Supporting Information

Nonafluorobutanesulfonyl Azide: A Shelf-Stable Diazo Transfer Reagent for the Synthesis of Azides from Primary Amines

José Ramón Suárez,[a] Beatriz Trastoy,[a] M. Eugenia Pérez-Ojeda,[b] Rubén Marín-Barrios,[a] and Jose Luis Chiara[a,]*

[a] Instituto de Química Orgánica General, C.S.I.C., Juan de la Cierva 3, E-28006 Madrid, Spain
Fax: (+34)-915644853; e-mail: jl.chiara@iqog.csic.es
[b] Instituto de Química-Física "Rocasolano", C.S.I.C., Serrano 119, E-28006 Madrid, Spain

General methods. All melting points were measured with a Reicher Jung Thermovar micro-melting apparatus. Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR or ^{13}C NMR) spectra were recorded on a BRUKER AMX-300 (300 and 75 MHz, respectively), a Varian INOVA 300 (300 and 75 MHz, respectively), a Varian INOVA 400 (400 and 100 MHz, respectively) or a Varian UNITY 500 (500 and 125 MHz, respectively) spectrometers. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual peaks of the deuterated NMR solvent used or to internal tetramethylsilane. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, b = broad), coupling constants in hertz (Hz), integration, and assignment. Proton and carbon-13 assignments are based on DQ-COSY, HSQC, and HMBC correlation experiments. Thin layer chromatography (TLC) was performed with Merck Silica Gel 60 F254 plates. Chromatograms were visualized using UV light and/or treatment with a solution of ammonium molybdate (50 g) and cerium(IV) sulphate (1 g) in 5 % aqueous H_2SO_4 (1 L) followed by charring on a hot plate. For

detection of azides, the chromatograms were first dipped in a 1% (w/v) solution of Ph_3P in EtOAc, dried at rt, then dipped in a 1% or 5% (w/v) solution of ninhydrin in 95% aqueous EtOH, and finally charred on a hot plate.[1] Column chromatography was performed with Merck silica gel, grade 60, 230–400 mesh. Mass spectra were recorded on an Agilent/HP 1100 LC/MSD spectrometer using ESI or APCI sources. High resolution mass spectra (HRMS) were recorded on an Agilent 6520 Q-TOF instrument with a ESI source. Elemental analyses were determined in a Heraus CHN-O analyser. Organic solvents were of HPLC grade and were used as provided. All reactions were carried out with magnetic stirring.

Substrates **10a** and **10b** were prepared as reported in the literature.[2]

Diazo transfer reaction. To a solution of the corresponding amine **3** (0.6 mmol) in water (0.8 mL) was added in sequence MeOH (2.2 mL), $NaHCO_3$ (0.201 g, 2.4 mmol), a solution of nonafluorobutanesulfonyl azide (0.295 g, 0.9 mmol) in Et_2O (1.2 mL) and $CuSO_4 \cdot 5H_2O$ (14 mg, 0,06 mmol). The reaction mixture was stirred at room temperature for 6 h. The mixture was concentrated at reduced pressure, CH_2Cl_2 (10 mL) was added, and the resultant solution was washed with a saturated aqueous solution of $NaHCO_3$ (5×10 mL). The organic layer were separated, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. The corresponding azide **4** was obtained in pure form without any further purification.

Benzyl azide (4a):
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.36 (s, 2 H), 7.33-7.45 (m, 5 H).

2-Phenylethyl azide (4b): ^{1}H NMR was in agreement with that reported in the literature.[3]
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.89 (t, J = 7.3 Hz, 2 H), 3.52 (t, J = 7.3 Hz, 2 H), 7.18-7.23 (m, 2 H), 7.23-7.41 (m, 5 H).

6-Azido-1-hexanol (4c): ^{1}H NMR was in agreement with that reported in the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$): 1.27-1.39 (m, 4 H), 1.53-1.62 (m, 4 H), 2.14 (br s, 1 H), 3.24 (t, *J* = 6.9 Hz, 2 H), 3.60 (t, *J* = 6.5 Hz, 2 H).

4-(2-azidoethyl)-1,2-dimethoxybenzene (4d):

^{1}H NMR (300 MHz, $CDCl_3$): 2.83 (t, *J* = 6.0 Hz, 2 H), 3.47 (t, *J* = 6.0 Hz, 2 H), 3.85 (s, 3 H), 3.87 (s, 3 H), 6.73-6.83 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): 34.9 (CH_2), 52.5 (CH_2), 55.7 (CH_3), 55.8 (CH_3), 111.3 (CH), 111.9 (CH), 120.6 (CH), 130.5 (C), 147.8 (C), 148.9 (C).

Anal, calcd for $C_{10}H_{13}N_3O_2$: C, 57.96, H, 6.32, N, 20.28; found: C, 58.04, H, 6.37, N, 19.99.

Ethyl 3-azidobenzoate (4e): ^{1}H NMR was in agreement with that reported in the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$): 1.40 (t, *J* = 7.3 Hz, 3 H), 4.38 (q, *J* = 7.3 Hz, 2 H), 7.18 (d, *J* = 8.0 Hz, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.70 (s, 1 H), 7.81 (d, *J* = 7.7 Hz, 1 H).

(*S*)-Ethyl α-azidoisovalerate (4f): ^{1}H NMR was in agreement with that reported in the literature.[6]

^{1}H NMR (300 MHz, $CDCl_3$): 1.00 (t, *J* = 6.0 Hz, 6 H), 1.32 (t, *J* = 6.0 Hz, 6 H), 2.15-2.25 (m, 1 H), 3.66 (t, *J* = 6.0 Hz, 6 H), 4.24 (qd, *J* = 6.0, 1.2 Hz, 2 H).

(*S*)-2-Azido-3-phenylpropanoic acid (4g): ^{1}H NMR was in agreement with that reported in the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$): 3.09 (dd, *J* = 13.5, 6.0 Hz, 1 H), 3.29 (dd, *J* = 13.5, 4.9 Hz, 1 H), 4.15-4.21 (m, 1 H), 7.30-7.43 (m, 5 H), 8.75 (br s, 1 H).

(*S*)-2-azido-3-(4-hydroxyphenyl)propanoic acid (4h): ^{1}H NMR was in agreement with that reported in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$): 3.05 (dd, *J* = 14.0, 8.7 Hz, 1 H), 3.27 (dd, *J* = 14.0, 4.8 Hz, 1H), 4.19 (dd, *J* = 8.5, 4.9 Hz, 1 H), 6.91 (d, *J* = 8.5 Hz, 1 H), 7.27 (d, *J* = 8.5 Hz, 2 H).

1,3,4,6-Tetra-*O*-acetyl-2-azido-2-deoxy-D-glucopyranose (4i): To a solution of D-glucosamine hydrochloride (64 mg, 0.3 mmol) in water (0.8 mL) was added in sequence MeOH (1.1 mL), $NaHCO_3$ (0.100 g, 1.2 mmol), a solution of nonafluorobutanesulfonyl azide (0.153 g, 0.45 mmol) in Et_2O (1.2 mL) and $CuSO_4 \cdot 5H_2O$ (14 mg, 0,06 mmol). The reaction mixture was stirred at room temperature for 6 h. The mixture was concentrated at reduced pressure. The oily residue was suspended in dry pyridine (3 mL) and treated with Ac_2O (0.42 mL, 4.5 mmol) at 0 ºC. After stirring at this temperature for 4 h, the reaction was diluted with CH_2Cl_2 (10 mL) and washed with aqueous 1 M HCl (2 × 10 mL). The combined aqueous layers were extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. The product **4i** was obtained as a mixture of two diastereoisomers (α/β = 40:60 ratio) in 74% yield.

^{1}H NMR spectrum was agreement with that reported in the literature.[9]

^{1}H NMR (300 MHz, $CDCl_3$): 2.02, 2.04, 2.07, 2.09, 2.10 and 2.19 (8 × CH_3), 3.64-3.70 (m, 1 H), 3.72-3.77 (m, 2 H), 3.78-3.83 (m, 1 H, β-anomer), 4.02-4.10 (m, 3 H), 4.28 (dd, *J* = 4.2, 3.0 Hz, 1H, β-anomer), 4.30-4.33 (m, 1 H, α-anomer), 5.01-5.14 (m, 3 H), 5.46 (dd, *J* = 12.2, 7.7 Hz, 1 H, α-anomer), 5.55 (d, *J* = 8.6 Hz, 1 H, β-anomer), 6.29 (d, *J* = 3.7 Hz, 1 H, α-anomer).

Hexaazido-hepta-*O*-Acetyl Neomycin (4j): To a solution of neomycin trisulfate salt hydrate (80 mg, 0.088 mmol) in water (0.8 mL) was added in sequence MeOH (1.1 mL), $NaHCO_3$ (0.100 g, 1.2 mmol), a solution of nonafluorobutanesulfonyl azide (0.257 g, 0.792 mmol) in Et_2O (1.2 mL) and $Cu_2SO_4 \cdot 5H_2O$ (14 mg, 0,06 mmol). The reaction mixture was stirred at room temperature for 6 h. The mixture was concentrated at reduced pressure. The residue was dissolved in dry pyridine (3 mL) was treated at 0ºC with Ac_2O (0.45 mL, 4.4 mmol) and stirred for 4 h at this temperature. Then, the volatiles were removed under reduced pressure and the residue was redissolved in 10 mL of ethyl acetate, and extracted twice with 8 mL of 1 M aqueous HCl. The organic layer was concentrated and the residue was purified by flash column chromatography eluting with 2:1 hexane/EtOAc to afford **4j** in 62% yield as a white solid.

^{1}H NMR was in agreement with that reported in the literature.[10]

^{1}H NMR (300 MHz, $CDCl_3$): 2.09 (CH_3), 2.12 (CH_3), 2.14 (CH_3), 2.15 (CH_3), 2.20 (3 × CH_3), 3.17 (dd, *J* = 10.7, 3.7 Hz, 1 H), 3.27-3.76 (m, 11 H), 3.93 (t, *J* = 8.9 Hz, 1H), 4.11-4.15 (m, 1 H), 4.26-4.37 (m, 2 H), 4.42-4.51 (m, 3 H), 4.73 (br s, 1 H), 4.91 (br s, 2 H), 4.97-5.07 (m, 4 H), 5.38 (d, *J* = 2.6 Hz, 1 H), 5.50 (d, *J* = 9.4 Hz, 2 H), 5.98 (d, *J* = 3.6 Hz, 1 H).

One pot Diazo transfer and intermolecular 1,3-Dipolar-cycloaddition reaction. To a solution of the corresponding amine **3** (0.6 mmol) in water (0.8 mL) was added in sequence MeOH (2.2 mL), $NaHCO_3$ (0.201 g, 2.4 mmol), a solution of nonafluorobutanesulfonyl azide (0.295 g, 0.9 mmol) in Et_2O (1.2 mL) and $CuSO_4 \cdot 5H_2O$ (14 mg, 0.06 mmol). The reaction mixture was stirred at room temperature for 6 h. Then, phenylacetylene (0.06 mL, 0.65 mmol) and sodium ascorbate (178 mg, 0.9 mmol) were added and the reaction was stirred at room temperature overnight. The mixture was concentrated at reduced pressure, CH_2Cl_2 (15 mL) was added, and the resultant solution was washed with a saturated aqueous solution of $NaHCO_3$ (4 × 10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. The residue was purified by flash column chromatography to afford the corresponding triazol **5-9**.

1-Benzyl-4-hexyl-1*H*-1,2,3-triazole (5): White solid. M.p. 50-51ºC. R_f = 0.41 (hexane/EtOAc 3:2).

^{1}H NMR (300 MHz, $CDCl_3$): 0.86 (t, *J* = 6.1 Hz, 3 H), 1.26-1.37 (m, 6 H), 1.58-1.67 (m, 2 H), 2.67 (t, *J* = 7.7 Hz, 2 H), 5.48 (s, 2 H), 7.18 (br s, 1 H), 7.23-7.27 (m, 2 H), 7.33-7.39 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.6 (CH_3), 23.1 (CH_2), 26.3 (CH_2), 29.5 (CH_2), 29.9 (CH_2), 32.1 (CH_2), 54.5 (CH_2), 121.0 (CH), 128.5 (2 × CH), 129.1 (CH), 129.6 (2 × CH), 135.5 (C), 149.5 (C).

HRMS (ESI) $(M+H)^+$ calcd for $C_{15}H_{22}N_3$: 244.1808, found: 244.1819.

1-Benzyl-4-(p-tolyl)-1*H*-1,2,3-triazole (6): White solid. M.p.151-153ºC. R_f = 0.33 (hexane/EtOAc 3:2).

^{1}H NMR (300 MHz, $CDCl_3$): 2.36 (s, 3 H), 5.58 (s, 3 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 7.28-7.32 (m, 2 H), 7.35-7.39 (m, 3 H), 7.64 (s, 1 H), 7.69 (d, *J* = 7.8 Hz, 2 H).
^{13}C NMR (75 MHz, $CDCl_3$): 21.8 (CH_3), 54.7 (CH_2), 126.1 (2 × CH), 128.2 (C), 128.6 (2 × CH), 129.3 (CH), 129.7 (2 × CH), 130.0 (3 × CH), 135.2 (C), 138.6 (2 × C).
HRMS (ESI) $(M+H)^+$ calcd for $C_{16}H_{16}N_3$: 250.1339, found: 250.1349.

1-(3,4-Dimethoxyphenethyl)-4-phenyl-1*H*-1,2,3-triazole (7): Pale yellow oil. R_f = 0.36 (hexane/EtOAc 3:2).
^{1}H NMR (300 MHz, $CDCl_3$): 3.19 (t, *J* = 7.0 Hz, 2 H), 3.78 (s, 3 H), 3.85 (s, 3 H), 4.61 (t, *J* = 7.1 Hz, 2 H), 6.54 (d, *J* = 1.9 Hz, 1 H), 6.68 (dd, *J* = 8.1, 1.9 Hz, 1 H), 6.80 (d, *J* = 8.2 Hz, 1 H), 7.32 (t, *J* = 7.3 Hz, 1 H), 7.41 (t, *J* = 7.3 Hz, 2 H), 7.47 (s, 1 H), 7.76 (d, *J* = 7.1 Hz, 2 H).
^{13}C NMR (75 MHz, $CDCl_3$): 36.4 (CH_2), 52.0 (CH_2), 55.8 (CH_3), 55.9 (CH_3), 111.5 (CH), 111.9 (CH), 120.6 (CH), 125.7 (2 × CH), 128.1 (CH), 128.8 (2 × CH), 129.6 (2 × C), 130.6 (C), 148.1 (C), 149.1 (C).
MS (ESI): m/z (%): 310 (M^++H, 100), 239 (10), 165 (26), 102 (41). HRMS calcd for $C_{18}H_{20}N_3O_2$: 310.1481, found: 310.1556.

