Electronic Supplementary Information

Nucleophilic transformations of carbonyl compounds via protection of azido group

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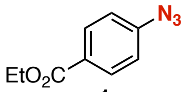
General Information

All reactions were performed with dry glassware under atmosphere of argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 1.05715. Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60, spherical, particle size 40–50 μm, Cat. No. 37562-85) by conventional manual method. Melting points (Mp) were measured on an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 MHz, or a Bruker AVANCE 400 spectrometer at 400 MHz. ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 126 MHz. All NMR measurements were carried out at 25 ºC. $CDCl_3$ (Kanto Chemical Co. Inc., Cat. No. 07663-23) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR in $CDCl_3$) or the solvent peak (δ 77.0 for ^{13}C NMR in $CDCl_3$) as an internal reference with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, br, and m signify singlet, doublet, triplet, quartet, broad, and multiplet, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1}. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^{+}) conditions.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Ethyl 4-azidobenzoate (**1a**),[S1] methyl 3-azido-4-methyl-2-thiophenecarboxylate (**1b**),[S2] methyl 3-azidoadamantane-1-carboxylate (**1f**),[S2] 2-azidobenzaldehyde (**7g**),[S3] 6-azidopropanal (**7h**),[S4] 5,6-didehydro-11,12-dihydrodibenzo[*a*,*e*]cyclooctene (**12**),[S5] methyl 3-azido-5-methylbenzoate,[S6] methyl 3-azido-5-(trifluoromethyl)benzoate,[S7] and methyl 3-azido-5-bromobenzoate[S6] were prepared according to the reported methods. Methyl 3-azido-5-methoxybenzoate (907 mg, 88%) was prepared from methyl 5-methoxybenzoate according to the reported method.[S6]

Structures of Azido-substituted Esters 1 and aldehydes 7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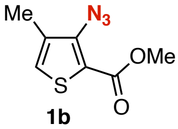
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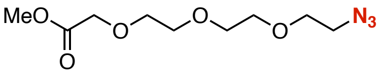
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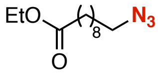
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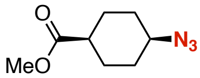
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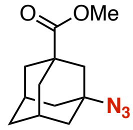
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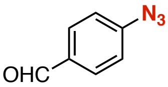
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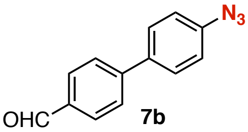
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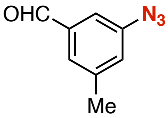
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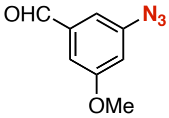
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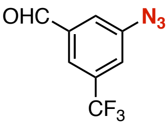
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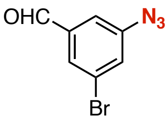
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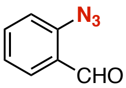
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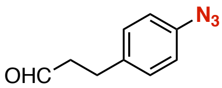
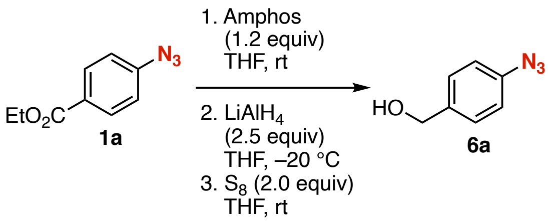

7h

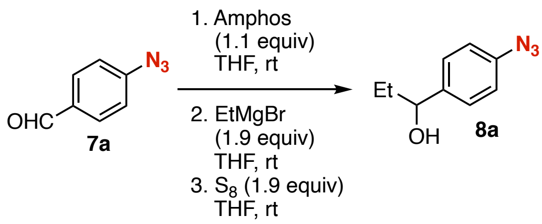
Experimental Procedures

*A typical procedure for LAH reduction of ester-substituted azides **6** through the phosphazide formation*



To a solution of 4-(ethoxycarbonyl)phenyl azide (**1a**) (37.9 mg, 0.198 mmol, 1.0 equiv) dissolved in THF (4.0 mL) was added di(*tert*-butyl)(4-(dimethylamino)phenyl)phosphine (Amphos) (63.7 mg, 0.240 mmol, 1.2 equiv) at room temperature. After stirring for 1 h at the same temperature, to this was added lithium aluminum hydride (18.5 mg, 0.487 mmol, 2.5 equiv) at –20 °C. After stirring for 4 h at the same temperature, to this was slowly added EtOAc (5 mL) and then aqueous saturated potassium sodium tartrate (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with brine (10 mL) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. To the residue dissolved in THF (2.0 mL) was added S_8 (12.9 mg, 0.400 mmol, 2.0 equiv) at room temperature. After stirring for 12 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 4-azidobenzyl alcohol (**6a**) (21.7 mg, 0.146 mmol, 74%) as a yellow solid.

*A typical procedure for the synthesis of azido-substituted alcohols **8***

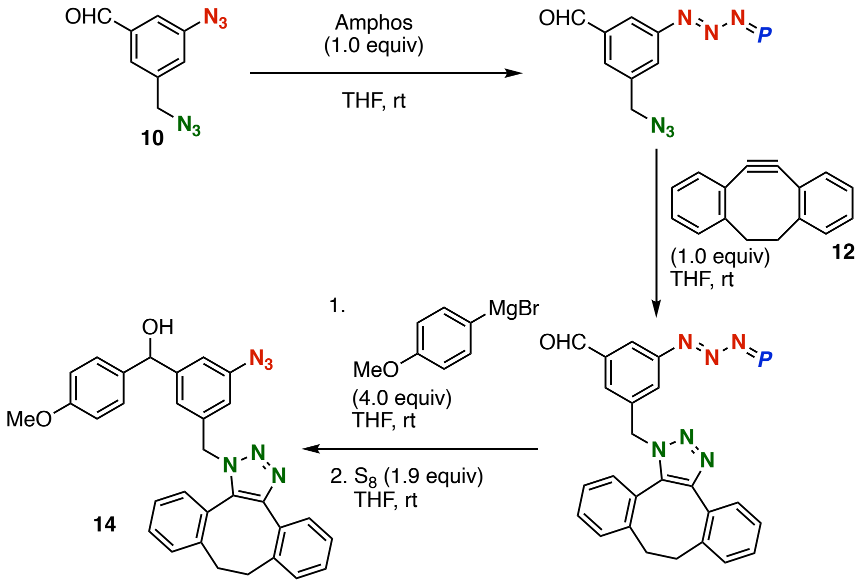


To a solution of 4-azidobenzaldehyde (**7a**) (30.0 mg, 0.212 mmol) dissolved in THF (4.0 mL) was added di(*tert*-butyl)(4-(dimethylamino)phenyl)phosphine (Amphos) (64.1 mg, 0.240 mmol, 1.1 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added ethylmagnesium bromide in THF (1.0 M, 0.407 mL, 0.41 mmol, 1.9 equiv). After stirring the mixture for 3 h at the same temperature, to the mixture was added aqueous ammonium chloride (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3), and washed with brine. The combined organic extract was dried (Na_2SO_4), and the mixture was concentrated under reduced pressure. The residue was dissolved in THF (2.0 mL) and to the solution was added S_8 (12.8 mg, 0.400 mmol, 1.9 equiv) at room temperature. After stirring for 24 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 3/1) to give 4-azidophenyl-1-propanol (**8a**) (30.2 mg, 0.170 mmol, 80%) as a brown oil.

*A procedure for the synthesis of azido-substituted alcohol **8a** at 1 mmol scale*

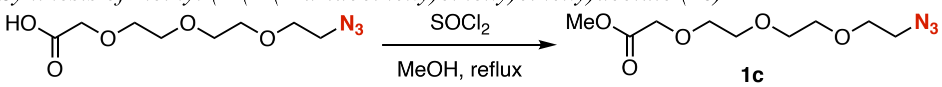
To a solution of 4-azidobenzaldehyde (**7a**) (148 mg, 1.01 mmol) dissolved in THF (20 mL) was added di(*tert*-butyl)(4-(dimethylamino)phenyl)phosphine (Amphos) (320 mg, 1.21 mmol, 1.2 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added ethylmagnesium bromide in THF (1.0 M, 2.0 mL, 2.00 mmol, 2.0 equiv). After stirring the mixture for 3 h at the same temperature, to the mixture was added aqueous ammonium chloride (30 mL). The mixture was extracted with CH_2Cl_2 (20 mL × 3), and washed with brine. The combined organic extract was dried (Na_2SO_4), and the mixture was concentrated under reduced pressure. The residue was dissolved in THF (10 mL) and to the solution was added S_8 (64.5 mg, 2.02 mmol, 2.0 equiv) at room temperature. After stirring for 24 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 15 g, *n*-hexane/EtOAc = 9/1 to 5/1) to give 4-azidophenyl-1-propanol (**8a**) (146 mg, 0.824 mmol, 82%) as brown oil.

*A procedure for the synthesis of (3-azido-5-((8,9-dihydro-1H-dibenzo[3,4:7,8]cycloocta[1,2-d][1,2,3]triazol-1-yl)methyl)phenyl)(4-methoxyphenyl)methanol (**13**)*



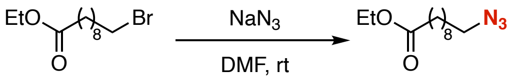
To a solution of 3-azido-5-(azidomethyl)benzaldehyde (**10**) (10.5 mg, 52.0 μmol) dissolved in THF (1.0 mL) was added di(*tert*-butyl)(4-(dimethylamino)phenyl)phosphine (Amphos) (13.8 mg, 52.0 μmol, 1.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added 5,6-didehydro-11,12-dihydrodibenzo[*a*,*e*]cyclooctene (**12**) (10.7 mg, 52.5 μmol, 1.0 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added 4-methoxyphenylmagnesium bromide in THF (1.11 M, 0.190 mL, 0.211 mmol, 4.0 equiv). After stirring the mixture for 3 h at room temperature, to the mixture was added aqueous ammonium chloride (5 mL). The mixture was extracted with CH_2Cl_2 (5 mL × 3), and washed with brine. The combined organic extract was dried (Na_2SO_4), and the mixture was concentrated under reduced pressure. The residue was dissolved in THF (1.0 mL) and to the solution was added S_8 (3.3 mg, 0.10 mmol, 1.9 equiv) at room temperature. After stirring for 24 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/1) to give (3-azido-5-((8,9-dihydro-1*H*-dibenzo[3,4:7,8]cycloocta[1,2-*d*][1,2,3]triazol-1-yl)methyl)phenyl)(4-methoxyphenyl)methanol (**14**) (22.7 mg, 44.1 μmol, 85%) as a yellow oil.

*Synthesis of methyl (2-(2-(2-azidoethoxy)ethoxy)ethoxy)acetate (**1c**)*



To a solution of (2-(2-(2-azidoethoxy)ethoxy)ethoxy)acetatic acid (2.00 g, 8.58 mmol) dissolved in methanol (60 mL) was added thionyl chloride (1.50 mL, 20.7 mmol, 2.4 equiv) at 0 °C. After stirring for 13 h at reflux (oil bath, bath temp.: 90 °C), the resulting mixture was concentrated under reduced pressure. Then, to the mixture was added water (50 mL). The mixture was extracted with EtOAc (30 mL × 3), and washed with saturated aqueous sodium bicarbonate (10 mL). The combined organic extract was dried (Na_2SO_4), and the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 40 g, *n*-hexane/EtOAc = 1/2) to give methyl (2-(2-(2-azidoethoxy)ethoxy)ethoxy)acetate (**1c**) (1.52 g, 6.13 mmol, 71%) as a colorless oil.

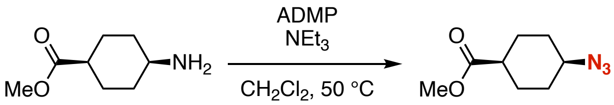
*Synthesis of ethyl 10-azidodecanoate (**1d**)*



1d

To a solution of ethyl 10-bromodecanoate (2.10 g, 7.54 mmol) dissolved in DMF (18.8 mL) was added sodium azide (1.47 g, 22.6 mmol, 3.0 equiv) at 0 °C. After stirring for 4 days at room temperature, to the mixture was added water (50 mL). The mixture was extracted with diethyl ether (30 mL × 3), and washed with water (10 mL × 3). The combined organic extract was dried (Na_2SO_4), and the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 40 g, *n*-hexane/EtOAc = 10/1) to give ethyl 10-azidodecanoate (**1d**) (1.78 g, 7.38 mmol, 96%) as a colorless oil.

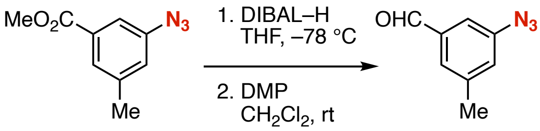
*Synthesis of cis-4-(methoxycarbonyl)cyclohexy azide (**1e**)*



1e

To a solution of *cis*-4-(methoxycarbonyl)cyclohexyamine (2.50 g, 12.9 mmol) and triethylamine (6.54 g, 64.5 mmol, 5.0 equiv) dissolved in dichloromethane (26 mL) was added a solution of 2-azido-1,3-dimethylimidazolinium hexafluorophosphate (ADMP) (4.23 g, 14.8 mmol, 1.2 equiv) dissolved in dichloromethane (26 mL) at room temperature. After stirring for 4 h at 50 °C (oil bath), to the mixture was added saturated aqueous sodium bicarbonate (20 mL). The mixture was extracted with dichloromethane (20 mL × 3), and washed with brine (10 mL). The combined organic extract was dried (Na_2SO_4), and the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 50 g, *n*-hexane/EtOAc = 1/1) to give *cis*-4-(methoxycarbonyl)cyclohexy azide (**1e**) (1.94 g, 10.6 mmol, 82%) as a colorless oil.

A typical procedure for the synthesis of azido-substituted aldehydes 7



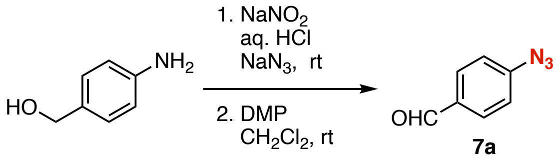
7c

To a solution of methyl 3-azido-5-methylbenzoate (855 mg, 4.47 mmol) dissolved in THF (18 mL) was added diisobutylaluminum hydride (1.03 M, hexane solution, 17.4 mL, 17.8 mmol, 4.0 equiv) at –78 °C. After stirring for 3 h at the same temperature, to the mixture was added ethylmagnesium bromide in THF (1.0 M, 0.407 mL, 0.41 mmol, 1.9 equiv). After stirring the mixture for 3 h at the same temperature, to the mixture was slowly added water (20 mL) and an aqueous hydrogen chloride (1 M) (40 mL). The mixture was extracted with EtOAc (30 mL × 3), and washed with brine. The combined organic extract was dried (Na_2SO_4), and the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 15 g, *n*-hexane/EtOAc = 4/1) to give 3-azido-5-methylbenzyl alcohol (645 mg, 3.95 mmol, 88%) as a yellow solid.

To a solution of 3-azido-5-methylbenzyl alcohol (645 mg, 3.95 mmol) dissolved in THF (10 mL) was added Dess–Martin periodinane (DMP) (2.28 g, 5.36 mmol, 1.2 equiv) at room temperature. After stirring for 3 h at the same temperature, the resulting mixture was filtered through a pad of silica-gel. The mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 30 g, *n*-hexane/EtOAc = 10/1) to give 3-azido-5-methylbenzaldehyde (**7c**) (536 mg, 3.33 mmol, <84%) as a yellow solid with a small amount of impurity. To remove a small amount of impurity, further purification was carried out by recycling preparative HPLC system (JAI, LC-9210) equipped with a refractive index detector and JAIGEL-1H and 2H columns (GPC) using $CHCl_3$ as an eluent, which provided 3-azido-5-methylbenzaldehyde (**7c**) (365 mg, 2.27 mmol, 57%) as a yellow solid.

According to the procedure for preparing 3-azido-5-methylbenzaldehyde (**7c**), 3-azido-5-methoxybenzaldehyde (**7d**) (249 mg, 86% (2 steps)), 3-azido-5-(trifluoromethyl)benzaldehyde (**7e**) (241 mg, 49% (2 steps)), and 3-azido-5-bromobenzaldehyde (**7f**) (264 mg, 83% (2 steps)) were prepared from the corresponding esters.

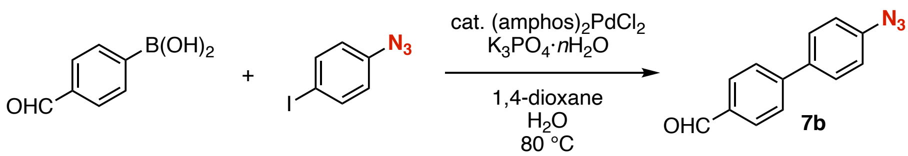
*Synthesis of 4-azidobenzaldehyde (**7a**)*



To a solution of 4-aminobenzyl alcohol (2.09 g, 17.0 mmol) dissolved in aqueous hydrochloric acid (5 M, 10 mL) was slowly added $NaNO_2$ (1.68 g, 1.5 equiv) dissolved in water (40 mL) at 0 °C. Then, to the mixture was added NaN_3 (4.20 g, 64.6 mmol, 3.8 equiv) at 0 °C. After stirring the mixture for 11 h at room temperature, to the mixture was added saturated aqueous sodium bicarbonate (20 mL). The mixture was extracted with EtOAc (30 mL × 3), and washed with brine. The combined organic extract was dried (Na_2SO_4), and the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 50 g, *n*-hexane/EtOAc = 1/1) to give 4-azidobenzyl alcohol (2.12 g, 14.2 mmol, 84%) as a yellow oil.

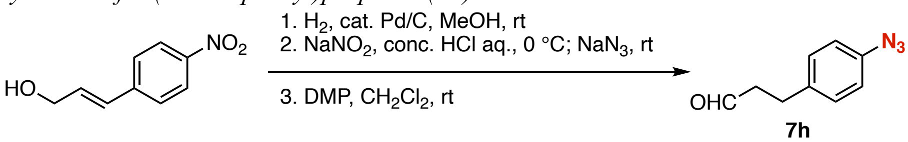
To a solution of 4-azidobenzyl alcohol (986 mg, 6.61 mmol) dissolved in dichloromethane (10 mL) was added Dess–Martin periodinane (DMP) (2.58 g, 6.09 mmol, 1.2 equiv) at room temperature. After stirring for 6 h at the same temperature, the resulting mixture was filtered through a pad of silica-gel. The mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 10 g, *n*-hexane/EtOAc = 1/1) to give 3-azido-5-methylbenzaldehyde (**7c**) (694 mg, 4.72 mmol, 71%) as a yellow oil.

*Synthesis of 4-(4-azidophenyl)benzaldehyde (**7b**)*



To a mixture of 4-formylphenylboronic acid (55.8 mg, 0.372 mmol, 1.2 equiv), 4-iodophenyl azide (75.6 mg, 0.309 mmol), potassium phosphate n-hydrate (131 mg, ca. 0.62 mmol, ca. 2.0 equiv), and bis(di(tert-butyl)(4-(dimethylamino)phenyl)phosphine)palladium dichloride (11.6 mg, 15.3 μmol, 5.0 mol %) were added 1,4-dioxane (3.0 mL) and water (0.30 mL) at room temperature. After stirring for 25 h at 80 °C (oil bath), to the mixture was added water (3 mL). The mixture was extracted with EtOAc (10 mL × 3), and washed with brine. The combined organic extract was dried (Na_2SO_4), and the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 9/1) to give 4-(4-azidophenyl)benzaldehyde (**7b**) (28.7 mg, 0.129 mmol, 42%) as a yellow solid.

*Synthesis of 3-(4-azidophenyl)propanal (**7h**)*



To a solution of 4-nitrocynnamyl alcohol (181 mg, 1.01 mmol) in methanol was added Pd/C (10 wt%, 55.6 mg, 5 mol %) at room temperature. Then, hydrogen (1 atm) was filled into the reaction flask. After stirring for 15 h at the same temperature, hydrogen gas was removed under reduced pressure and argon was filled. The reaction mixture was filtered with Celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 4 g, *n*-hexane/EtOAc = 1/1 to 1/2) to give 3-(4-aminophenyl)propanol (110 mg, 0.728 mmol, 72%) as a pale brown oil.

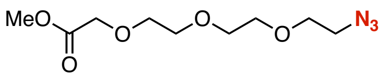
To a mixture of 3-(4-aminophenyl)propanol (110 mg, 0.728 mmol) and water (3.0 mL) was added conc. HCl (12M, 0.30 mL, 3.6 mmol, 5.0 equiv) at 0 °C. Then, to the mixture was added $NaNO_2$ (50.2 mg, 0.727 mmol, 1.0 equiv) dissolved in water (1.0 mL) at the same temperature. After stirring 10 min at the same temperature, to the mixture was added NaN_3 (56.7 mg, 0.872 mmol, 1.2 equiv) at the same temperature. After stirring 1.5 h at room temperature, the mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was dried with Na_2SO_4. The mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 4 g, *n*-hexane/EtOAc = 3/2) to give 3-(4-azidophenyl)propanol (121 mg, 0.682 mmol, 94%) as a pale brown oil.

To a solution of 3-(4-azidophenyl)propanol (116 mg, 0.651 mmol) in dichloromethane (2.0 mL) was added was added Dess–Martin periodinane (DMP) (332 mg, 0.782 mmol, 1.2 equiv) at room temperature. After stirring for 3 h at the same temperature, the resulting mixture was filtered through a pad of silica-gel. The mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 6 g, *n*-hexane/EtOAc = 9/1) to give 3-(4-azidophenyl)propanal (**7h**) (91.0 mg, 0.520 mmol, 80%) as a yellow oil.

Characterization Data of New Compounds

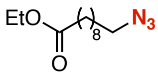
4-Azidobenzaldehyde (**7a**)[S8] and 1-(4-azidophenyl)-3-buten-1-ol (**8g**)[S9] were identical in spectra data with those reported in the literature.

