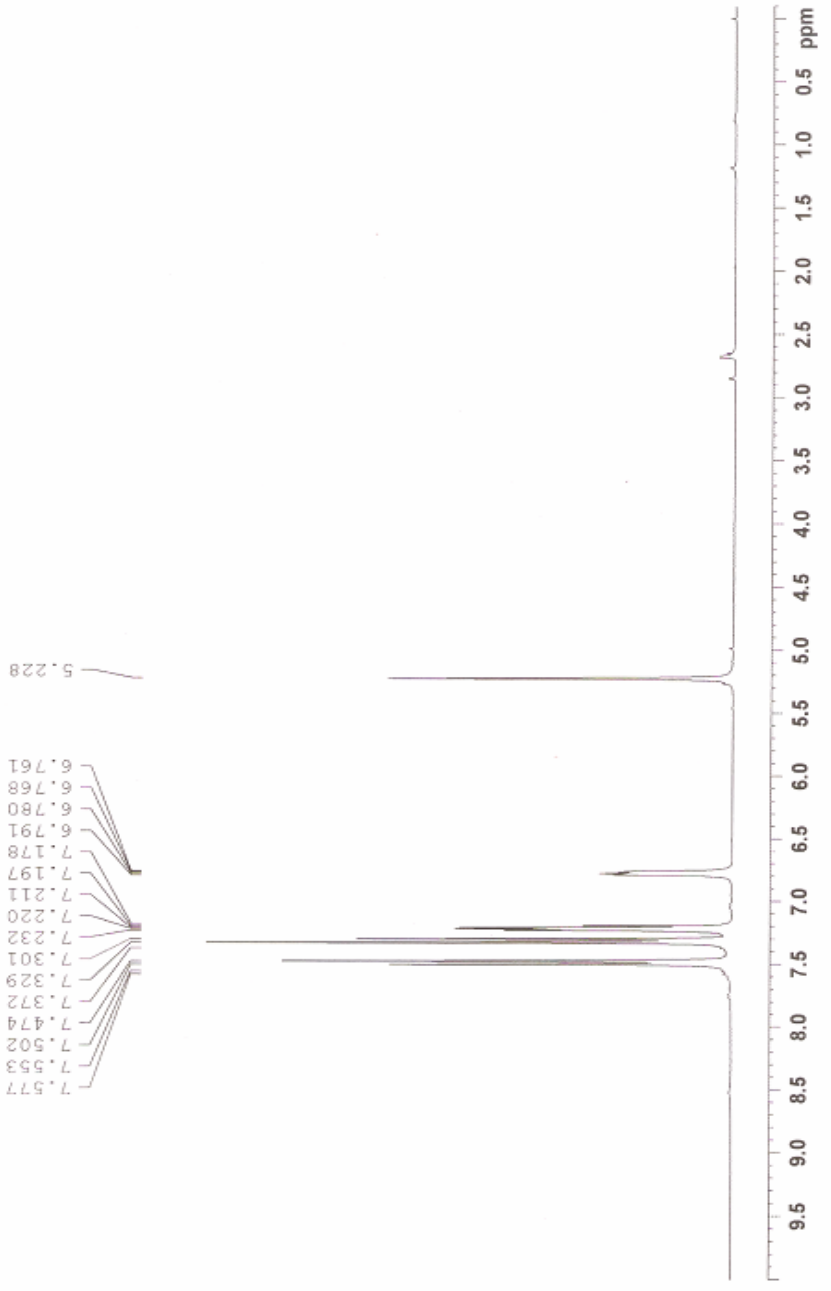


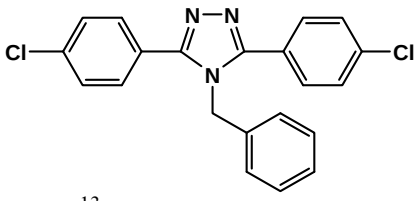
ESI Figure 19. ^{13}C NMR spectrum of the triazole **6h**



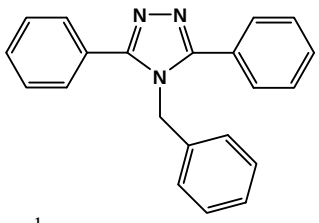


ESI Figure 20. ^{1}H NMR spectrum of the triazole **6i**

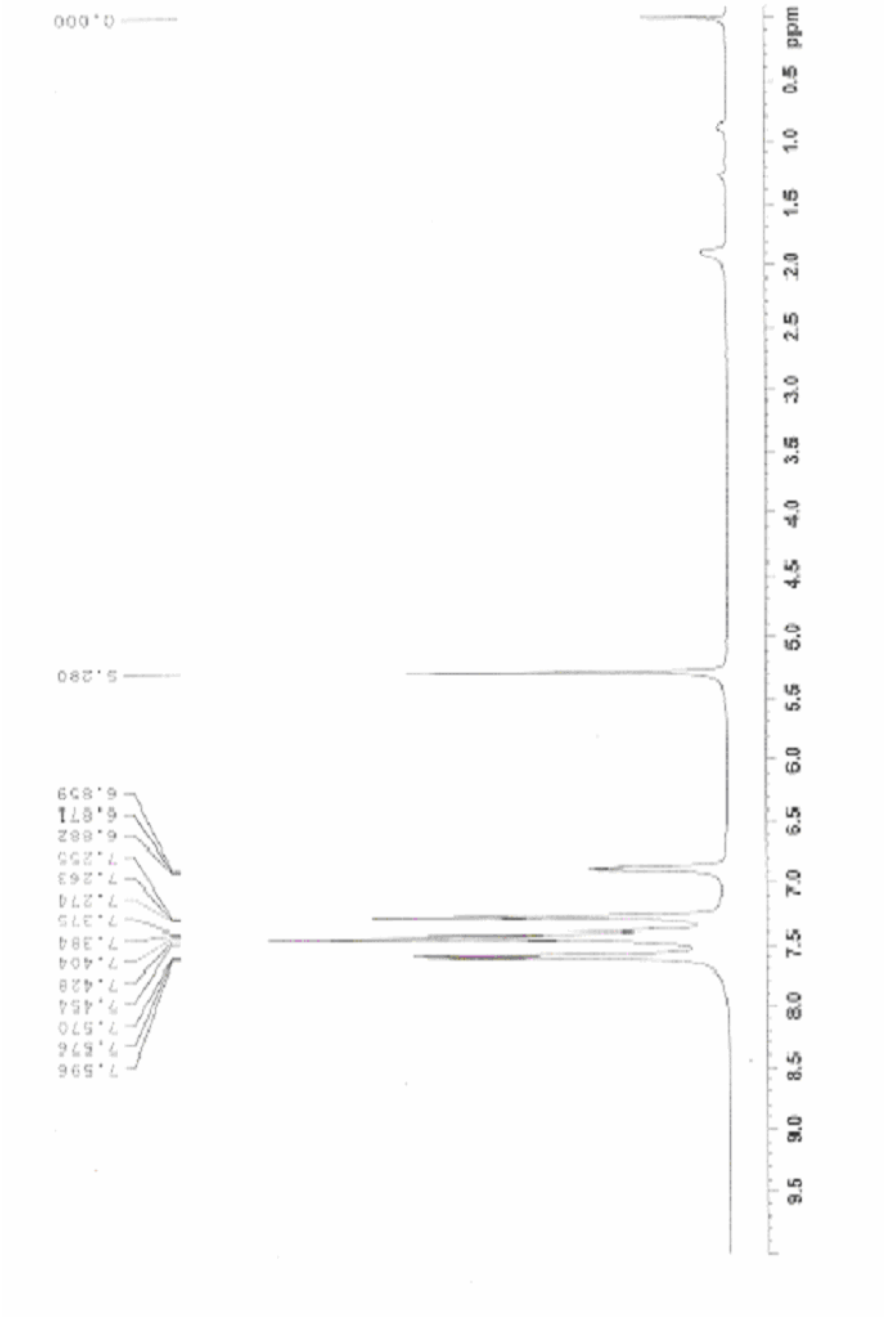


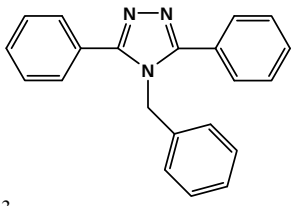


ESI Figure 21. ^{13}C NMR spectrum of the triazole **6i**

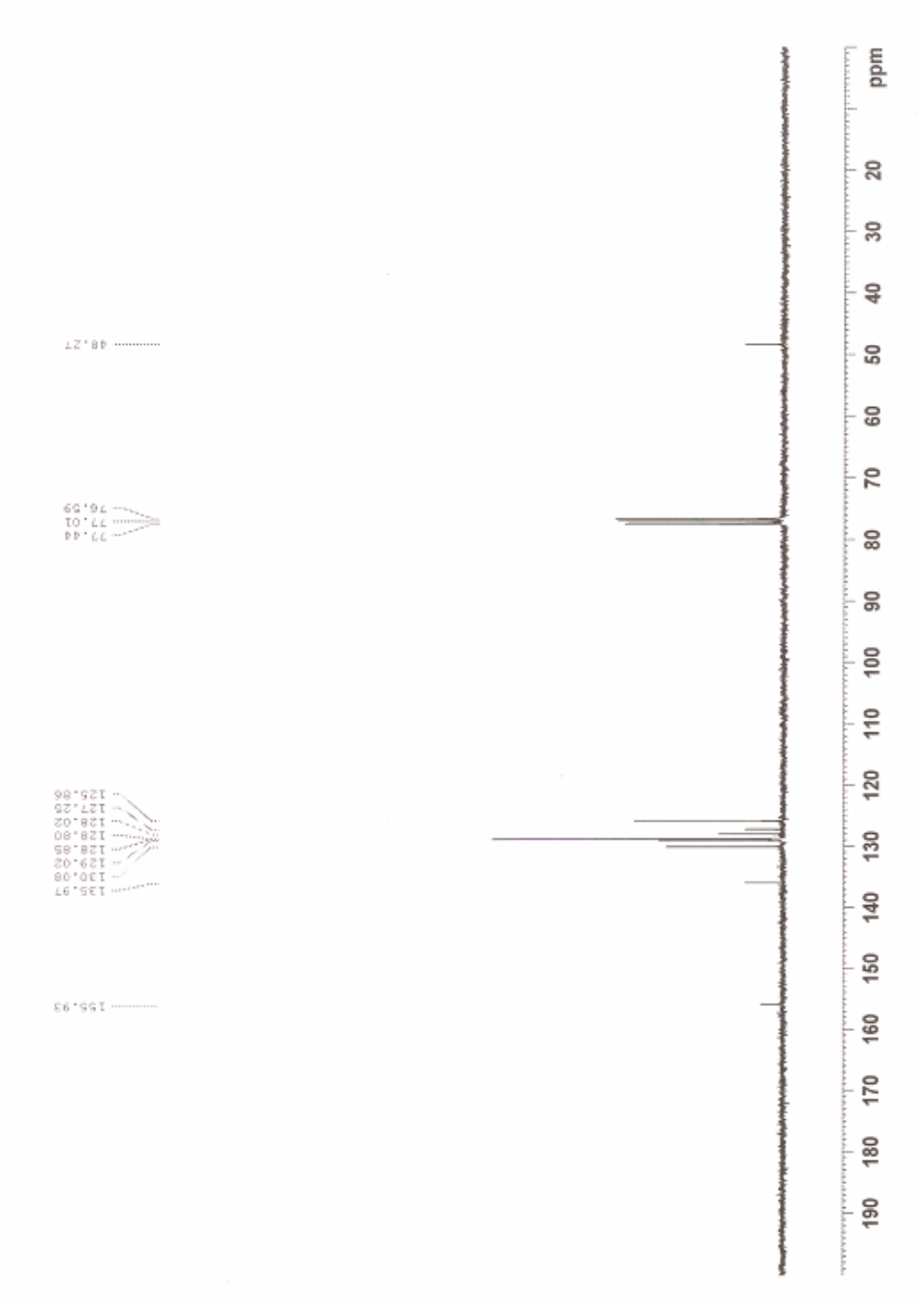


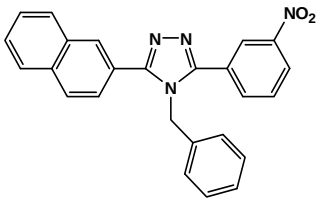
ESI Figure 22. ^{1}H NMR spectrum of the triazole **6j**



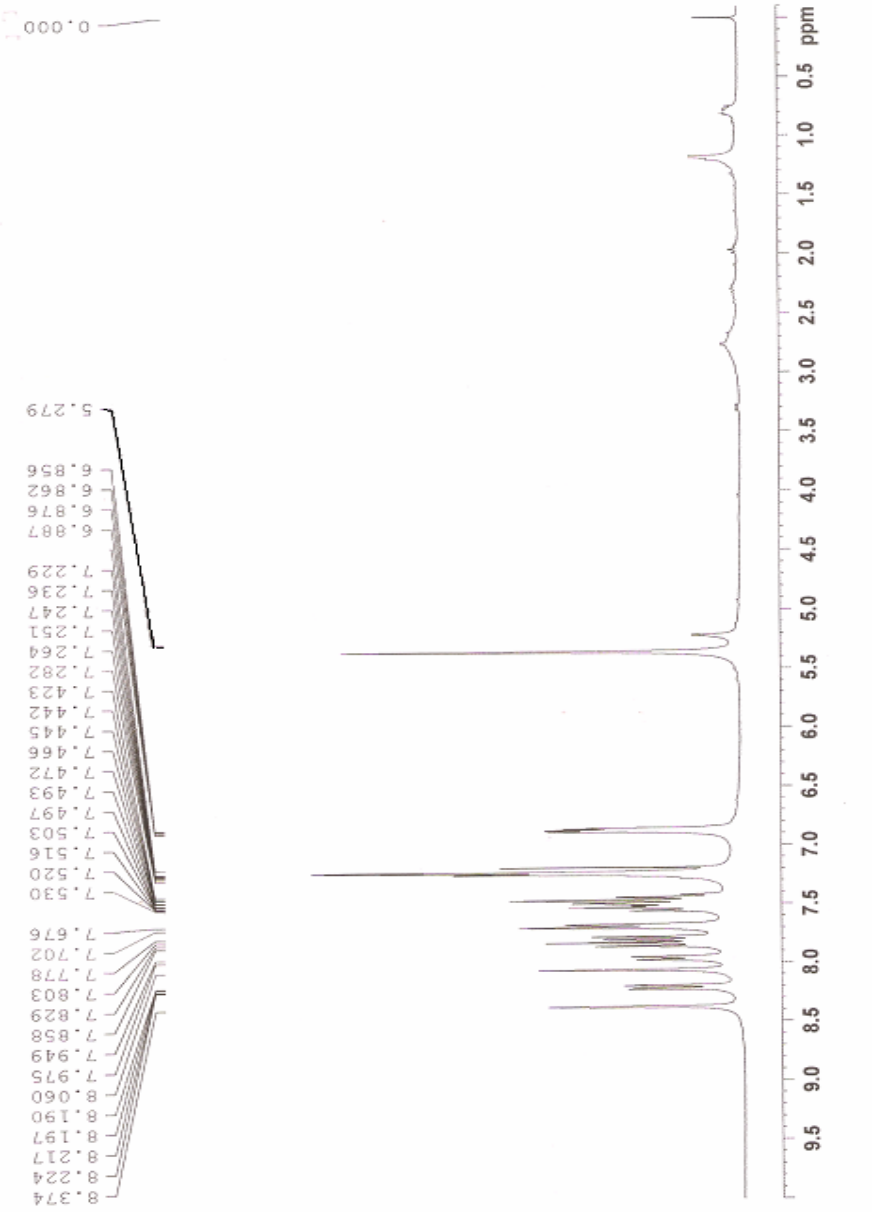


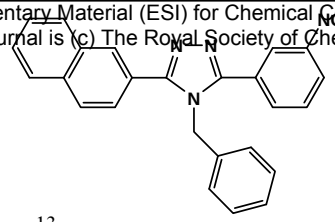
ESI Figure 23. ^{13}C NMR spectrum of the triazole **6j**