Ethyl 3-(4-hexyl-1*H*-1,2,3-triazol-1-yl)benzoate (8): Pale yellow oil. R_f = 0.54 (hexane/EtOAc 7:3).
^{1}H NMR (300 MHz, $CDCl_3$): 0.87 (t, *J* = 7.0 Hz, 3 H), 1.26-1.34 (m, 6 H), 1.39 (t, *J* = 7.1 Hz, 3 H), 1.65-1.75 (m, 2 H), 2.77 (t, *J* = 7.0 Hz, 2 H), 4.39 (q, *J* = 7.1 Hz, 2 H), 7.56 (app. t, *J* = 7.9 Hz, 1 H), 7.80 (s, 1 H), 7.98 (ddd, *J* = 8.1, 2.0, 1.1 Hz, 1 H), 8.05 (ddd, *J* = 5.5, 3.4, 2.0 Hz, 1 H), 8.29-8.30 (m, 1 H).
^{13}C NMR (75 MHz, $CDCl_3$): 14.5 (CH_3), 14.7 (CH_3), 23.0 (CH_2), 26.1 (CH_2), 29.4 (CH_2), 29.8 (CH_2), 32.0 (CH_2), 62.0 (CH_2), 119.3 (C), 121.4 (CH), 125.0 (CH), 129.7 (CH), 130.3 (CH), 132.6 (CH), 137.8 (C), 150.0 (C), 165.9 (C).
HRMS (ESI) $(M+H)^+$ calcd for $C_{17}H_{24}N_3O_2$: 302.1863, found: 302.1877.

Ethyl 3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzoate (9): Colorless oil. R_f = 0.42 (hexane/EtOAc 3:2).

^{1}H NMR (300 MHz, $CDCl_3$): 1.43 (t, *J* = 7.1 Hz, 1 H), 4.44 (q, *J* = 7.1 Hz, 1 H), 7.35-7.41 (m, 1 H), 7.44-7.50 (m, 2 H), 7.64 (app. t, *J* = 7.9 Hz, 1 H), 7.89-7.94 (m, 2 H), 8.06-8.15 (m, 2 H), 8.28 (s, 1 H), 8.38 (dd, *J* = 8.4, 6.7 Hz, 1 H).
^{13}C NMR (75 MHz, $CDCl_3$): 14.3 (CH_3), 61.7 (CH_2), 117.6 (CH), 121.0 (CH), 124.7 (CH), 125.9 (2 × CH), 128.6 (CH), 129.0 (2 × CH), 129.6 (CH), 129.9 (C), 130.0 (CH), 132.2 (C), 137.1 (C), 148.7 (C), 165.4 (C).
MS (ESI): m/z (%): 294 (M^++H, 100), 194 (10), 180 (22). HRMS calcd for $C_{17}H_{16}N_3O_2$: 294.1167, found: 294.1242.

One pot Diazo transfer and intramolecular 1,3-Dipolar-cycloaddition reaction. To a solution of the corresponding amine **10** (0.6 mmol) in water (0.8 mL) was added in sequence MeOH (2.2 mL), $NaHCO_3$ (0.201 g, 2.4 mmol), and a solution of nonafluorobutanesulfonyl azide (0.295 g, 0.9 mmol) in CH_2Cl_2 (1.2 mL). After stirring the reaction mixture at room temperature for 12 h, $CuSO_4 \cdot 5H_2O$ (14 mg, 0.06 mmol) and sodium ascorbate (178 mg, 0.9 mmol) were added and the reaction was stirred at room temperature for 3 h. The mixture was concentrated at reduced pressure, CH_2Cl_2 (15 mL) was added, and the resultant solution was washed with a saturated aqueous solution of $NaHCO_3$ (4 × 10 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated at reduced pressure. The residue was purified by flash column chromatography to afford the corresponding tricyclic triazol **11**.

4*H*-Benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazine (11a): Yellow oil. R_f = 0.35 (hexane/EtOAc 3:2).
^{1}H NMR (300 MHz, $CDCl_3$): 5.39 (s, 2 H), 7.09-7.18 (m, 2 H), 7.26 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.63 (s, 1 H), 8.06 (dd, *J* = 8.0, 1.6 Hz, 1 H).
^{13}C NMR (75 MHz, $CDCl_3$): 62.4 (CH_2), 117.3 (CH), 118.3 (CH), 123.6 (CH), 124.5 (C), 127.9 (C), 129.5 (2 × CH), 145.7 (C).
HRMS (ESI) $(M+H)^+$ calcd for $C_9H_8N_3O_2$: 174.0772, found: 174.0220.

7-Methoxy-4*H*-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazine (11b): Yellow solid. R_f = 0.38 (hexane/EtOAc 3:2).

^{1}H NMR (300 MHz, $CDCl_3$): 3.87 (s, 3 H), 5.34 (s, 2 H), 6.84 (dd, J = 9.0, 3.0 Hz, 1 H), 7.05 (d, J = 9.0 Hz, 1 H), 7.62 (d, J = 3.0 Hz, 1 H), 7.64 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): 56.2 (CH_3), 61.9 (CH_2), 101.6 (CH), 115.6 (CH), 119.1 (CH), 124.4 (CH), 127.9 (C), 129.3 (C), 139.1 (C), 135.6 (C).

HRMS (ESI) $(M+H)^+$ calcd for $C_{10}H_{10}N_3O_2$: 204.0768, found: 204.0770.

References:

1) Punna, S.; Finn, M. G. *Synlett* **2004**, 99-100.

2) Gabriele, B.; Salerno, G.; Veltri, L.; Mancuso, R.; Li, Z.; Crispini, A.; Anna Bellusci, A. *J. Org. Chem.* **2006**, *71*, 7895-7898.

3) Benati, L.; Bencivenni, G.; Leardini, R.; Nanni, D.; Minozzi, M.; Spagnolo, P.;Scialpi, R.; Zanardi, G. *Org. Lett.* **2006**, *8*, 2499-2502.

4) Malkoch, M.; Schleicher, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P.; Wu, P.; Fokin V. V. *Macromolecules* **2005**, *38*, 3663–3678.

5) Hu, M.; Li, J.; Yao, S.Q. *Org. Lett.* **2008**, *10*, 5529-5531.

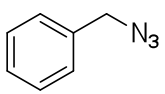
6) Manis, P. A.; Rathke, M. W. *J. Org. Chem.* **1980**, *45*, 4952-4954-5032.

7) Shi, H.; Liu, K.; Xu, A.; Yao, S. Q. *Chem. Commun.* **2009**, 5030-5032.

8) Bock, V. D.; Speijer, D.; Hiemstraa, H.; van Maarseveen, J. H. *Org. Biomol. Chem. 2007*, ***5***, 971-975.

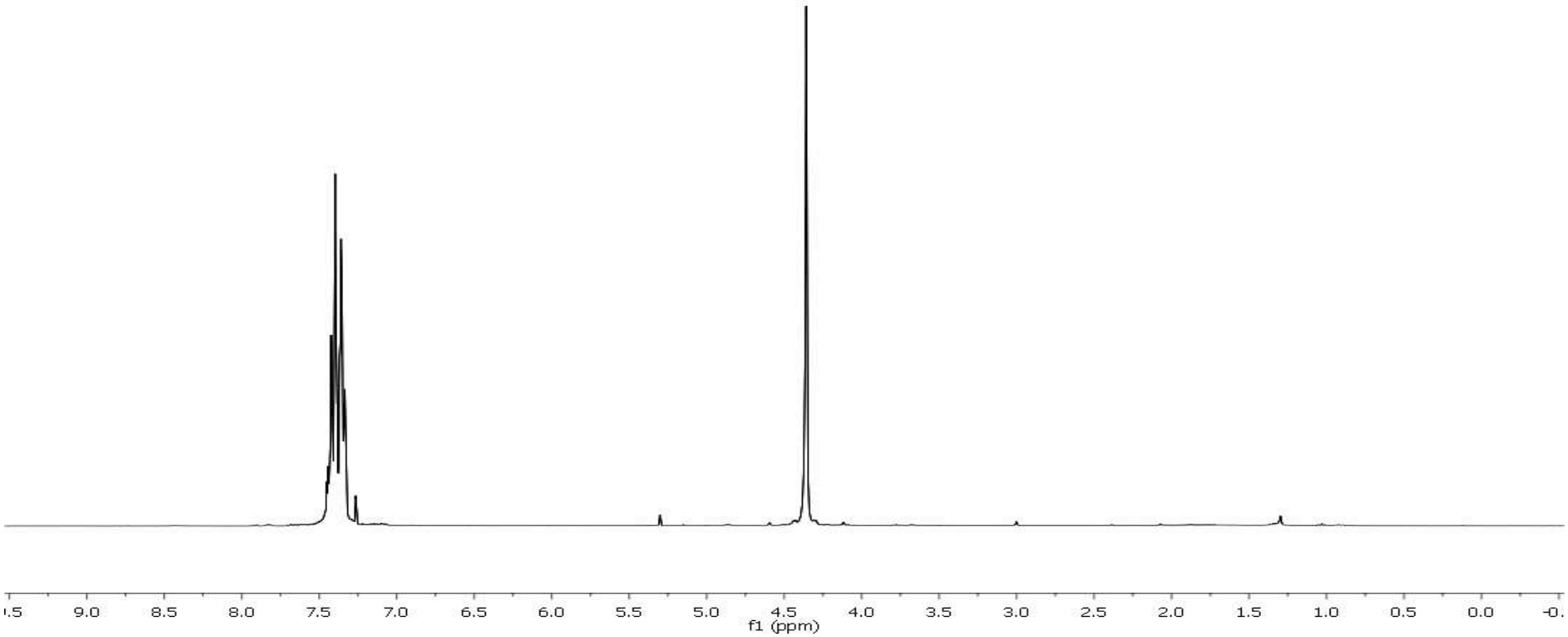
9) Vasella, A.; Witzig, C.; Chiara, J. L.; Martín-Lomas, M. *Hev. Chim. Acta* **1991**, *74*, 2073-2077.

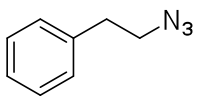
10) Greenberg, W. A.; Priestley, E. S.; Sears, P. S.; Alper, P. B.; Rosenbohm, C.; Hendrix, M.; Hung, S-C.; Wong, C-H. *J. Am. Chem. Soc.* **1999,** *121,* 6527-6541.



(^{1}H NMR, $CDCl_3$, 300 MHz)