Methyl (2-(2-(2-azidoethoxy)ethoxy)ethoxy)acetate (**1c**)



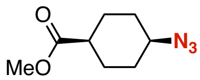
Colorless oil; TLC *R*f 0.25 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.39 (t, 2H, *J* = 5.1 Hz), 3.66–3.75 (m, 10H), 3.76 (s, 3H), 4.18 (s, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 50.8, 52.0, 68.8, 70.2, 70.80, 70.82, 70.9, 71.1, 171.0; IR (KBr, cm^{-1}) 1123, 1211, 1285, 1439, 1755, 2106, 2870; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{17}N_3NaO_5^+$ 270.1060; Found 270.1065.

Ethyl 10-azidodecanoate (**1d**)



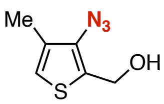
Colorless oil; TLC *R*f 0.34 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23–1.42 (m, 13H), 1.55–1.66 (m, 4H), 2.29 (t, 2H, *J* = 7.6 Hz), 3.25 (t, 2H, *J* = 7.2 Hz), 4.12 (q, 2H, *J* = 7.2 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 14.4, 25.1, 26.8, 29.0, 29.2 (two signals overlapped), 29.3, 29.4, 34.5, 51.6, 60.3, 174.0; IR (KBr, cm^{-1}) 1180, 1256, 1371, 1464, 1736, 2095, 2855, 2930; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{23}N_3NaO_2^+$ 264.1682; Found 264.1677.

cis-4-(methoxycarbonyl)cyclohexy azide (**1e**)



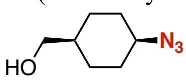
Colorless oil; TLC *R*f 0.29 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.62–1.82 (m, 6H), 1.86–1.94 (m, 2H), 2.41 (tt, 1H, *J* = 3.2, 7.3 Hz), 3.63–3.73 (m, 4H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 24.2, 28.9, 41.1, 51.8, 57.6, 175.4; IR (KBr, cm^{-1}) 1038, 1169, 1200, 1231, 1256, 1329, 1341, 1435, 1449, 1734, 2099, 2949; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_8H_{13}N_3NaO_2^+$ 206.0900; Found 206.0898.

(3-Azido-4-methylthiophen-2-yl)methanol (**6b**)



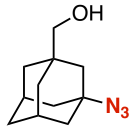
Brown oil; TLC *R*f 0.19 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.83 (brs, 1H), 2.22 (d, 3H, *J* = 1.0 Hz), 4.76 (s, 2H), 6.84 (q, 1H, *J* = 1.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 14.2, 57.1, 120.4, 129.6, 132.2, 133.0; IR (KBr, cm^{-1})745, 999, 1285, 1389, 1447, 1560, 1597, 2104, 2292, 3325; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_6H_7N_3NaOS^+$ 192.0202; Found192.0203.

cis-(4-Azidocyclohexy)methanol (**6e**)



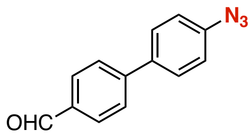
Brown oil; TLC *R*f 0.20 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.28–1.38 (m, 3H), 1.51–1.63 (m, 5H), 1.81–1.88 (m, 2H), 3.50 (d, 2H, *J* = 5.0 Hz), 3.81–3.86 (m, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 24.0, 29.1, 39.2, 58.0, 67.8; IR (KBr, cm^{-1}) 1022, 1263, 2100, 2859, 2928, 3329; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_7H_{13}N_3NaO^+$ 178.0951; Found 178.0952.

(3-Azido-1-adamantyl)methanol (**6f**)



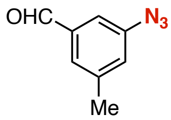
Colorless oil; TLC R_f 0.17 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.48 (d, 4H, J = 2.5 Hz), 1.57–1.65 (m, 4H), 1.71–1.83 (m, 4H), 2.23–2.37 (m, 2H), 3.30 (d, 2H, J = 4.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 29.7, 35.6, 37.6, 37.7, 41.3, 43.1, 59.6, 72.6; IR (KBr, cm^{-1}) 679, 1038, 1146, 1248, 1449, 2087, 2853, 2911, 3316; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{18}N_3O^+$ 208.1444; Found 208.1447.

4-(4-Azidobiphenyl)benzaldehyde (**7b**)



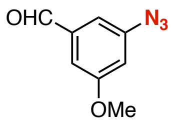
Yellow solid; Mp 63–64 °C; TLC R_f 0.23 (*n*-hexane/EtOAc = 15/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.12–7.16 (AA'BB', 2H), 7.62–7.66 (AA'BB', 2H), 7.71–7.74 (AA'BB', 2H), 7.94–7.97 (AA'BB', 2H), 10.05 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 119.8, 127.5, 128.9, 130.5, 135.4, 136.5, 140.6, 146.2, 192.0; IR (KBr, cm^{-1}) 812, 1192, 1308, 1493, 1599, 1694, 2102, 2129; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_9N_3NaO^+$ 246.0638; Found 246.0641.

3-Azido-5-methylbenzaldehyde (**7c**)



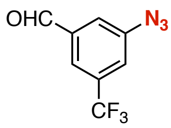
Yellow solid; Mp 27–28 °C; TLC R_f 0.41 (*n*-hexane/EtOAc = 9/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 7.06–7.09 (br, 1H), 7.35 (s, 1H), 7.46 (s, 1H), 9.95 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 21.3, 116.7, 125.6, 127.5, 137.9, 141.1, 141.4, 191.6; IR (KBr, cm^{-1}) 675, 854, 1233, 1310, 1387, 1464, 1589, 1612, 1701, 2108; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_8H_8N_3O^+$ 162.0662; Found 162.0660.

3-Azido-5-methoxybenzaldehyde (**7d**)



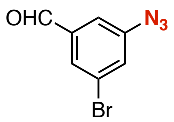
Brown solid; Mp 50–51 °C; TLC R_f 0.30 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.87 (s, 3H), 6.79 (dd, 1H, J = 1.5, 1.5 Hz), 7.16 (dd, 1H, J = 1.2, 2.2 Hz), 7,18 (dd, 1H, J = 1,2, 2,2 Hz), 9.93 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 56.0, 110.5, 111.4, 112.9, 138.9, 142.7, 161.5, 191.2; IR (KBr, cm^{-1}) 671, 851, 1055, 1150, 1240, 1310, 1339, 1470, 1591, 1701, 2112; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_8H_7N_3NaO_2^+$ 200.0430; Found 200.0431.

3-Azido-5-(trifluoromethyl)benzaldehyde (**7e**)



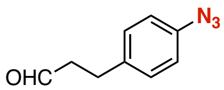
Brown oil; TLC R_f 0.34 (*n*-hexane/EtOAc = 9/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (s, 1H), 7.73 (s, 1H), 7.89 (s, 1H), 10.04 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 121.5 (q, J = 3.7 Hz), 122.1, 123.1 (q, J = 272.9 Hz), 123.0 (q, J = 3.7 Hz), 133.6 (q, J = 34.0 Hz), 138.4, 142.8, 189.8; IR (KBr, cm^{-1}) 692, 878, 1134, 1182, 1279, 1348, 1389, 1456, 1466, 1605, 1713, 2114; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_8H_4F_3N_3NaO^+$ 238.0199; Found 238.0201.

3-Azido-5-bromobenzaldehyde (**7f**)



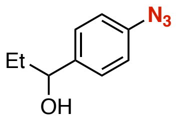
Yellow solid; Mp 60–61 °C; TLC R_f 0.28 (*n*-hexane/EtOAc = 20/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.42 (br, 1H), 7.46–7.48 (br, 1H), 7.75–7.77 (br, 1H), 9.93 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 118.2, 124.3, 127.7, 129.3, 139.0, 143.0, 189.8; IR (KBr, cm^{-1}) 665, 856, 1194, 1292, 1449, 1574, 1705, 2108; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_7H_4BrN_3NaO^+$ 247.9430; Found 247.9430.

3-(4-Azidophenyl)propanal (**7h**)



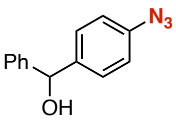
Yellow oil; TLC R_f 0.48 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.77 (t, J = 7.5 Hz, 2H), 2.94 (t, J = 7.5 Hz, 2H), 6.93–6.97 (AA'BB', 2H), 7.16–7.20 (AA'BB', 2H), 9.81 (t, J = 1.3 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 27.6, 45.4, 119.3, 129.8, 137.3, 138.2, 201.3; IR (KBr, cm^{-1}) 826, 1128, 1287, 1506 1722, 2112; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_9H_9N_3NaO^+$ 198.0638; Found 198.0640.

1-(4-Azidophenyl)-1-propanol (**8a**)



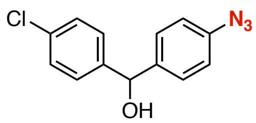
Brown oil; TLC R_f 0.36 (*n*-hexane/EtOAc = 5/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.91 (t, 3H, J = 7.5 Hz), 1.68–1.86 (m, 3H), 4.60 (dd, 1H, J = 8.5, 8.5 Hz), 6.99–7.03 (AA'BB', 2H), 7.31–7.35 (AA'BB', 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 10.2, 32.1, 75.6, 119.1, 127.6, 139.3, 141.5; IR (KBr, cm^{-1}) 534, 831, 1098, 1288, 1506, 1607, 2118, 2932, 2965, 3356; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_9H_{11}N_3NaO^+$ 200.0794; Found 200.0792.

1-(4-Azidophenyl)-1-phenylmethanol (**8b**)



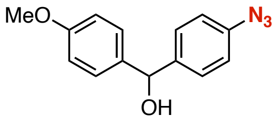
Brown oil; TLC R_f 0.23 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.21 (br s, 1H), 5.83 (s, 1H), 6.97–7.01 (AA'BB', 2H), 7.26–7.38 (m, 7H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 75.9, 119.2, 126.6, 127.9, 128.2, 128.8, 139.4, 140.7, 143.7; IR (KBr, cm^{-1}) 700, 1288, 1504, 1605, 2120, 3354; HRMS (ESI) *m/z*: [M +H]$^+$ Calcd for $C_{13}H_{12}N_3O^+$ 226.0975; Found 226.0979.

1-(4-Azidophenyl)-1-(4-chlorophenyl)methanol (**8c**)



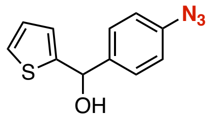
Brown solid; Mp 67–68 °C; TLC R_f 0.19 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.21–2.25 (br, 1H), 5.80 (d, 1H, J = 3.2 Hz), 6.98–7.01 (AA'BB', 2H), 7.28–7.31 (m, 4H), 7.31–7.34 (AA'BB', 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 75.2, 119.3, 128.0, 128.2, 128.9, 133.7, 139.7, 140.3, 142.1; IR (KBr, cm^{-1}) 534, 783, 829, 1013, 1090, 1288, 1504, 1605, 2122, 3356; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{13}H_{10}ClN_3NaO^+$ 282.0405; Found 282.0404.

1-(4-Azidophenyl)-1-(4-methoxyphenyl)methanol (**8d**)



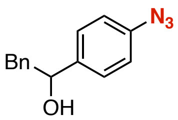
Brown solid; Mp 40–42 °C ; TLC R_f 0.30 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.19 (br s, 1H), 3.79 (s, 3H), 5.78 (s, 1H), 6.85–6.88 (AA'BB', 2H), 6.97–7.00 (AA'BB', 2H), 7.24–7.27 (AA'BB', 2H), 7.33–7.37 (AA'BB', 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 55.4, 75.4, 114.1, 119.2, 128.0 (two signals overlapped), 136.1, 139.2, 141.0, 159.4; IR (KBr, cm^{-1}) 831, 1032, 1173, 1248, 1288, 1510, 1607, 2120, 3383; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{14}H_{13}N_3NaO_2^+$ 278.0900; Found 278.0899.

1-(4-Azidophenyl)-2-thienylmethanol (**8e**)



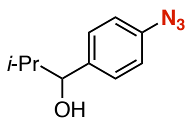
Brown solid; Mp 41–42 °C ; TLC R_f 0.24 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (d, 1H, J = 3.2 Hz), 6.05 (d, 1H, J = 3.2 Hz), 6.87–6.91 (m, 1H), 6.93–6.97 (m, 1H), 7.00–7.05 (AA'BB', 2H), 7.25–7.29 (m, 1H), 7.41–7.46 (AA'BB', 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 72.0, 119.2, 125.1, 125.8, 126.9, 127.9, 139.8, 140.0, 148.0; IR (KBr, cm^{-1}) 704, 833, 1288, 1504, 1605, 2116, 3358; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_9N_3NaOS^+$ 254.0359; Found 254.0359.

1-(4-Azidophenyl)-2-phenylethanol (**8f**)



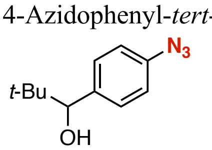
Brown solid; Mp 30–32 °C ; TLC R_f 0.27 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.94–1.97 (br, 1H), 2.95–3.04 (m, 2H), 4.86–4.91 (m, 1H), 6.98–7.02 (AA'BB', 2H), 7.15–7.19 (m, 2H), 7.22–7.26 (m, 1H), 7.28–7.35 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 46.3, 74.9, 119.1, 126.9, 127.6, 128.7, 129.7, 137.8, 139.4, 140.7; IR (KBr, cm^{-1}) 546, 700, 743, 833, 1032, 1045, 1288, 1506, 1605, 2100, 2124, 3377; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{14}H_{13}N_3NaO^+$ 262.0951; Found 262.0950.

1-(4-Azidophenyl)2-methyl-1-propanol (**8h**)



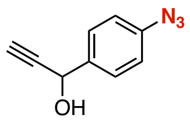
Brown oil; TLC R_f 0.31 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.79 (d, 3H, J = 6.8 Hz), 0.98 (d, 3H, J = 6.8 Hz), 1.79 (brs, 1H), 1.93 (dqq, 1H, J = 6.8, 6.8, 6.8 Hz), 4.36 (d, 1H, J = 6.5 Hz), 7.00 (d, 2H, J = 8.3 Hz), 7.30 (d, 2H, J = 8.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 18.3, 19.0, 35.5, 79.6, 118.9, 128.1, 139.2, 140.6; IR (KBr, cm^{-1}) 534, 839, 1013, 1028, 1290, 1506, 1605, 2118, 2891, 2959, 3383; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{10}H_{13}N_3NaO^+$ 214.0951; Found 214.0949.

4-Azidophenyl-*tert*-butyl-methylalcohol (**8i**)



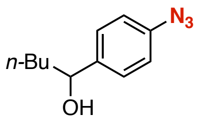
Brown solid; Mp 49–51 °C ; TLC R_f 0.38 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.91 (s, 9H), 1.84 (br s, 1H), 4.38 (d, 1H, J = 2.0 Hz), 6.97–6.99 (AA'BB', 2H), 7.29–7.31 (AA'BB', 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 26.0, 35.9, 82.0, 118.3, 129.1, 139.1; IR (KBr, cm^{-1}) 833, 1007, 1288, 1506, 1607, 2079, 2116, 2870, 2955, 3449; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_{15}N_3NaO^+$ 228.1107; Found 228.1105.

1-(4-Azidophenyl)propargyl alcohol (**8j**)



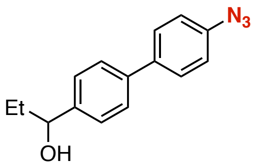
Brown solid; Mp 43–44 °C; TLC R_f 0.21 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.19 (d, 1H, J = 5.6 Hz), 2.68 (dd, 1H, J = 0.8, 2.0 Hz), 5.45 (d, 1H, J = 5.6 Hz), 7.04 (d, 2H, J = 8.2 Hz), 7.54 (d, 2H, J = 8.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 64.0, 75.3, 83.3, 119.4, 128.4, 136.9, 140.5; IR (KBr, cm^{-1}) 831, 1015, 1288, 1504, 1607, 2114, 3292, 3356; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_7N_3NaO^+$ 196.0481; Found 196.0480.

1-(4-Azidophenyl)-1-pentanol (**8k**)



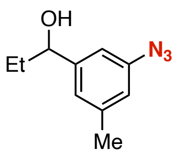
Brown oil; TLC R_f 0.29 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, 3H, J = 7.0 Hz), 1.19–1.45 (m, 4H), 1.63–1.84 (m, 3H), 4.66 (ddd, 1H, J = 2.0, 7.2, 7.2 Hz), 6.99–7.03 (AA'BB', 2H), 7.31–7.35 (AA'BB', 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 14.1, 22.7, 28.0, 39.0, 74.3, 119.2, 127.6, 139.3, 141.8; IR (KBr, cm^{-1}) 833, 1288, 1506, 1605, 2114, 2930, 2955, 3352; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{15}N_3NaO^+$ 228.1107; Found 228.1104.

1-(4-Azidobiphenyl)-1-propanol (**8l**)



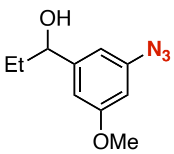
Brown solid; Mp 96–98 °C; TLC R_f 0.34 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.95 (t, 3H, J = 7.4 Hz), 1.72–1.97 (m, 3H), 4.64 (dd, 1H, J = 6.0, 6.0 Hz), 7.06–7.11 (AA'BB', 2H), 7.38–7.43 (AA'BB', 2H), 7.51–7.60 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 10.3, 32.1, 75.9, 119.6, 126.7, 127.0, 128.5, 137.8, 139.3, 139.5, 143.9; IR (KBr, cm^{-1}) 532, 741, 814, 1009, 1130, 1298, 1495, 2095, 2126, 2963, 3360; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{15}N_3NaO^+$ 276.1107; Found 276.1106.

1-(3-Azido-5-methylphenyl)-1-propanol (**8m**)



Brown oil; TLC R_f 0.31 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (t, 3H, J = 7.4 Hz), 1.67–1.87 (m, 3H), 2.34 (s, 3H), 4.55 (ddd, 1H, J = 1.8, 6.9, 6.9 Hz), 6.75 (s, 1H), 6.82 (s, 1H), 6.92 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 10.2, 21.5, 32.0, 75.7, 113.8, 118.8, 123.6, 140.09, 140.13, 146.7; IR (KBr, cm^{-1}) 698, 845, 1231, 1306, 1458, 1609, 2106, 2965, 3323; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{13}N_3NaO^+$ 214.0951; Found 214.0950.

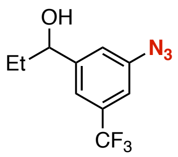
1-(3-Azido-5-methoxyphenyl)-1-propanol (**8n**)



Brown oil; TLC R_f 0.22 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, 3H, J = 7.4 Hz), 1.69–

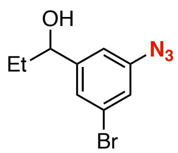
1.88 (m, 3H), 3.80 (s, 3H), 4.56 (ddd, 1H, *J* = 2.0, 6.8, 6.8 Hz), 6.45 (dd, 1H, *J* = 2.0, 2.0 Hz), 6.63–6.66 (br, 1H), 6.67–6.71 (br, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 10.2, 32.0, 55.6, 75.7, 104.0, 108.5, 109.0, 141.4, 148.0, 161.0; IR (KBr, cm^{-1}) 694, 843, 1059, 1157, 1242, 1306, 1331, 1433, 1464, 1597, 2108, 2965, 3343; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{13}N_3NaO_2^+$ 230.0900; Found 230.0900.

1-(3-Azido-5-trifluoromethylphenyl)-1-propanol (**8o**)



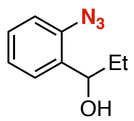
Colorless solid; Mp 37–38 °C; TLC R_f 0.27 (*n*-hexane/EtOAc = 5/1); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.95 (t, 3H, *J* = 7.4 Hz), 1.72–1.82 (m, 2H), 1.95–1.99 (br, 1H), 4.65–4.72 (m, 1H), 7.16 (s, 1H), 7.22 (s, 1H), 7.37 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 10.0, 32.3, 75.0, 115.1 (q, *J* = 3.8 Hz), 119.3 (q, *J* = 3.7 Hz), 119.7, 123.7 (q, *J* = 273.2 Hz), 132.5 (q, *J* = 32.8 Hz), 141.3, 148.0; IR (KBr, cm^{-1}) 691, 874, 1130, 1173, 1279, 1341, 1454, 1605, 2112, 2970, 3341; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{10}F_3N_3NaO^+$ 268.0668; Found 268.0668.

1-(3-Azido-5-bromophenyl)-1-propanol (**8p**)



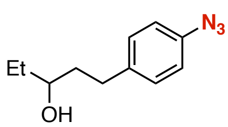
Yellow oil; TLC R_f 0.24 (*n*-hexane/EtOAc = 7/1); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.93 (d, 3H, *J* = 7.4 Hz), 1.70–1.81 (m, 2H), 1.87 (d, 1H, *J* = 3.4 Hz), 4.58 (ddd, 1H, *J* = 3.4, 6.6, 6.6 Hz), 6.95 (dd, 1H, *J* = 1.5, 1.5 Hz), 7.08 (dd, 1H, *J* = 1.5, 1.5 Hz), 7.25–7.28 (br, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 10.0, 32.1, 75.0, 115.5, 121.2, 123.3, 125.7, 141.7, 148.6; IR (KBr, cm^{-1}) 691, 706, 854, 1198, 1290, 1441, 1574, 1599, 2106, 2967, 3323; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{10}BrN_3NaO^+$ 277.9899; Found 277.9899.

1-(2-Azidophenyl)-1-propanol (**8q**)



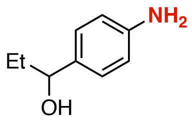
Brown oil; TLC R_f 0.31 (*n*-hexane/EtOAc = 5/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.95 (t, 3H, *J* = 7.5 Hz), 1.78 (dq, 2H, *J* = 7.5, 7.5 Hz), 2.08–2.12 (br, 1H), 4.78–4.84 (m, 1H), 7.13–7.18 (m, 2H), 7.29–7.34 (m, 1H), 7.41–7.45 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 10.4, 30.8, 71.6, 118.2, 125.1, 127.5, 128.6, 135.8, 136.8; IR (KBr, cm^{-1}) 752, 1294, 1449, 1485, 1582, 2099, 2126, 2934, 2965, 3354; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{11}N_3NaO^+$ 200.0794; Found 200.0790.