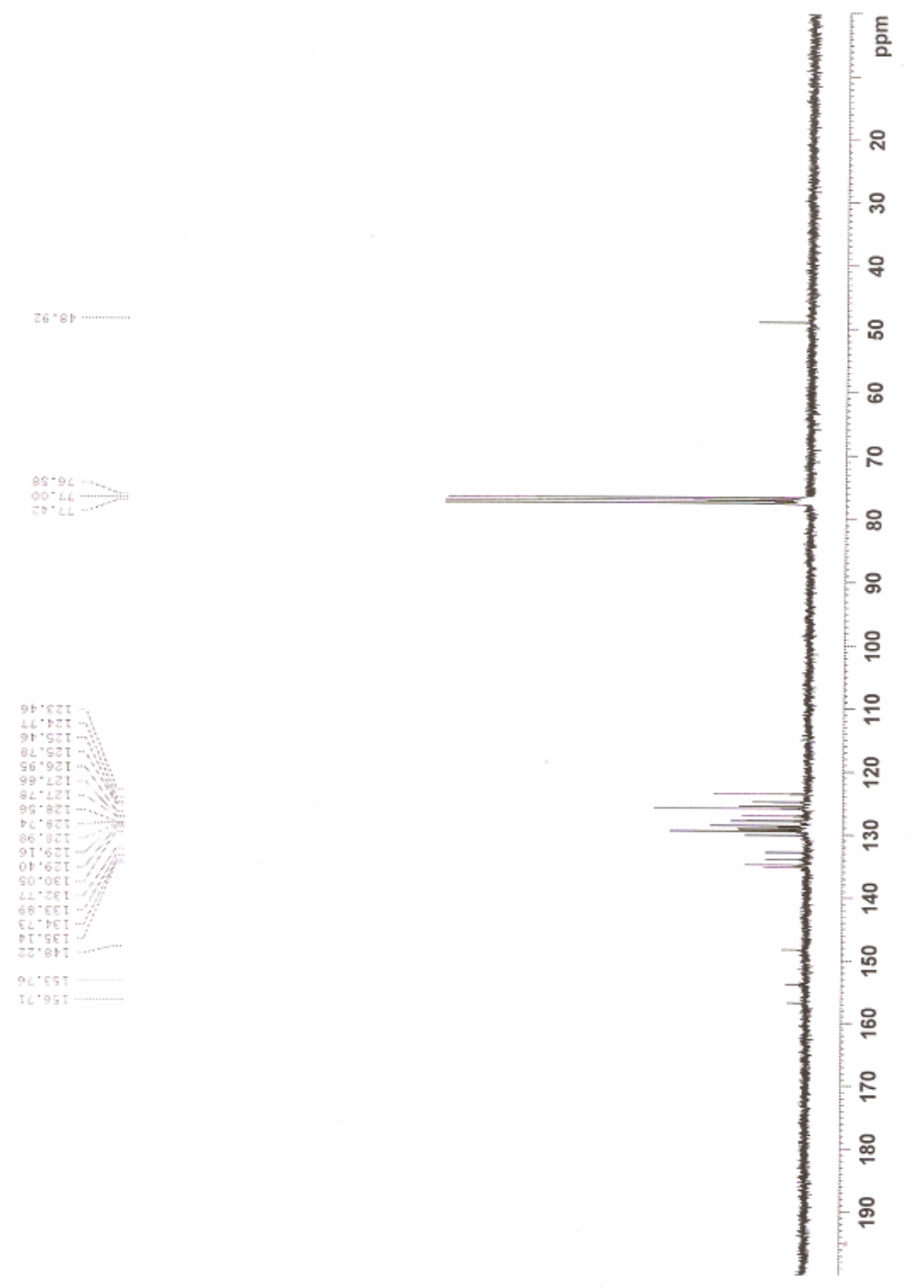


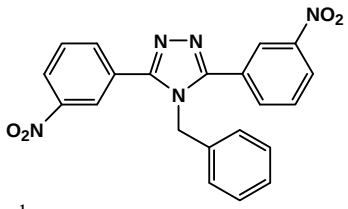
ESI Figure 24. ^{1}H NMR spectrum of the triazole **6k**



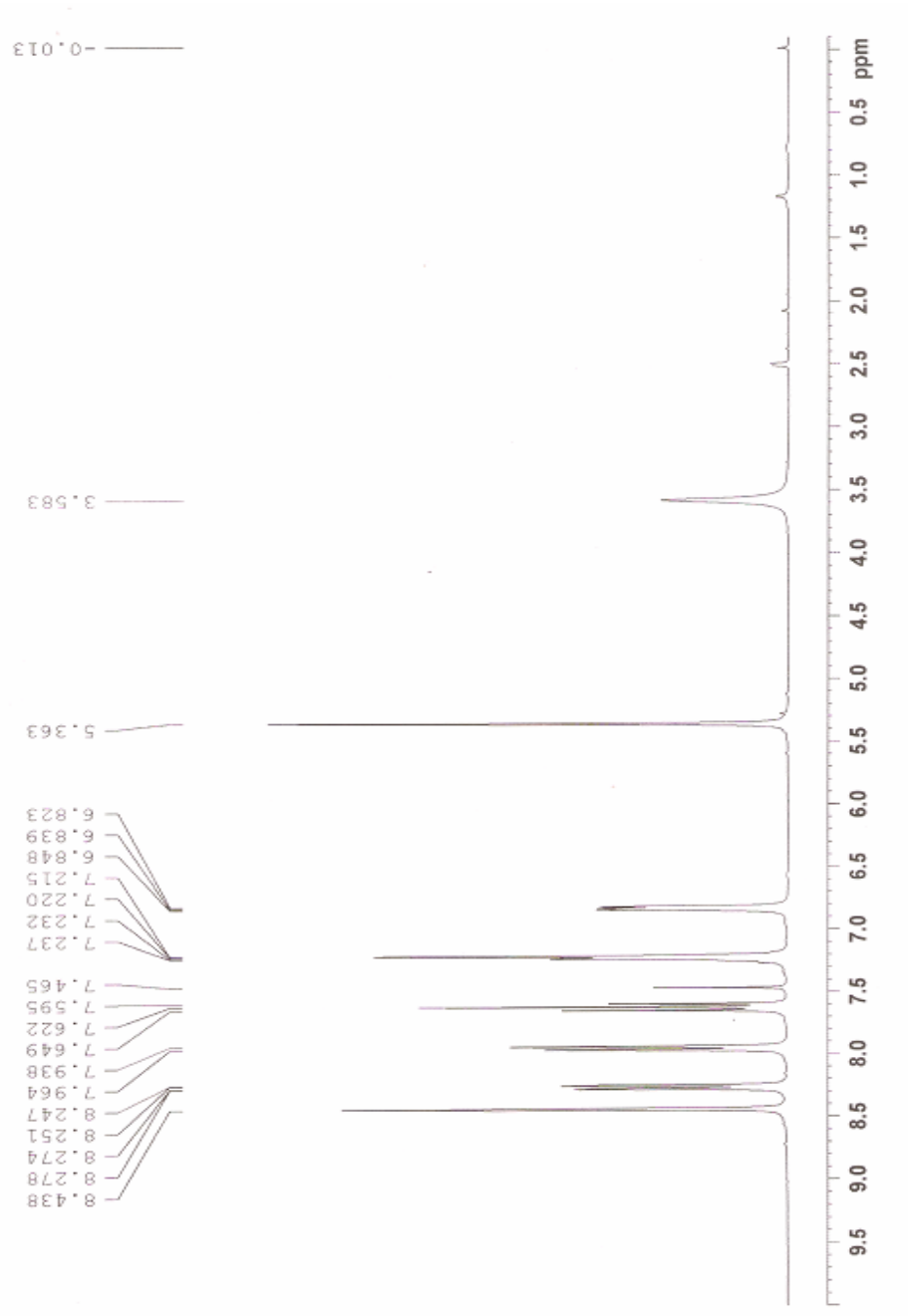


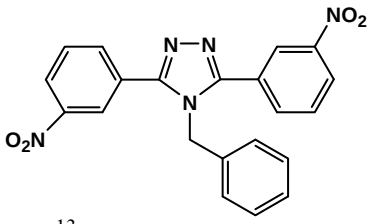
ESI Figure 25. ^{13}C NMR spectrum of the triazole **6k**



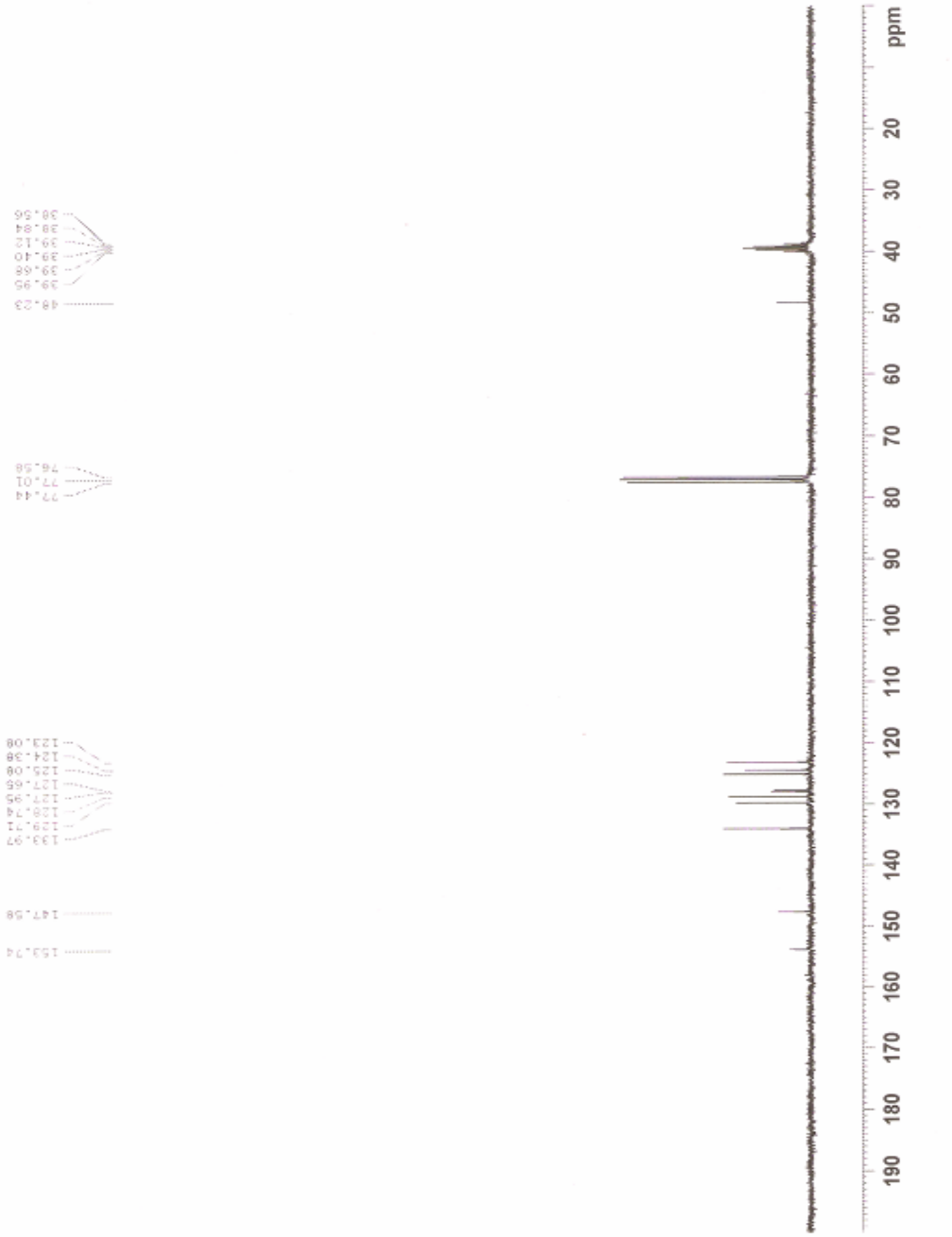


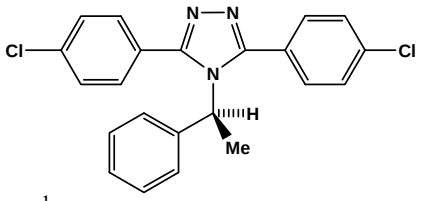
ESI Figure 26. ^{1}H NMR spectrum of the triazole **6l**



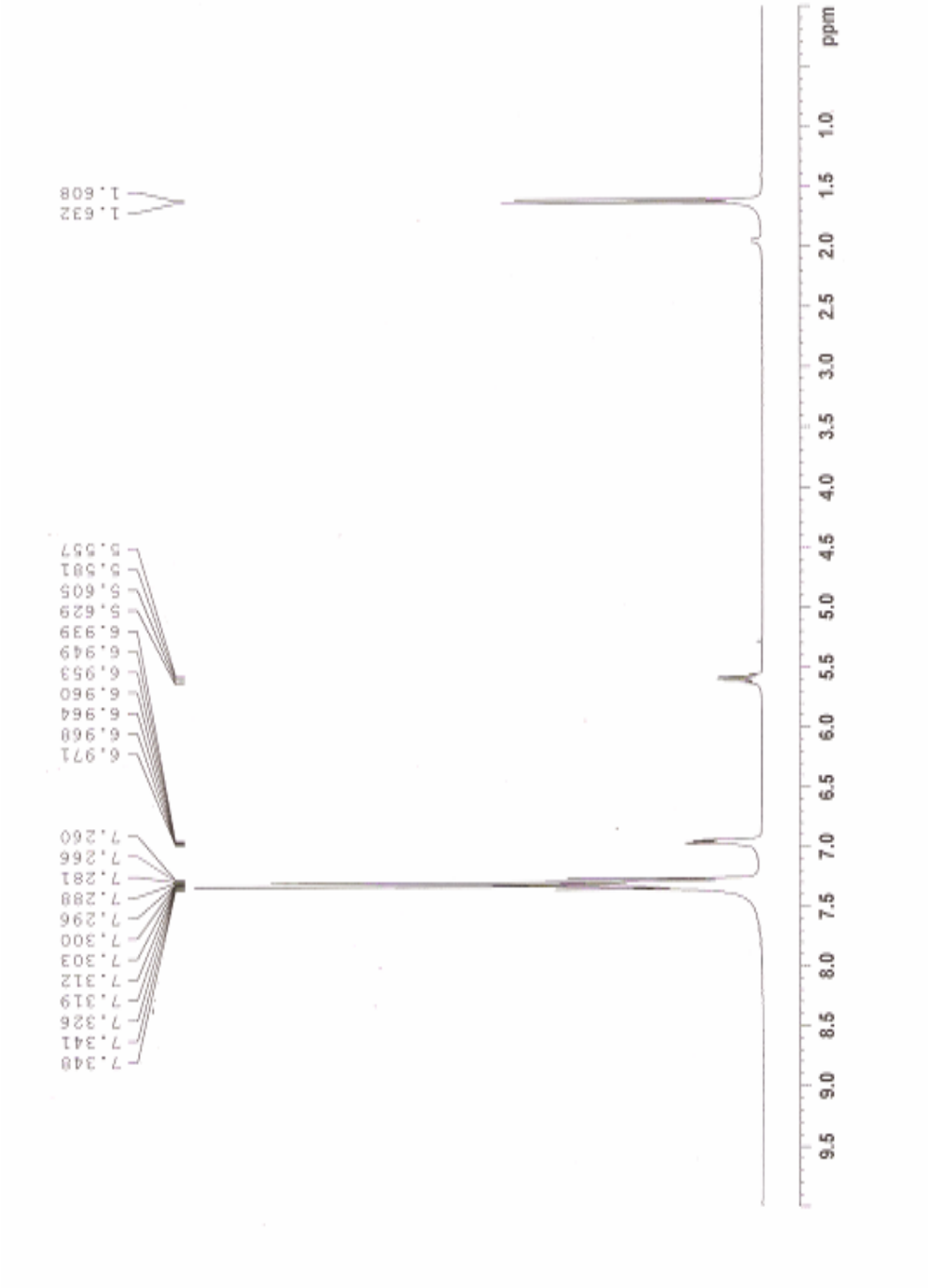


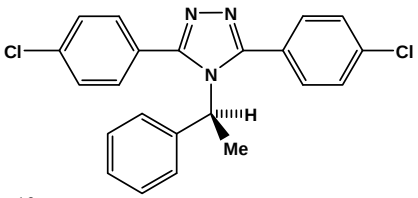
ESI Figure 27. ^{13}C NMR spectrum of the triazole **6l**



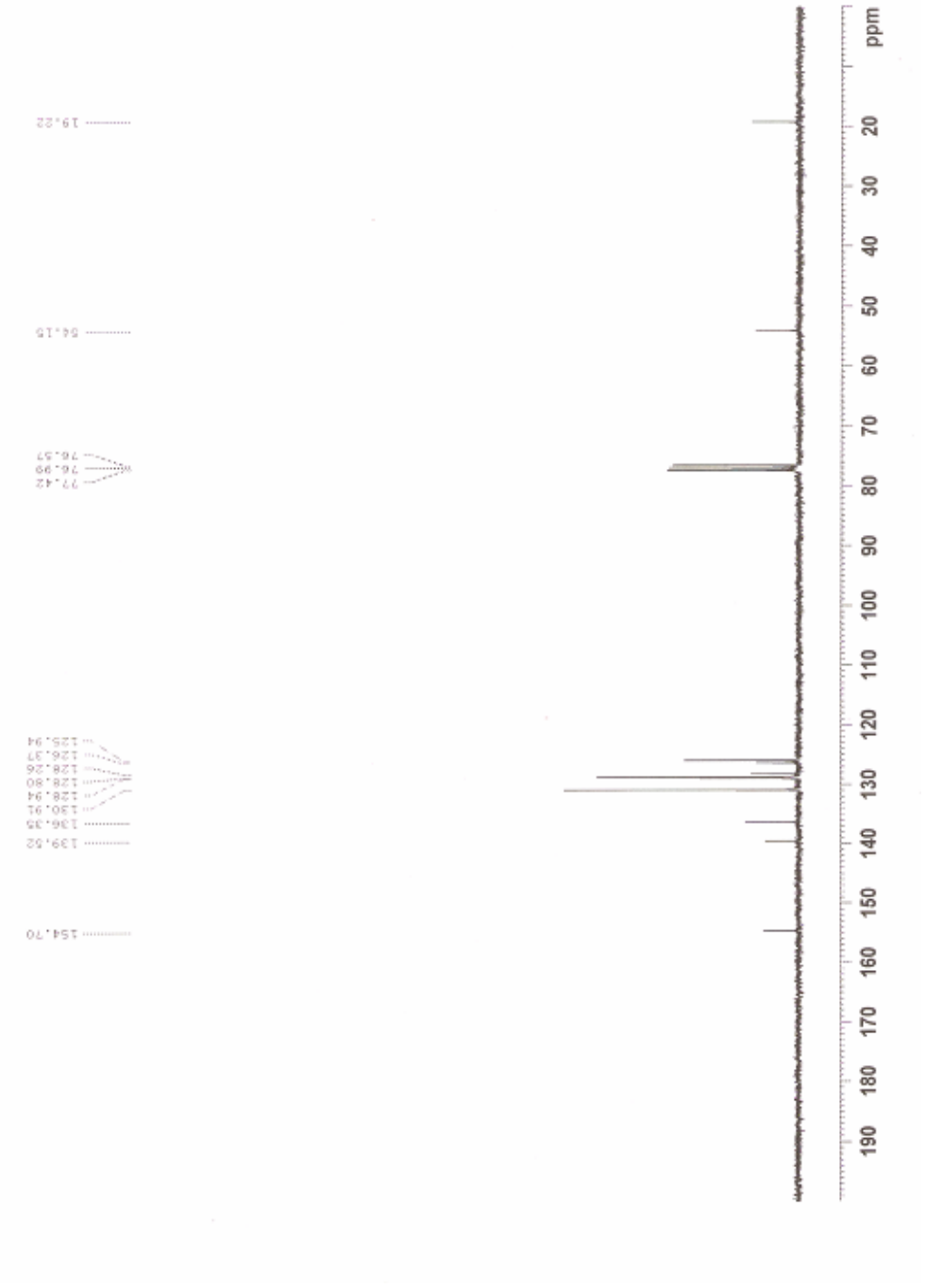


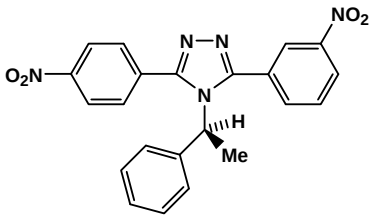
ESI Figure 28. ^{1}H NMR spectrum of the chiral triazole **6o**