4 a





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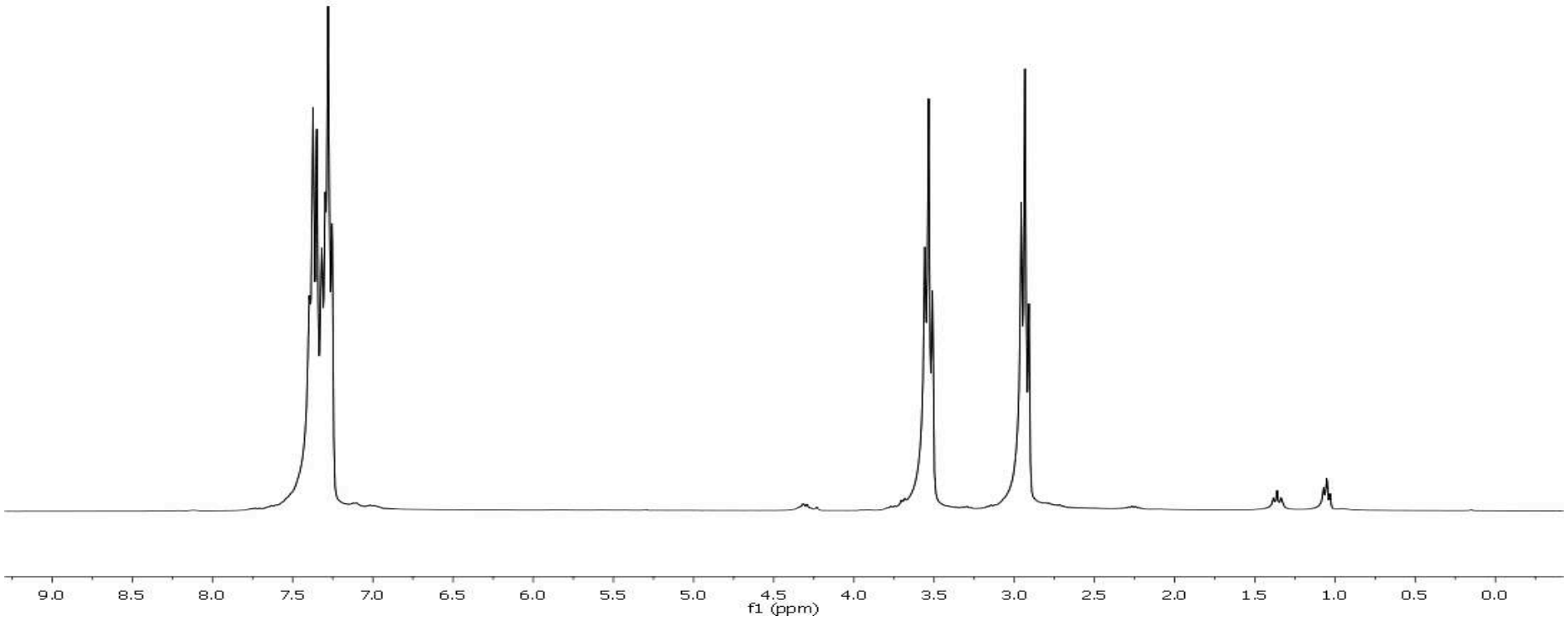
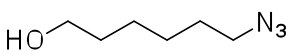
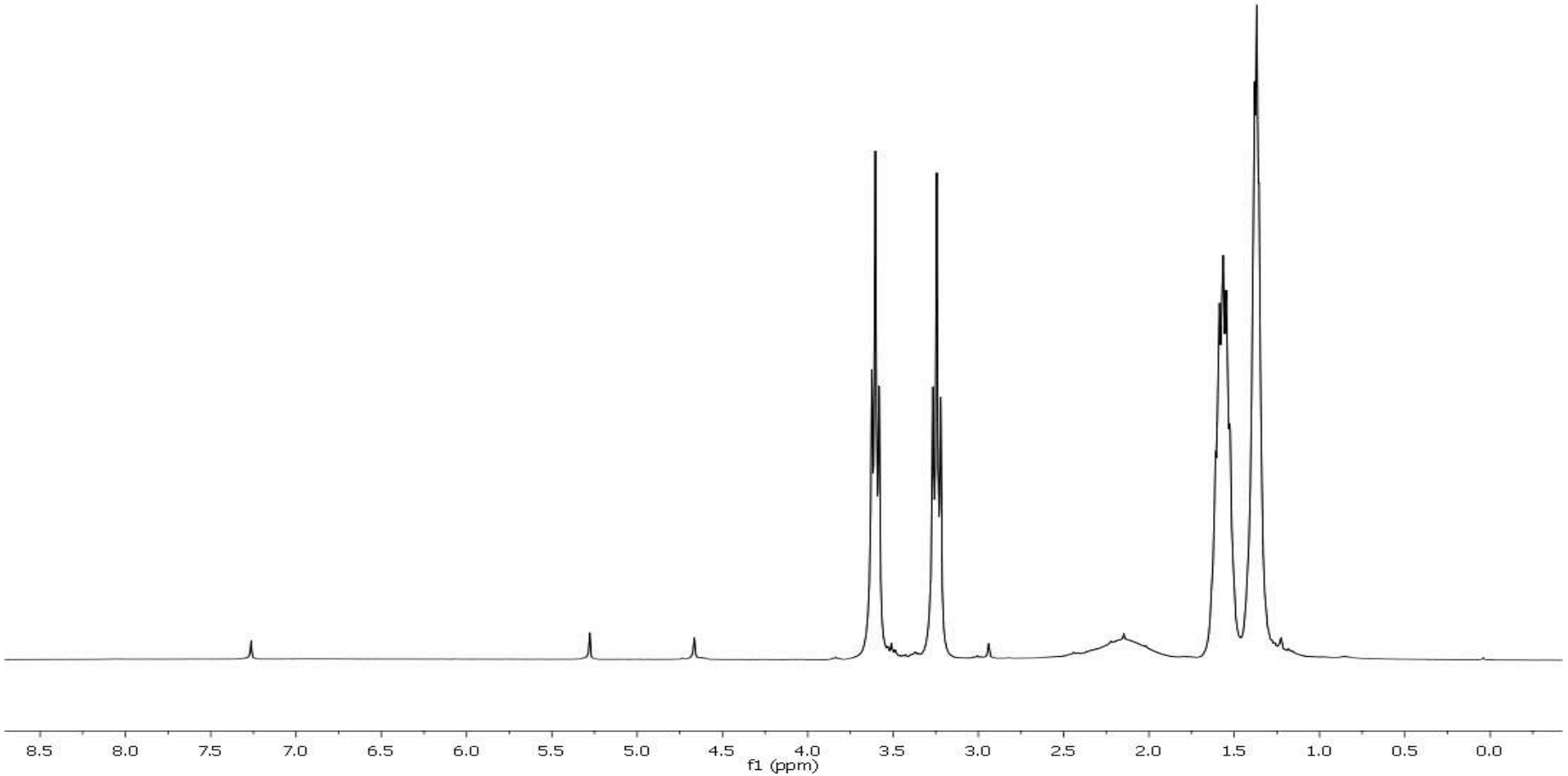
4b

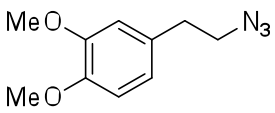




(^{1}H NMR, $CDCl_3$, 300 MHz)

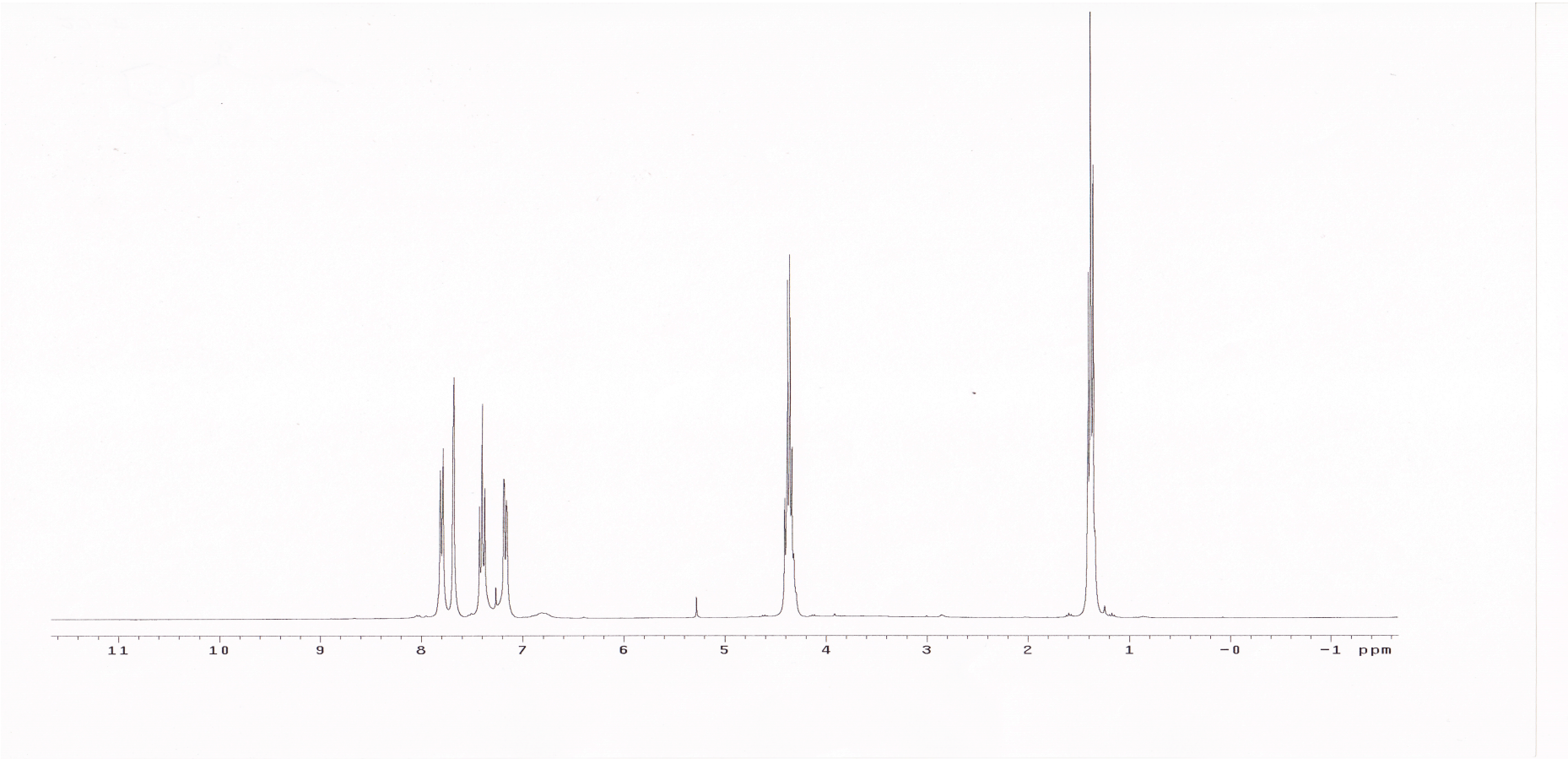
4c

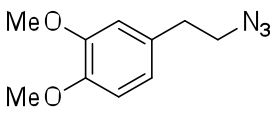




(^{1}H NMR, $CDCl_3$, 300 MHz)

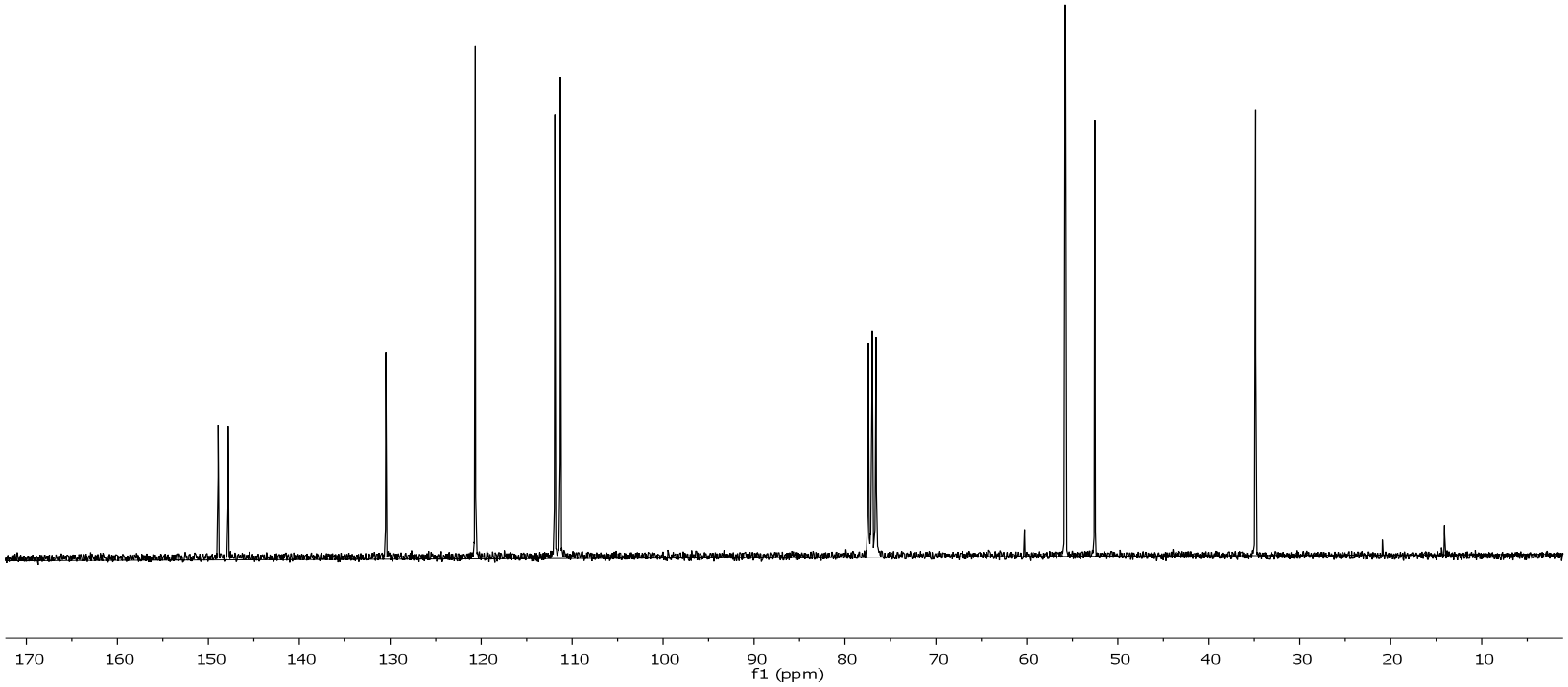
4d

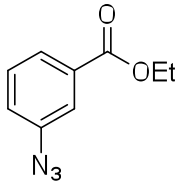




(^{1}H NMR, $CDCl_3$, 300 MHz)