1-(4-Azidophenyl)pentan-3-ol (**8r**)



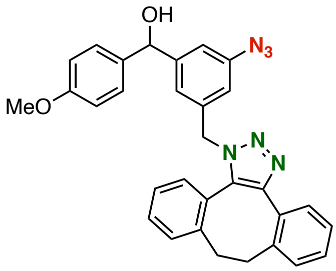
Yellow oil; TLC R_f 0.23 (*n*-hexane/EtOAc = 3/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.95 (dd, *J* = 7.5, 7.5 Hz, 3H), 1.42–1.59 (m, 4H), 1.66–1.80 (m, 2H), 2.65 (ddd, *J* = 7.0, 9.6, 14.0 Hz, 1H), 2.78 (ddd, *J* = 5.6, 9.8, 14.0 Hz, 1H), 3.50–3.58 (m, 1H), 6.93–6.97 (AA'BB', 2H), 7.17–7.21 (AA'BB', 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 10.0, 30.5, 31.6, 38.7, 72.7, 119.2, 129.9, 137.7, 139.2; IR (KBr, cm^{-1}) 827, 1288, 1506, 2108, 2932, 3360; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{15}N_3NaO^+$ 228.1107; Found 228.1108.

1-(4-Aminophenyl)-1-propanol (**9**)



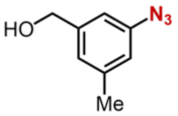
Brown solid; Mp 60–61 °C; TLC R_f 0.23 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.89 (t, 3H, *J* = 7.0 Hz), 1.70 (dq, 1H, *J* = 7.0, 7.0 Hz), 1.81 (dq, 1H, *J* = 7.0, 7.0 Hz), 2.50–4.00 (br, 2H), 4.48 (dd, 1H, *J* = 7.0, 7.0 Hz), 6.65–6.68 (AA'BB', 2H), 7.12–7.15 (AA'BB', 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 10.4, 31.7, 76.0, 115.2, 127.3, 134.8, 145.9; IR (KBr, cm^{-1}) 542, 831, 1177, 1265, 1516, 1614, 2963, 3339; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_9H_{14}NO^+$ 152.1070; Found 152.1071.

(3-Azido-5-((8,9-dihydro-1*H*-dibenzo[3,4:7,8]cycloocta[1,2-*d*][1,2,3]triazol-1-yl)methyl)phenyl)(4-methoxyphenyl)methanol (**14**)



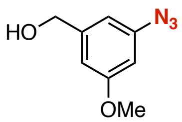
Yellow oil; TLC R_f 0.31 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.14 (br s, 1H), 2.61–2.82 (m, 2H), 2.94–3.07 (m, 1H), 3.20–3.31 (m, 1H), 3.78 (s, 3H), 5.52 (s, 2H), 5.65 (s, 1H), 6.52–6.59 (br, 1H), 6.77–6.87 (m, 3H), 6.98 (br s, 1H), 7.05–7.10 (m, 1H), 7.11–7.25 (m, 7H), 7.27–7.34 (m, 1H), 7.50–7.54 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 32.9, 36.5, 52.0, 55.4, 75.2, 114.2, 116.6, 116.8, 117.07, 117.12, 122.2, 126.2, 126.3, 126.5, 128.1, 128.3, 129.1, 129.8, 130.0, 130.3, 131.0, 131.8, 134.1, 135.5, 137.5, 137.8, 140.9, 141.7, 146.9, 147.2, 159.5; IR (KBr, cm^{-1}) 573, 702, 750, 764, 835, 1030, 1173, 1250, 1260, 1304, 1454, 1508, 1609, 2110, 2359, 3053, 3316; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{31}H_{27}N_6O_2^+$ 515.2190; Found 515.2190.

3-Azido-5-methylbenzyl alcohol



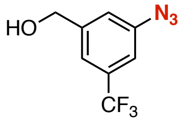
Yellow solid; Mp 32–33 °C; TLC R_f 0.25 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.66 (t, 1H, *J* = 5.6 Hz), 2.35 (s, 3H), 4.65 (d, 2H, *J* = 5.6 Hz), 6.76 (s, 1H), 6.86 (s, 1H), 6.95 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 21.5, 65.0, 114.7, 118.9, 124.3, 140.31, 140.34, 142.8; IR (KBr, cm^{-1}) 748, 841, 1040, 1053, 1234, 1308, 1460, 1593, 1611, 2104, 2156, 2920, 3323; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_8H_{10}N_3O^+$ 164.0818; Found 164.0819.

3-Azido-5-methoxybenzyl alcohol



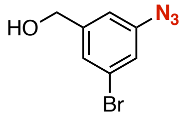
Yellow solid; Mp 29–31 °C; TLC R_f 0.38 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.74 (t, 1H, *J* = 6.0 Hz), 3.81 (s, 3H), 4.66 (d, 1H, *J* = 6.0 Hz), 6.47 (dd, 1H, *J* = 2.2, 2.2 Hz), 6.65–6.68 (br, 1H), 6.69–6.72 (br, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 55.6, 65.0, 104.2, 109.0, 109.6, 141.6, 144.1, 161.1; IR (KBr, cm^{-1}) 839, 1043, 1059, 1153, 1242, 1308, 1331, 1433, 1466, 1595, 2108, 2940, 3331; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_8H_9N_3NaO_2^+$ 202.0587; Found 202.0587.

3-Azido-5-(trifluoromethyl)benzyl alcohol



White solid; Mp 40–41 °C; TLC R_f 0.17 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.86 (t, 1H, *J* = 5.7 Hz), 4.77 (d, 2H, *J* = 5.7 Hz), 7.17 (s, 1H), 7.24 (s, 1H), 7.39 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 64.2, 115.2 (q, *J* = 3.6 Hz), 119.8 (q, *J* = 3.6 Hz), 120.2, 123.6 (q, *J* = 272.9 Hz), 132.6 (q, *J* = 32.7 Hz), 141.5, 144.1; IR (KBr, cm^{-1}) 691, 862, 1128, 1171, 1279, 1346, 1458, 1607, 2112, 3318; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_8H_7F_3N_3O^+$ 218.0536; Found 218.0536.

3-Azido-5-bromobenzyl alcohol



Yellow solid; Mp 79–80 °C; TLC R_f 0.27 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.76–1.94 (br, 1H), 4.64-4.71 (br, 2H), 6.97 (s, 1H), 7.09 (s, 1H), 7.28 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 64.1, 116.0, 121.3, 123.5, 126.2, 141.9, 144.7; IR (KBr, cm^{-1}) 829, 843, 1045, 1292, 1443, 1572, 1601, 2104, 3310; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_7H_6BrN_3NaO^+$ 249.9586; Found 249.9586.

References for Supporting Information

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S3 E. T. Pelkey and G. W. Gribble, *Tetrahedron Lett.*, 1997, **38**, 5603.
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S5 G.-J. Boons, J. Guo, X. Ning and M. Wolfert, WO 2009/067663, 2009.
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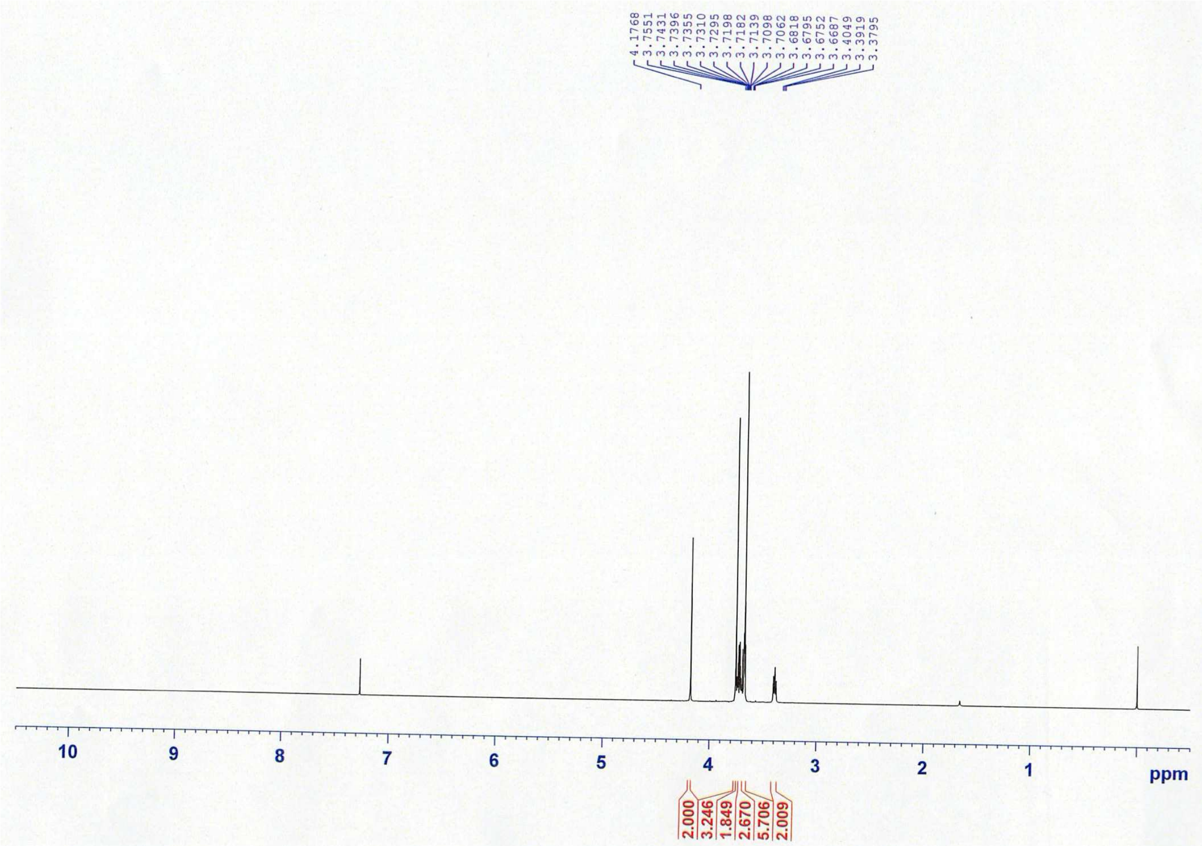
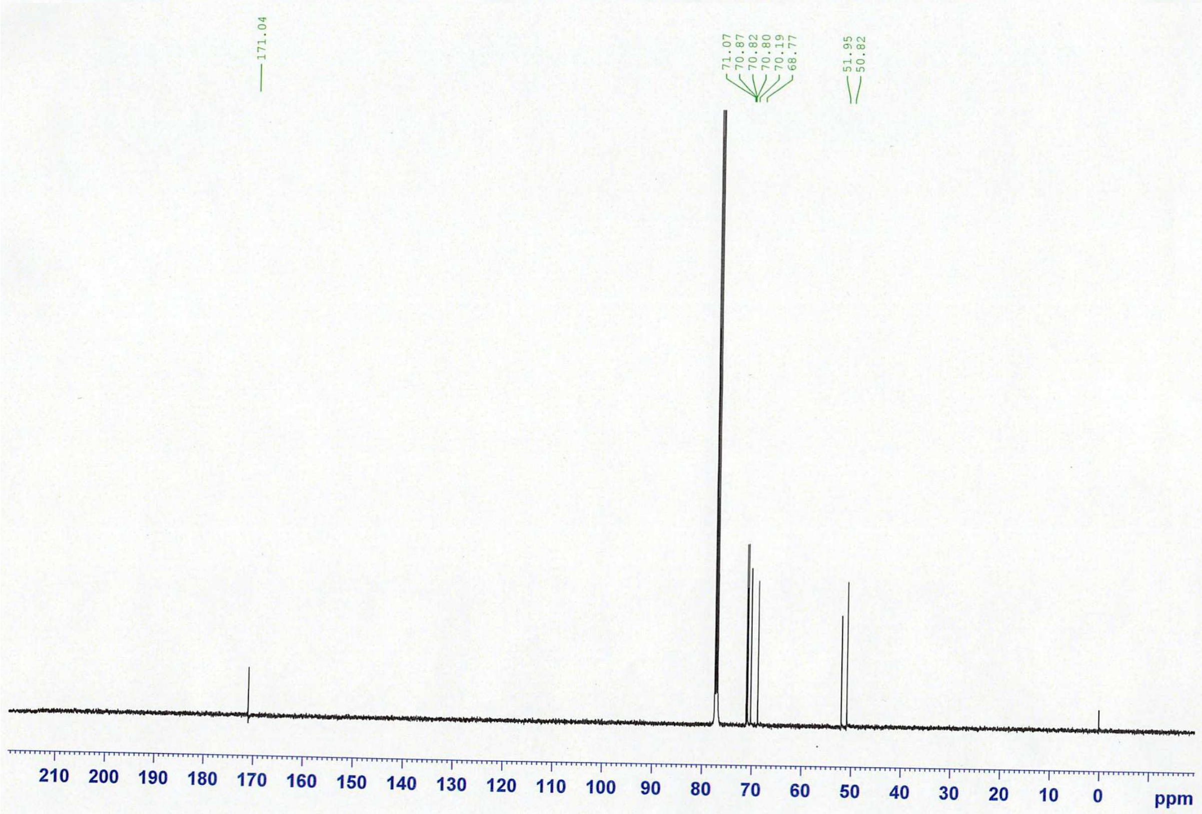
S8 G. Pelletier, W. S. Bechara and A. B. Charette, *J. Am. Chem. Soc.*, 2010, **132**, 12817.
S9 K. Morihiro, N. Ankenbruck, B. Lukasak and A. Deiters, *J. Am. Chem. Soc.*, 2017, **139**, 13909.

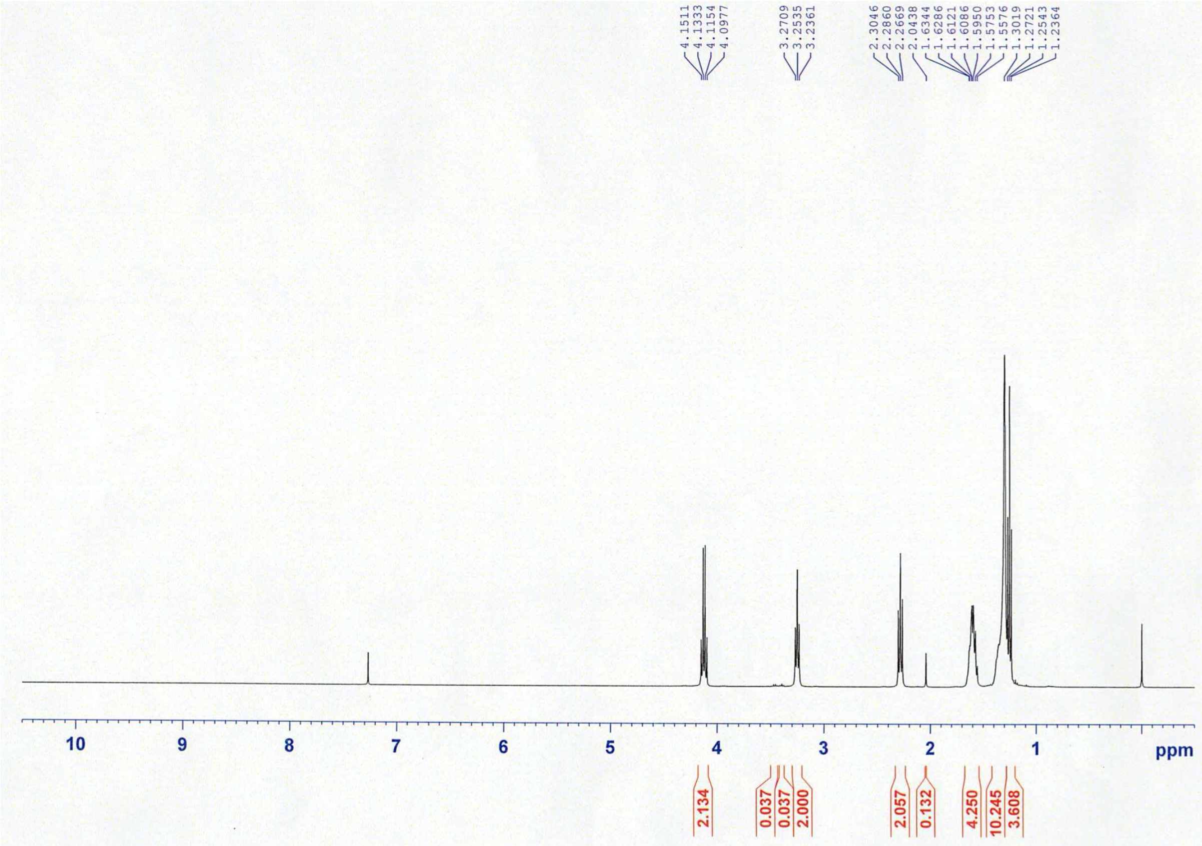
[1]H and [13]C NMR Spectra of Compounds

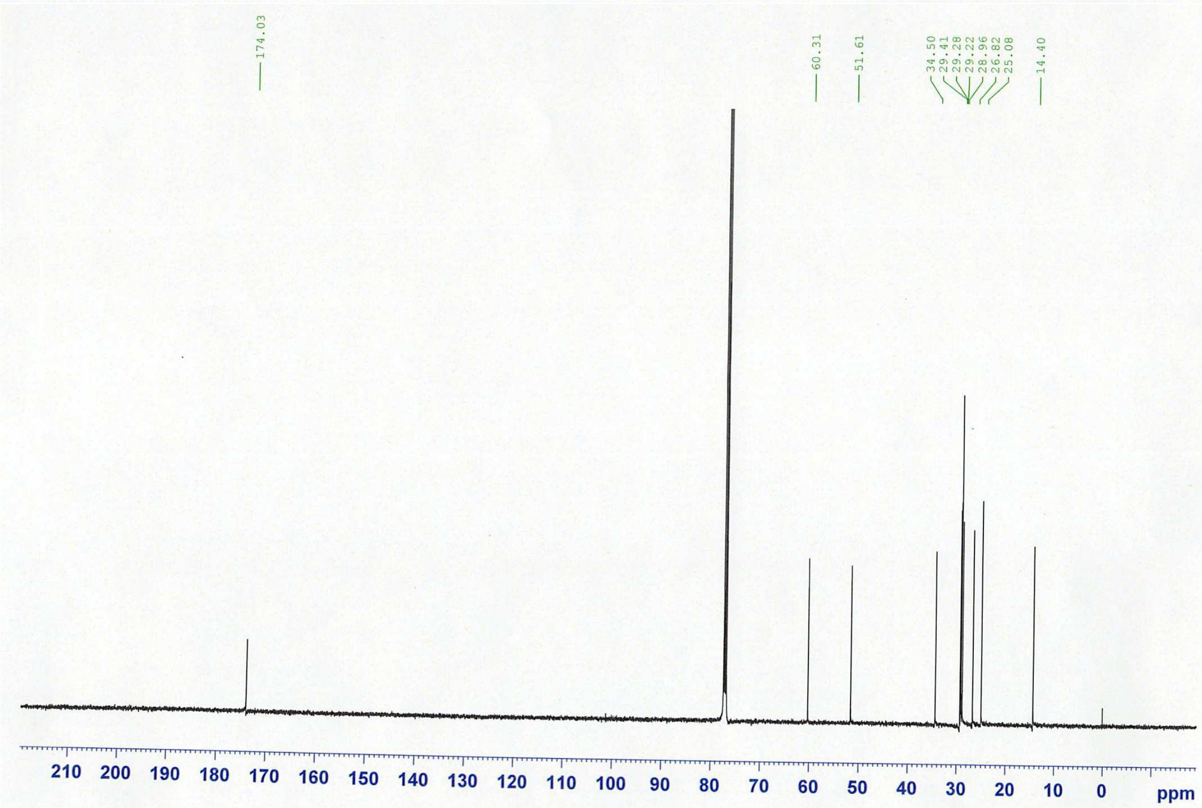
[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of methyl (2-(2-(2-azidoethoxy)ethoxy)ethoxy)acetate (**1c**) ($CDCl_3$)