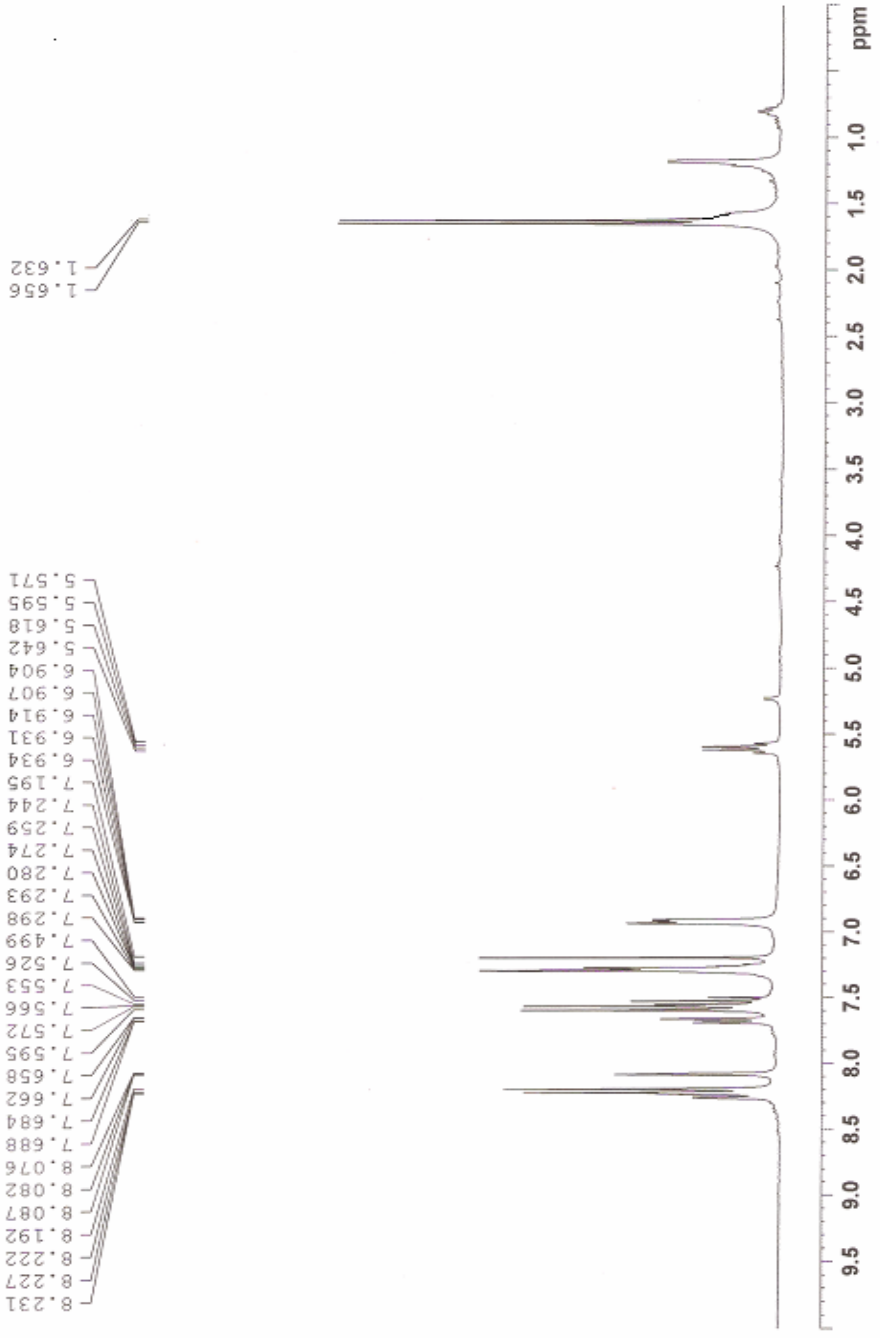


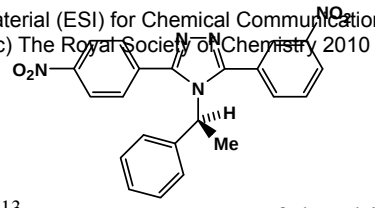
ESI Figure 29. ^{13}C NMR spectrum of the chiral triazole **6o**



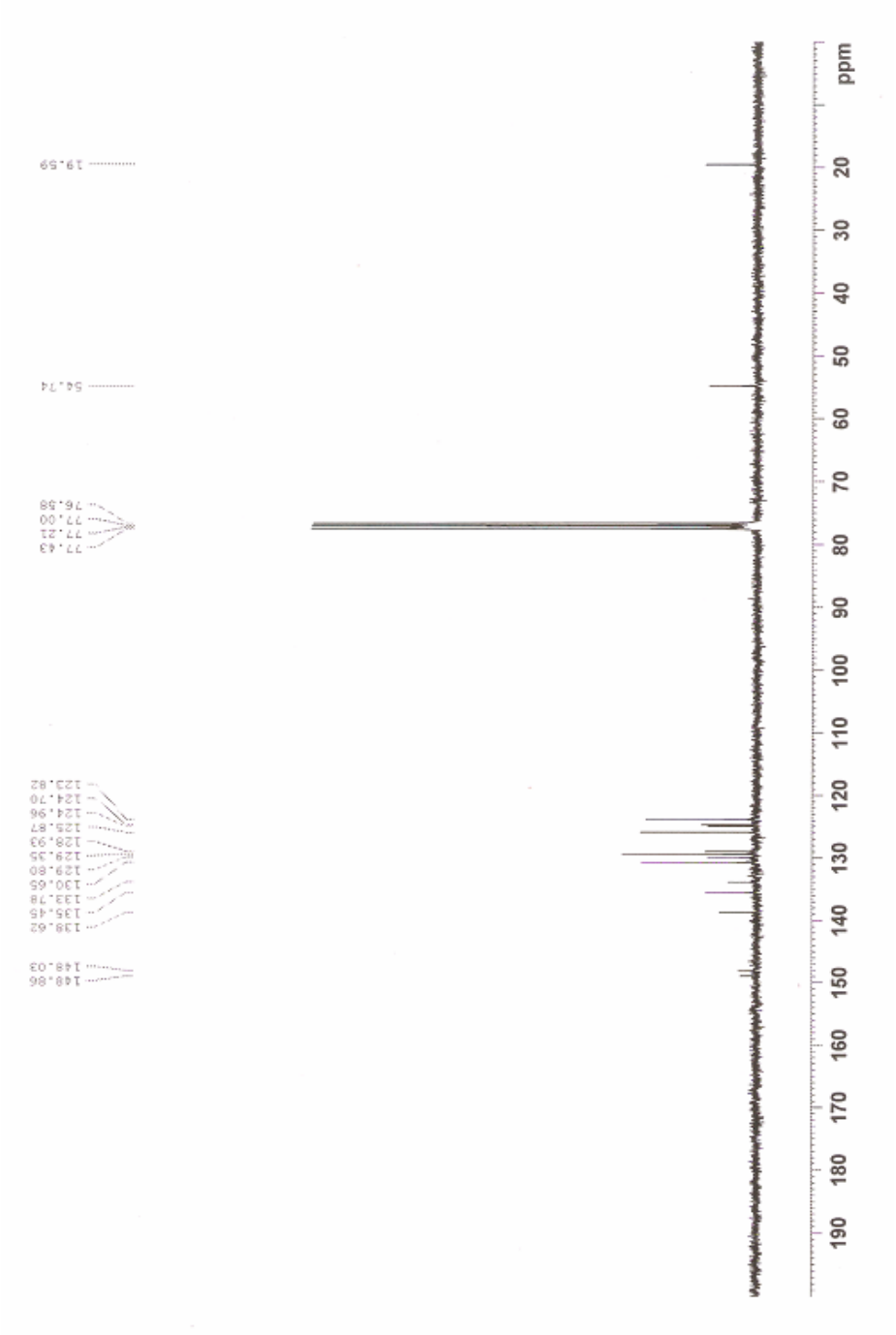


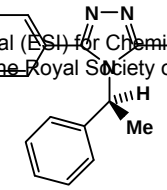
ESI Figure 30. ^{1}H NMR spectrum of the chiral triazole **6p**



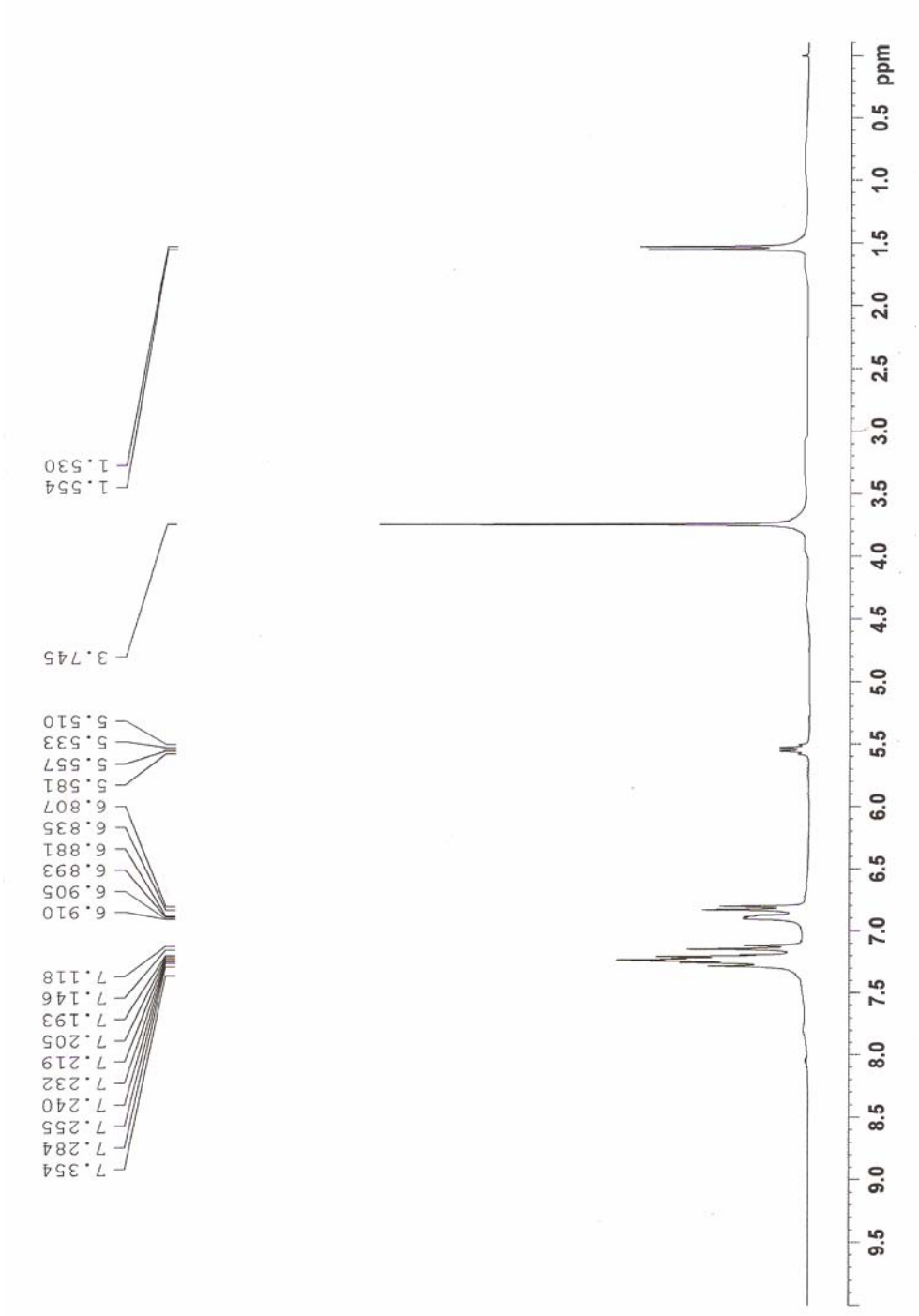


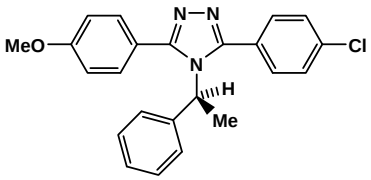
ESI Figure 31. ^{13}C NMR spectrum of the chiral triazole **6p**



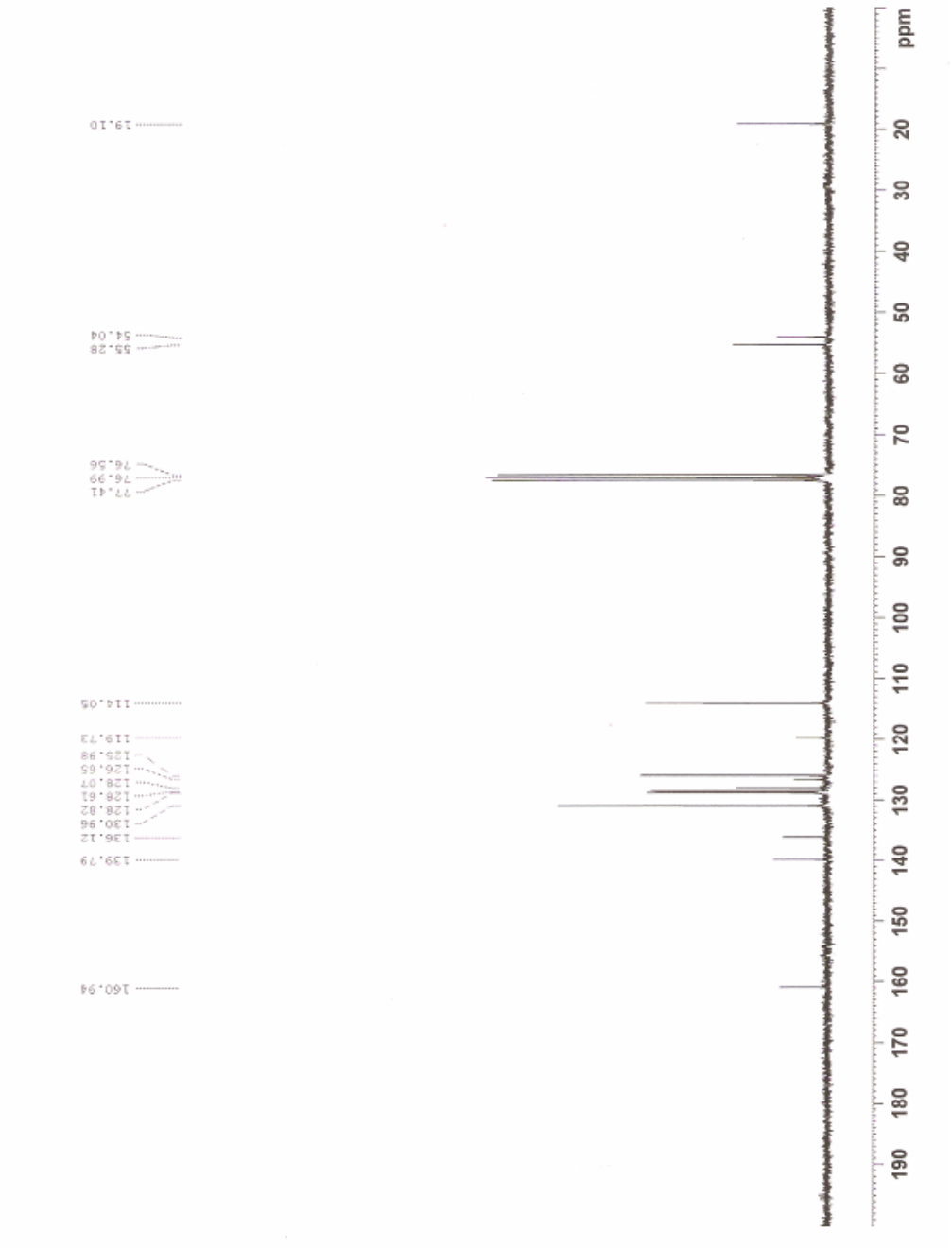


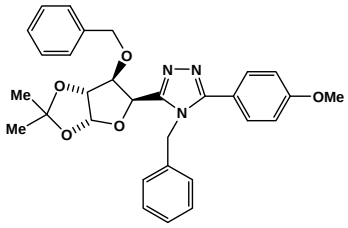
ESI Figure 32. ^{1}H NMR spectrum of the chiral triazole **6q**