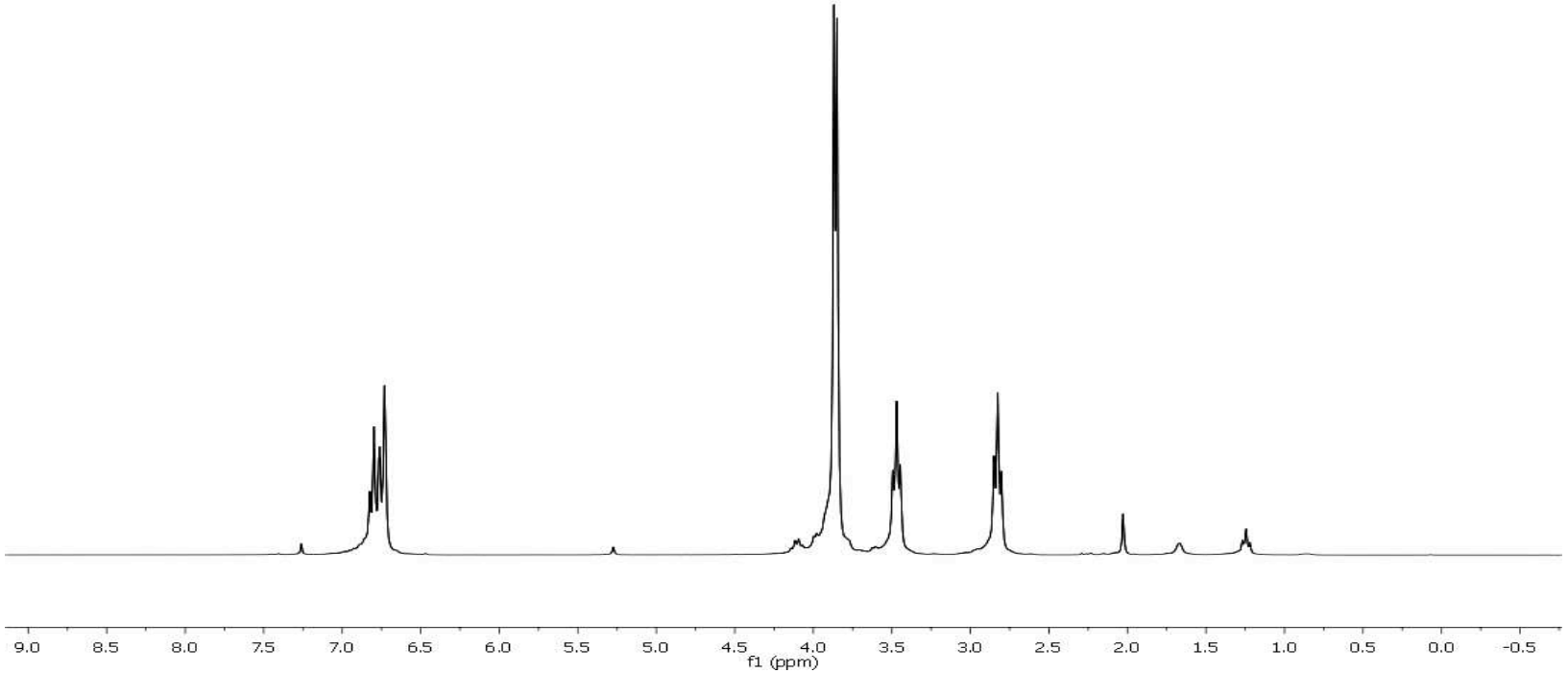
4 d

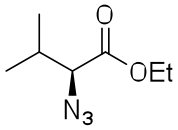




4e

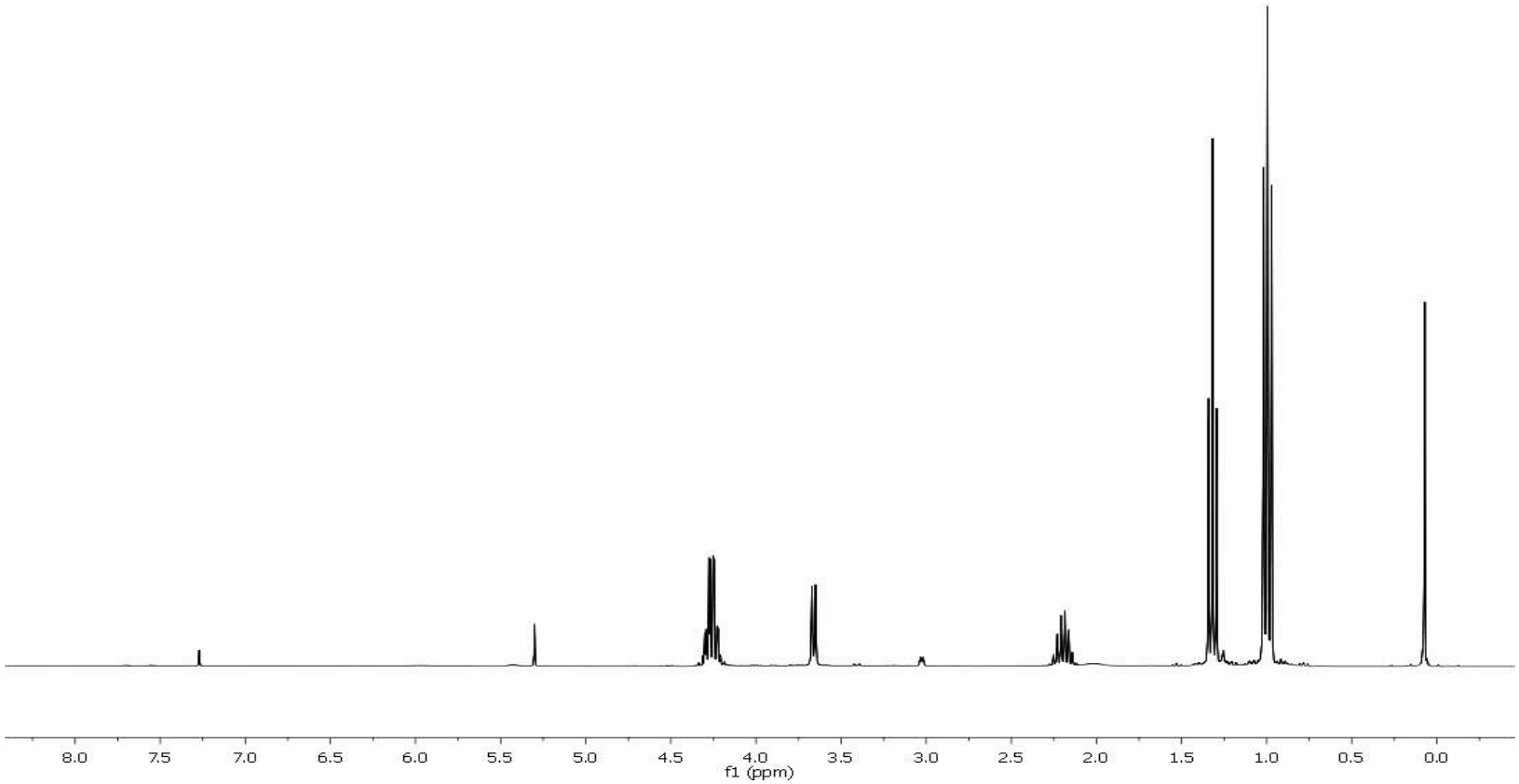
(^{1}H NMR, $CDCl_3$, 300 MHz)

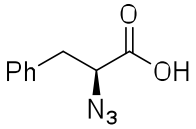




(^{1}H NMR, $CDCl_3$, 300 MHz)

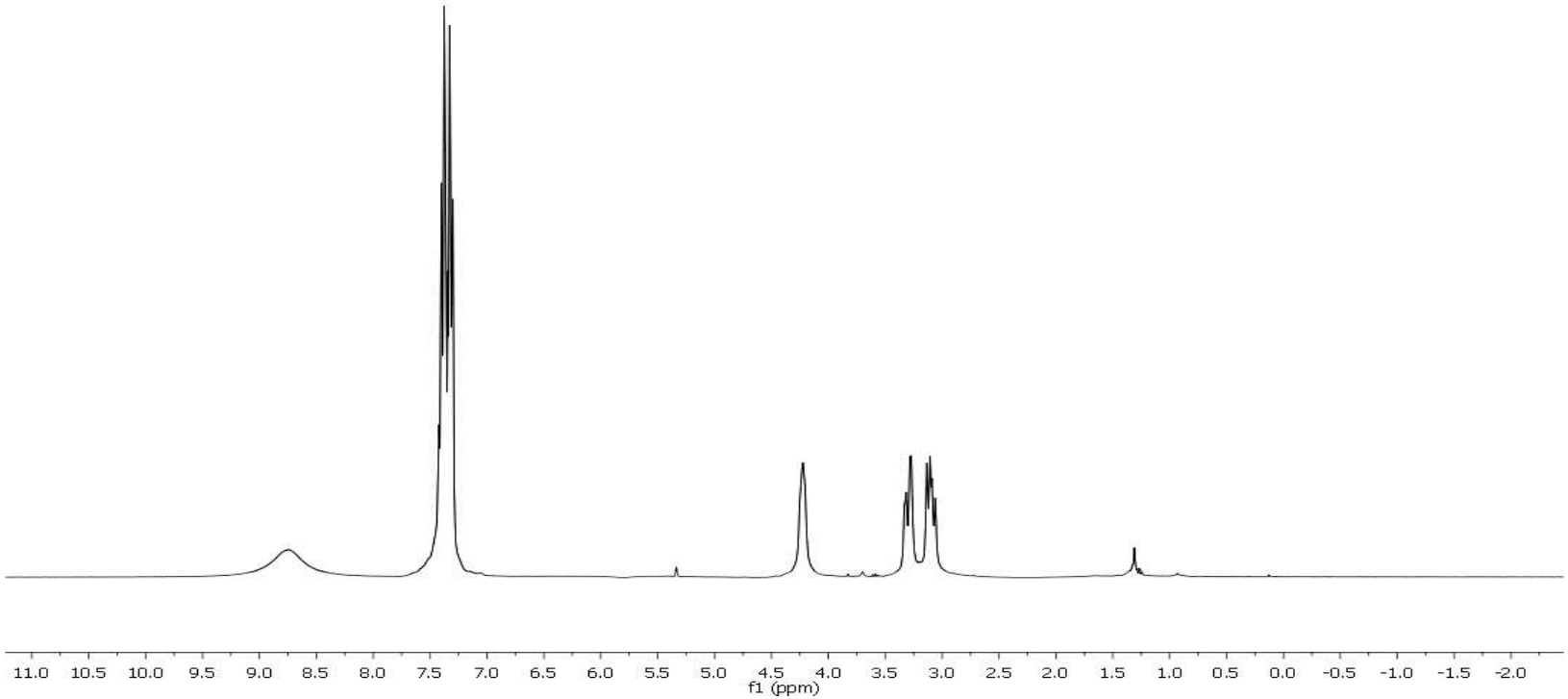
4f

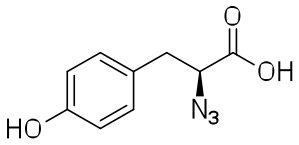




(^{1}H NMR, $CDCl_3$, 300 MHz)

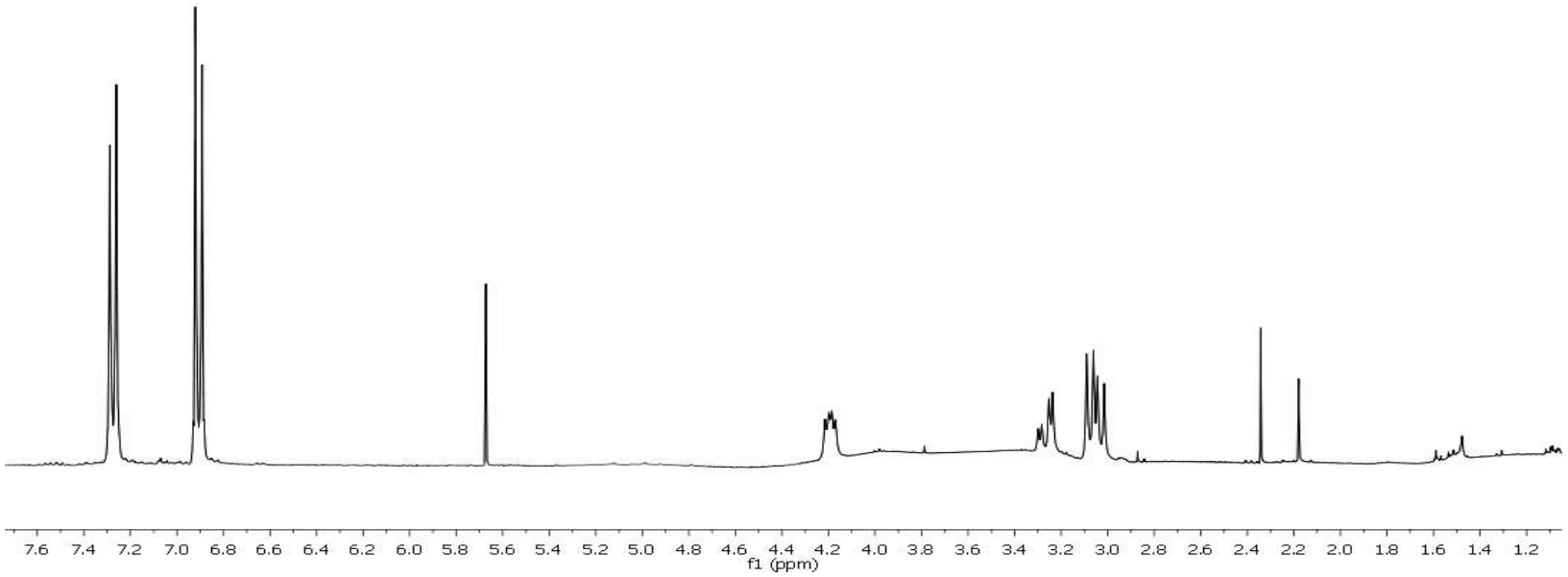
4g

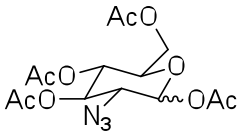




(¹H NMR, $CDCl_3$, 300 MHz)