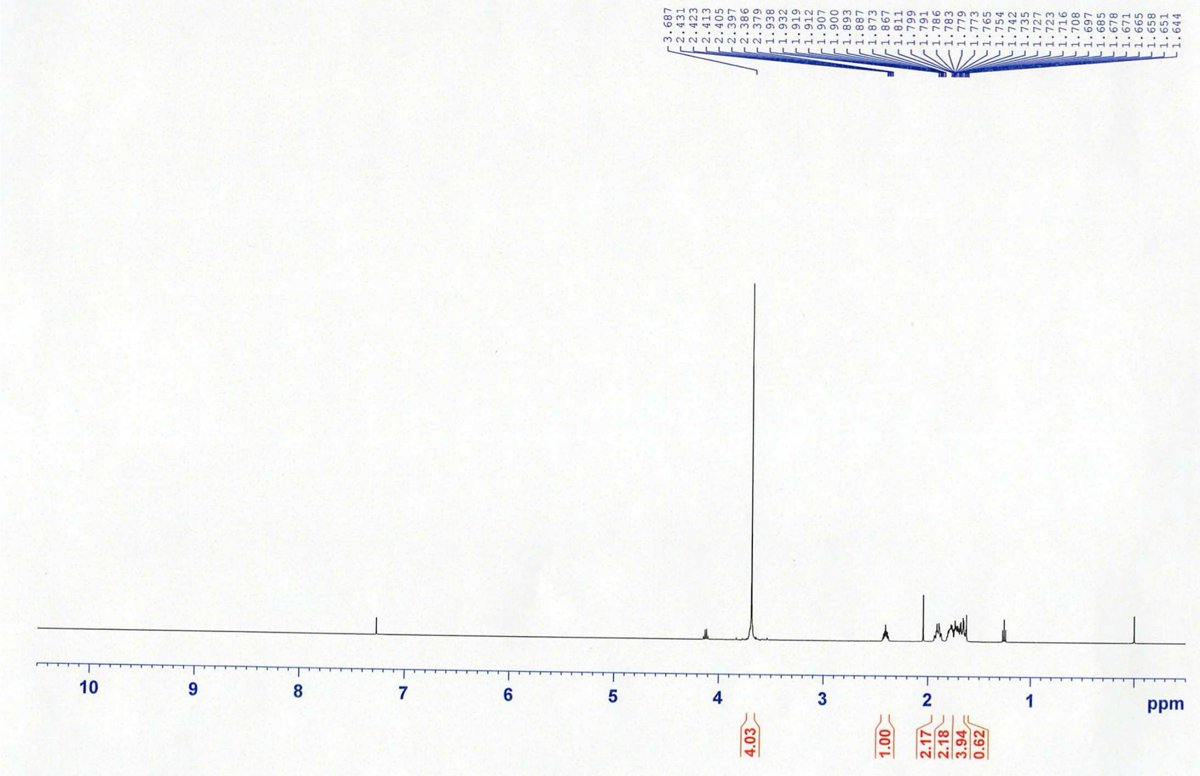


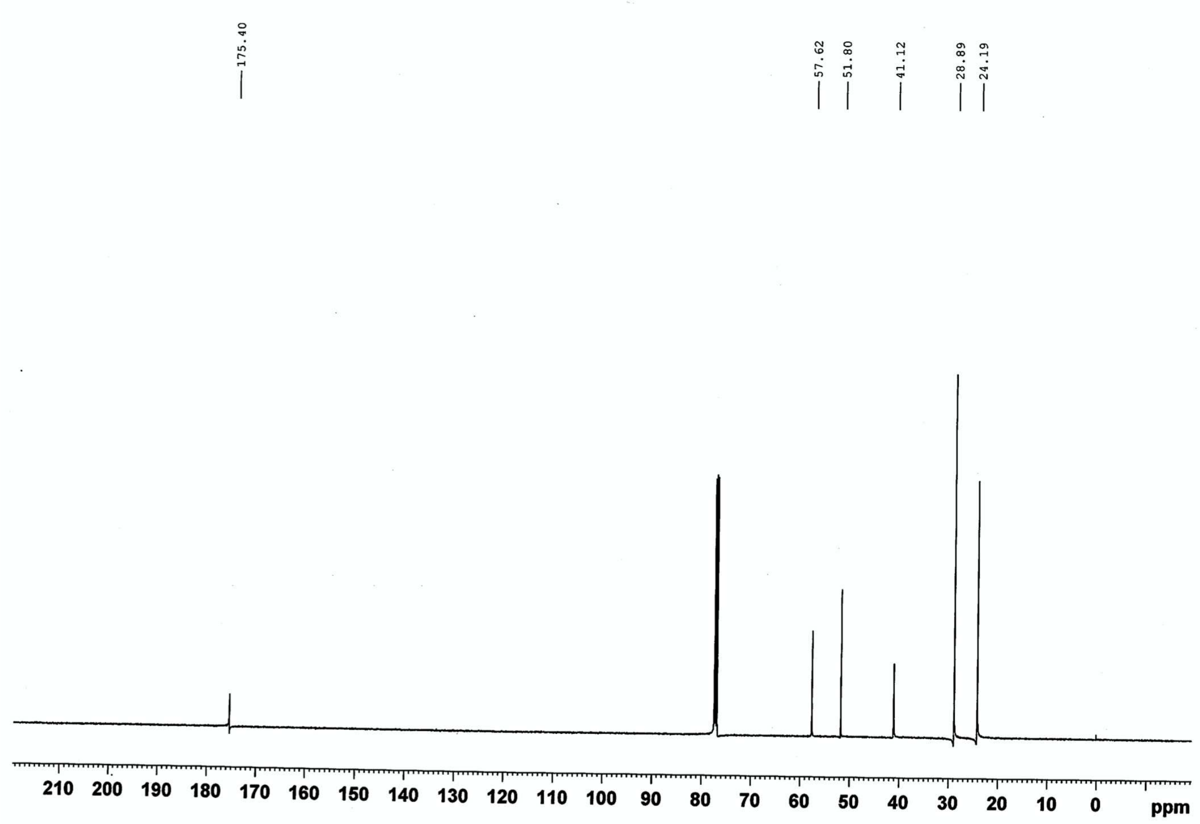
[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of ethyl 10-azidodecanoate (**1d**) ($CDCl_3$)



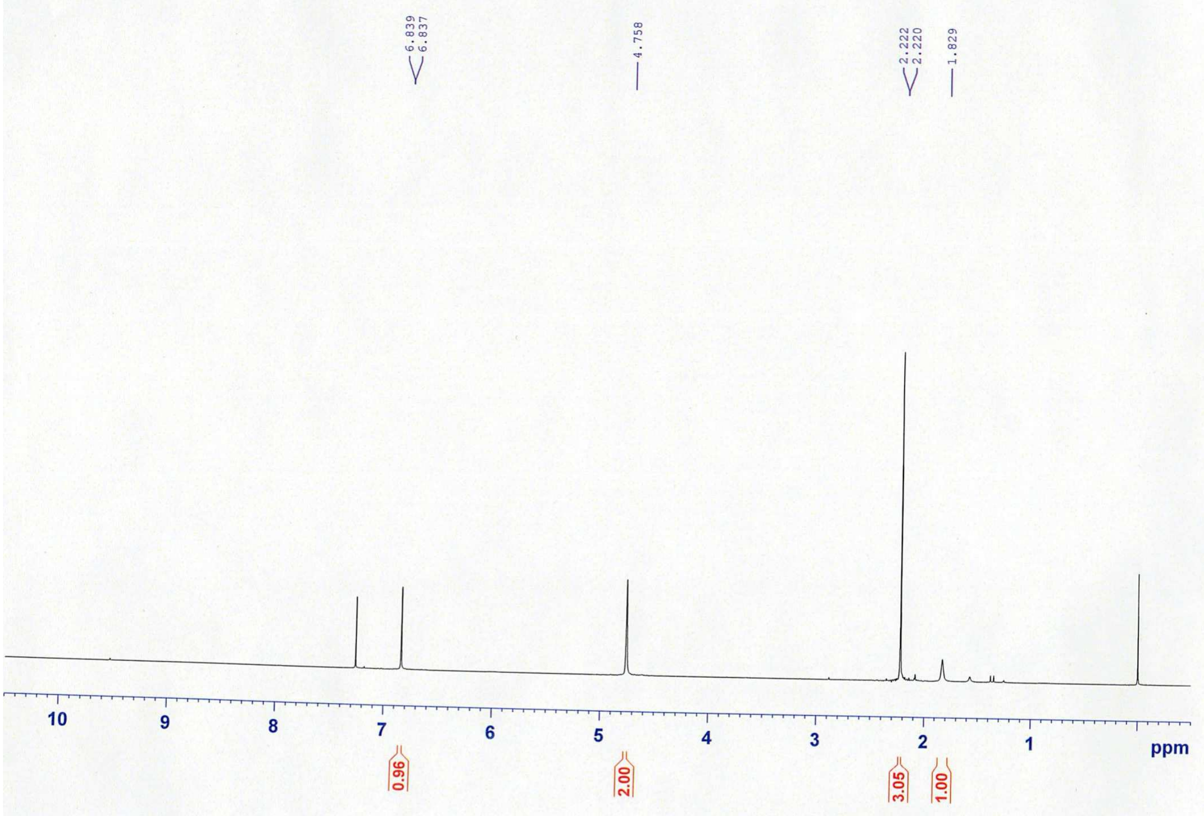


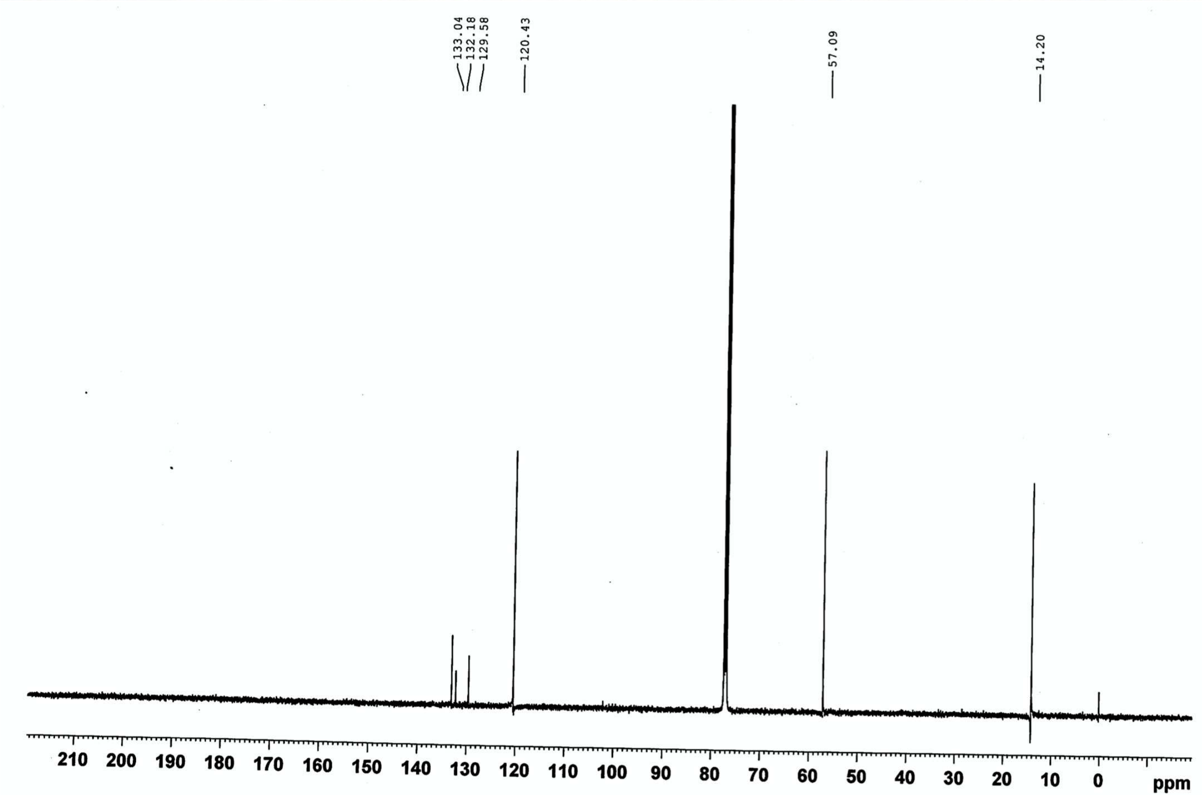
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *cis*-4-(methoxycarbonyl)cyclohexy azide (**1e**) ($CDCl_3$)



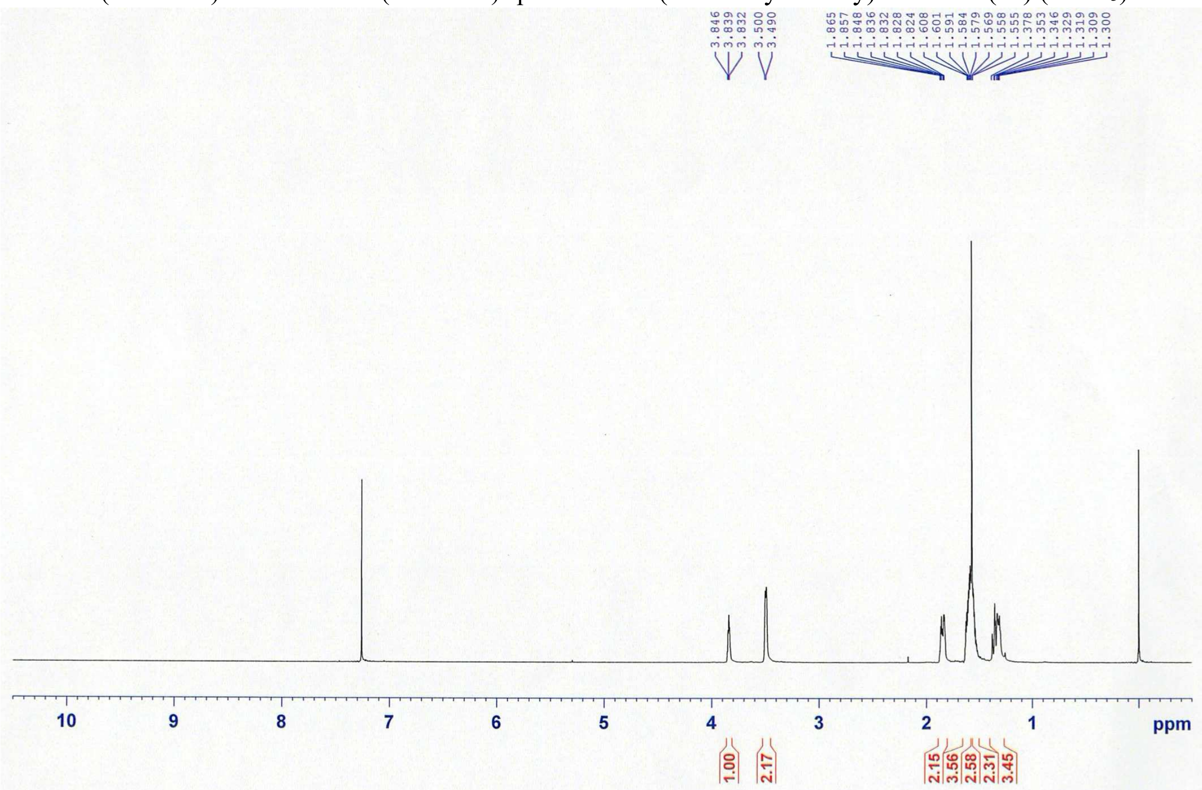


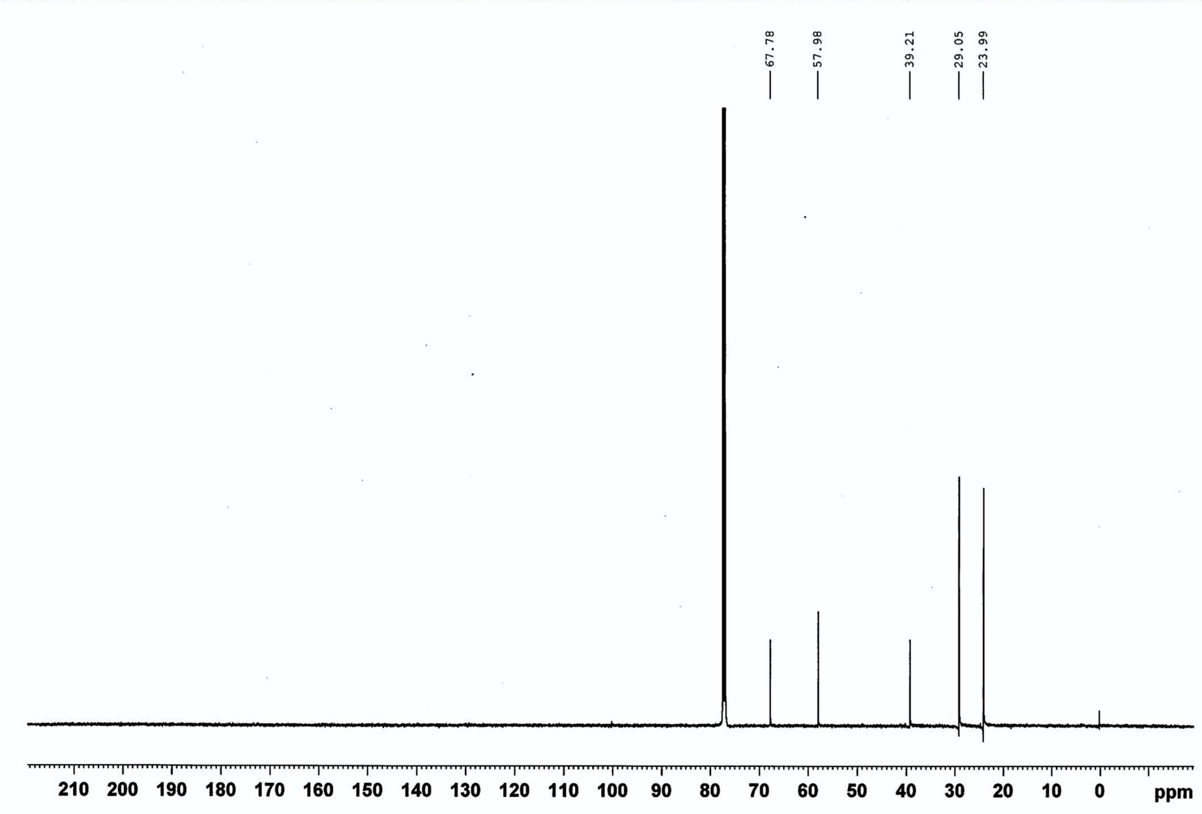
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of (3-azido-4-methylthiophen-2-yl)methanol (**6b**) ($CDCl_3$)



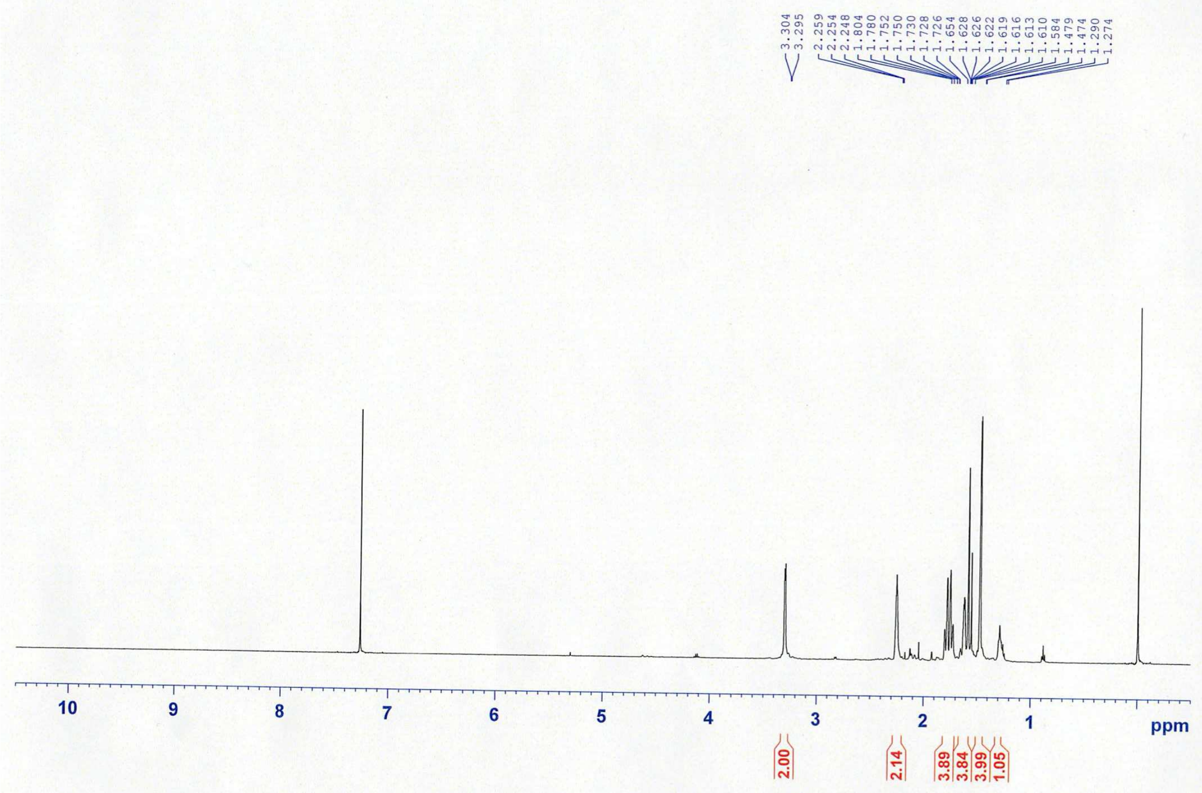


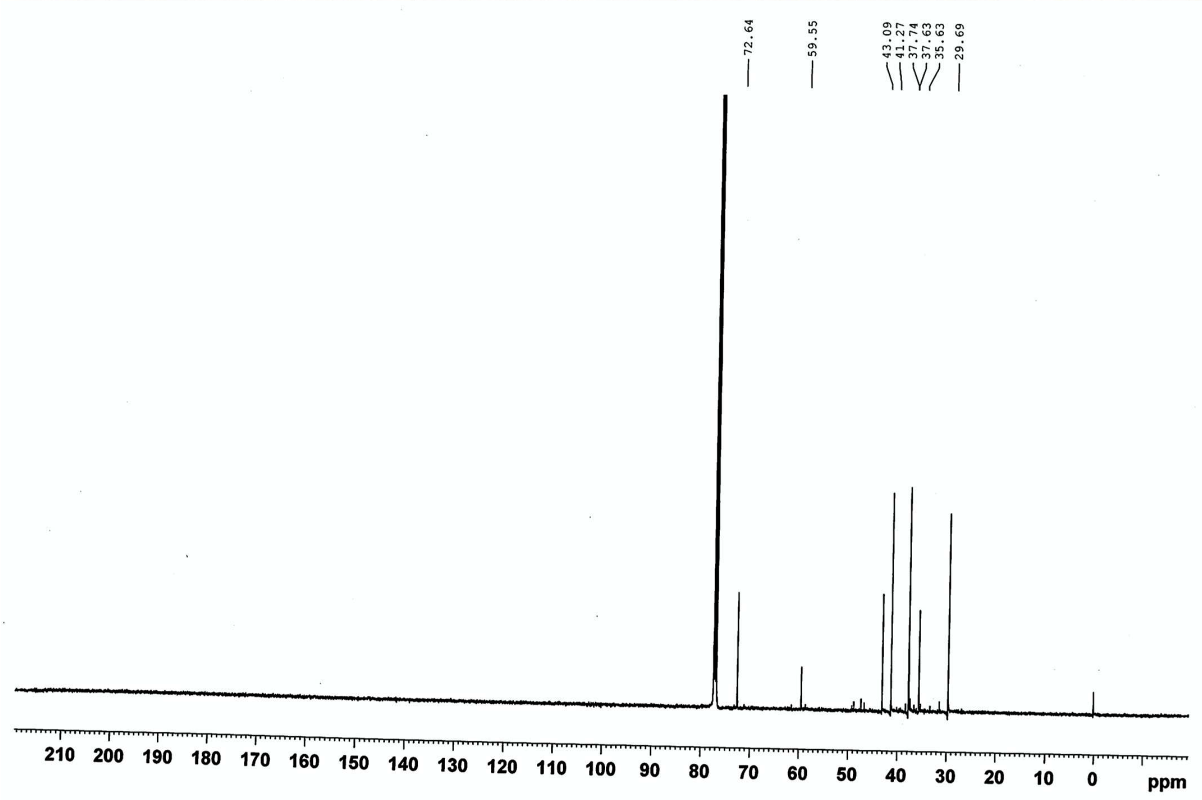
[1]H NMR (500 MHz) and [13]C NMR (126 MHz) spectra of *cis*-(4-azidocyclohexy)methanol (**6e**) ($CDCl_3$)