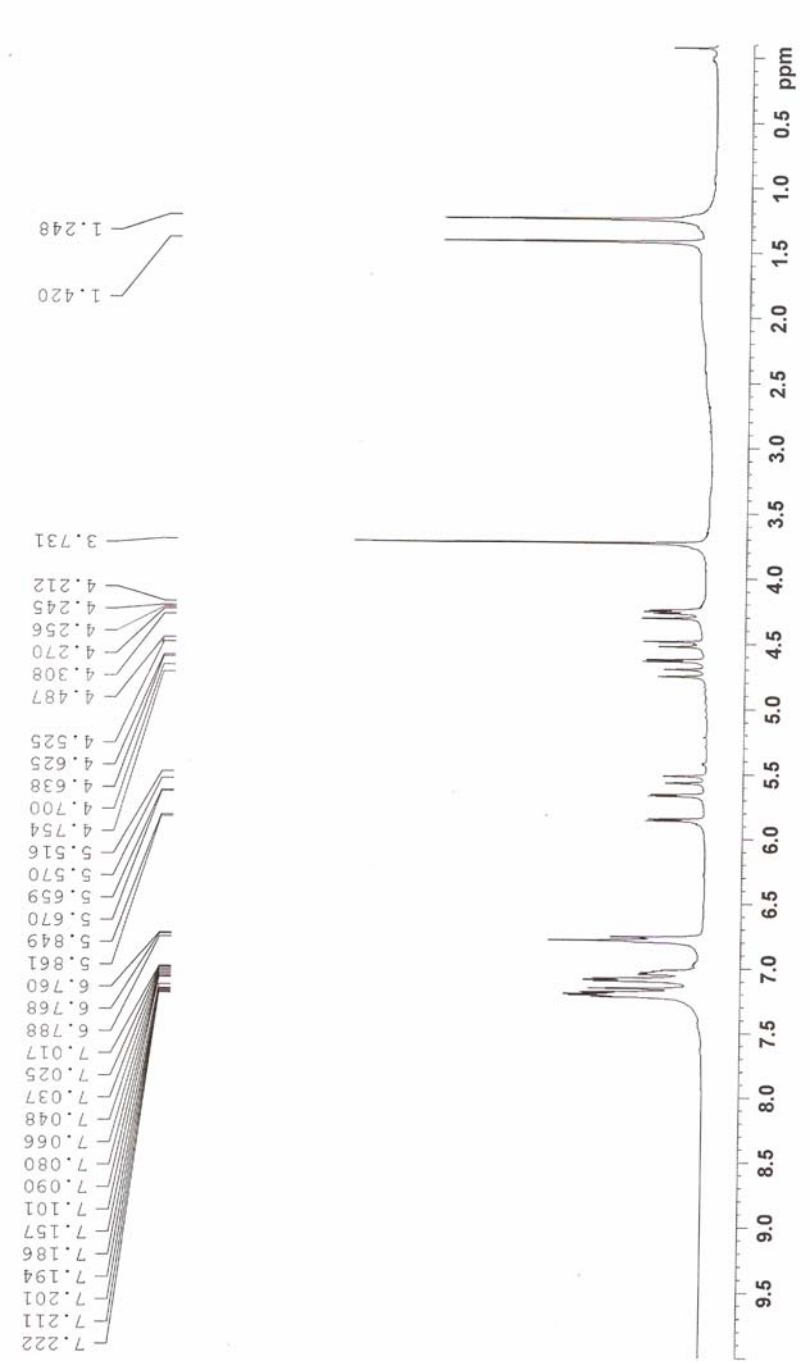


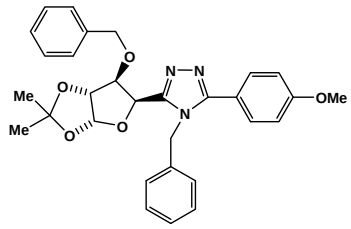
ESI Figure 33. ^{13}C NMR spectrum of the chiral triazole **6q**



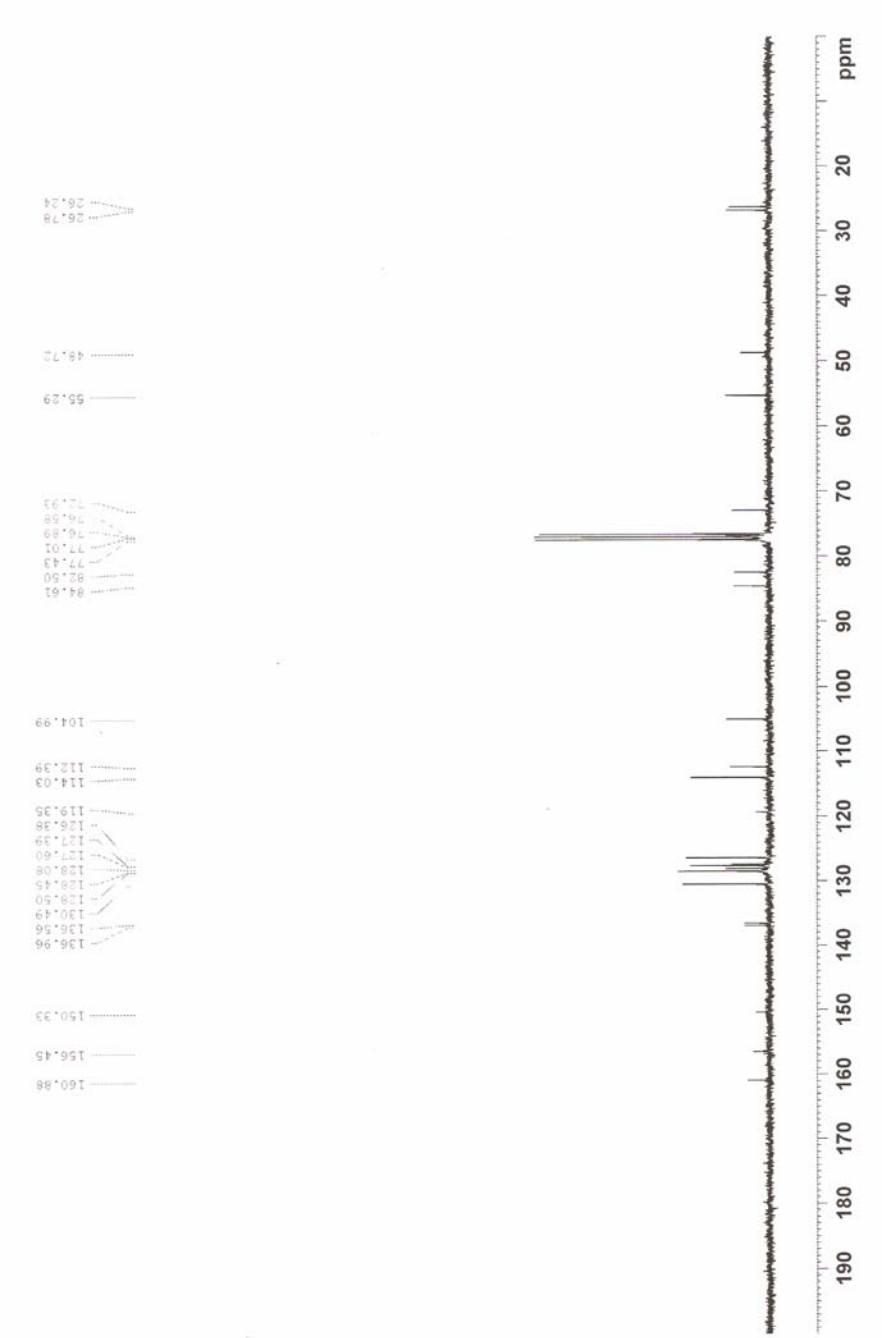


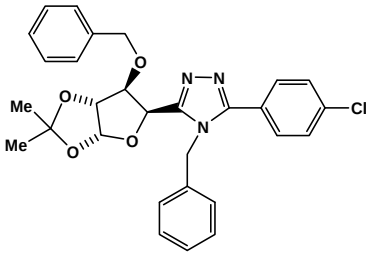
ESI Figure 34. ^{1}H NMR spectrum of the sugar-based triazole **6r**



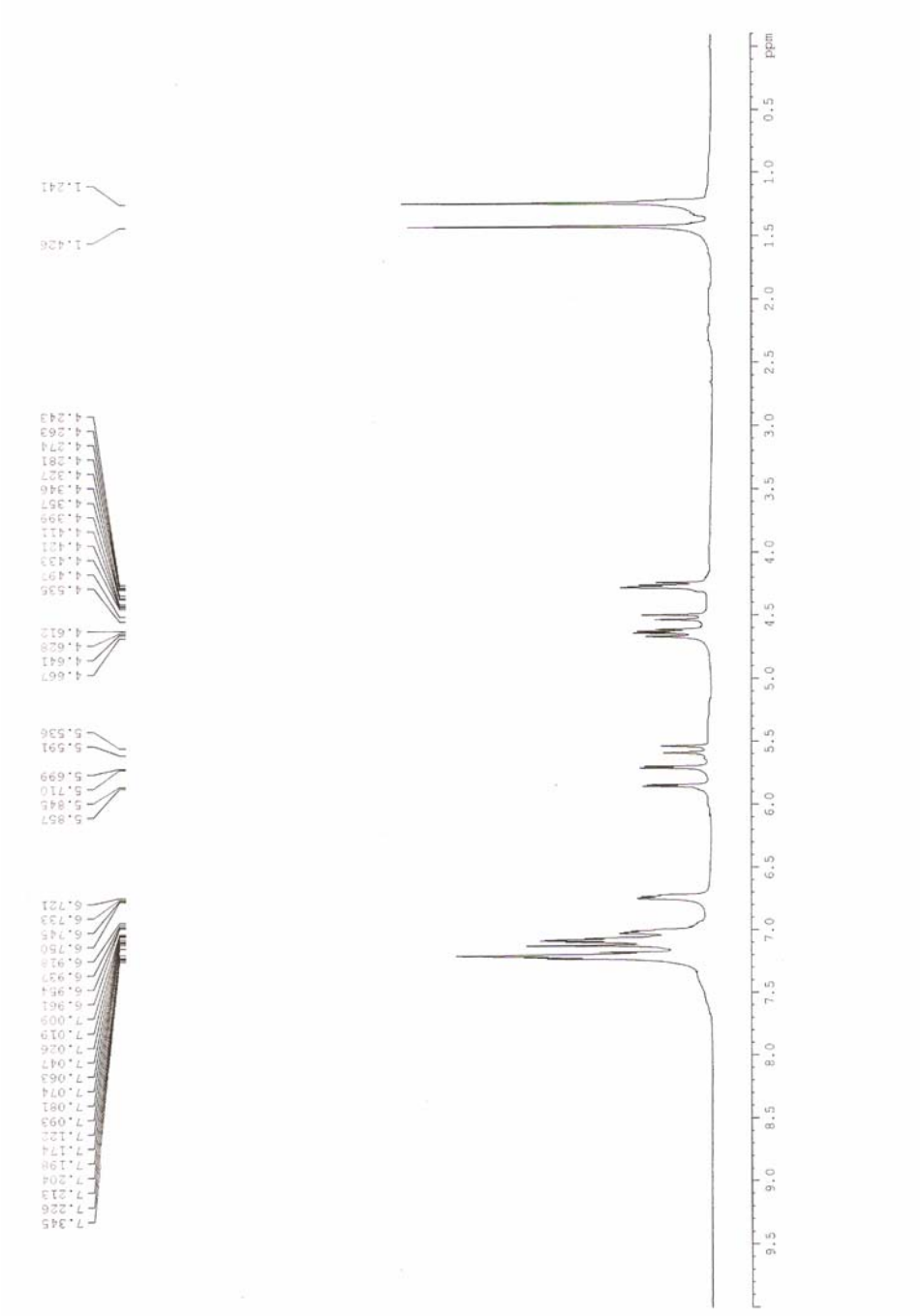


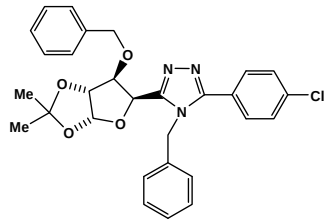
ESI Figure 35. ^{13}C NMR spectrum of the sugar-based triazole **6r**



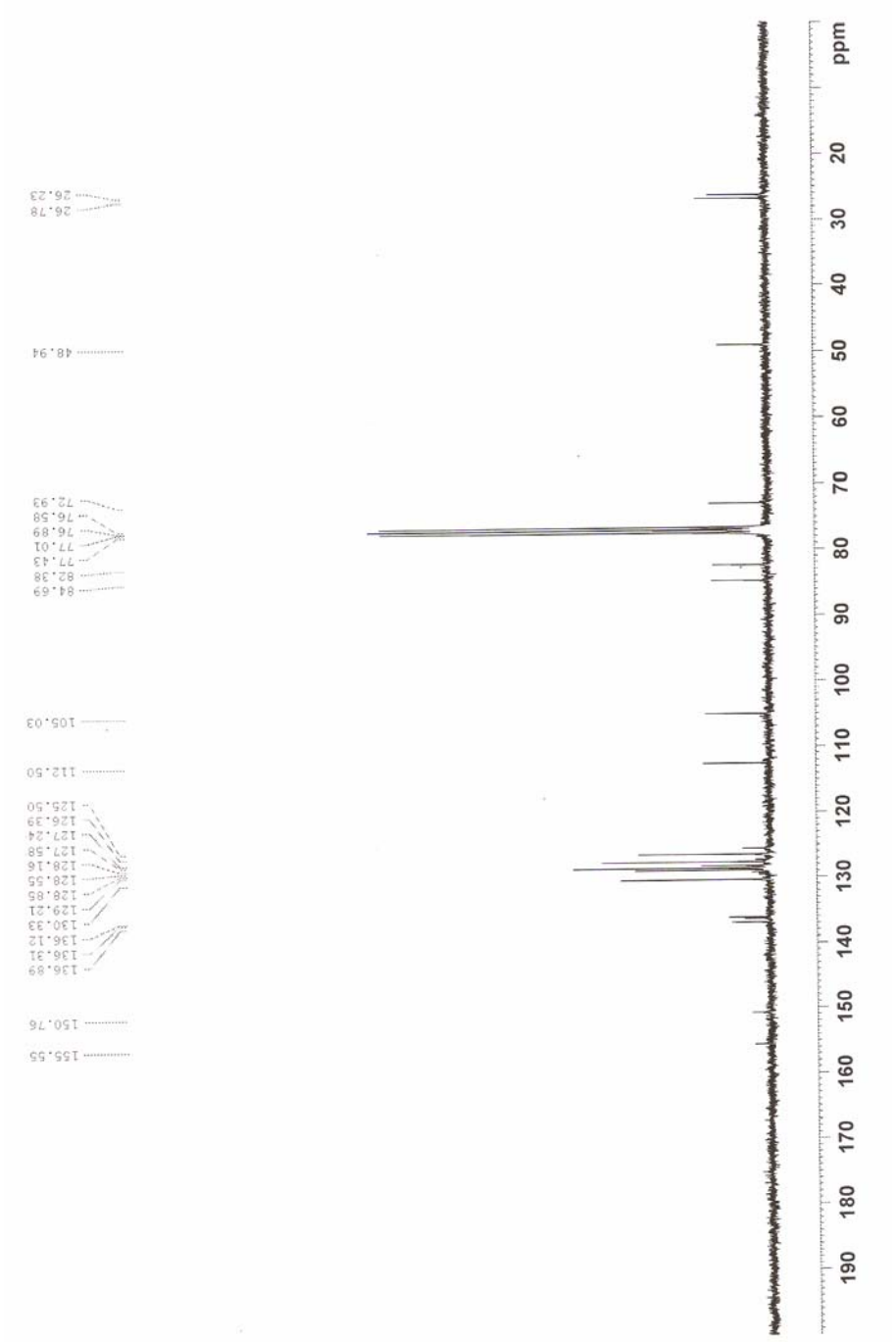


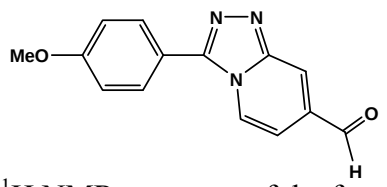
ESI Figure 36. ^{1}H NMR spectrum of the sugar-based triazole **6s**



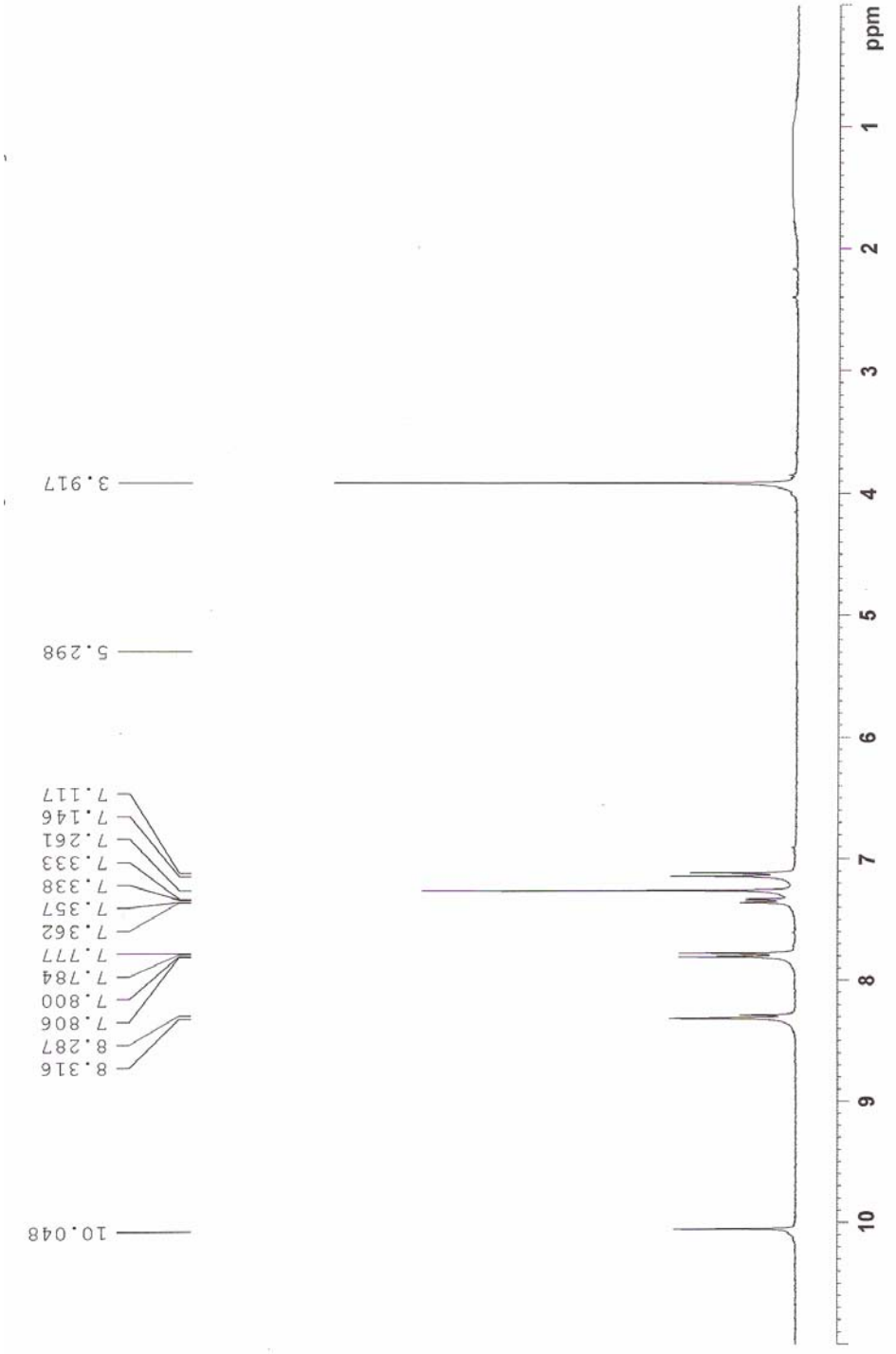


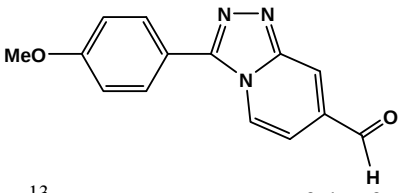
ESI Figure 37. ^{13}C NMR spectrum of the sugar-based triazole **6s**