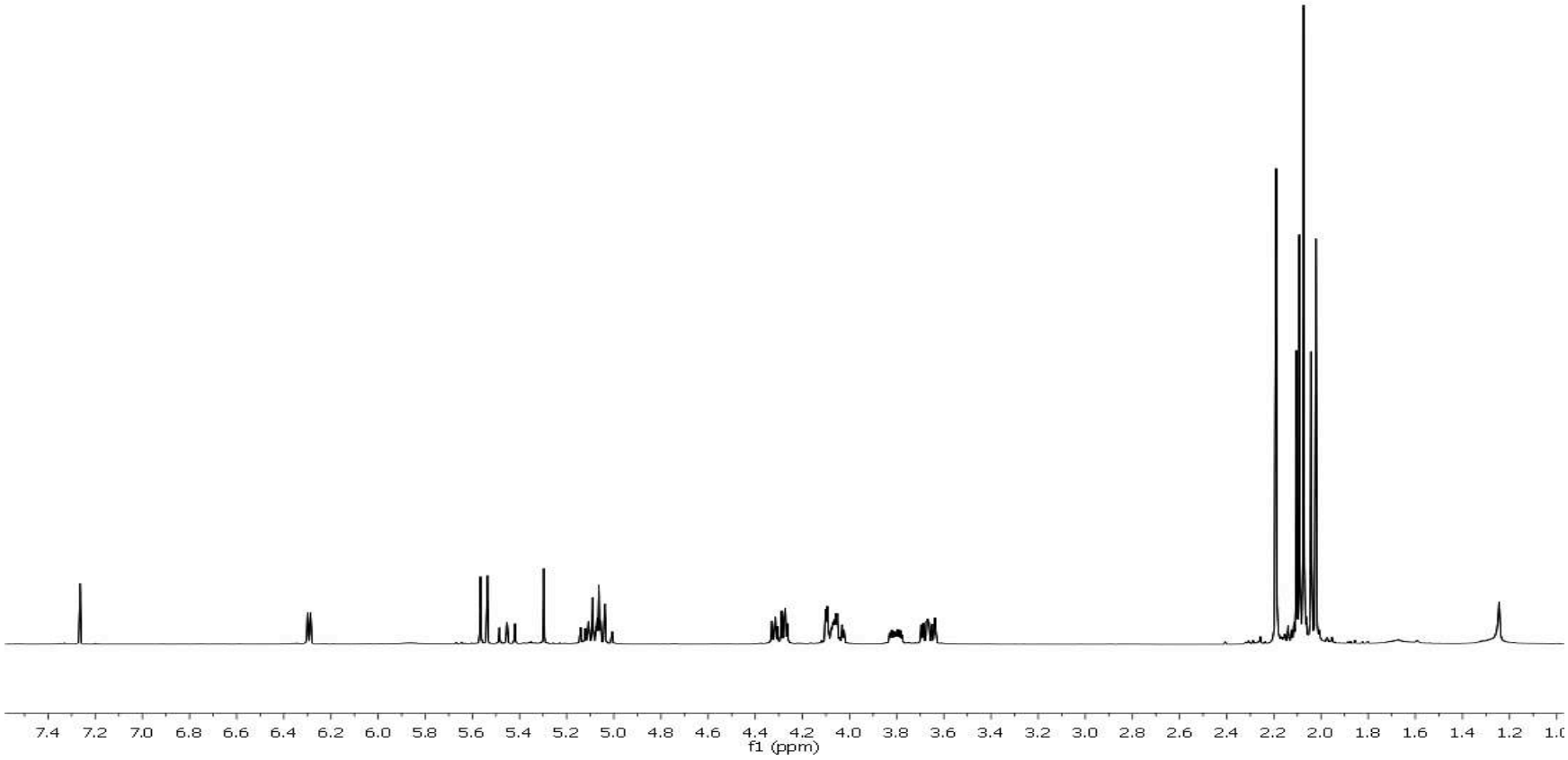
4h

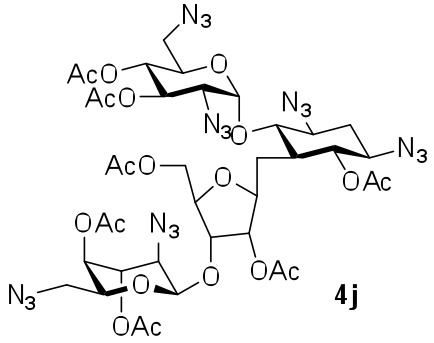




4i

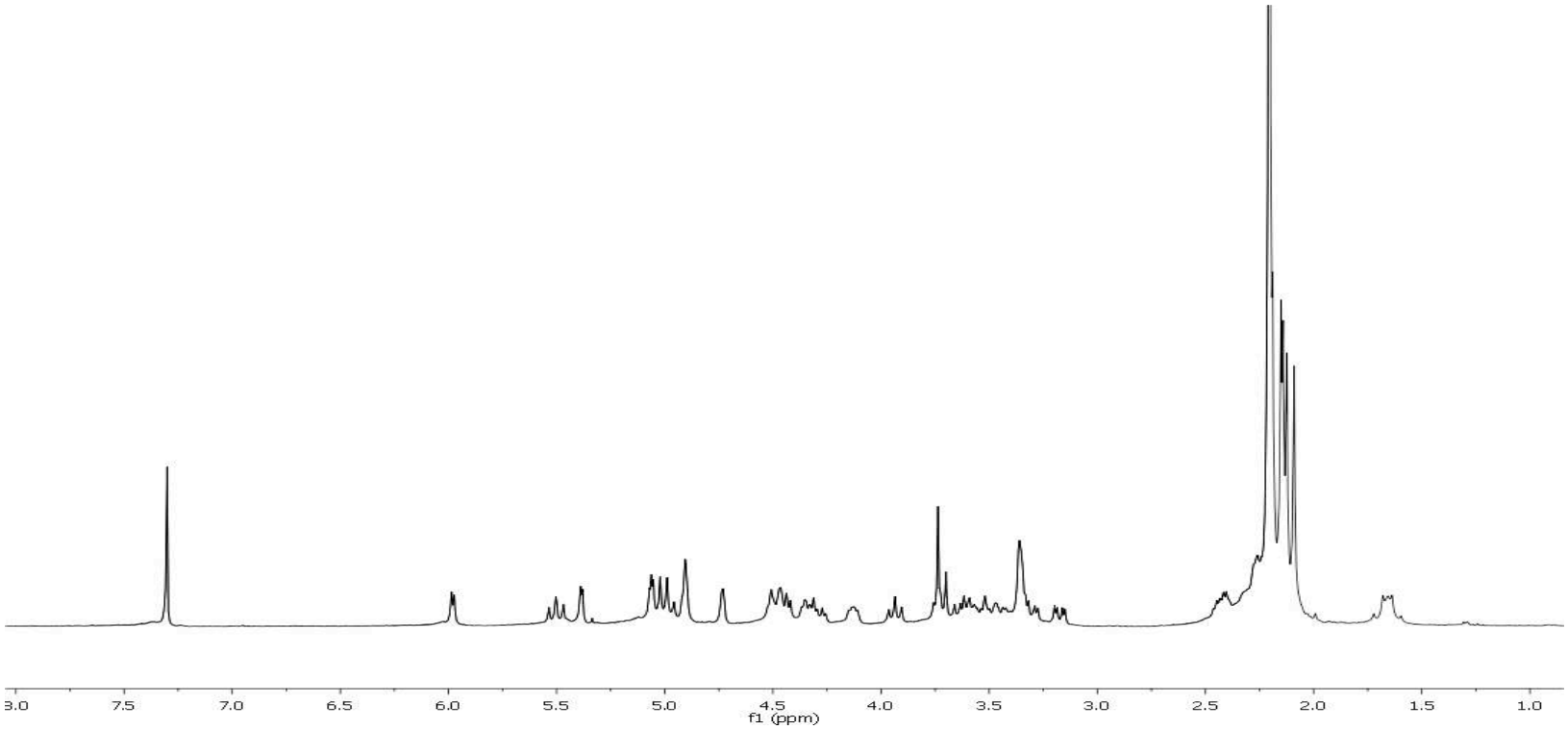
(^{1H} NMR, $CDCl_3$, 300 MHz)

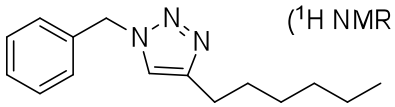




4j

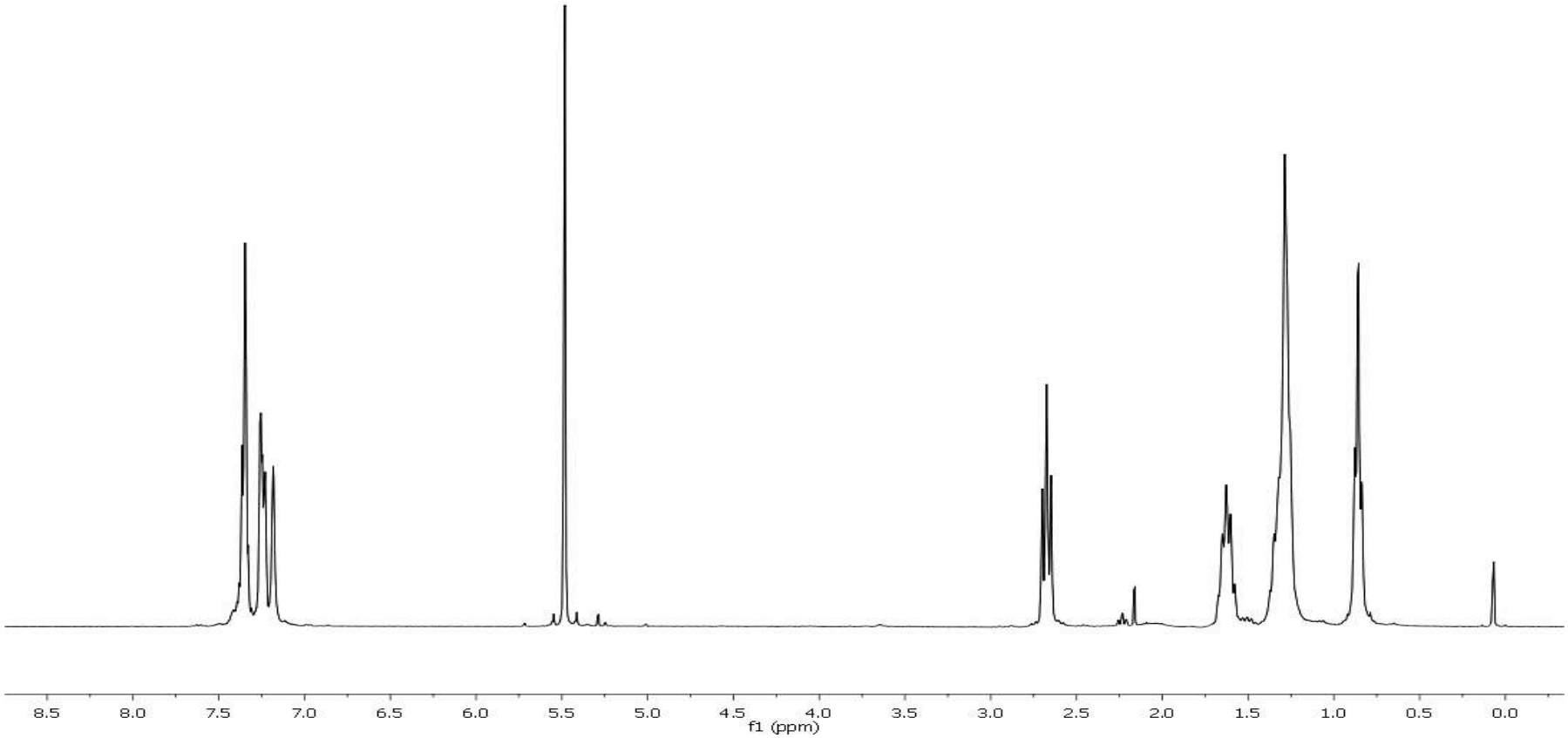
(^{1}H NMR, $CDCl_3$, 300 MHz)

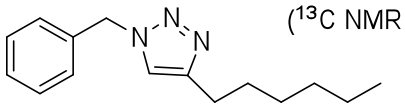




(^{1}H NMR, $CDCl_3$, 300 MHz)

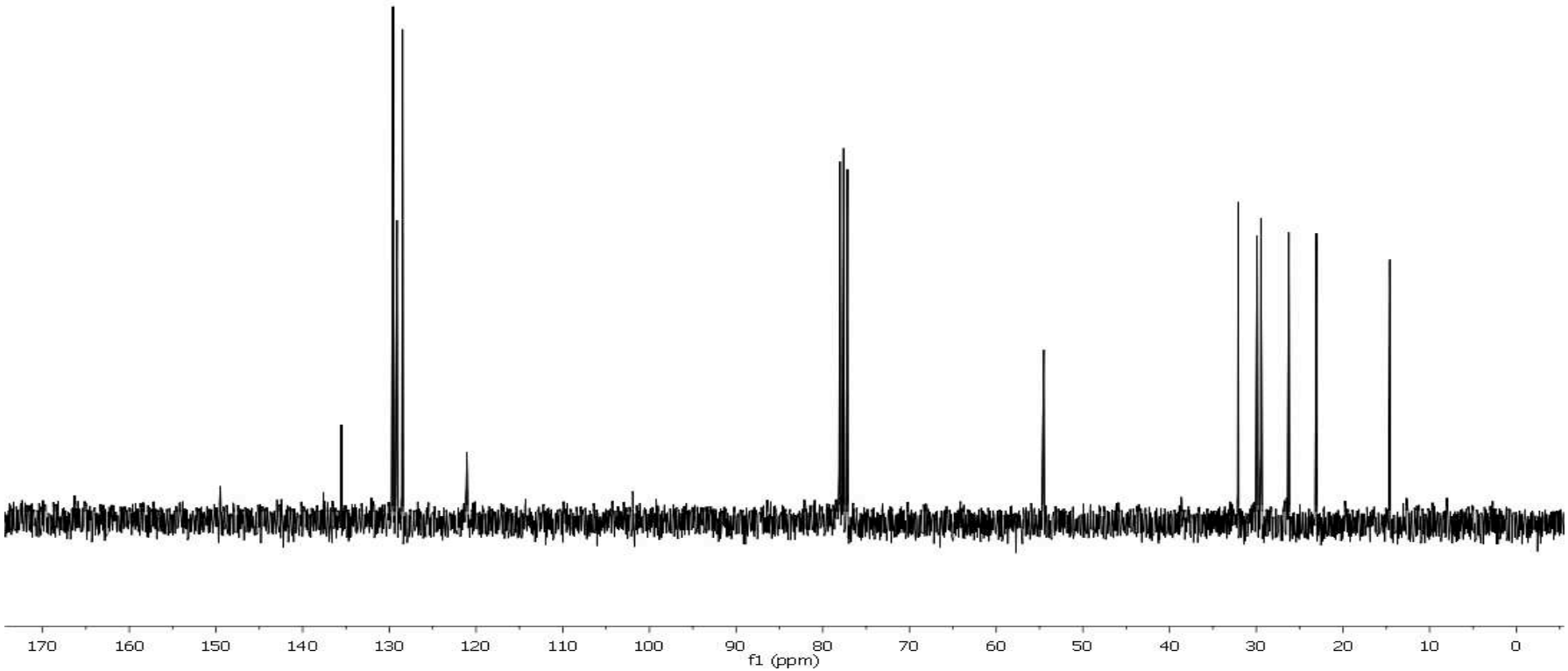
5

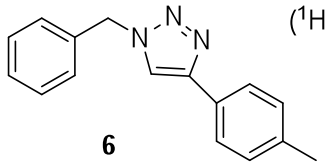




(^{13}C NMR, $CDCl_3$, 75 MHz)