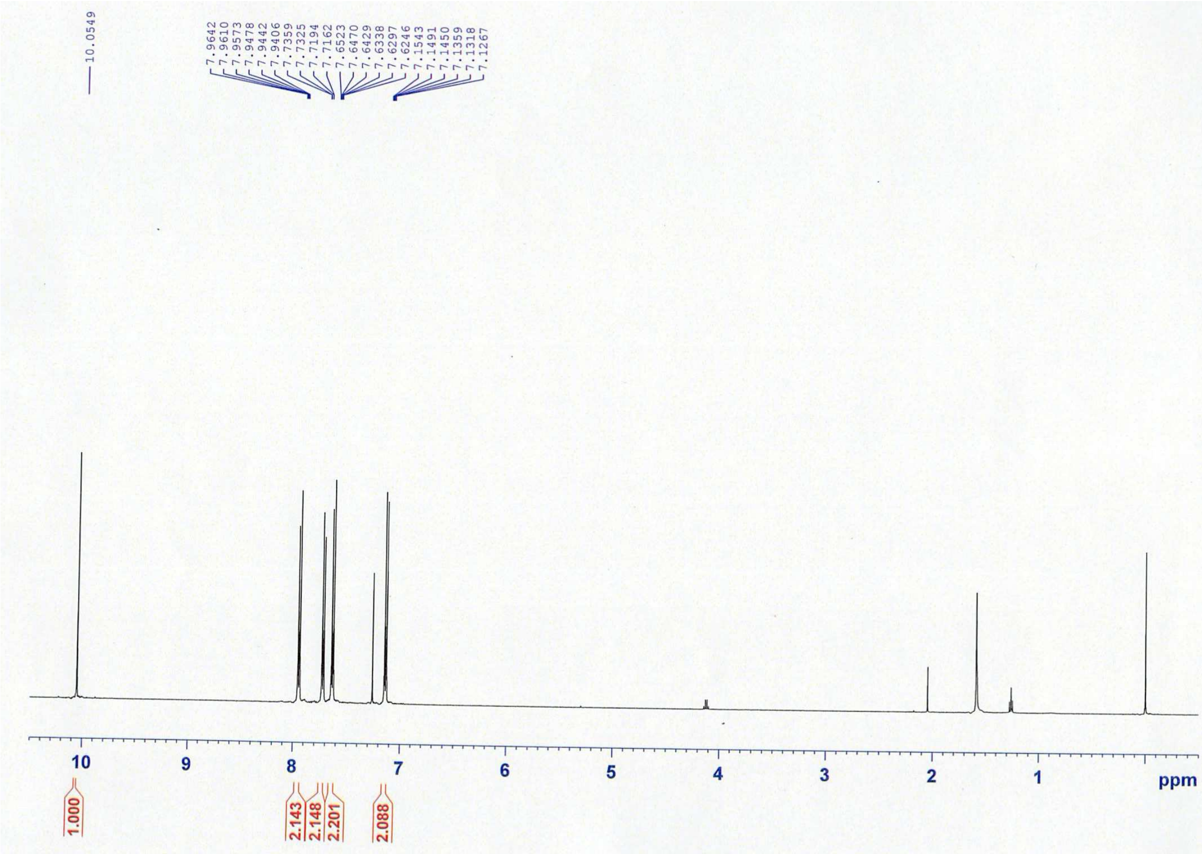


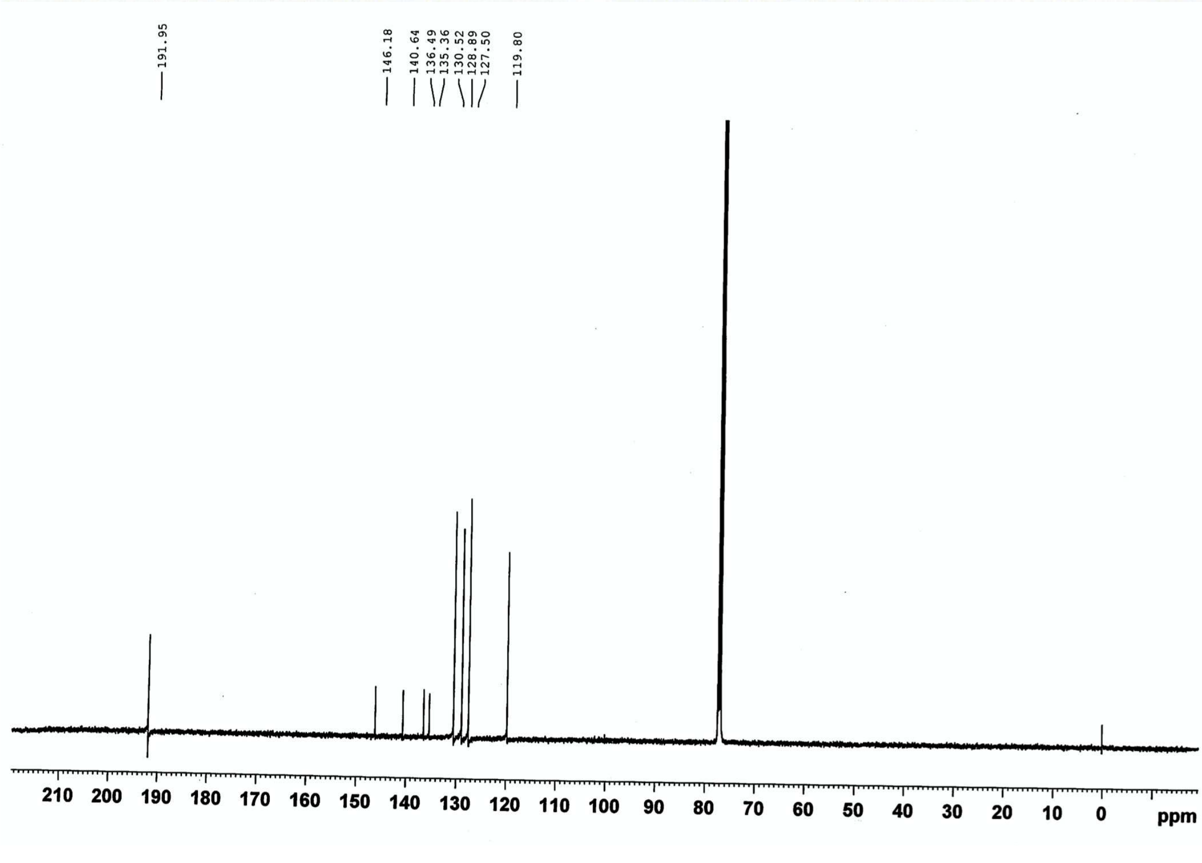
[1]H NMR (500 MHz) and [13]C NMR (126 MHz) spectra of (3-azido-1-adamantyl)methanol (**6f**) ($CDCl_3$)



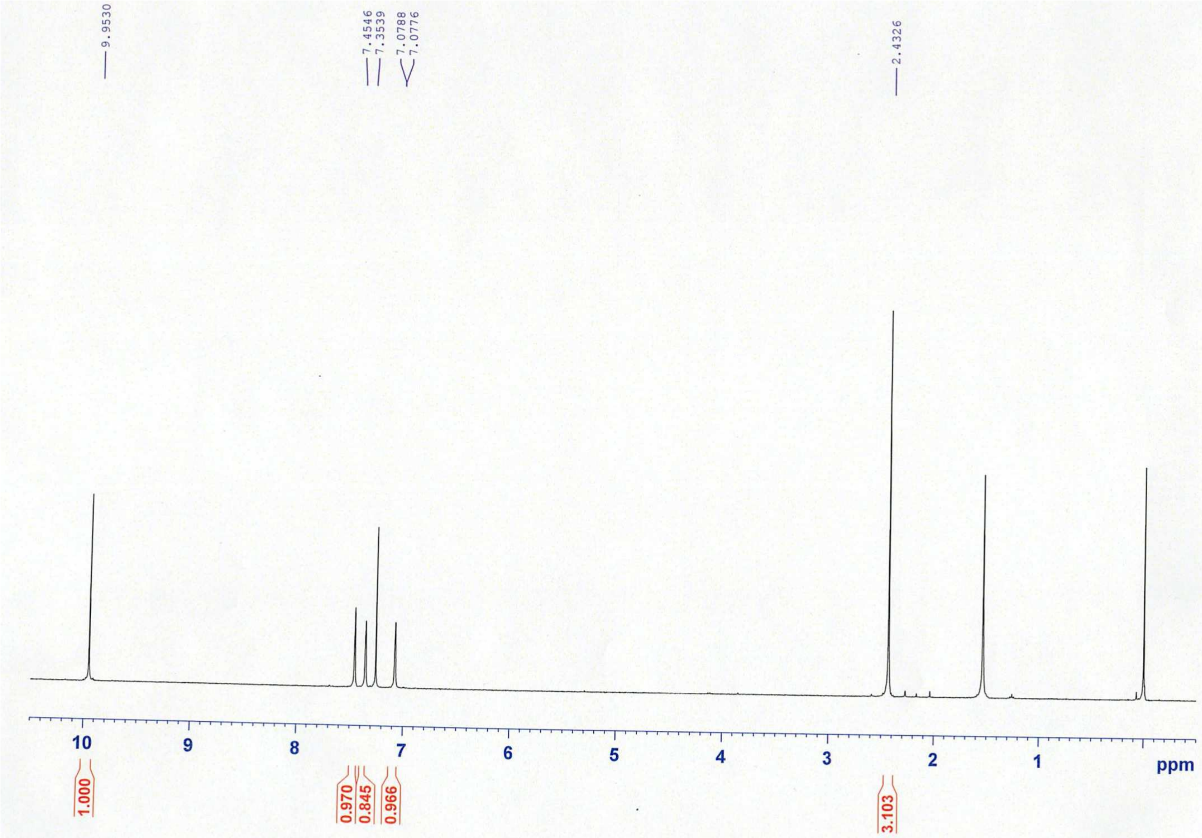


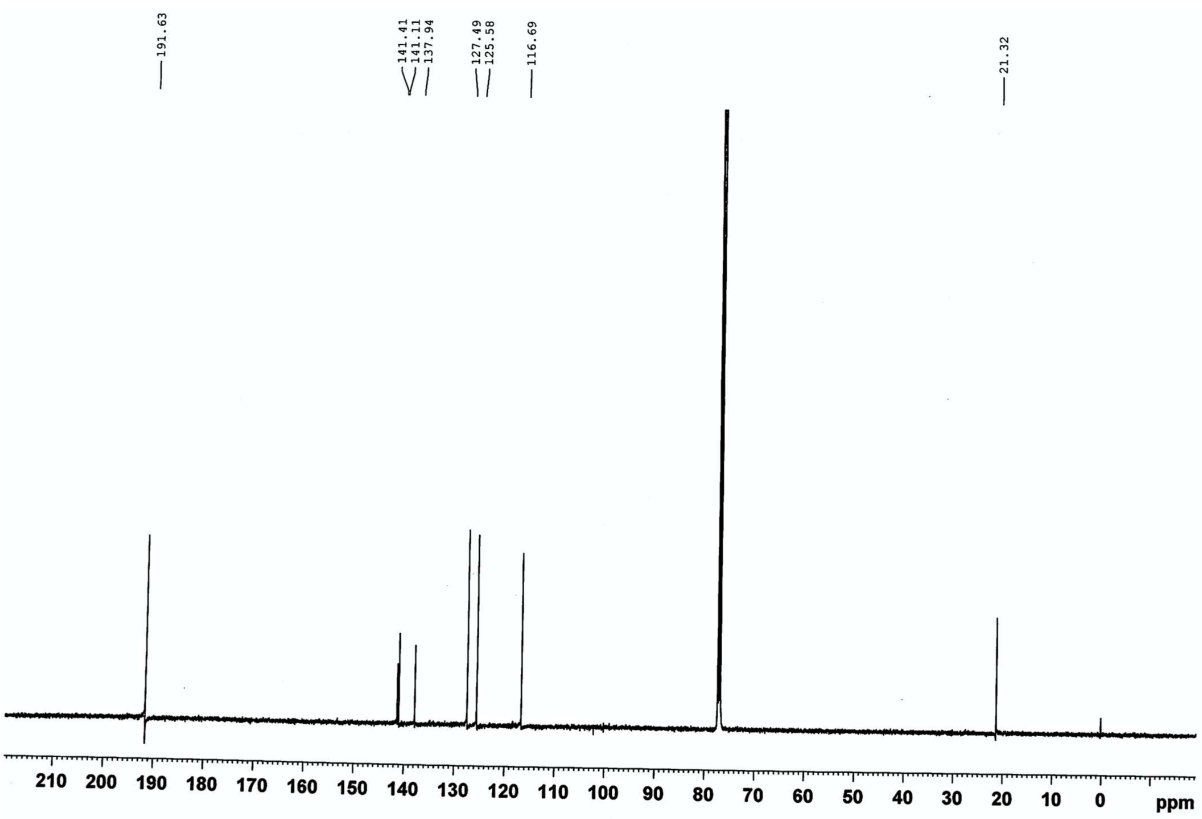
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-(4-azidobiphenyl)benzaldehyde (**7b**) ($CDCl_3$)



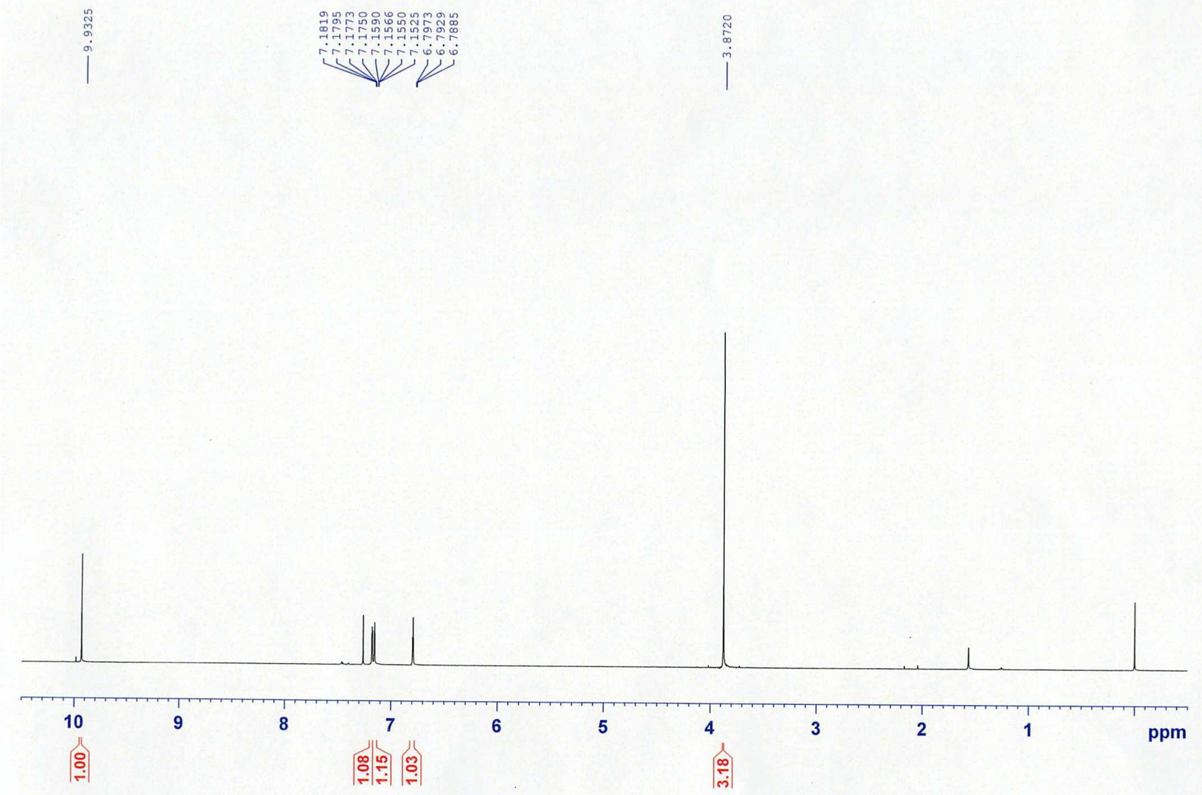


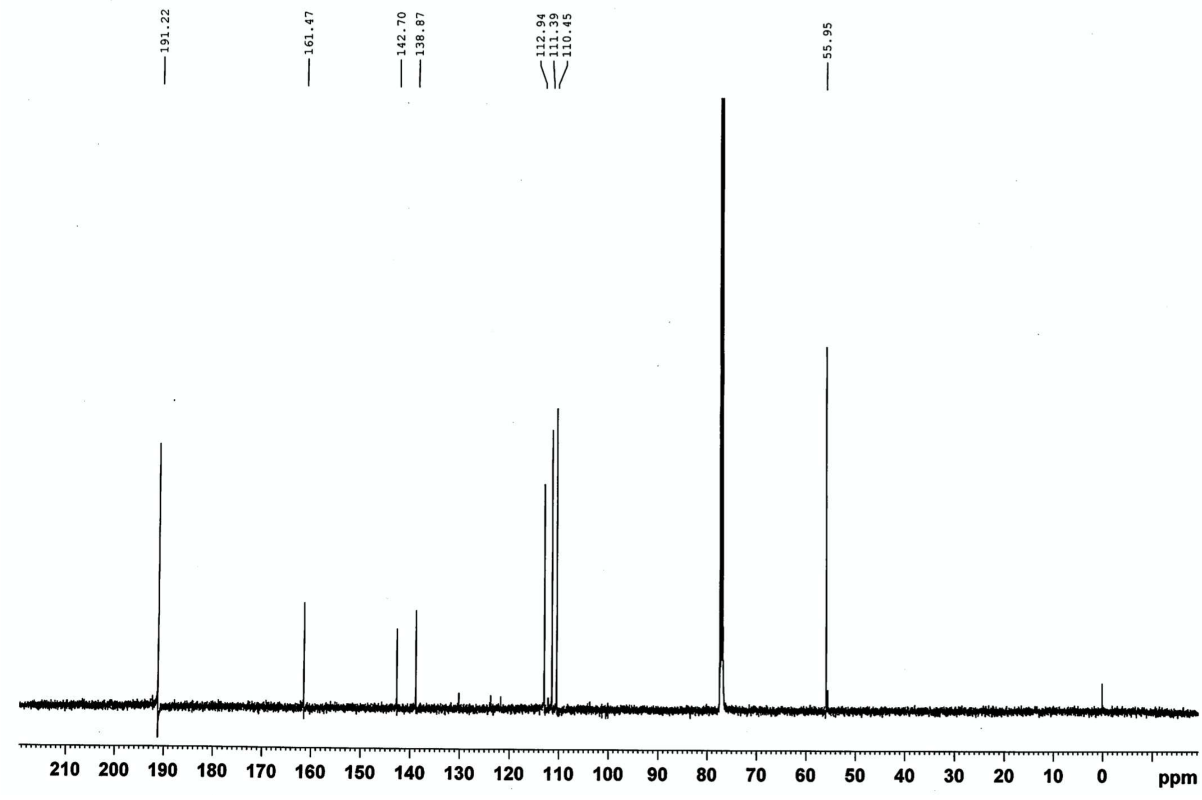
^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 3-azido-5-methylbenzaldehyde (**7c**) ($CDCl_3$)