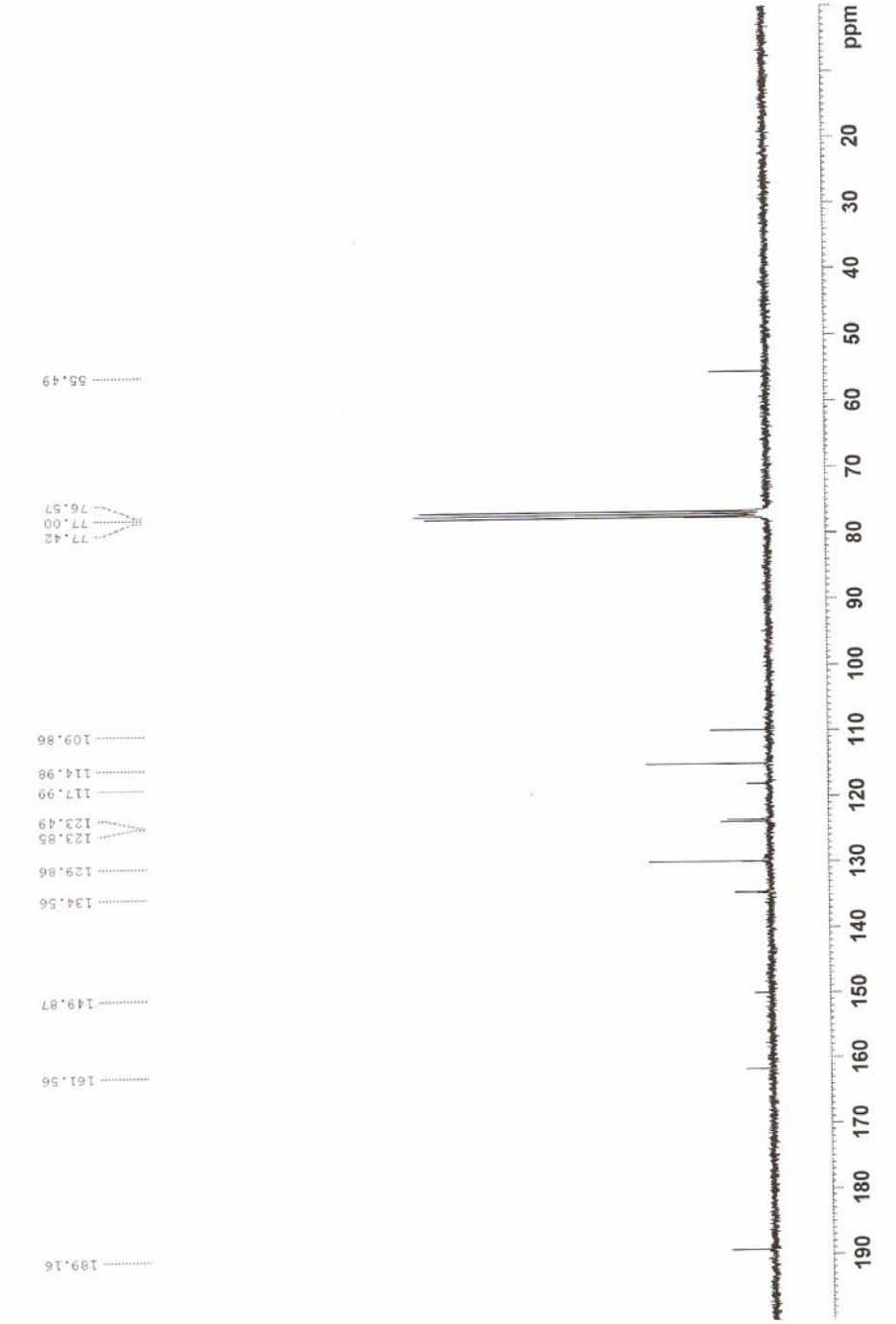


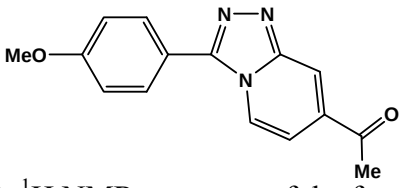
ESI Figure 38. ^{1}H NMR spectrum of the fused triazole **8a**



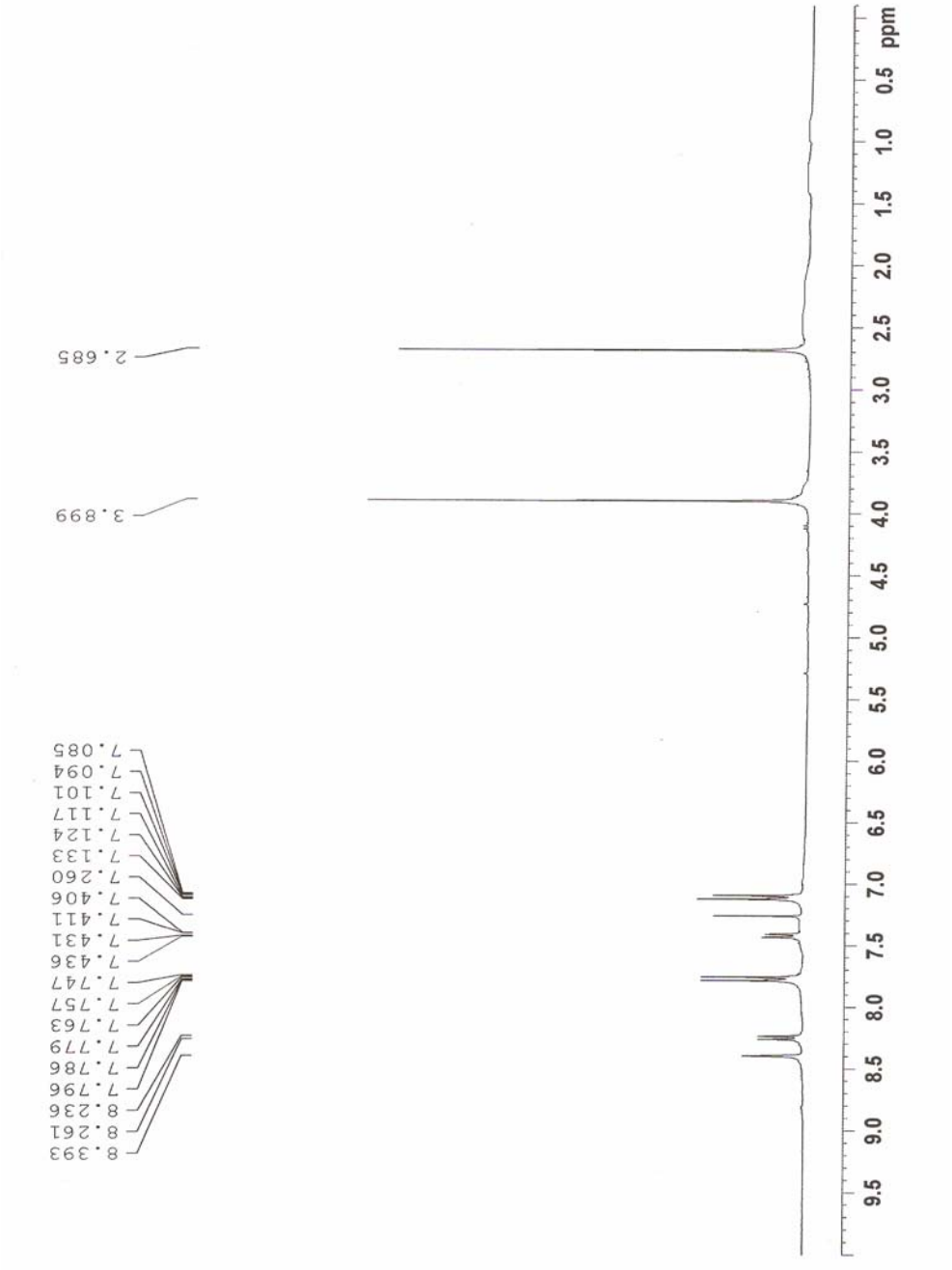


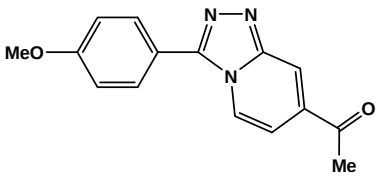
ESI Figure 39. ^{13}C NMR spectrum of the fused triazole **8a**



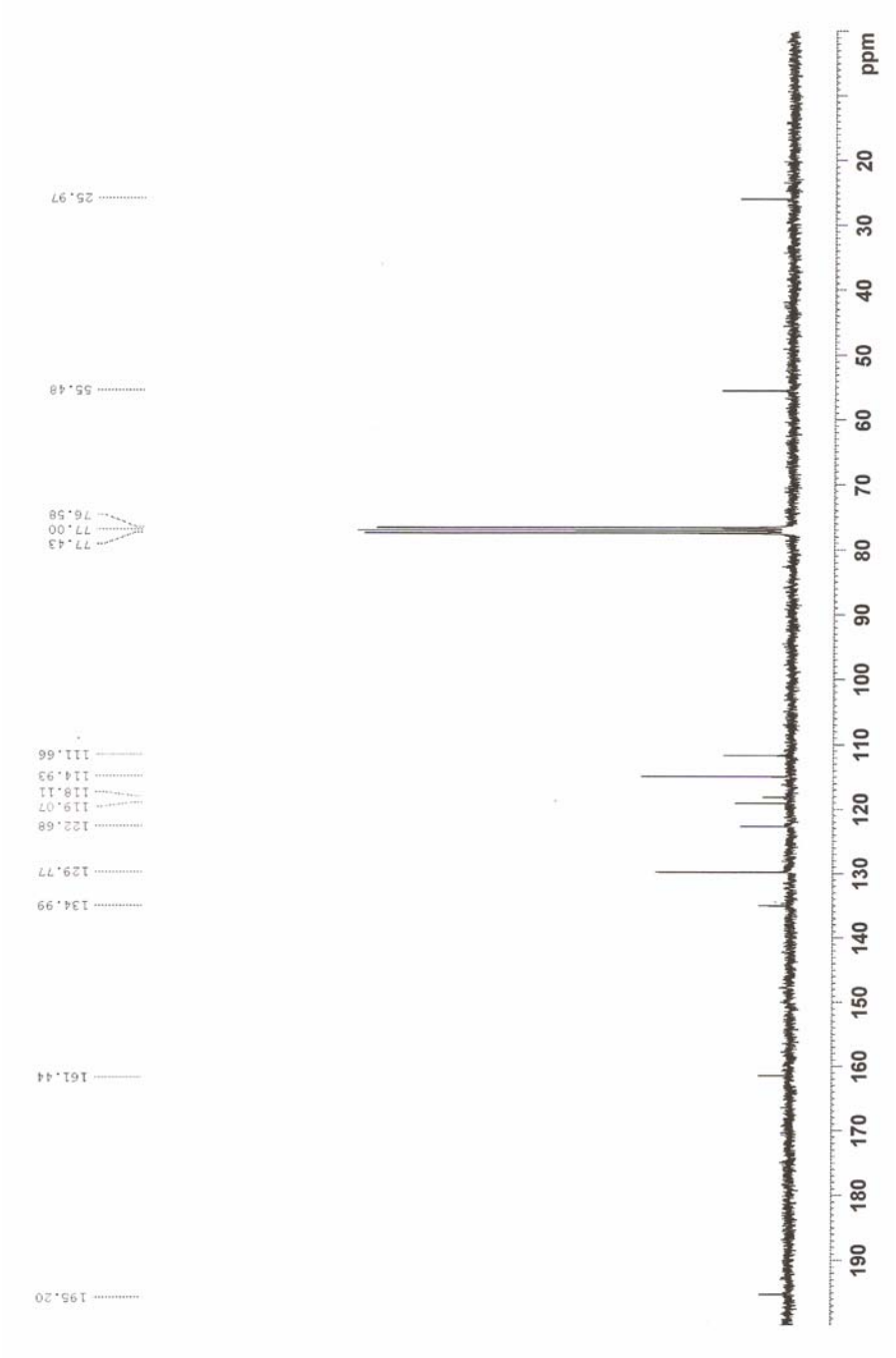


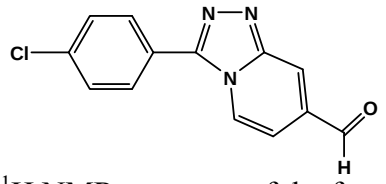
ESI Figure 40. ^{1}H NMR spectrum of the fused triazole **8b**



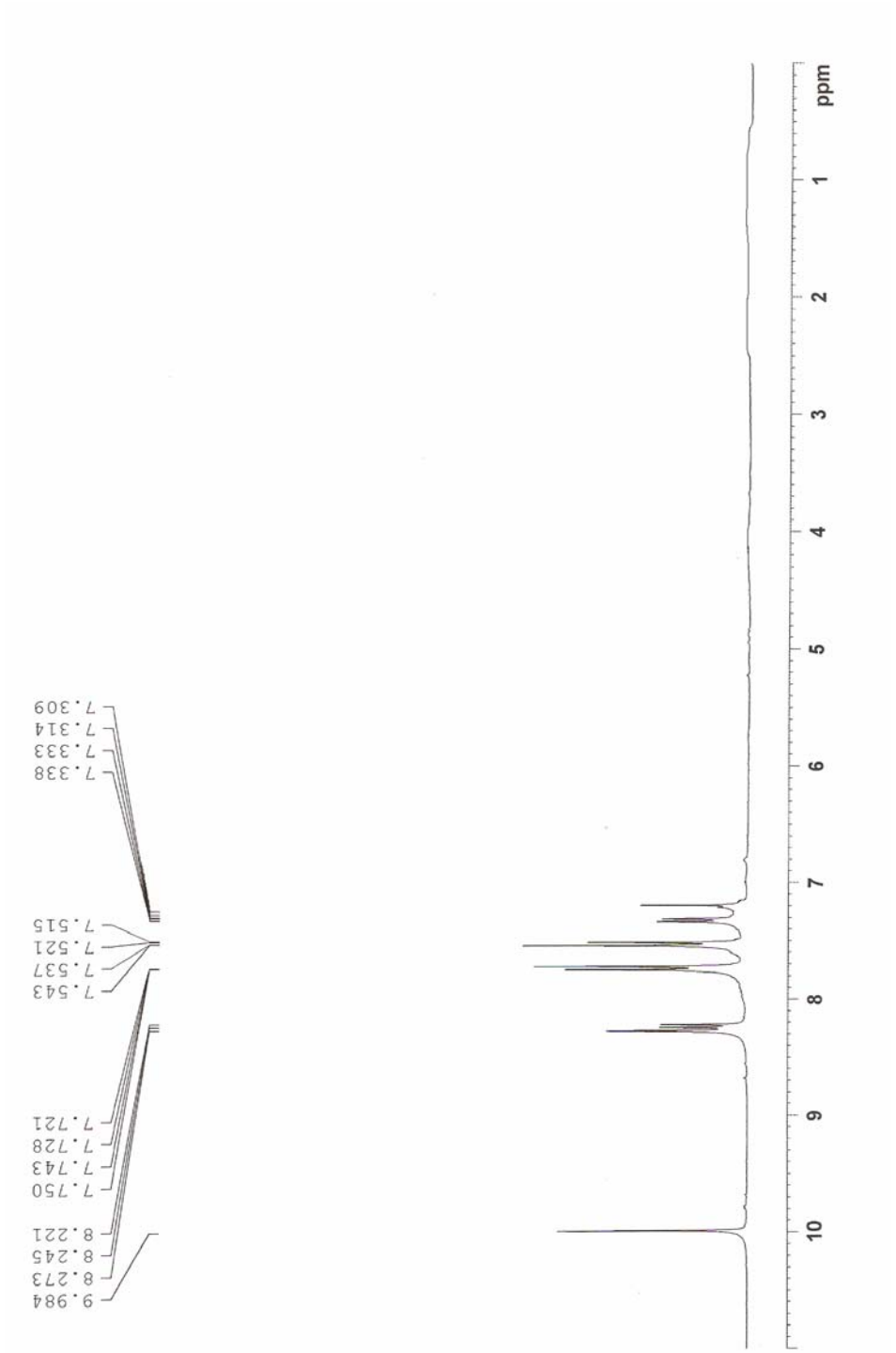


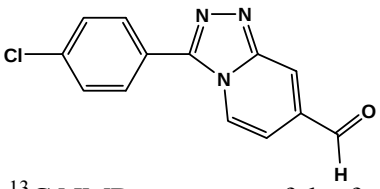
ESI Figure 41. ^{13}C NMR spectrum of the fused triazole **8b**