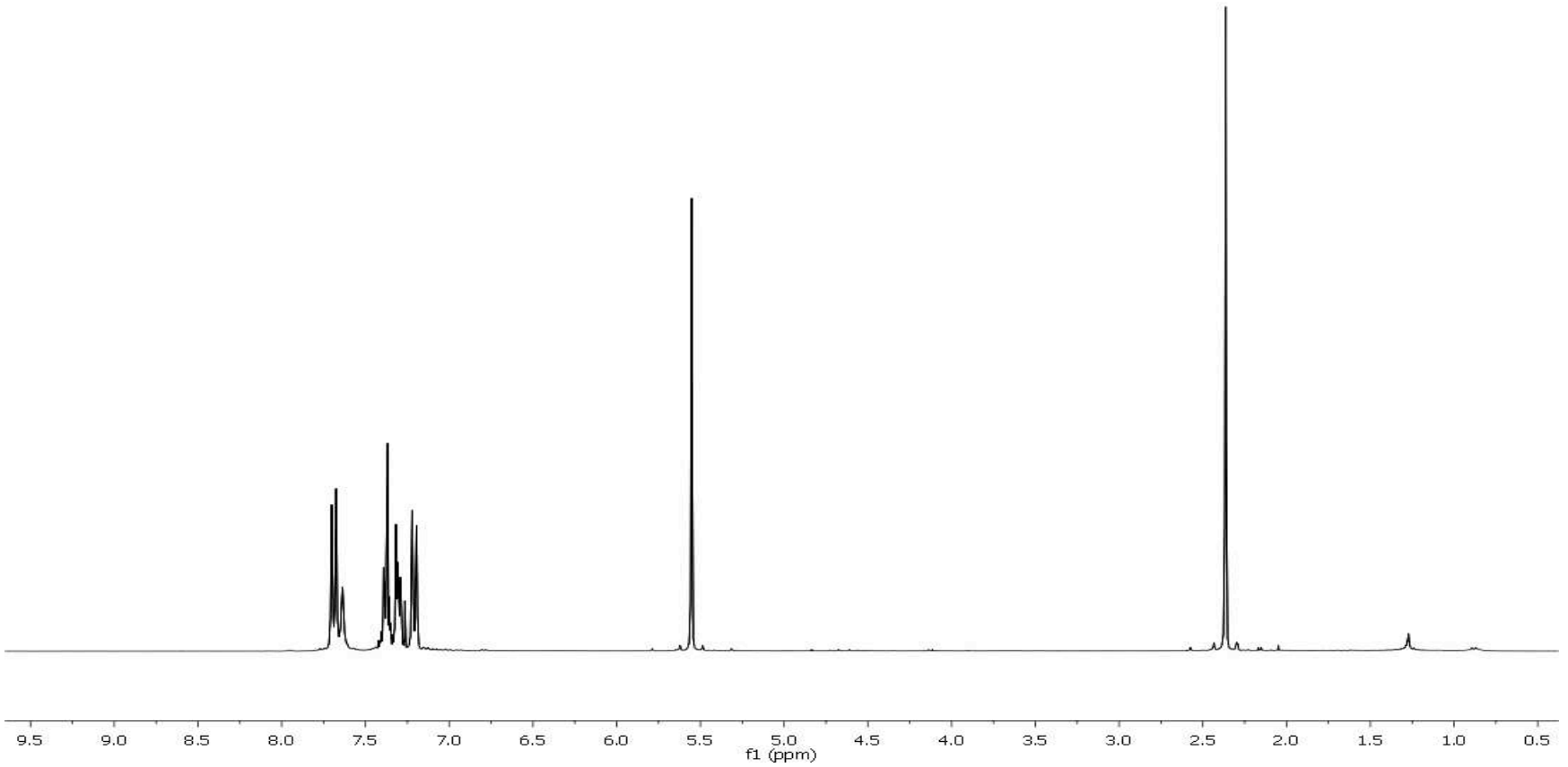
5

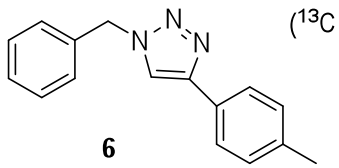




6

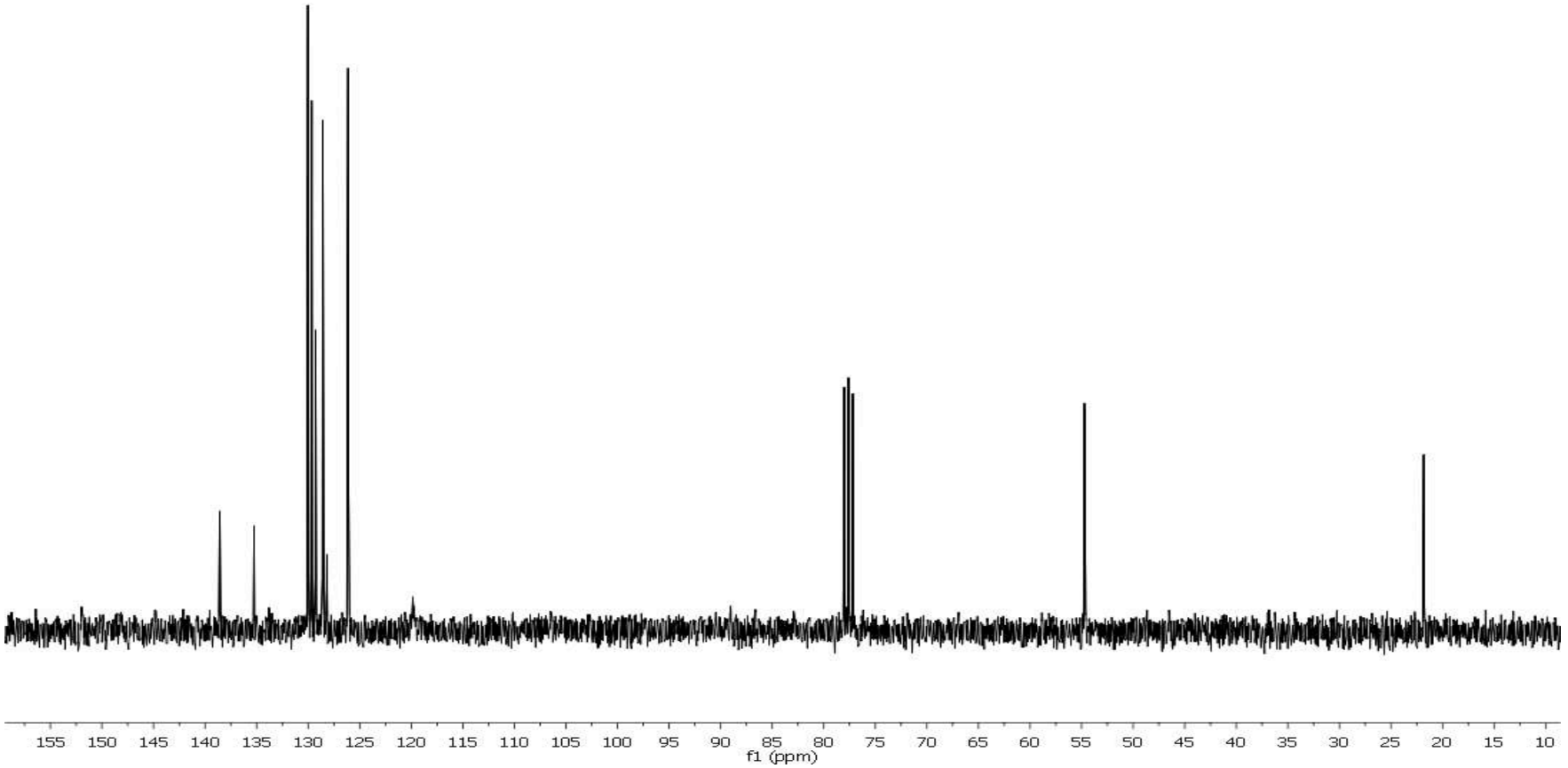
(^{1}H NMR, $CDCl_3$, 300 MHz)

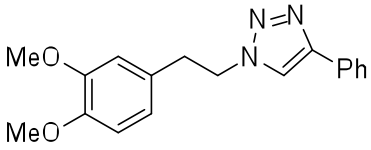




6

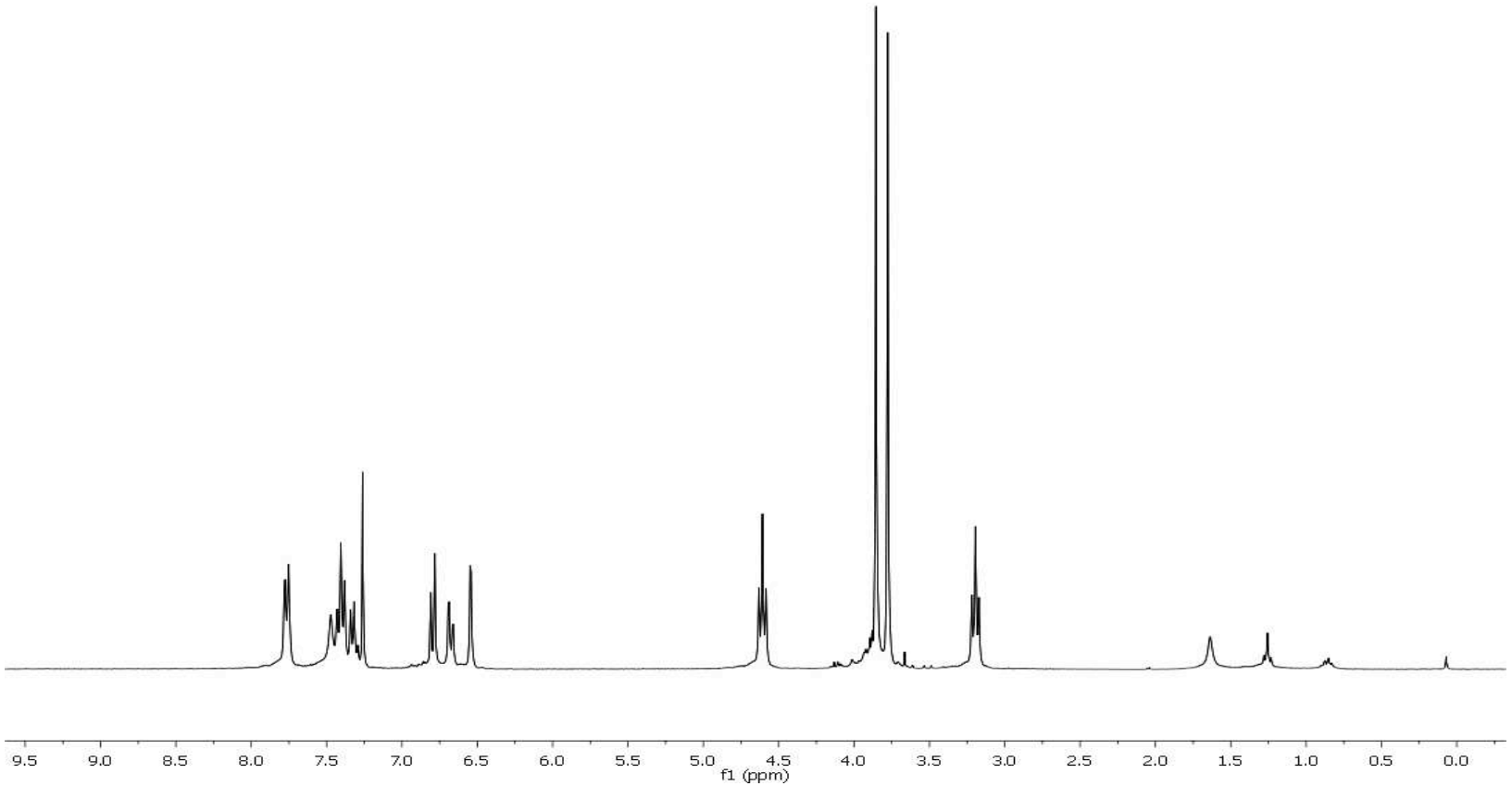
(^{13}C NMR, $CDCl_3$, 75 MHz)

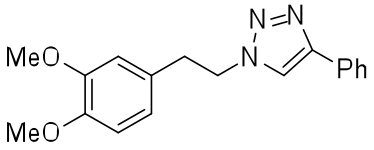




(¹H NMR, $CDCl_3$, 300 MHz)