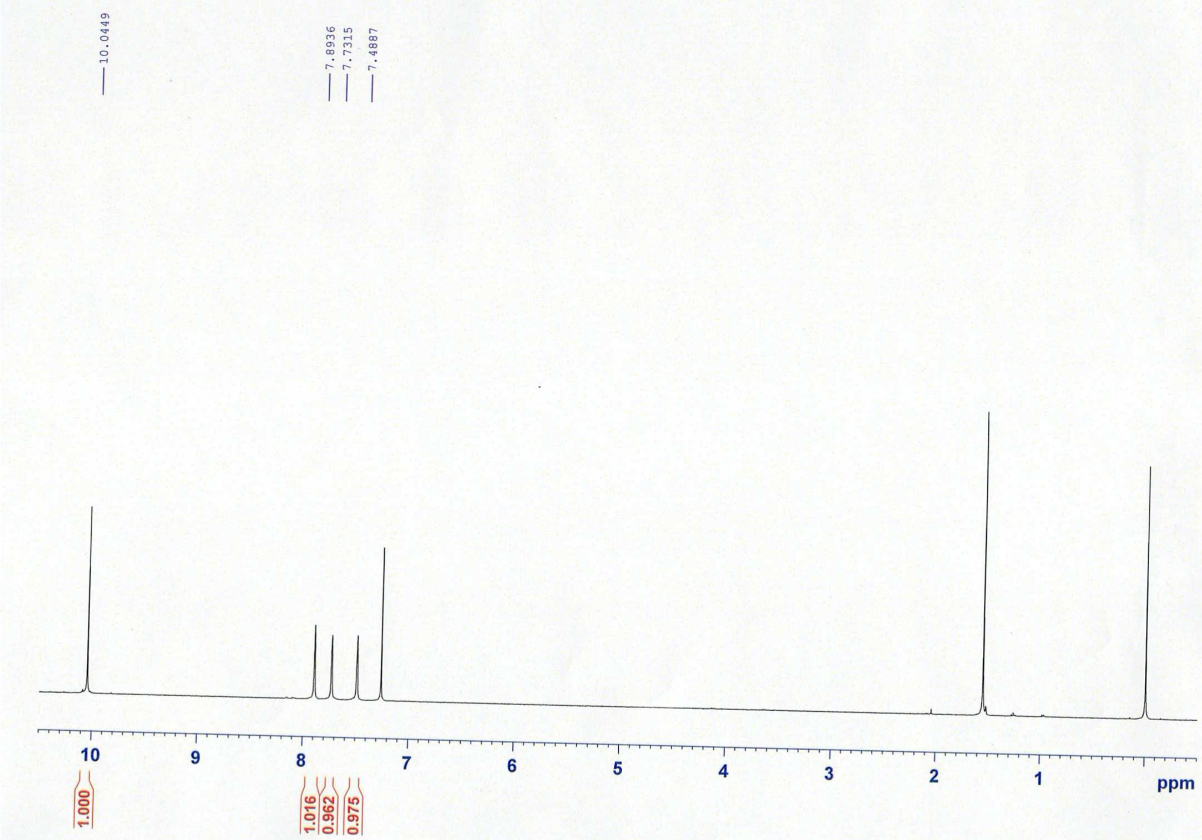


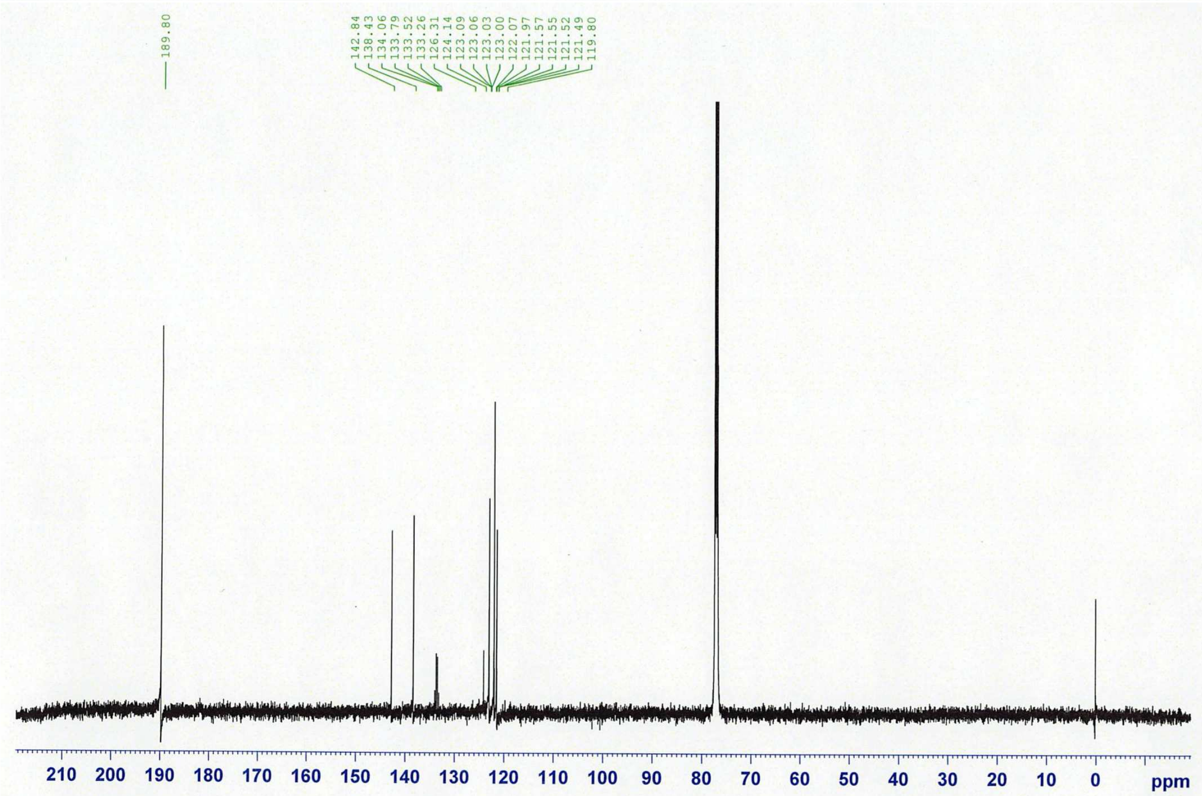
[1]H NMR (500 MHz) and [13]C NMR (126 MHz) spectra of 3-azido-5-methoxybenzaldehyde (**7d**) ($CDCl_3$)



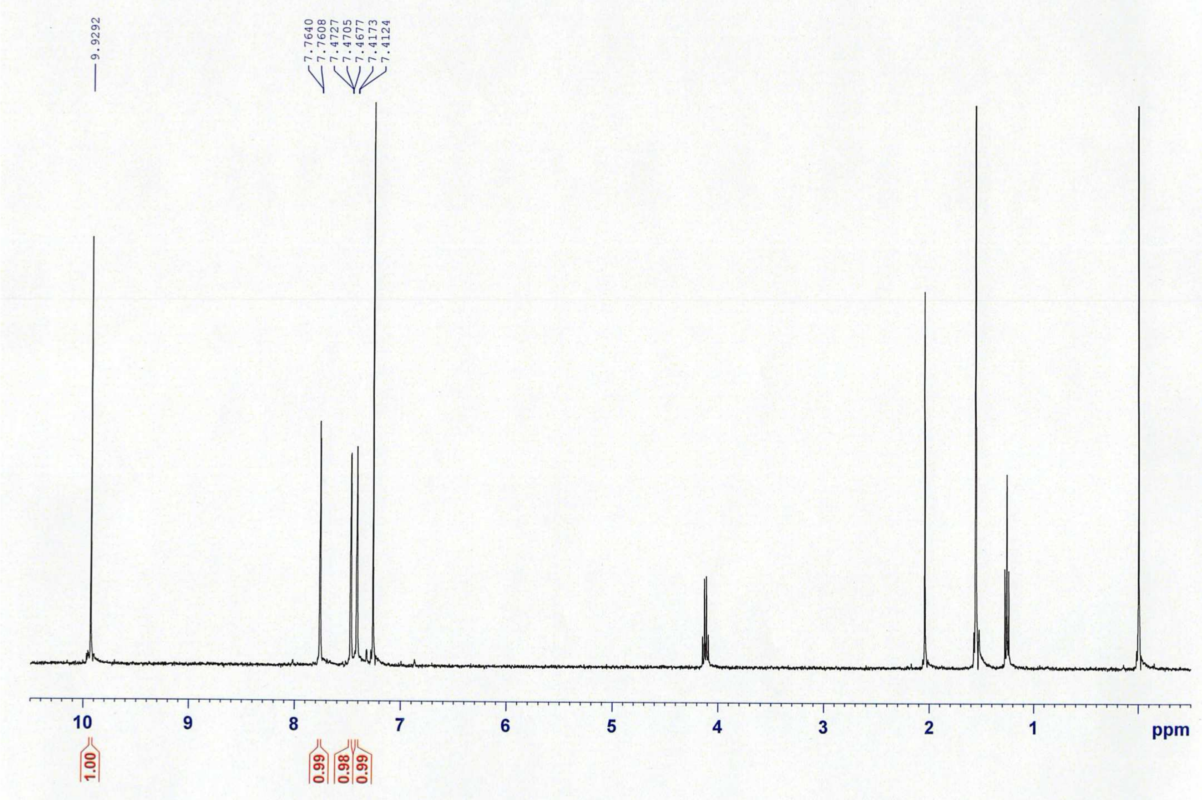


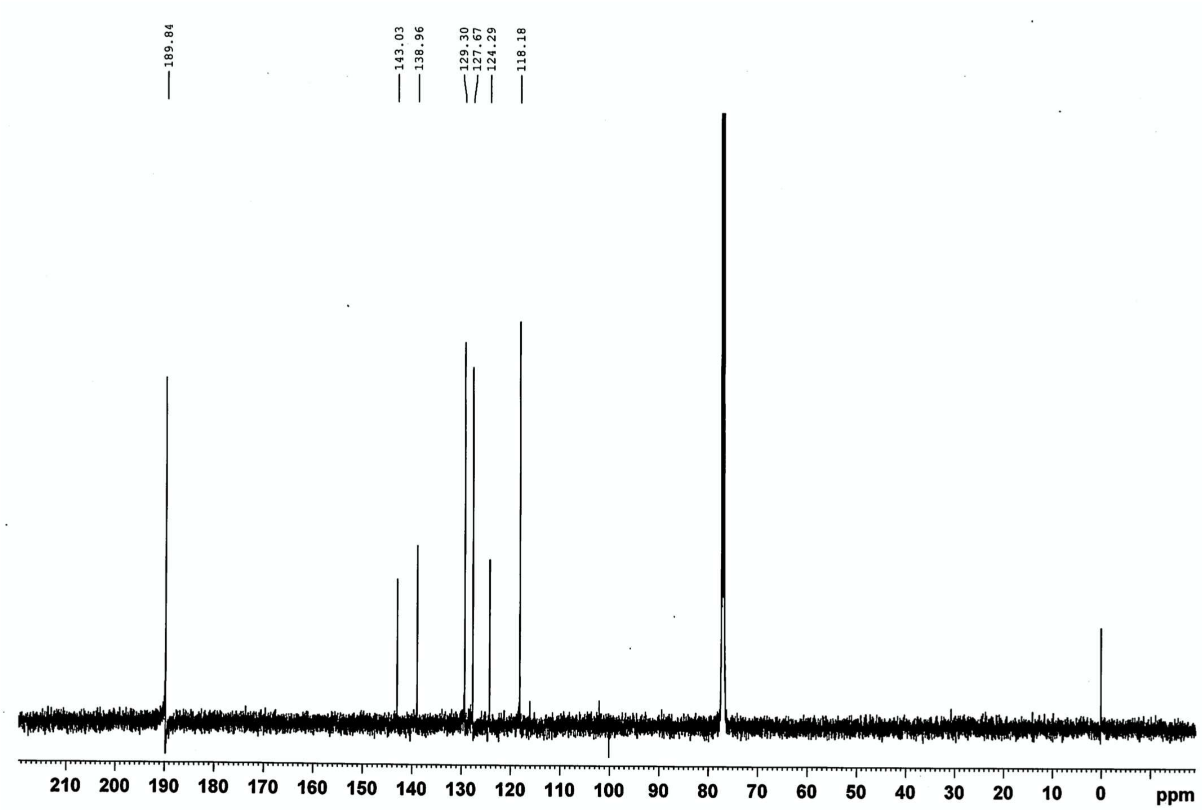
[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of 3-azido-5-(trifluoromethyl)benzaldehyde (**7e**) ($CDCl_3$)



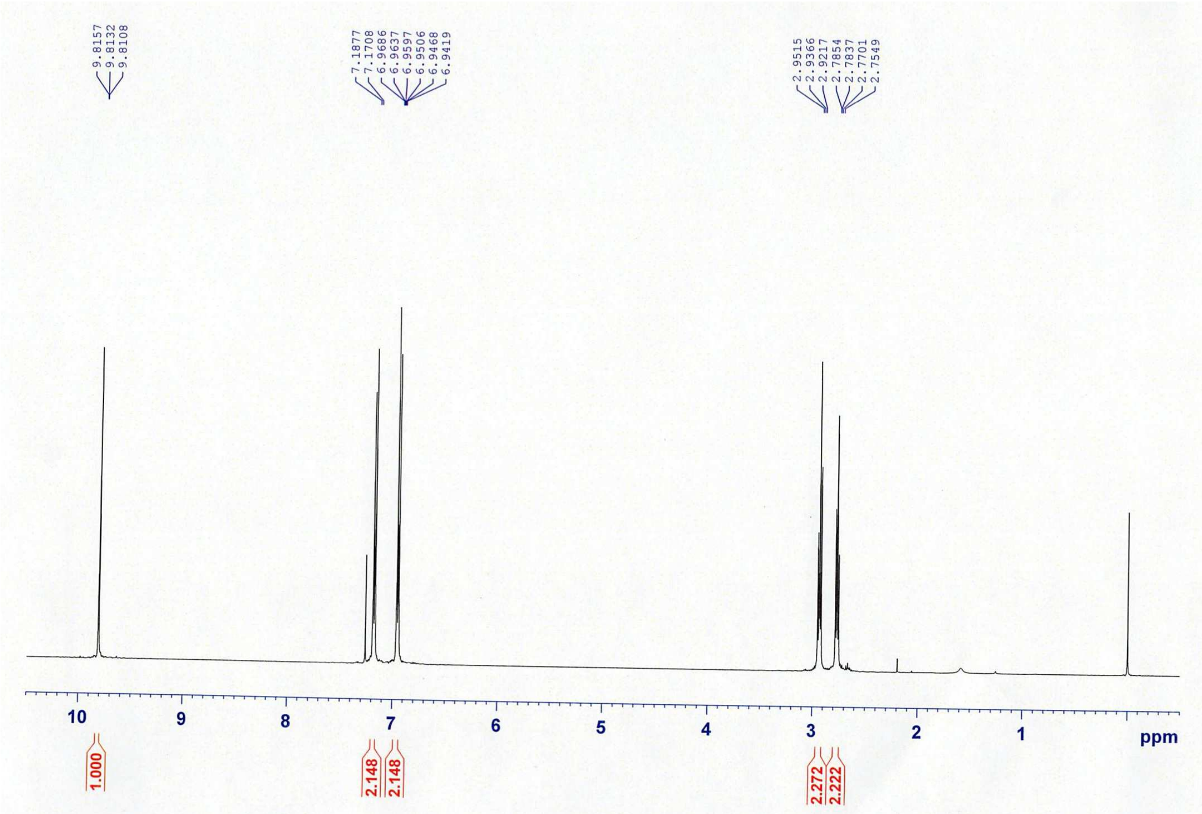


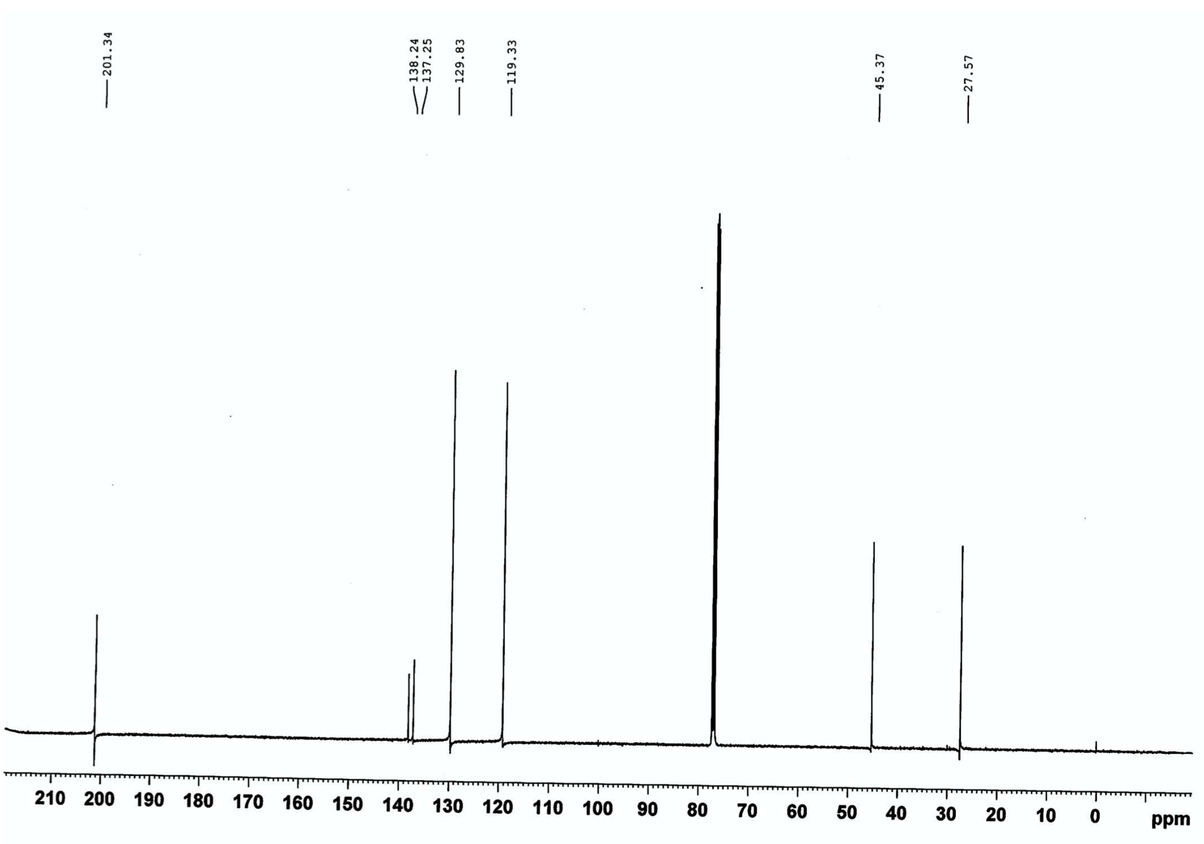
[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of 3-azido-5-bromobenzaldehyde (**7f**) ($CDCl_3$)



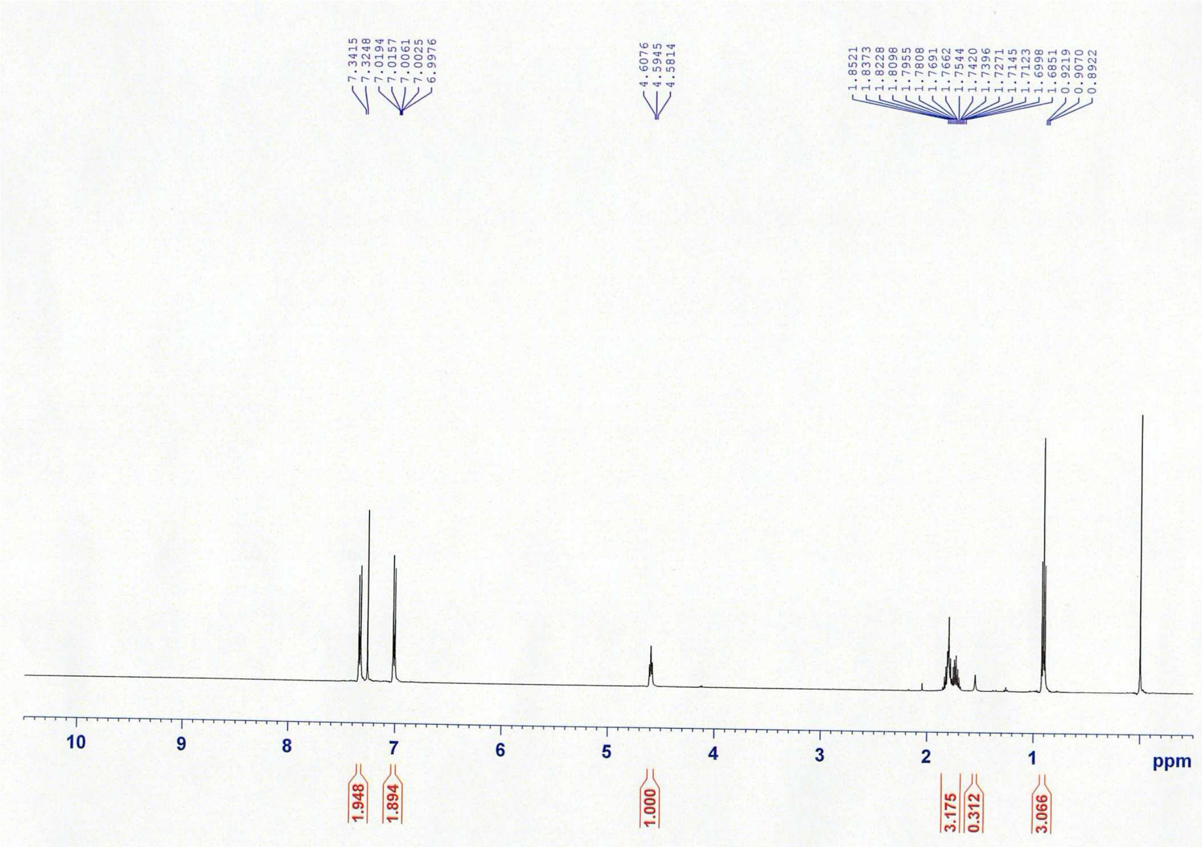


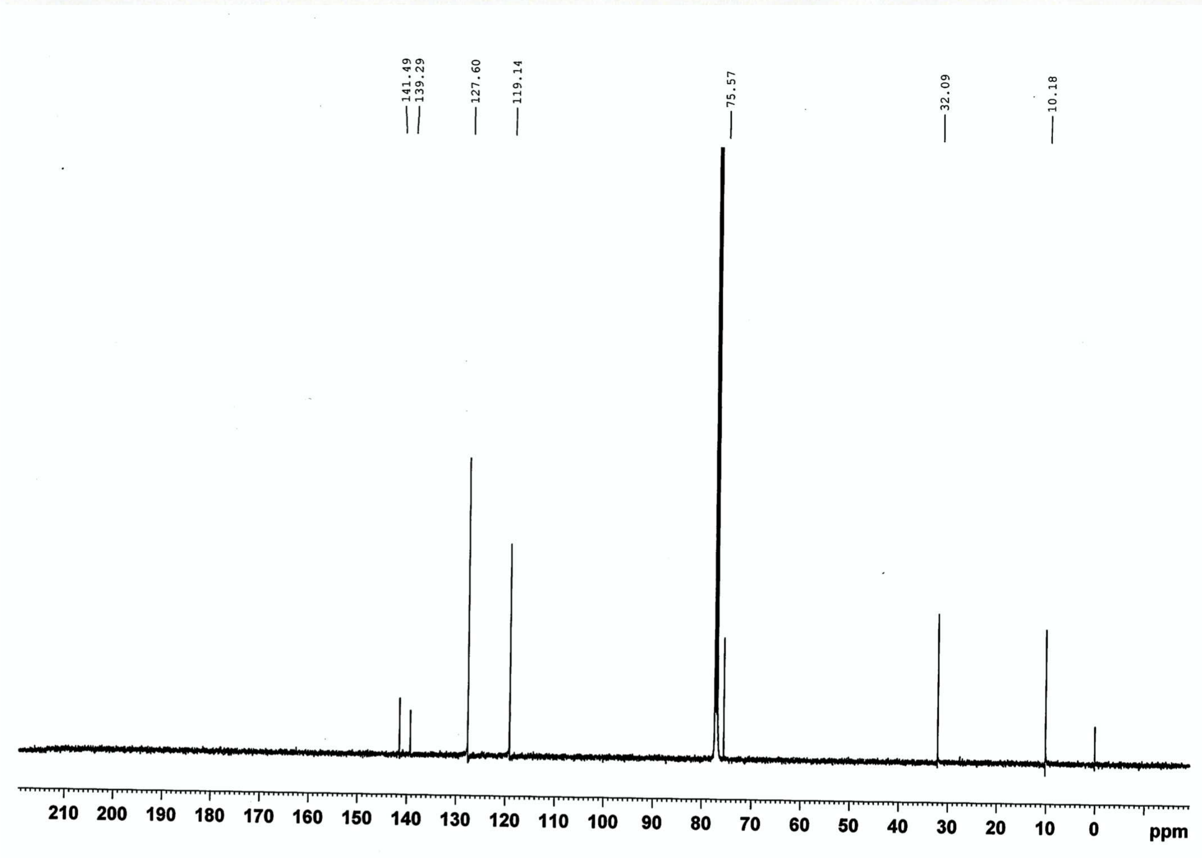
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-(4-azidophenyl)propanal (**7h**) ($CDCl_3$)