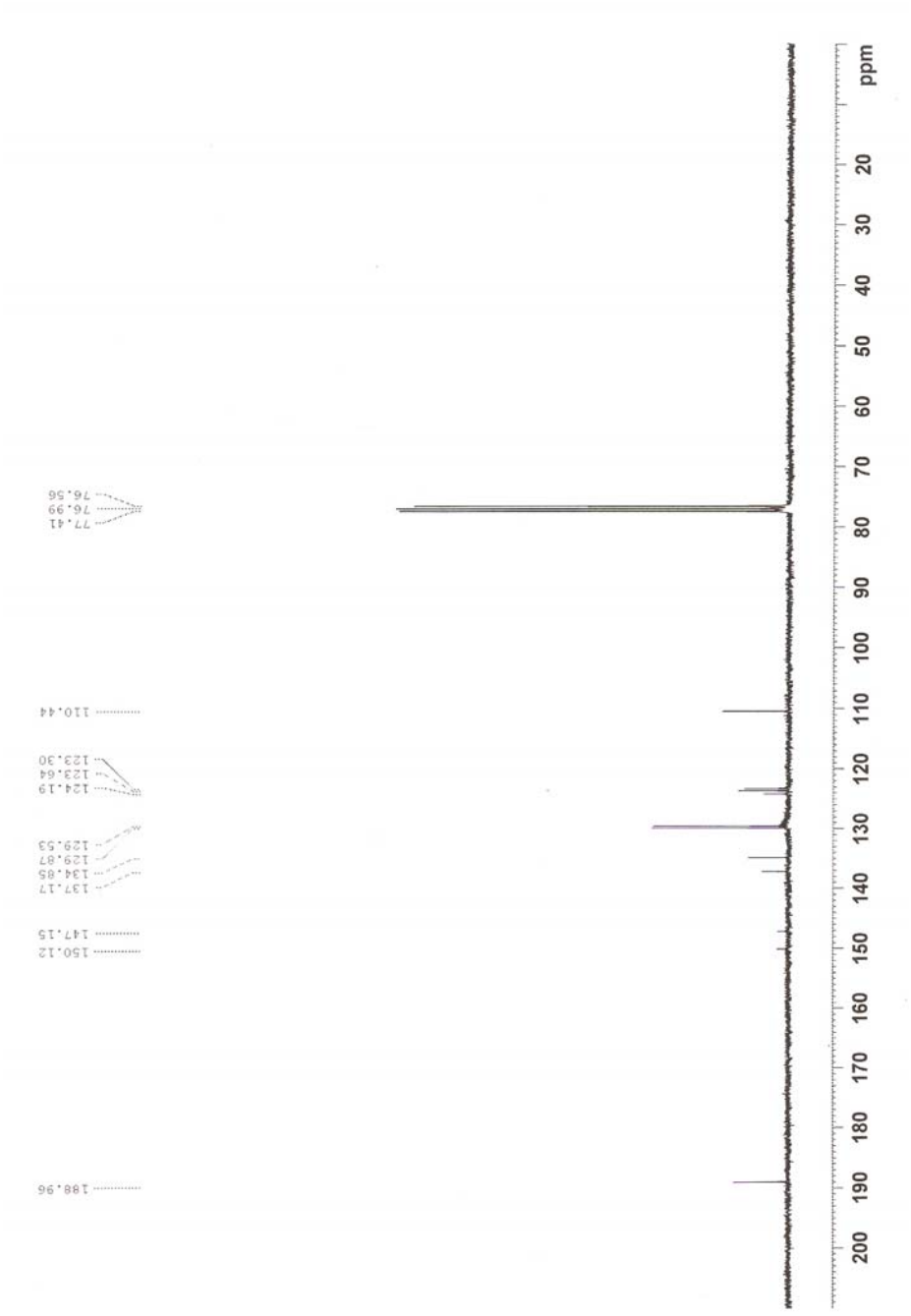


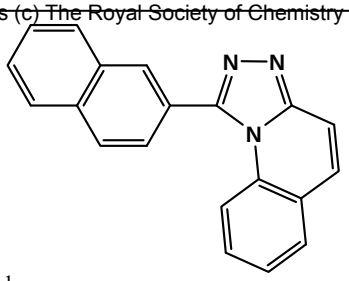
ESI Figure 42. ^{1}H NMR spectrum of the fused triazole **8c**



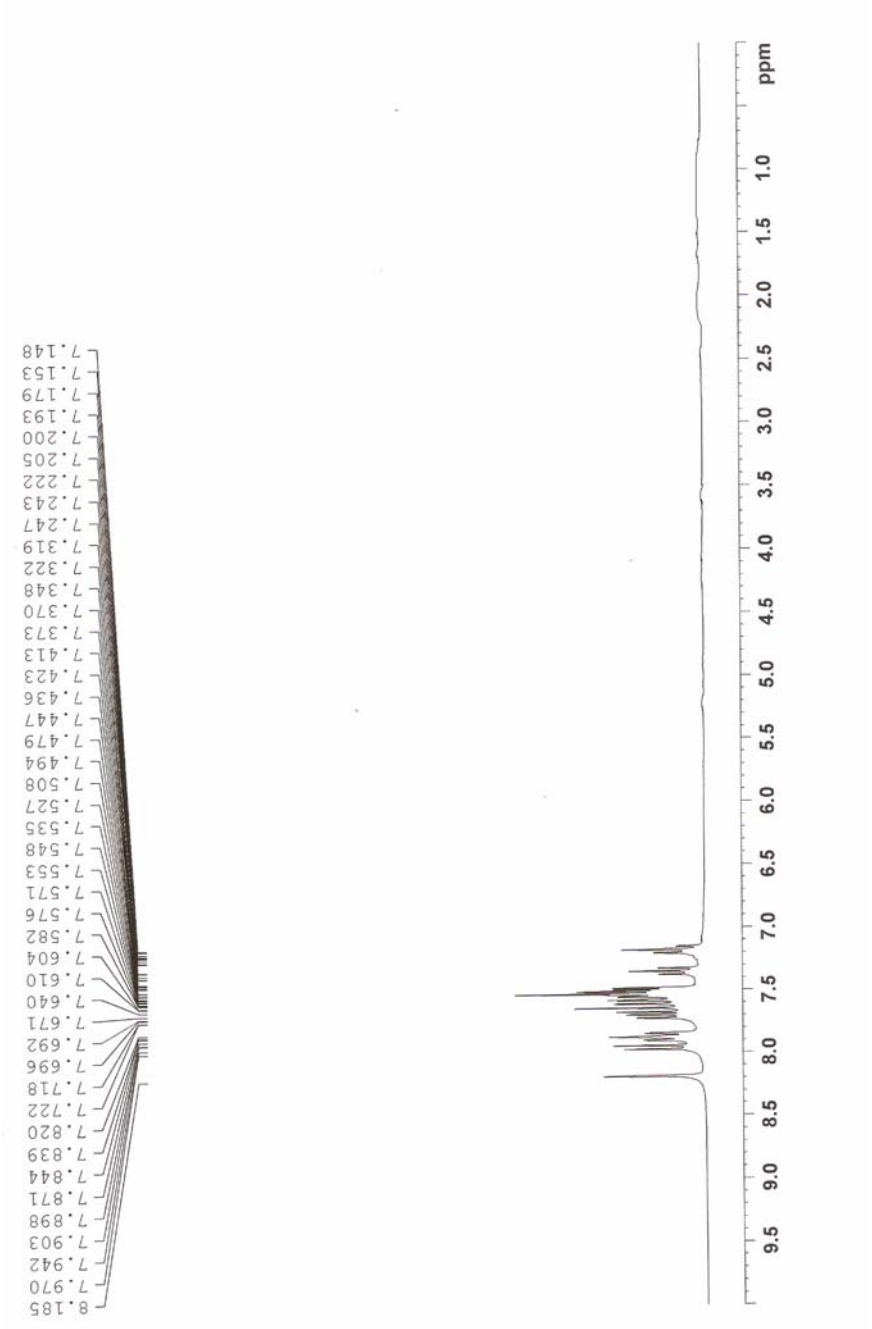


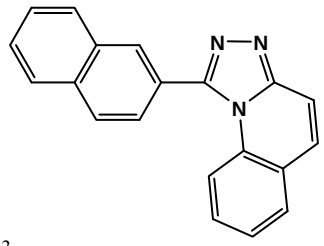
ESI Figure 43. ^{13}C NMR spectrum of the fused triazole **8c**



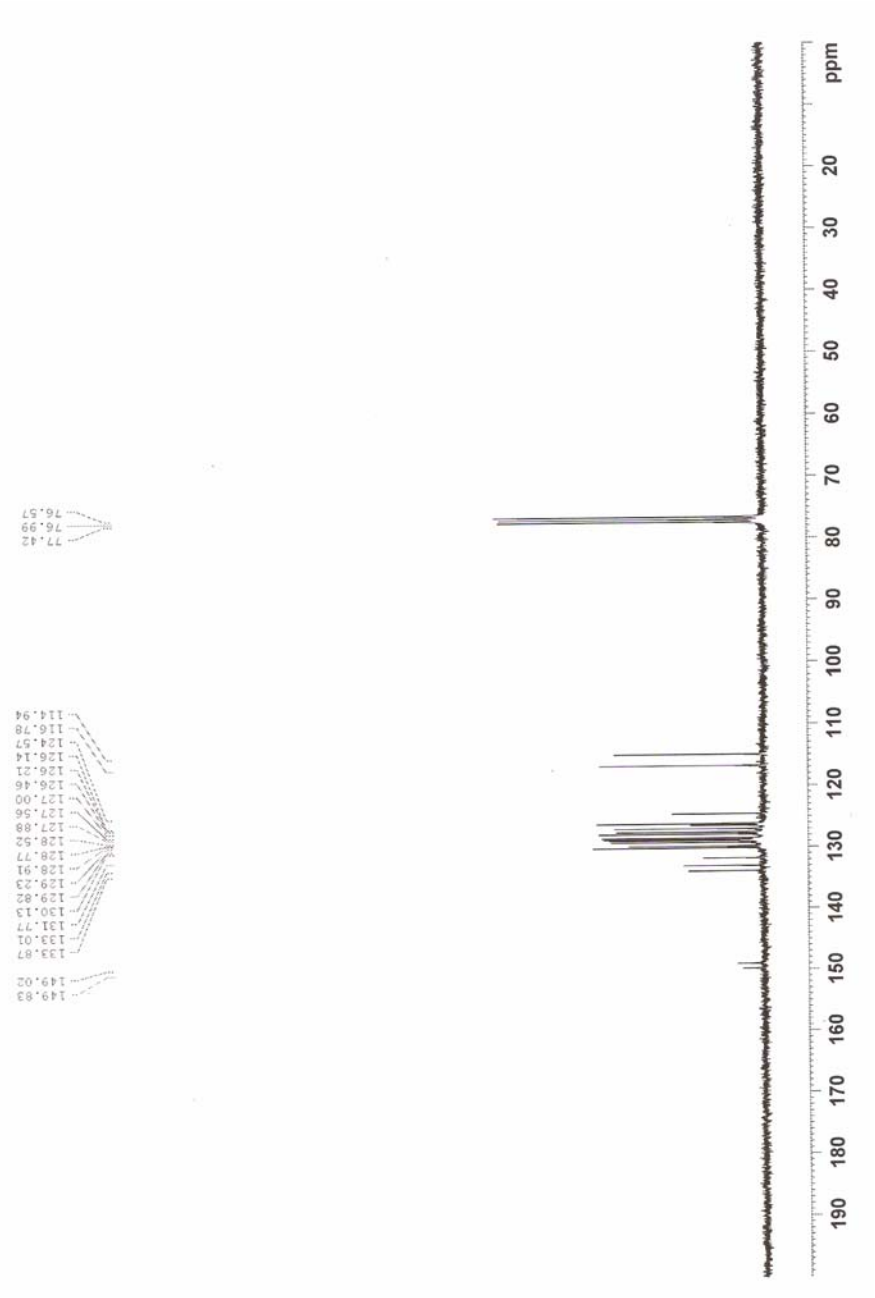


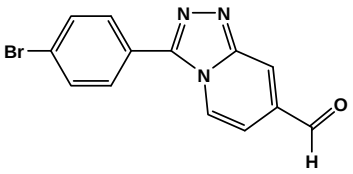
ESI Figure 44. ^{1}H NMR spectrum of the fused triazole **8d**



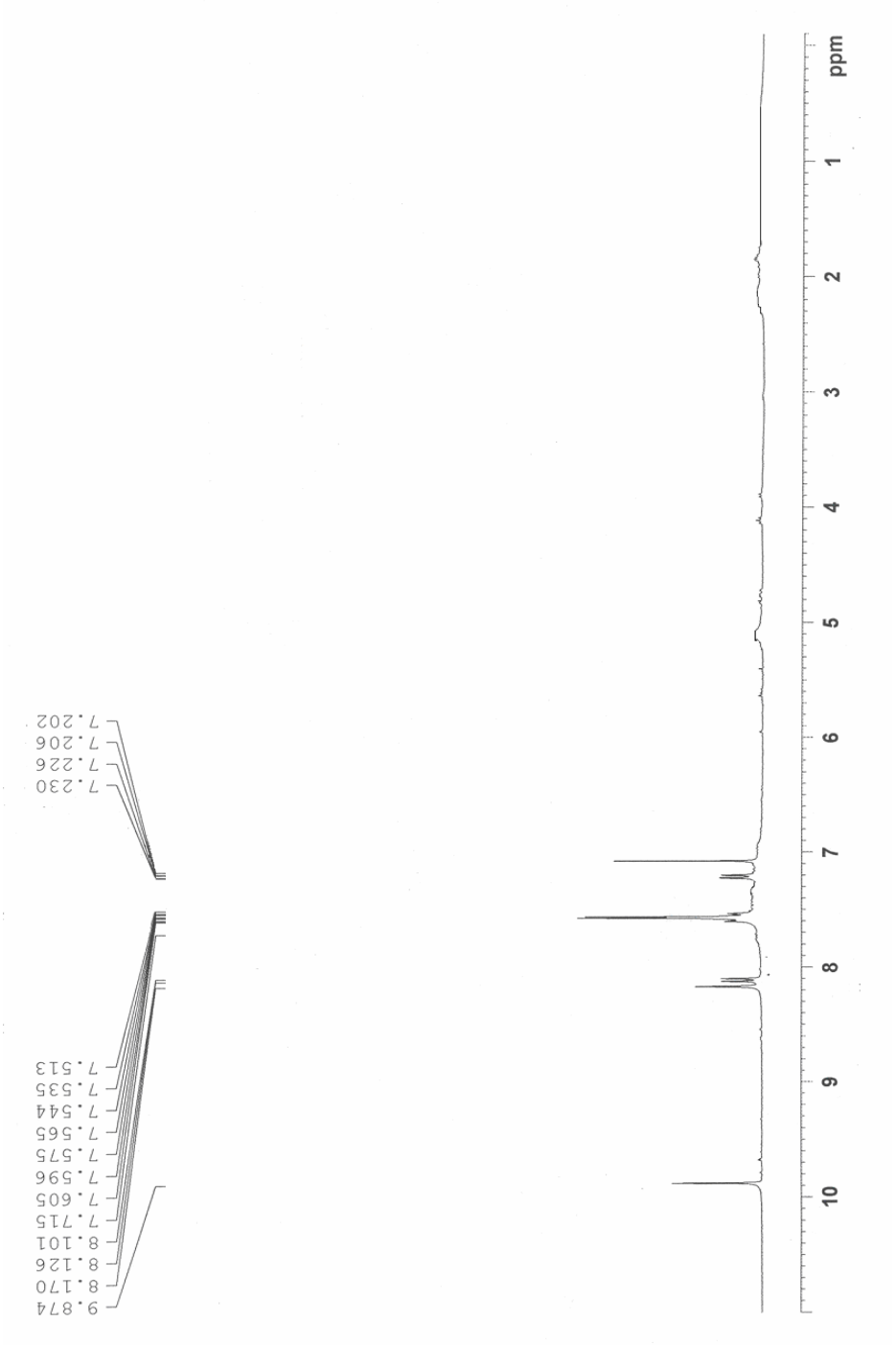


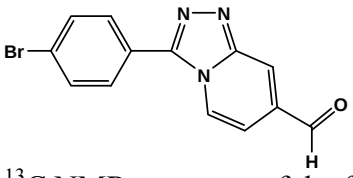
ESI Figure 45. ^{13}C NMR spectrum of the fused triazole **8d**