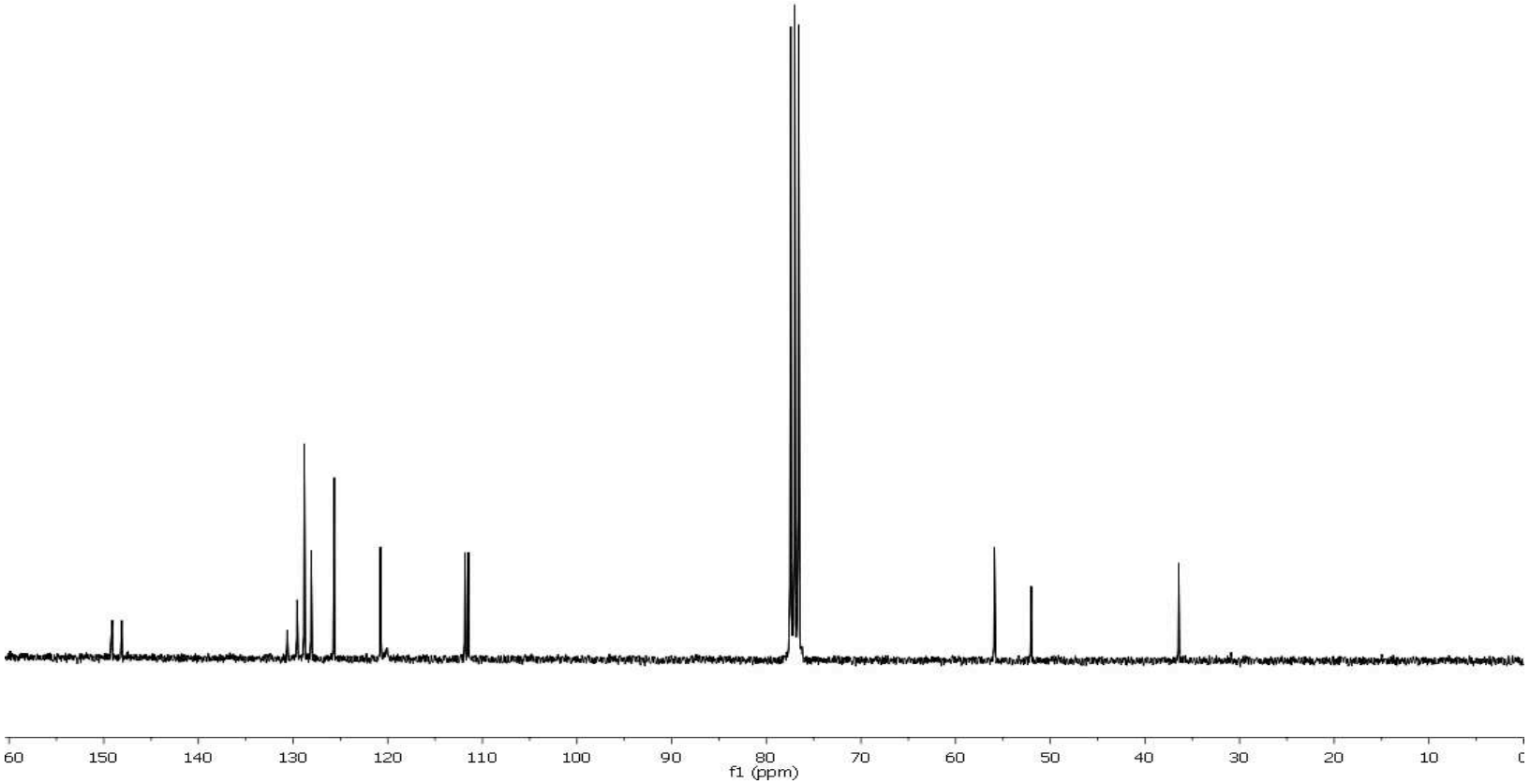
7

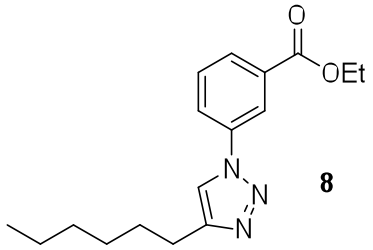




(^{13}C NMR, $CDCl_3$, 75 MHz)

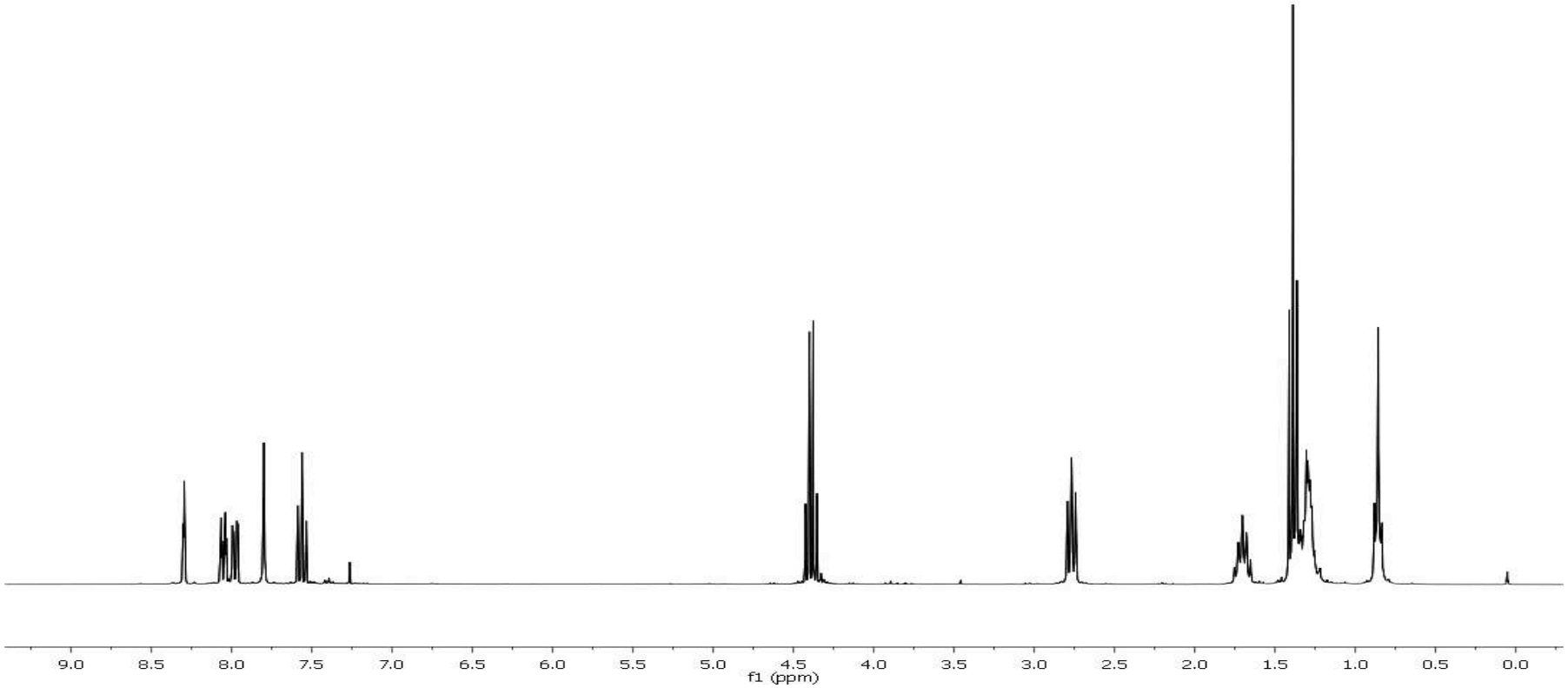
7

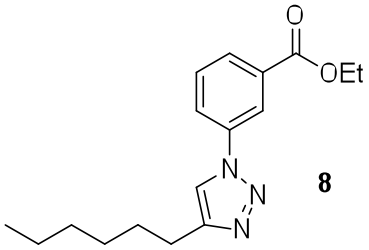




8

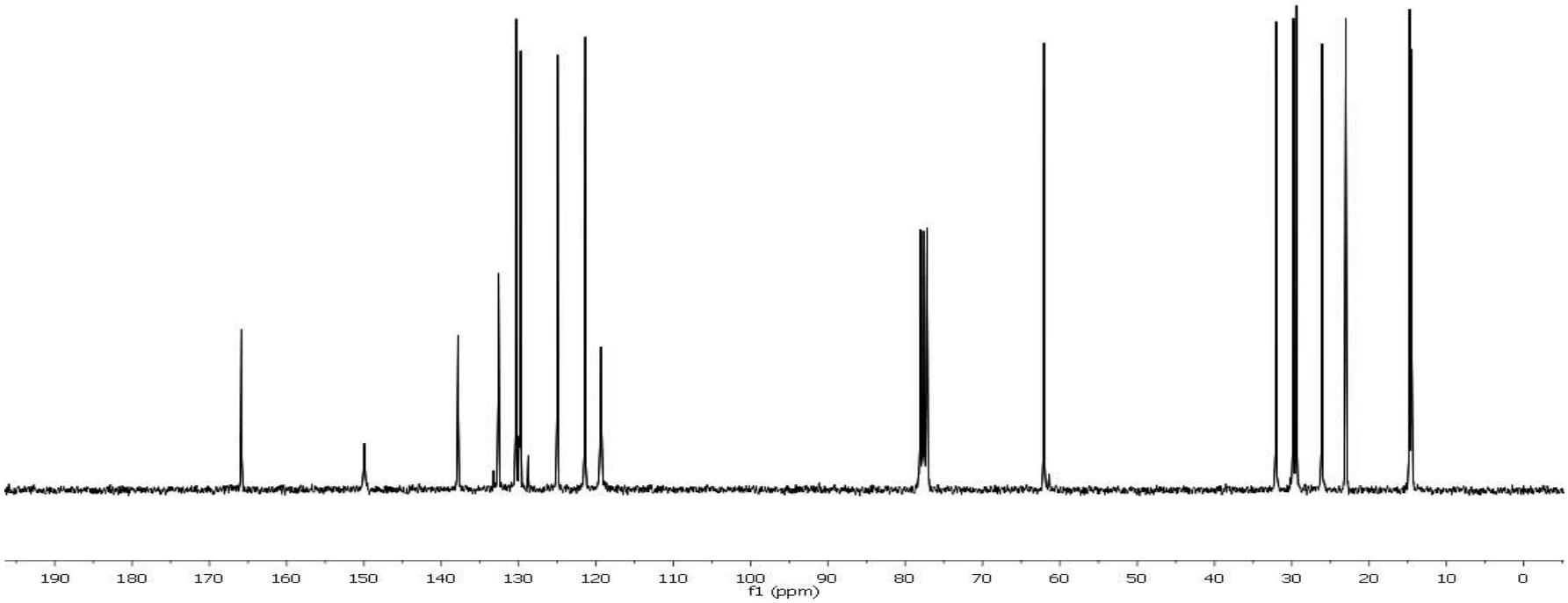
(^{1}H NMR, $CDCl_3$, 300 MHz)

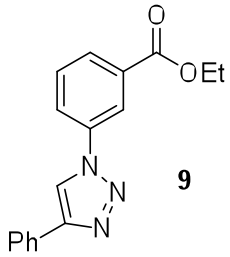




8

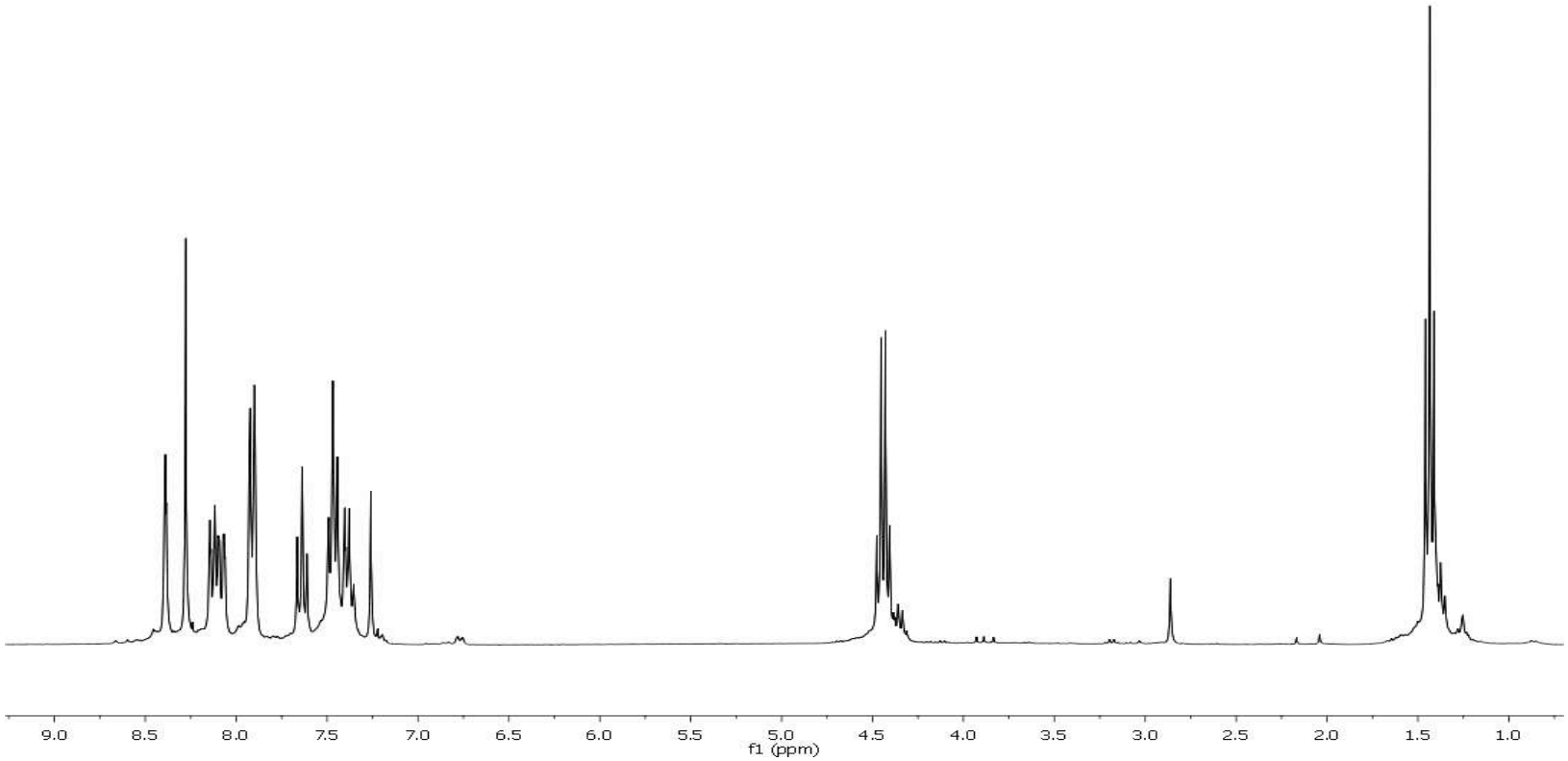
(^{13}C NMR, $CDCl_3$, 75 MHz)