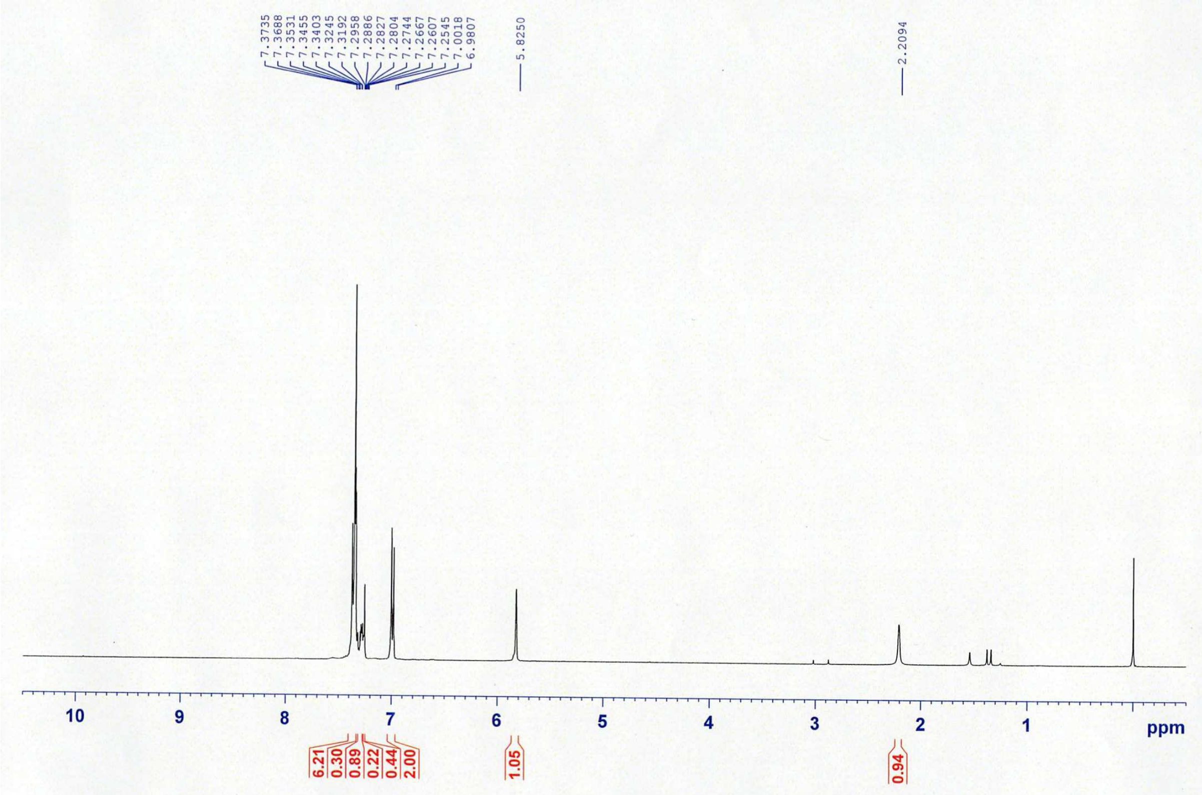


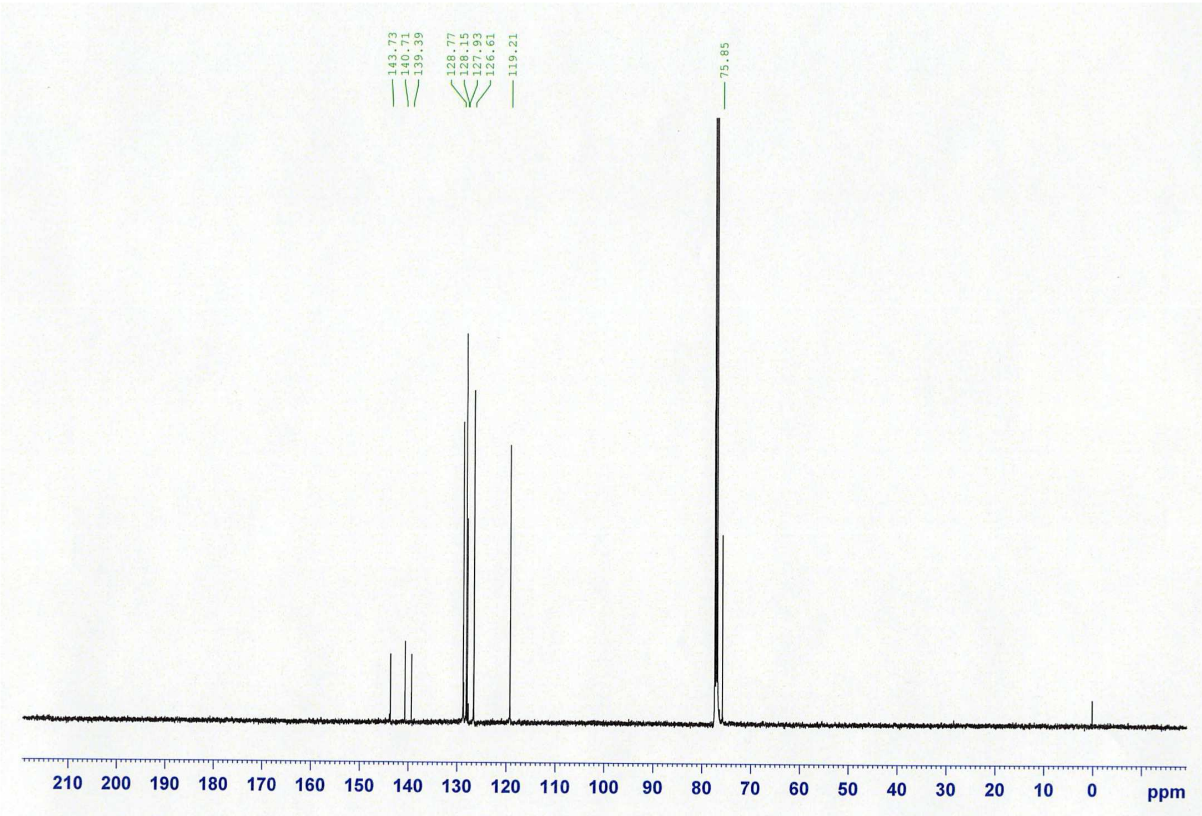
[1]H NMR (500 MHz) and [13]C NMR (126 MHz) spectra of 1-(4-azidophenyl)-1-propanol (**8a**) ($CDCl_3$)



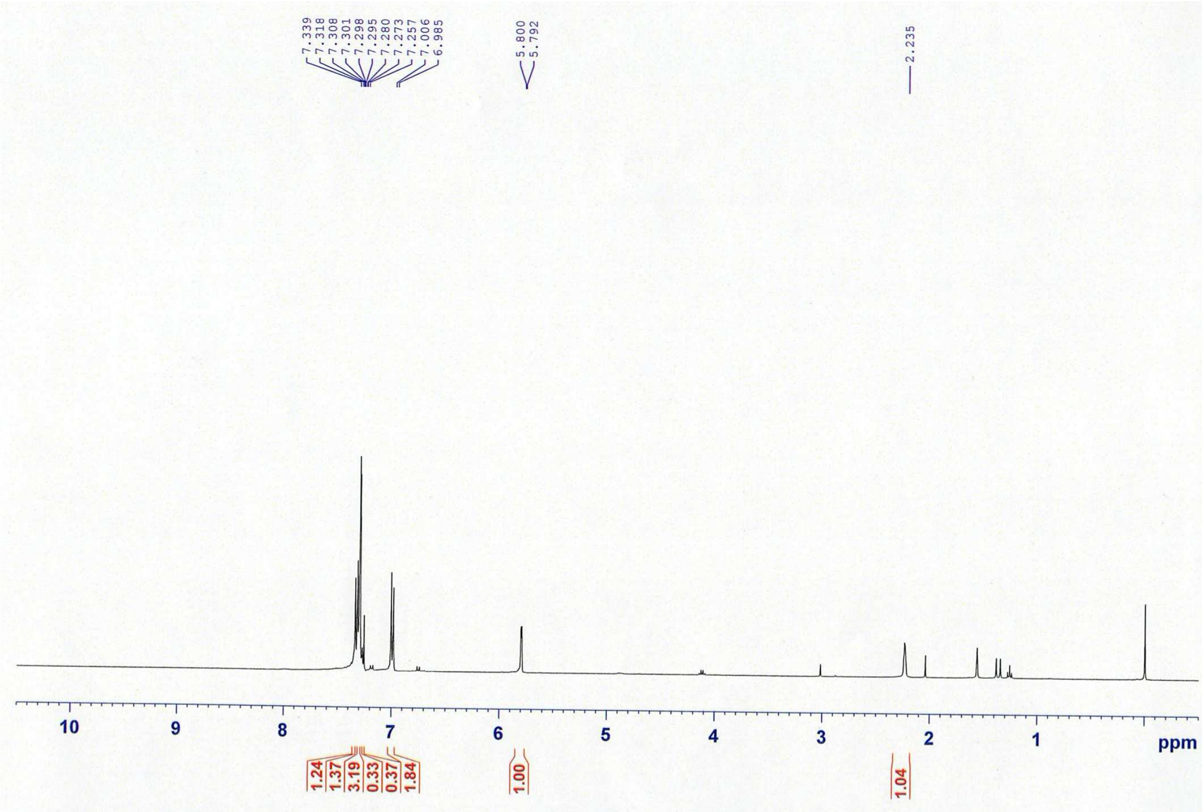


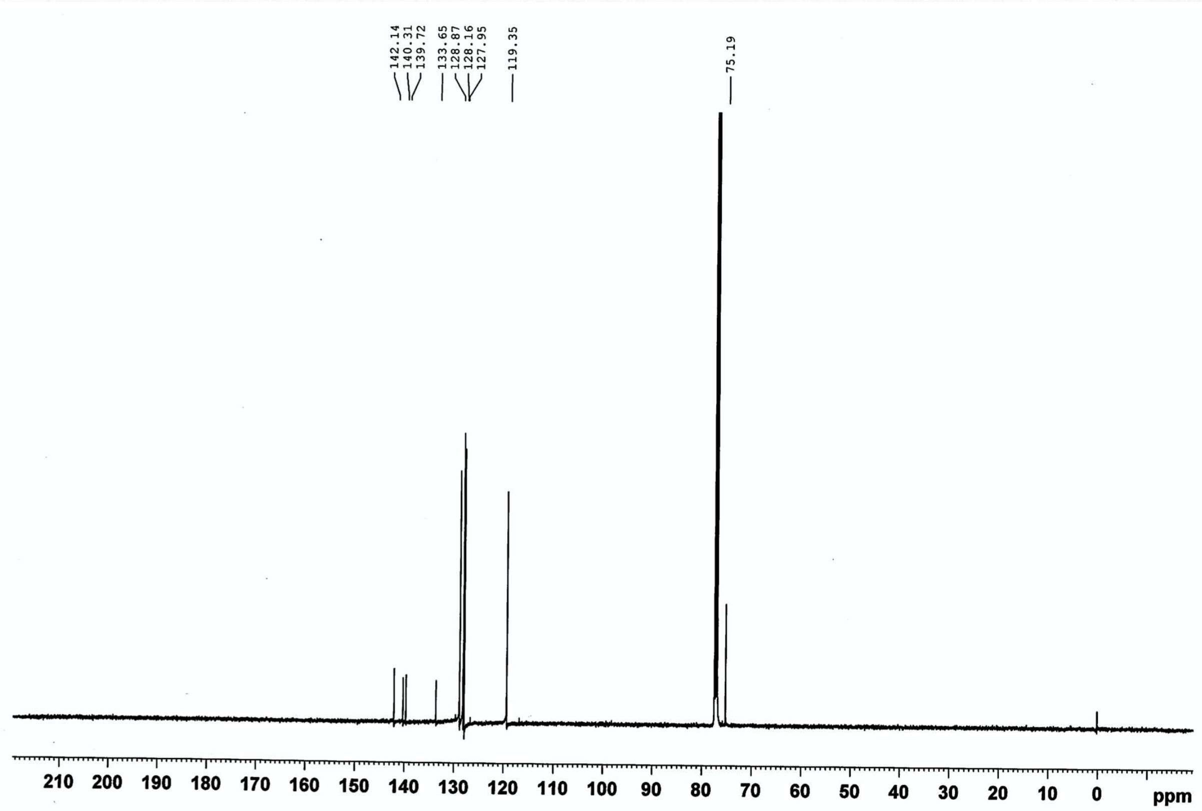
^1H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-Azidophenyl)-1-phenylmethanol (**8b**) ($CDCl_3$)



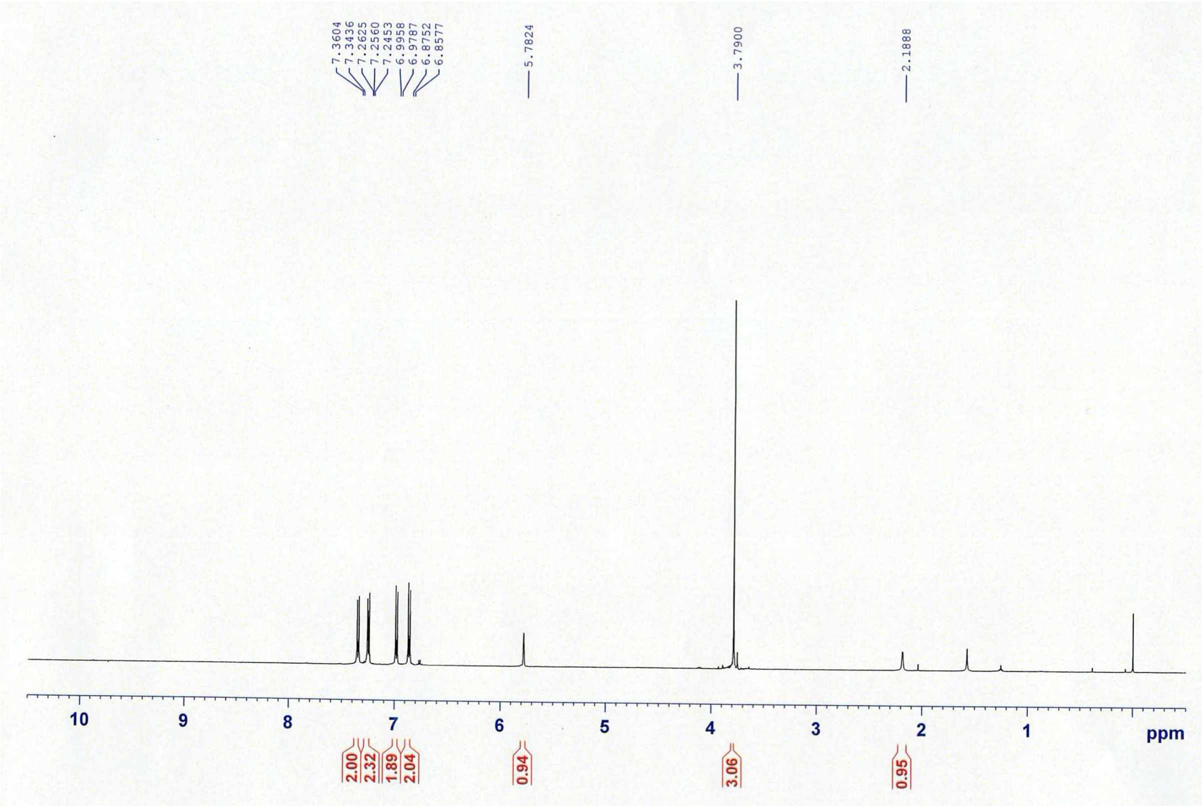


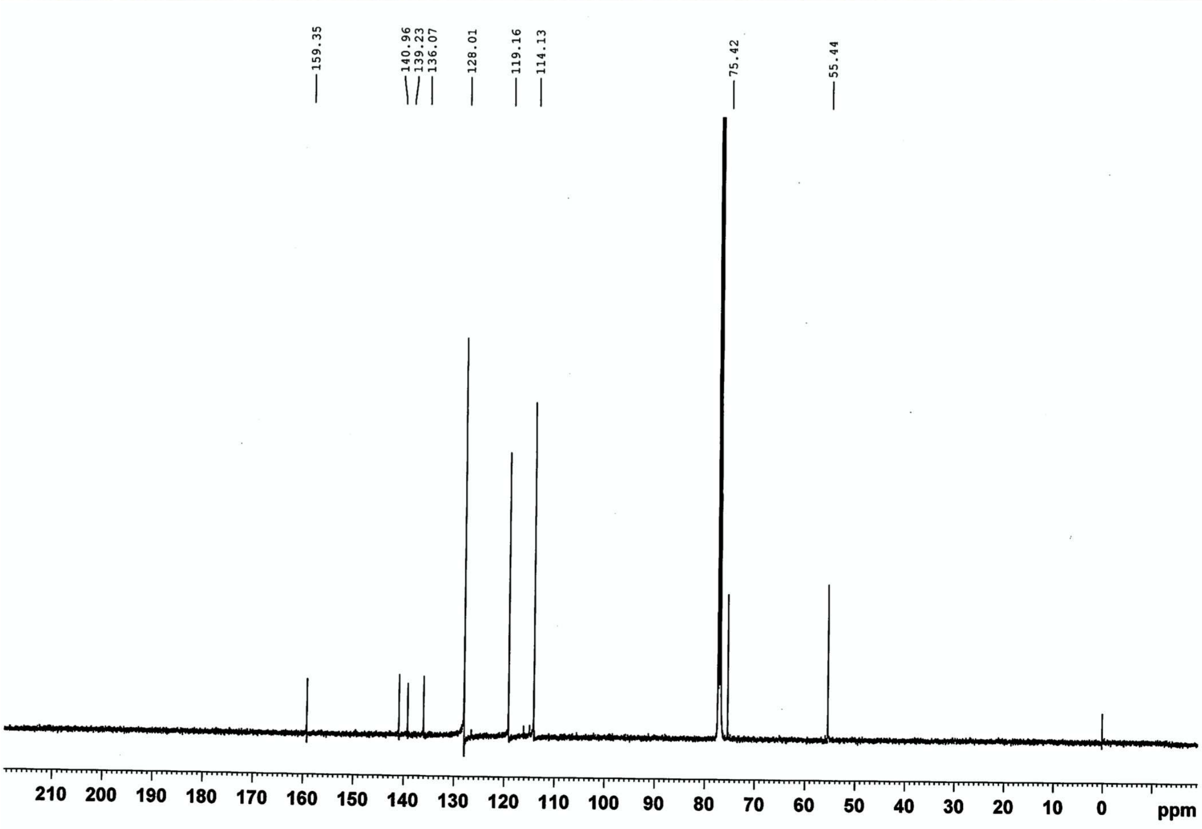
^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-azidophenyl)-1-(4-chlorophenyl)methanol (**8c**) ($CDCl_3$)