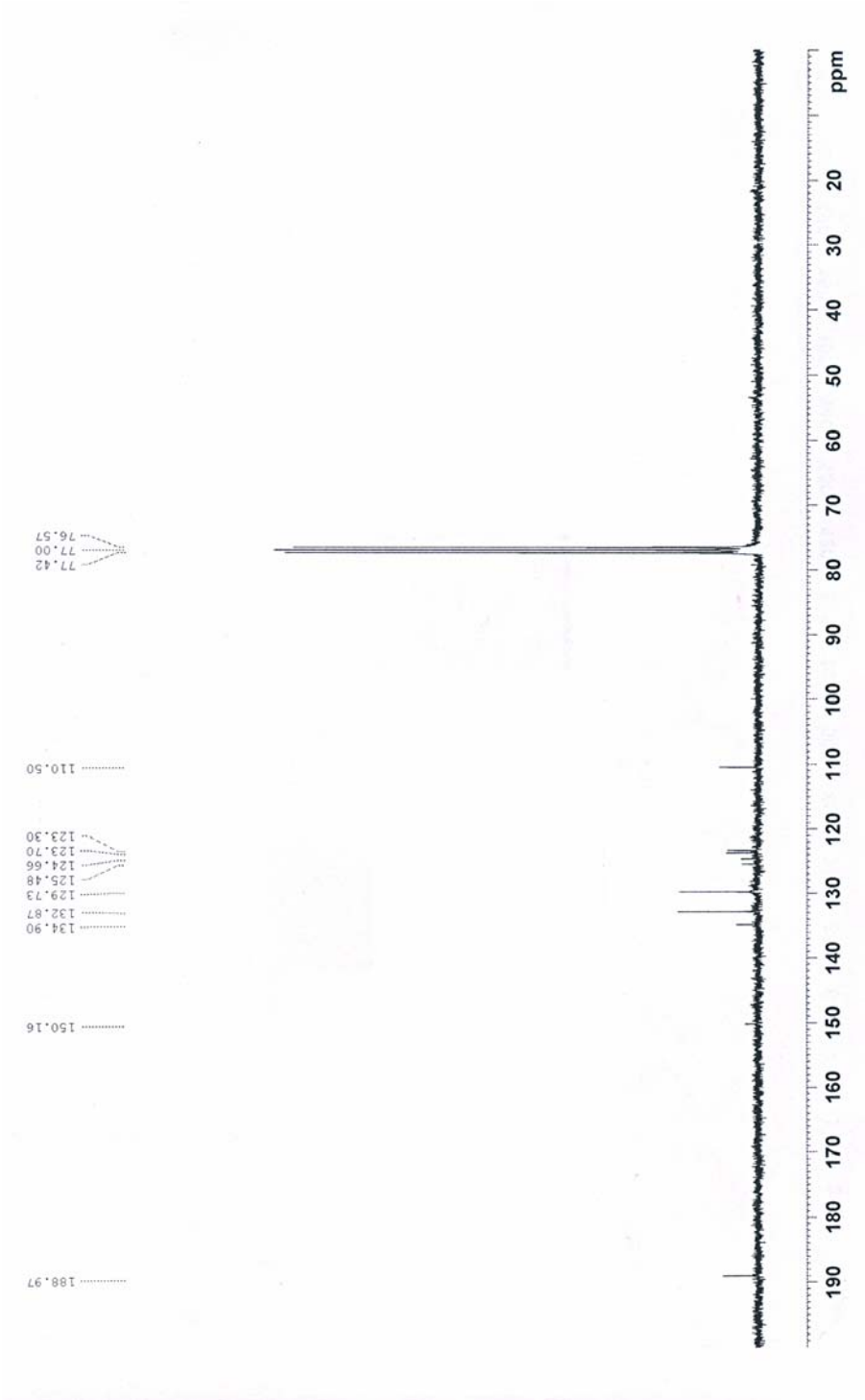


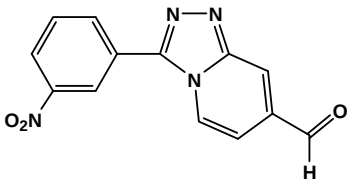
ESI Figure 46. ^{1}H NMR spectrum of the fused triazole **8e**



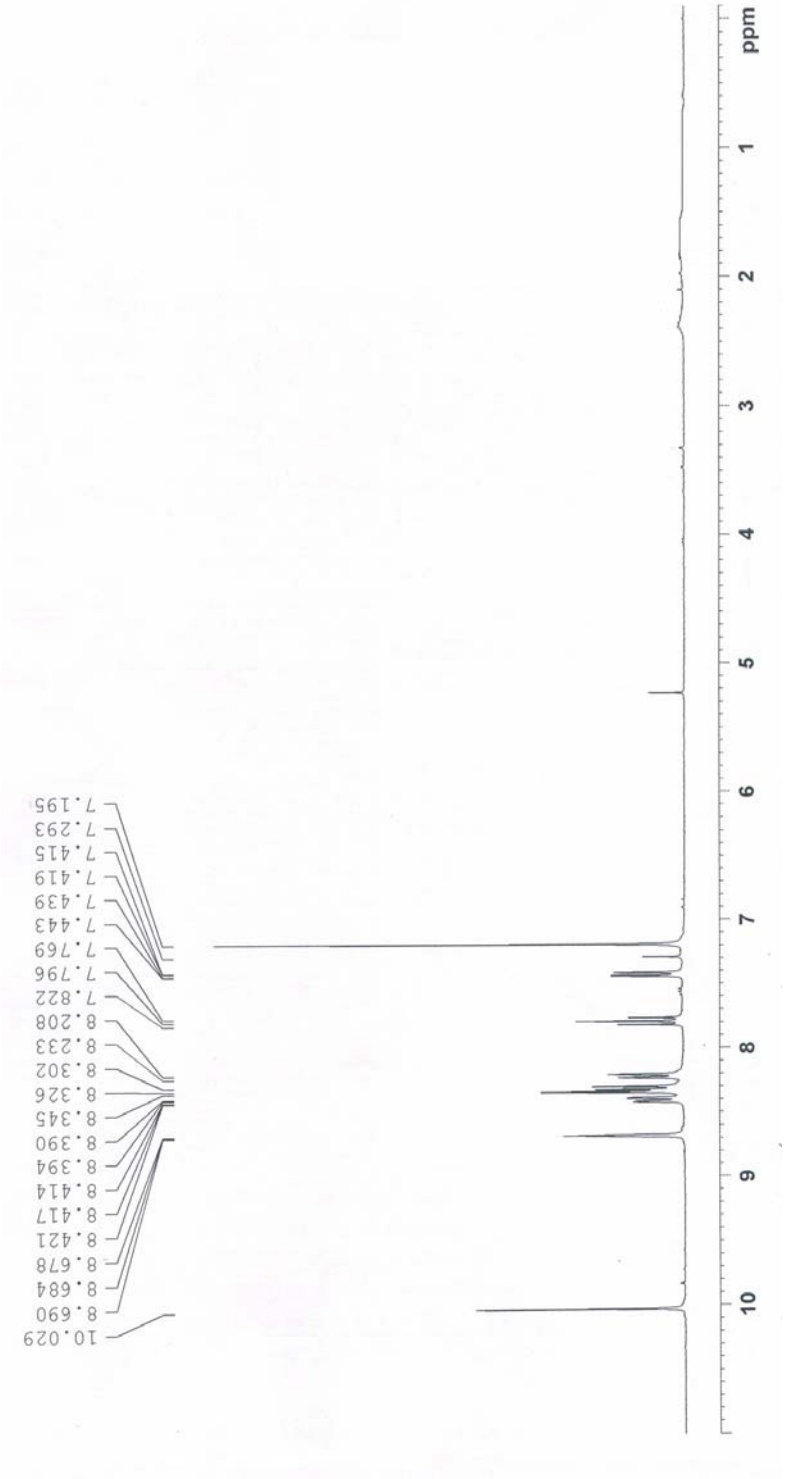


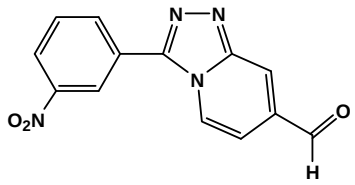
ESI Figure 47. ^{13}C NMR spectrum of the fused triazole **8e**



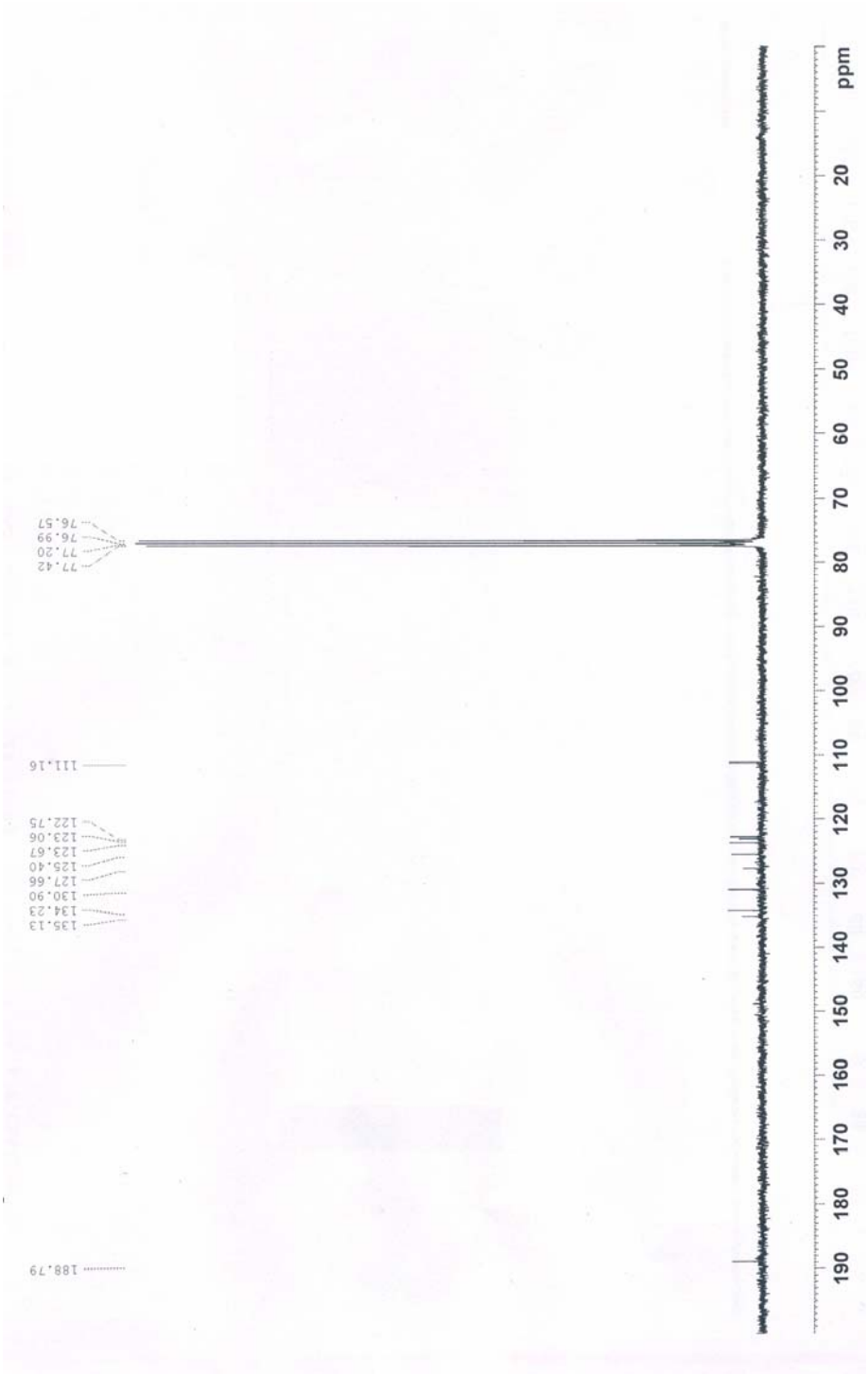


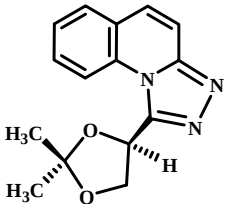
ESI Figure 48. ^{1}H NMR spectrum of the fused triazole **8f**



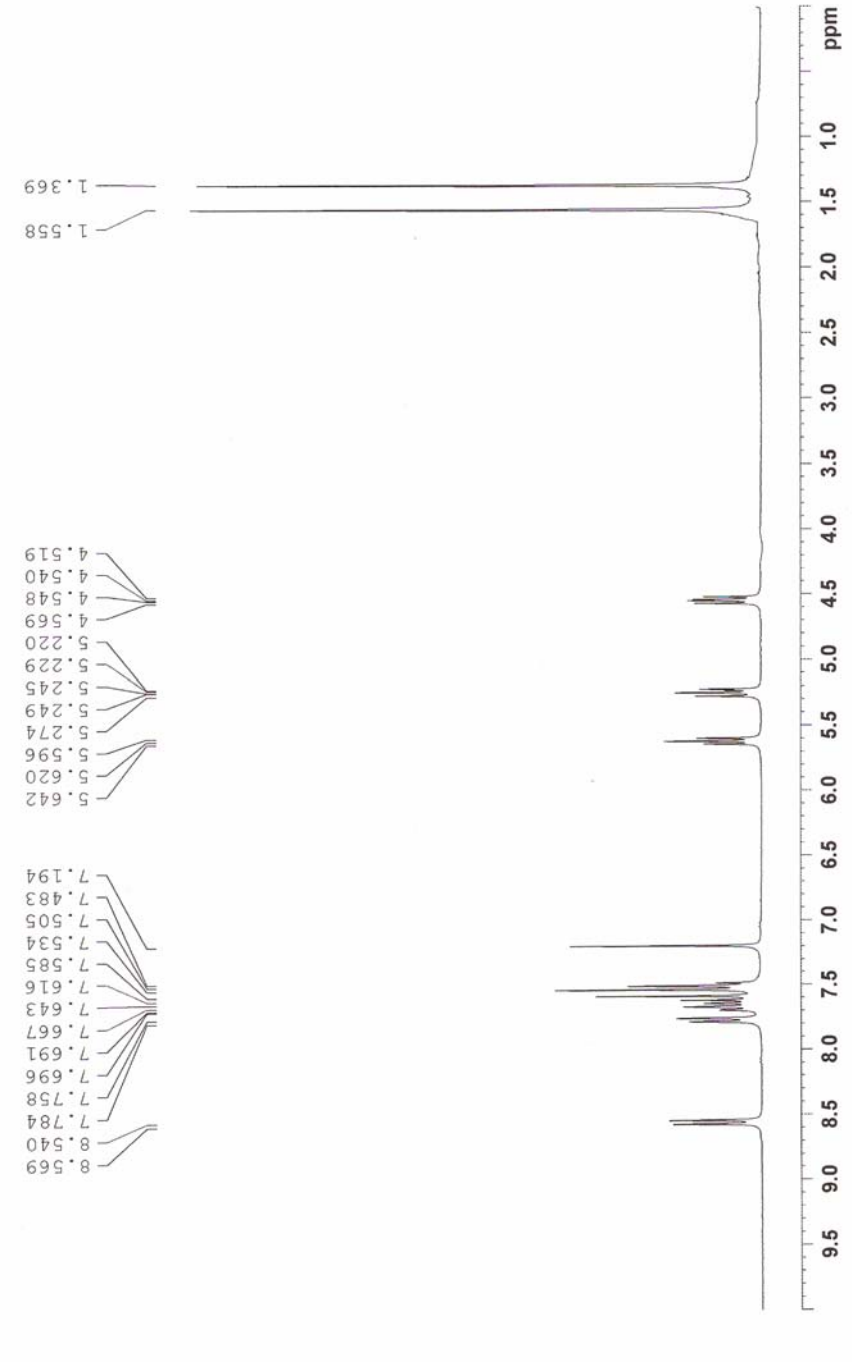


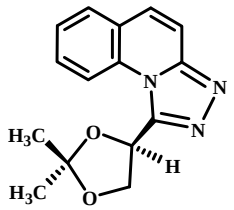
ESI Figure 49. ^{13}C NMR spectrum of the fused triazole **8f**



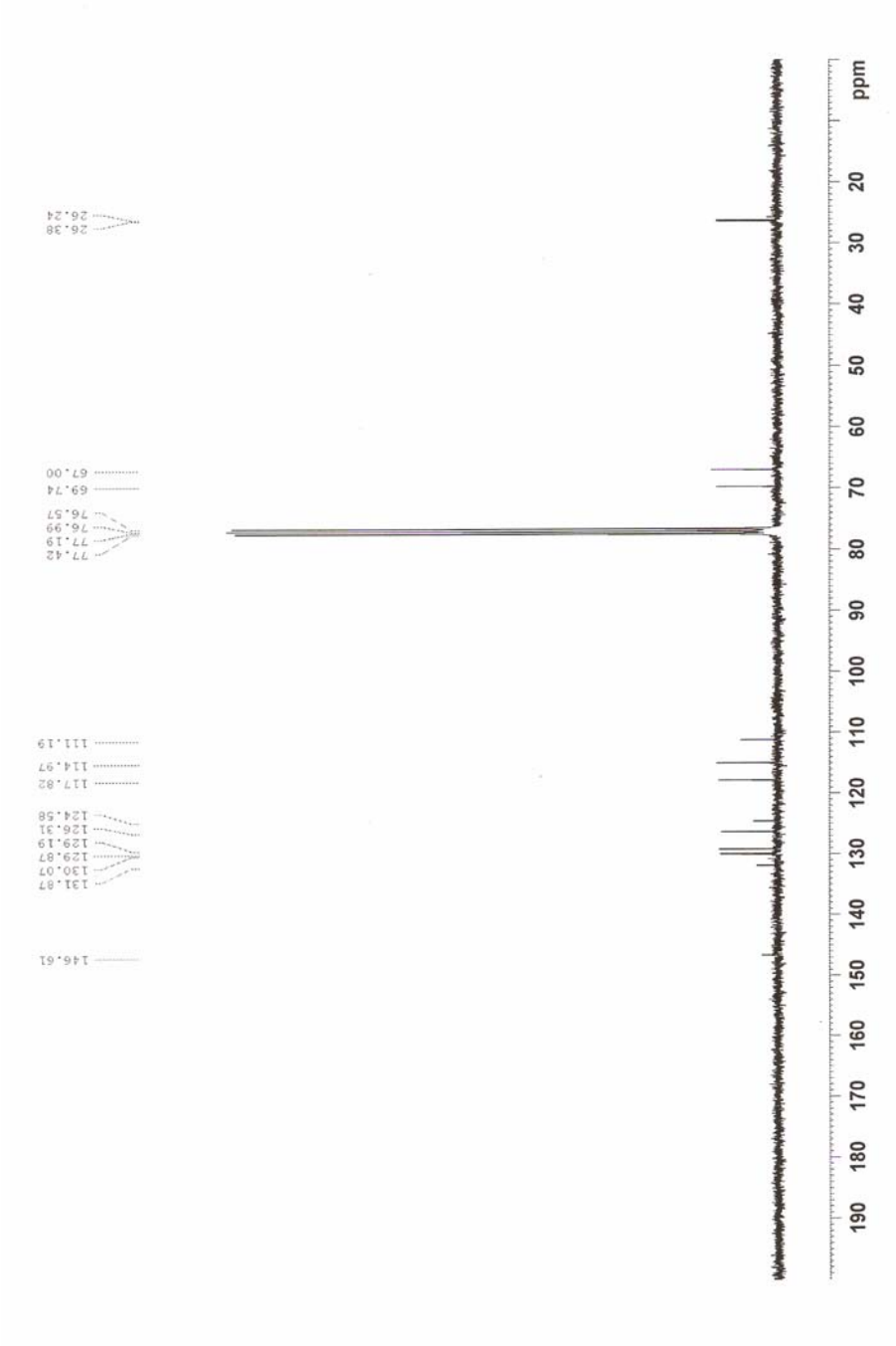


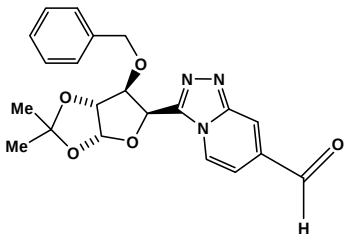
ESI Figure 50. ^{1}H NMR spectrum of the sugar-based fused triazole **8g**