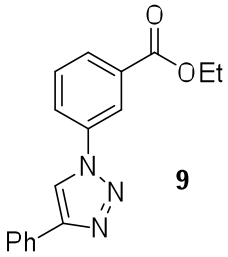




9

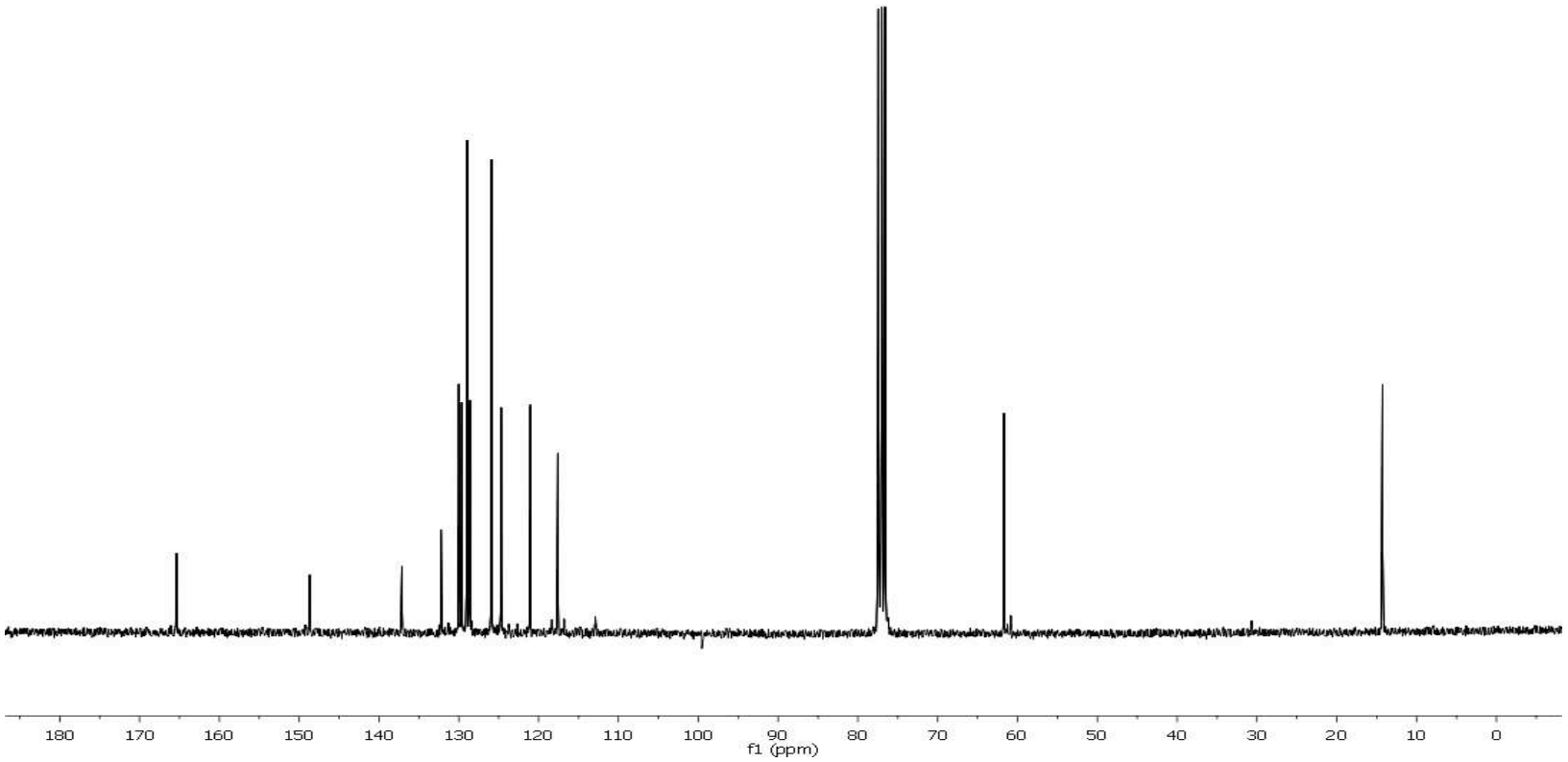
(^{1}H NMR, $CDCl_3$, 300 MHz)

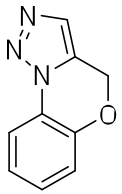




9

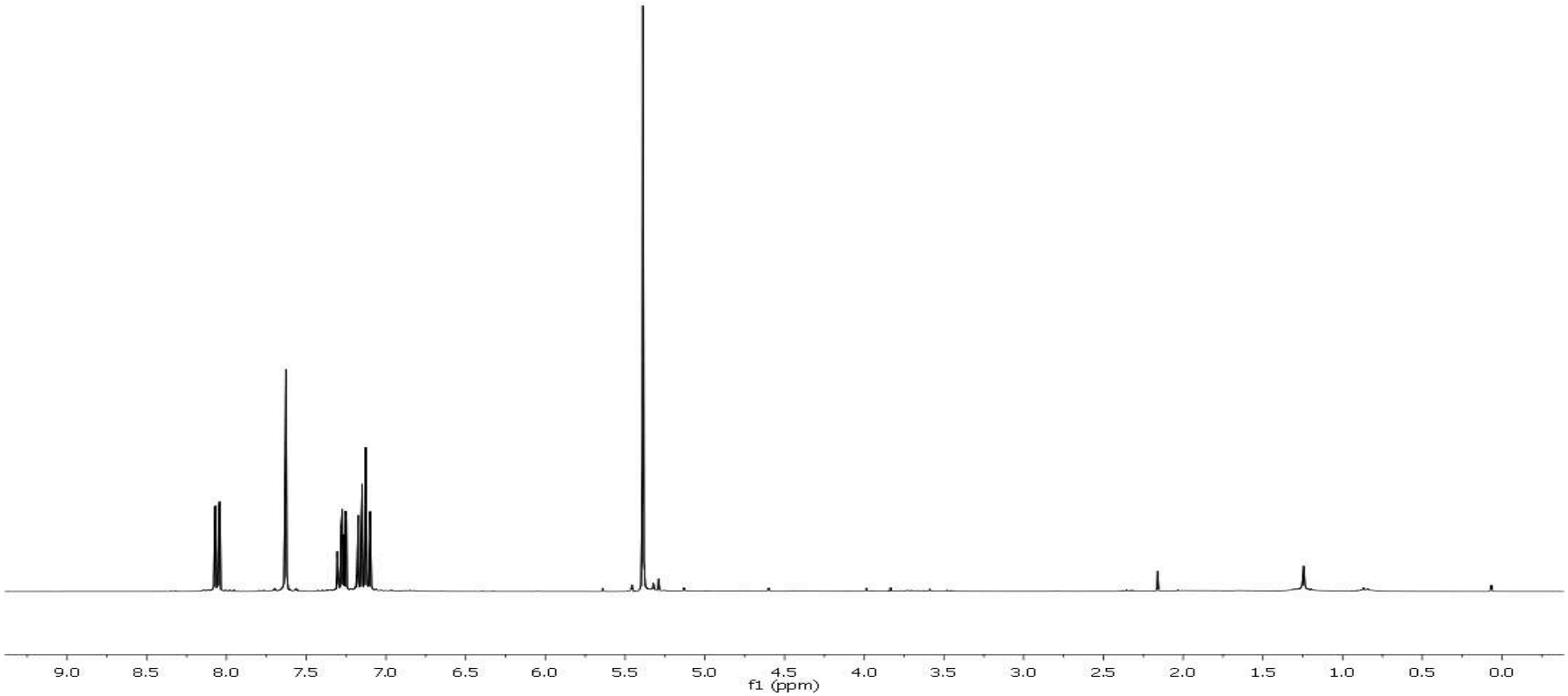
(^{13}C NMR, $CDCl_3$, 75 MHz)

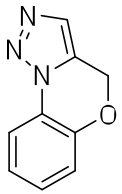




(^{1}H NMR, $CDCl_3$, 300 MHz)

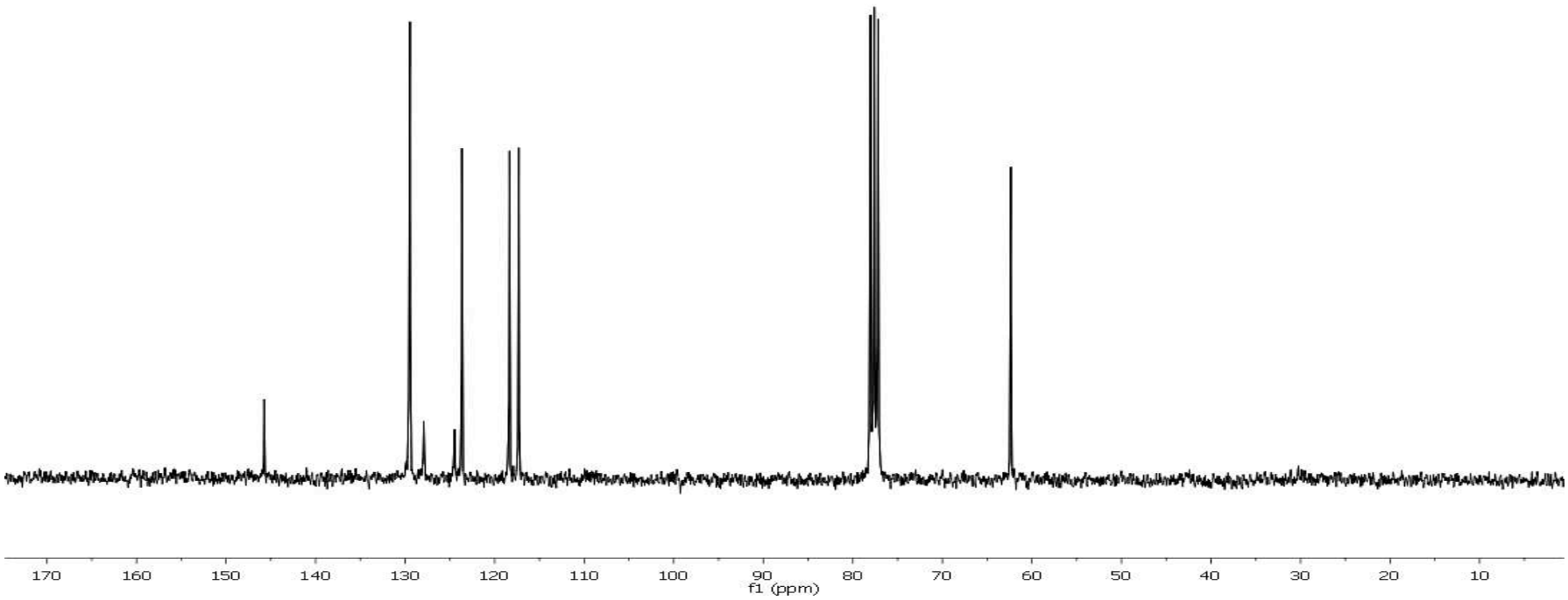
11a

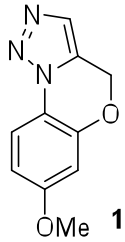




(^{13}C NMR, $CDCl_3$, 75 MHz)

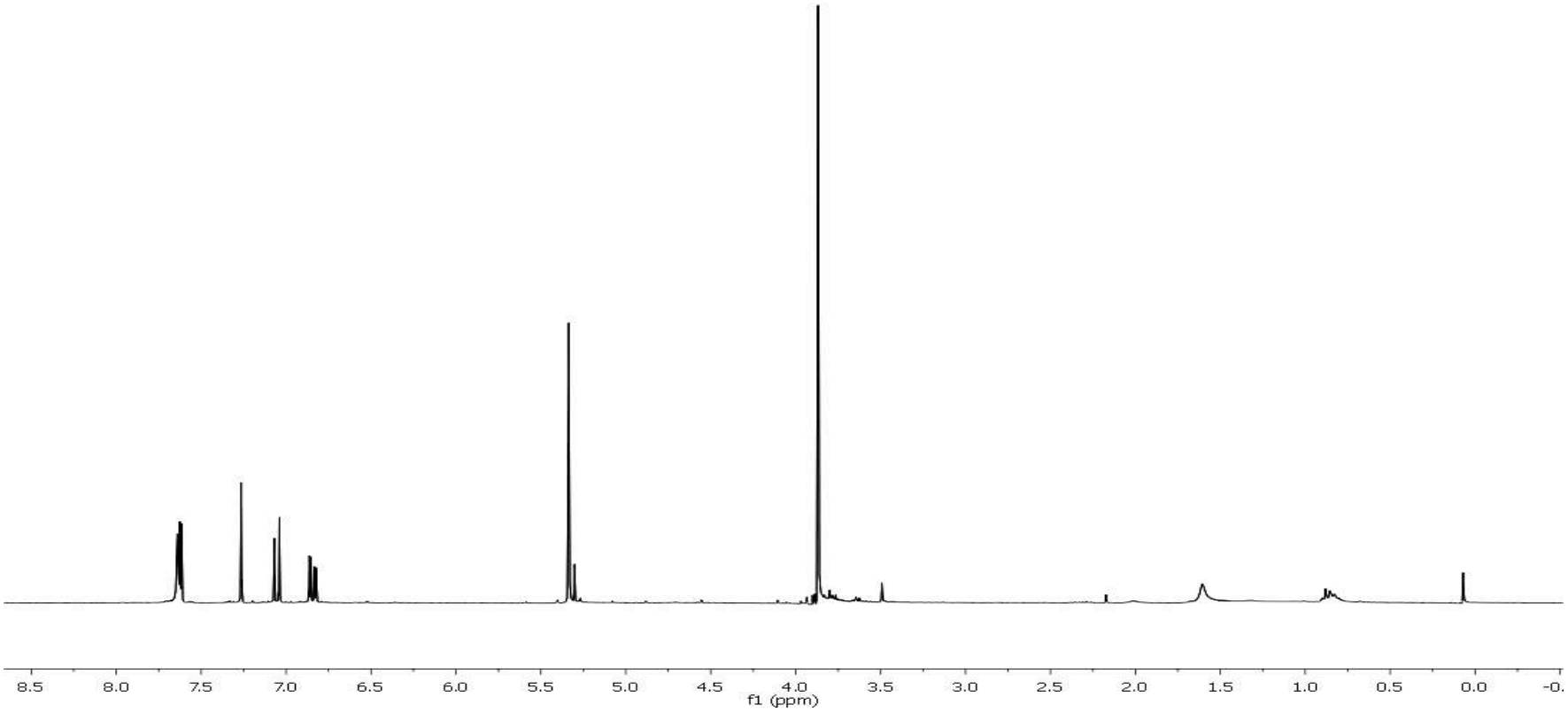
11a

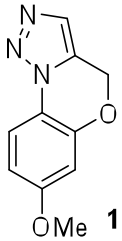




11b

(^{1}H NMR, $CDCl_3$, 300 MHz)





(^{13}C NMR, $CDCl_3$, 75 MHz)

11b