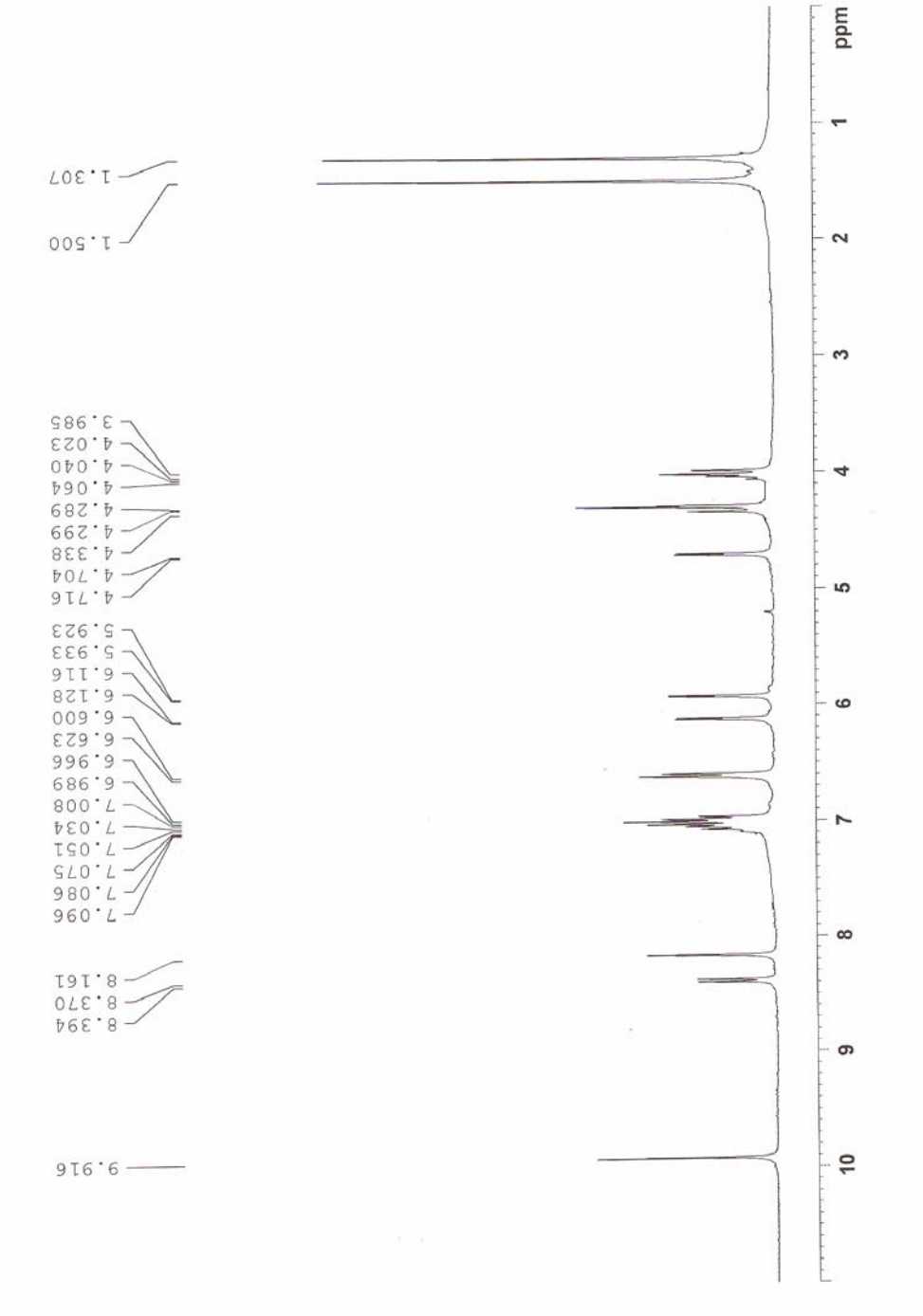


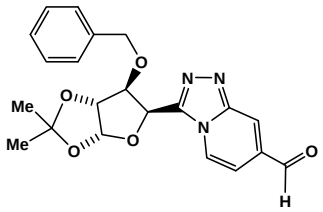
SI Figure 51. ^{13}C NMR spectrum of the sugar-based fused triazole **8g**



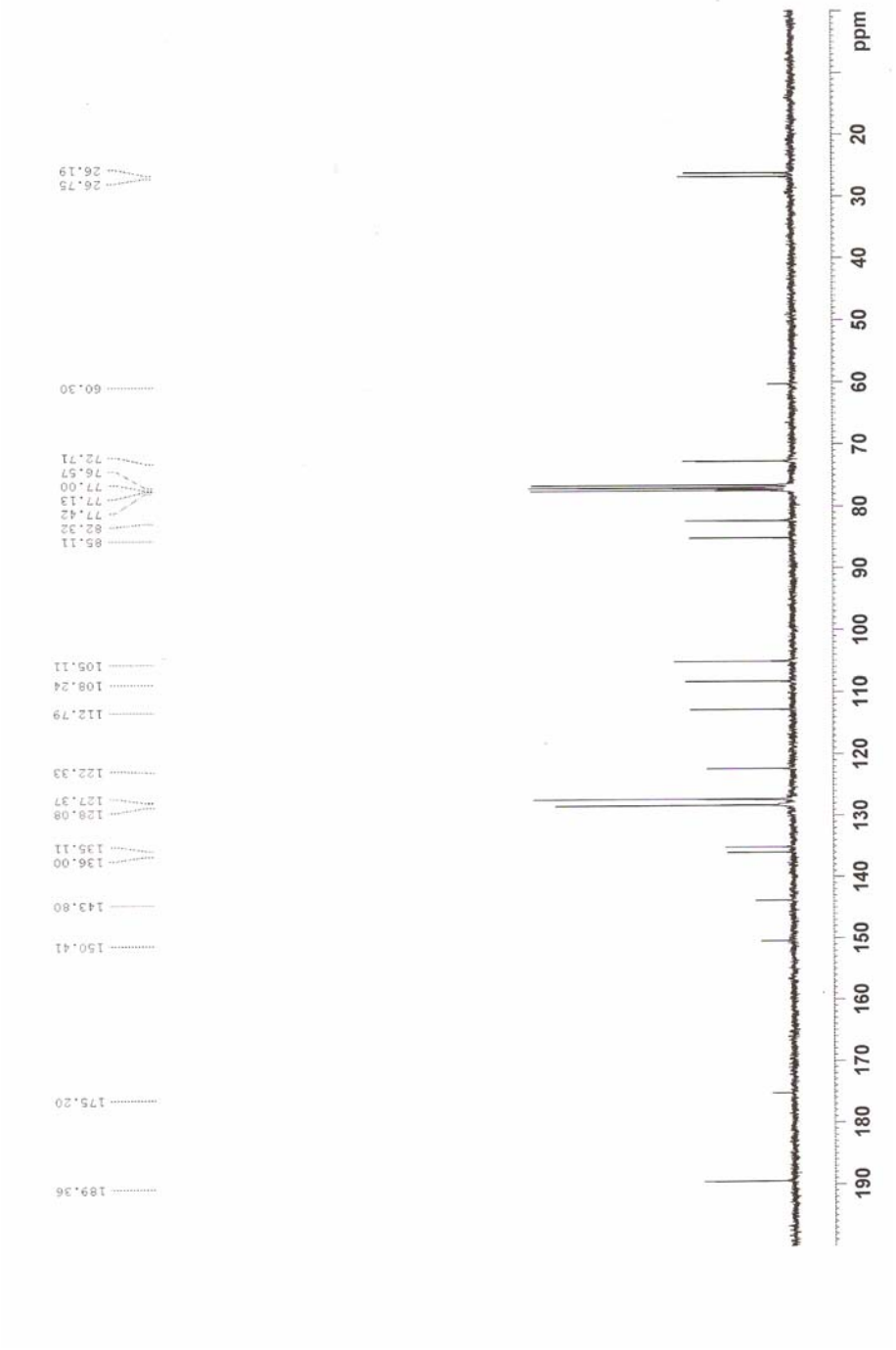


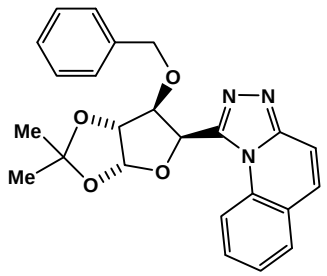
ESI Figure 52. ^{1}H NMR spectrum of the sugar-based fused triazole **8h**



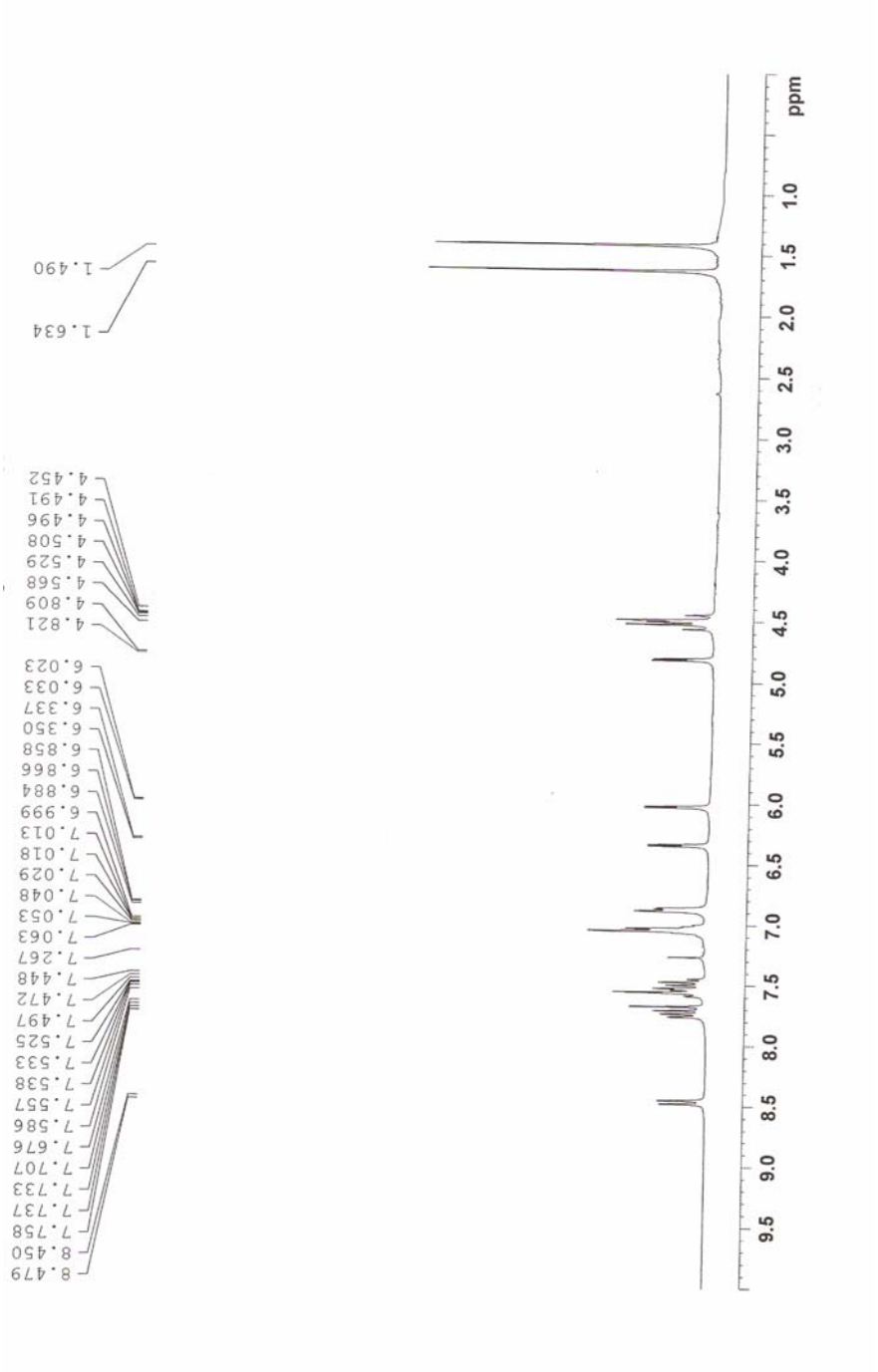


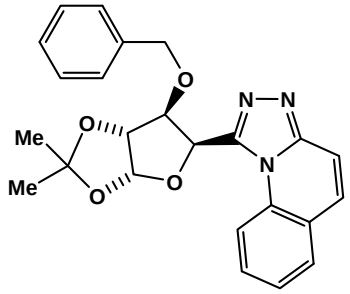
ESI Figure 53. ^{13}C NMR spectrum of the sugar-based fused triazole **8h**



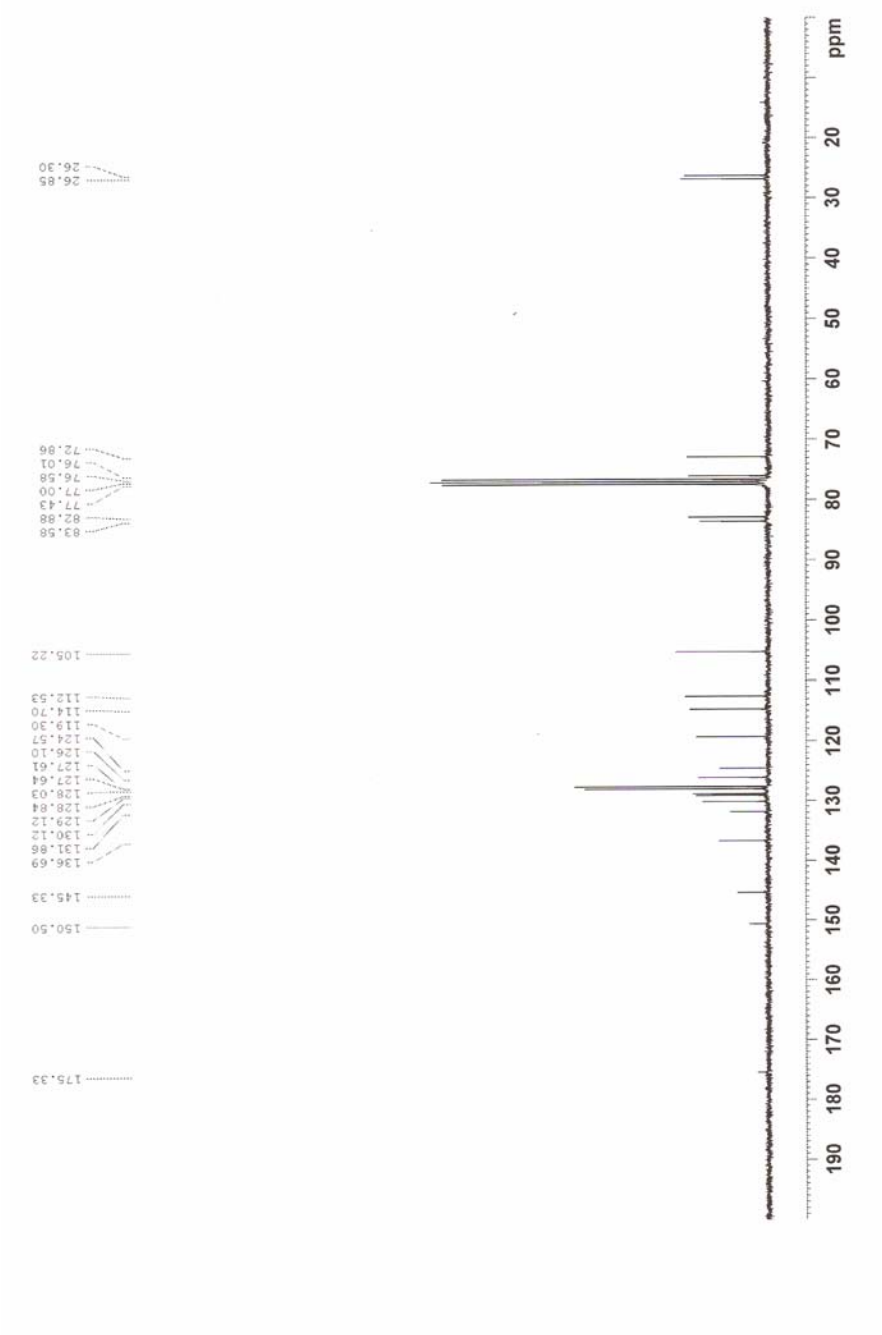


ESI Figure 54. ^{1}H NMR spectrum of the sugar-based triazole **8i**





ESI Figure 55. ^{13}C NMR spectrum of the sugar-based fused triazole **8i**



10. Summary of Data CCDC 741300

. Chemical formula and formula weight (M):	C21 H15 Cl2 N3 and 380.26
. Crystal system:	Orthorombic
. Unit-cell dimensions (angstrom or pm, degrees) and volume, with esds:	a 11.1316(8), b 14.5857(11), c 21.9255(15), 90.00, 90.00, 90.00, 3559.9 (4)
. Temperature:	296 (2)
. Space group symbol:	Pbca
. No. of formula units in unit cell (Z):	8
. Number of reflections measured and/or number of independent reflections, Rint:	2326
. Final R values (and whether quoted for all or observed data):	0.0597