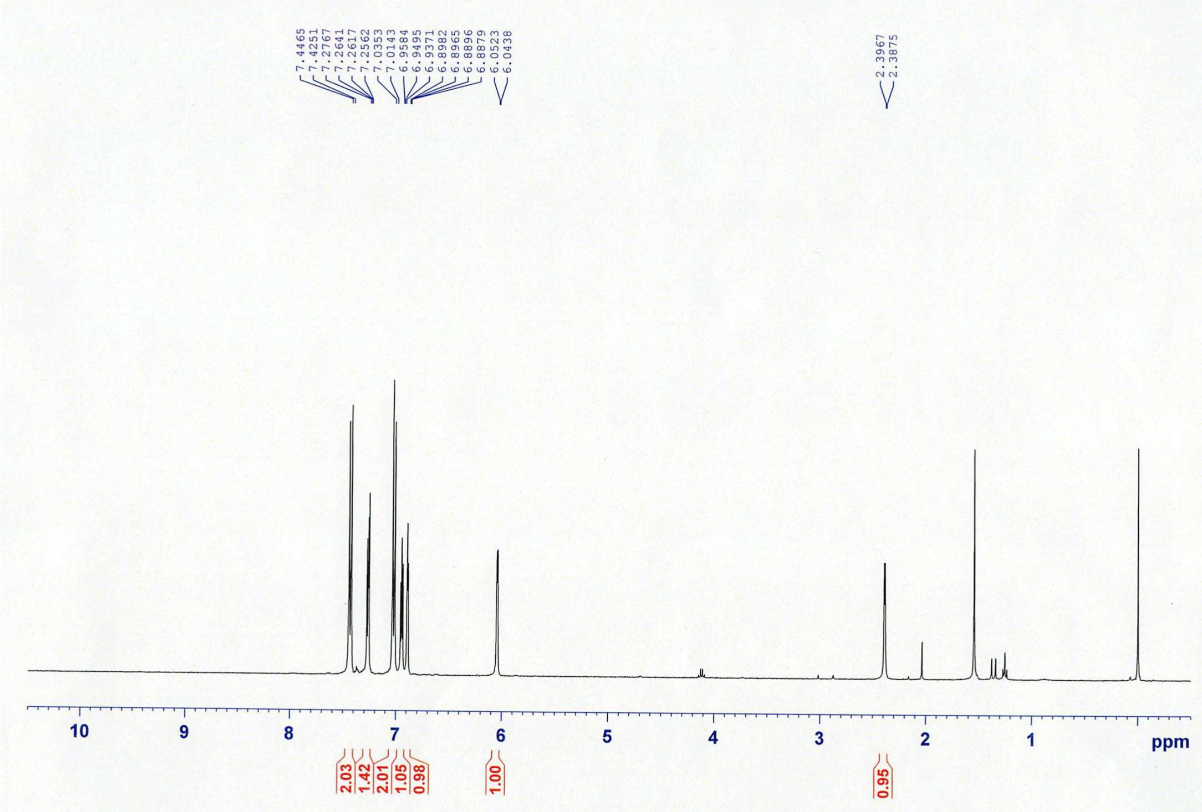


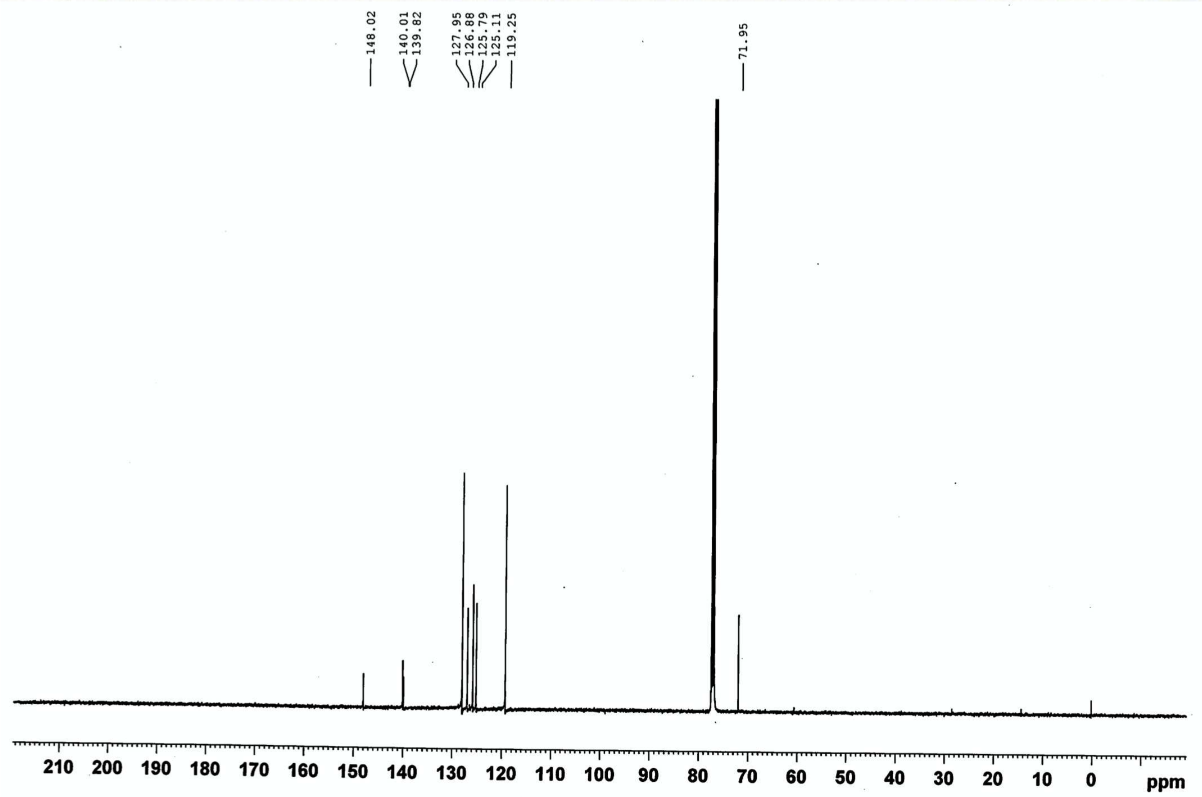
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-azidophenyl)-1-(4-methoxyphenyl)methanol (**8d**) ($CDCl_3$)



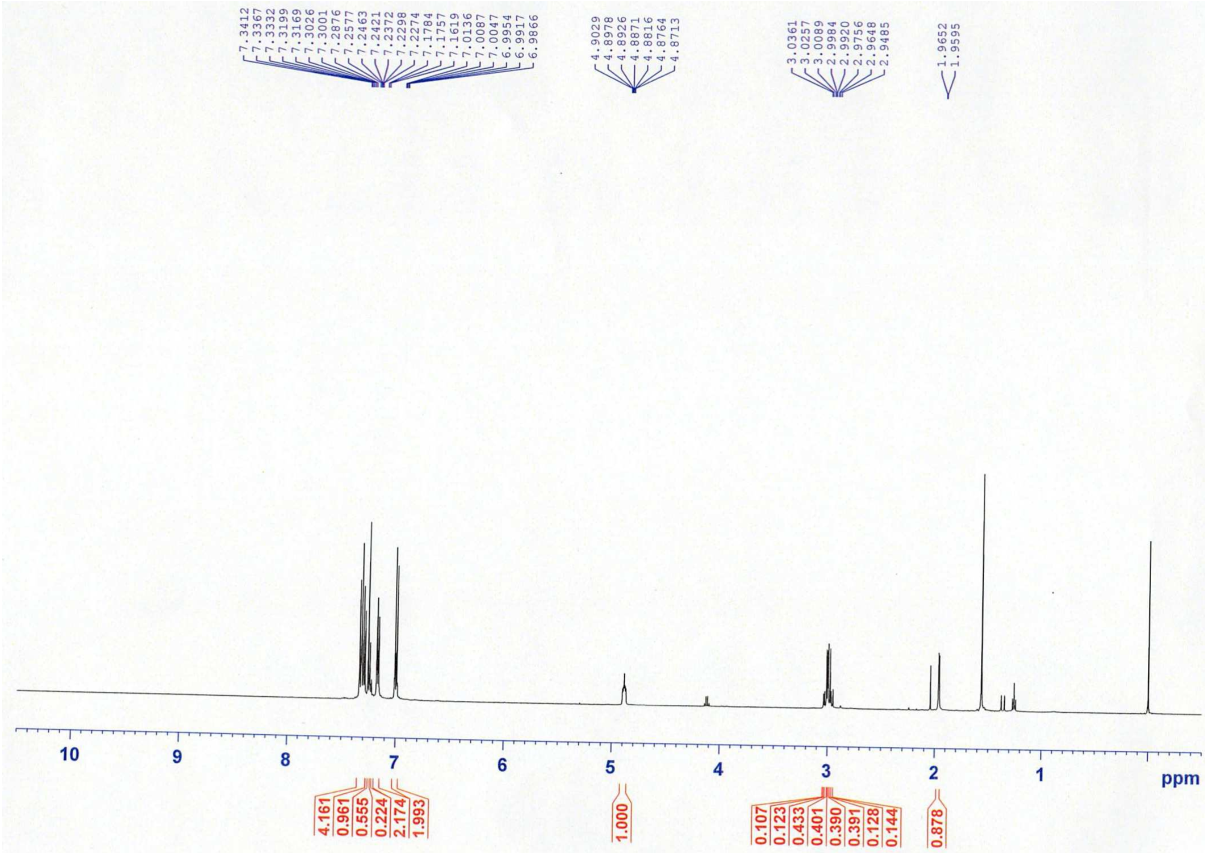


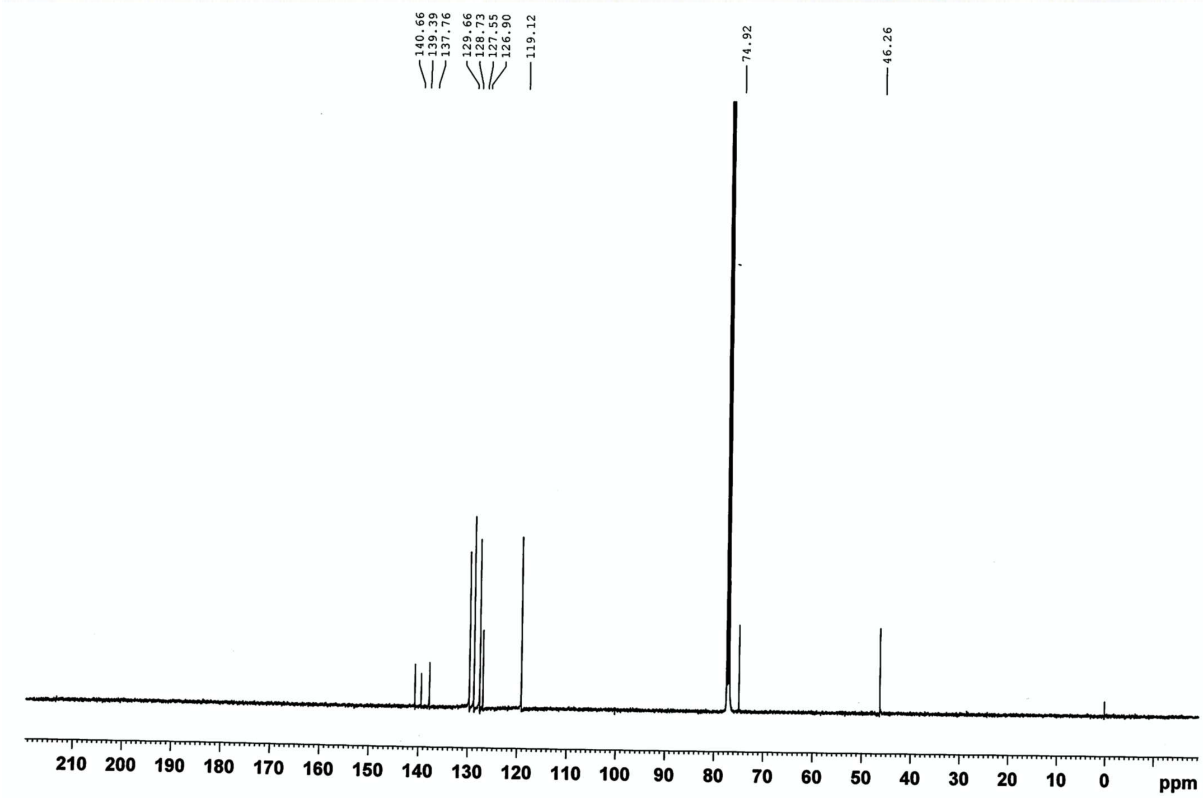
^1H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-azidophenyl)-2-thienylmethanol (**8e**) ($CDCl_3$)



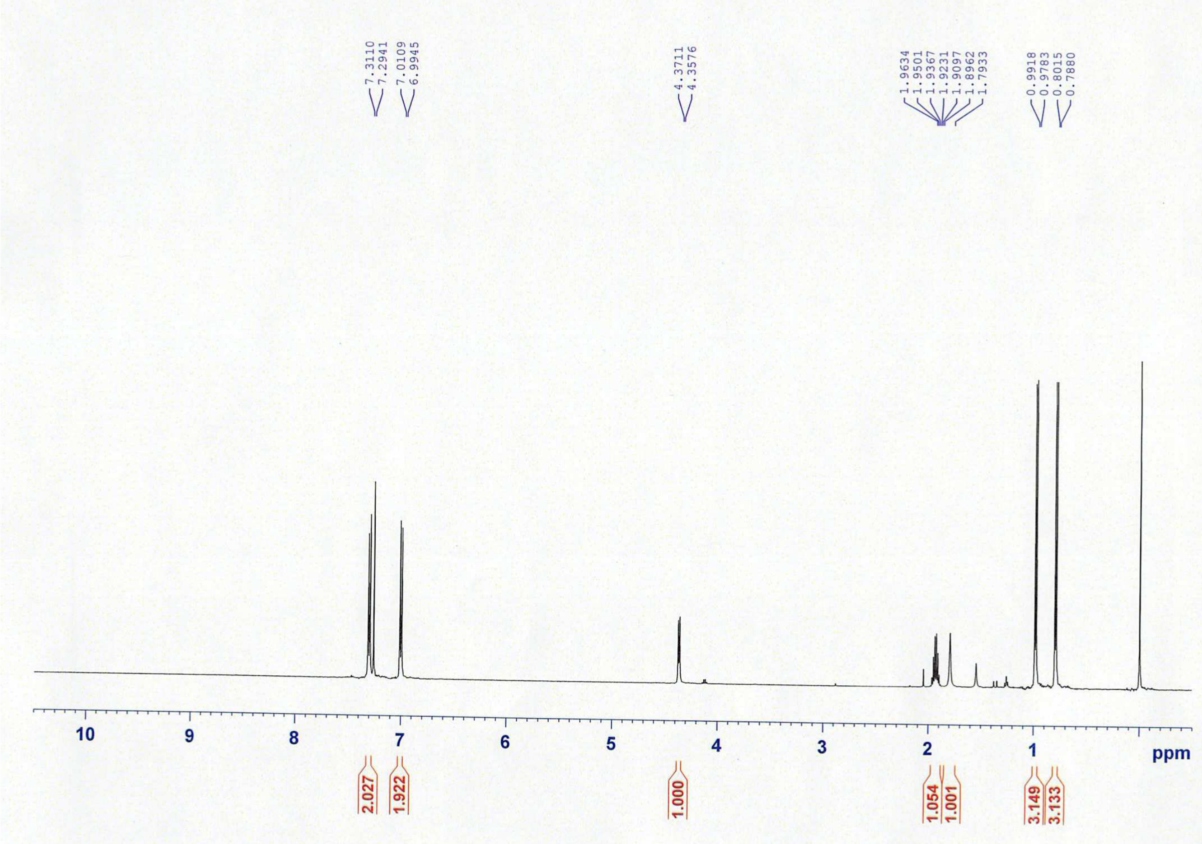


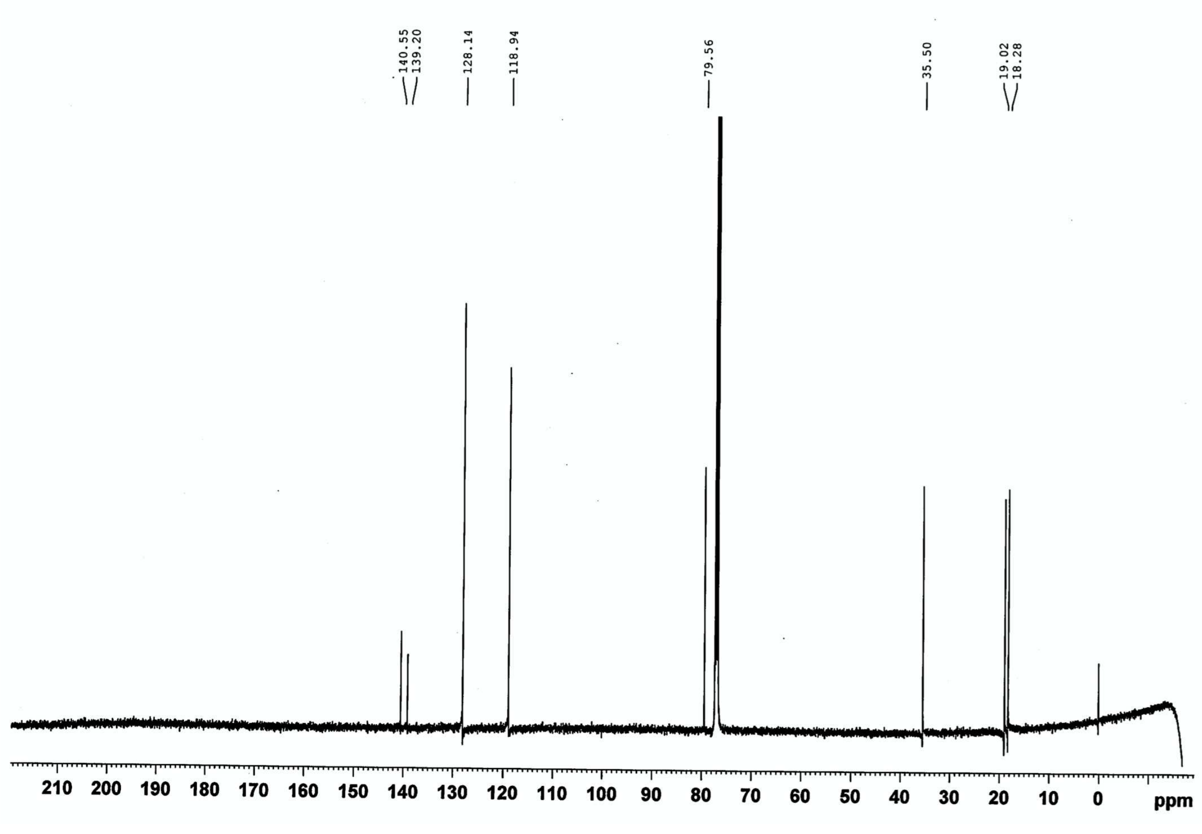
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-azidophenyl)-2-phenylethanol (**8f**) ($CDCl_3$)



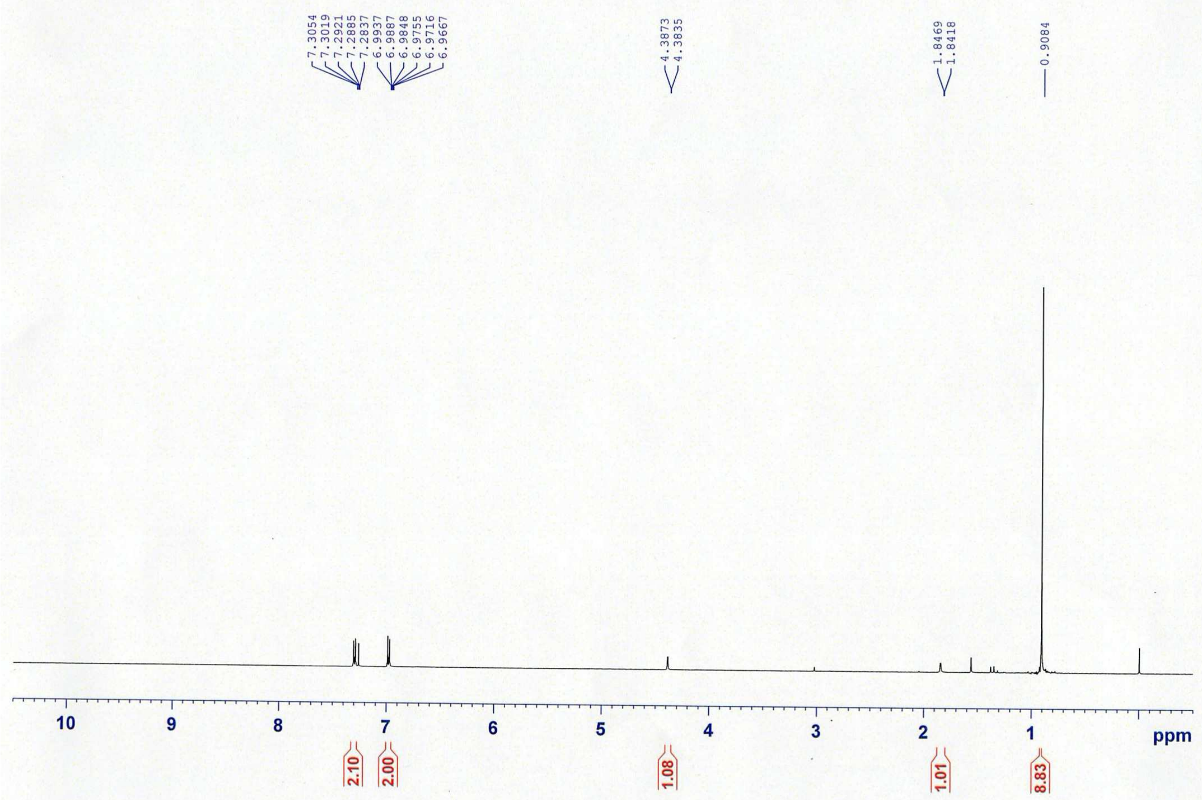


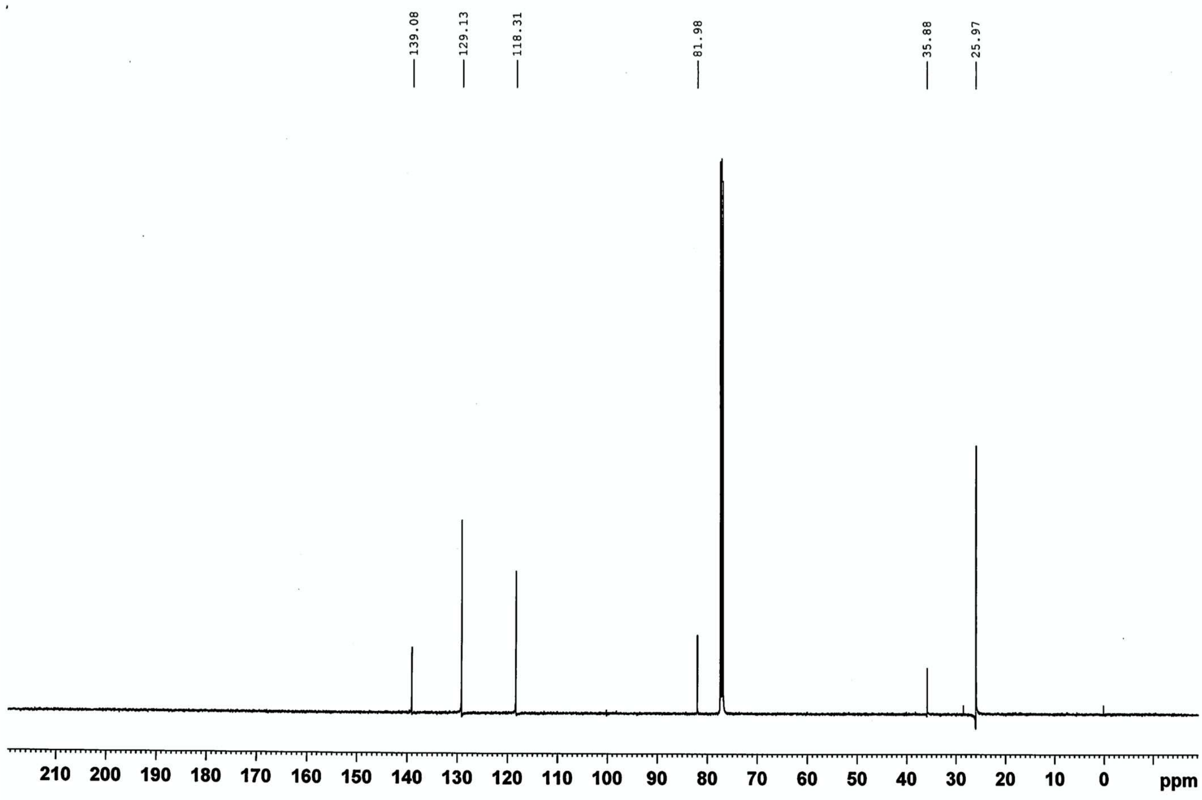
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-azidophenyl)2-methyl-1-propanol (**8h**) ($CDCl_3$)



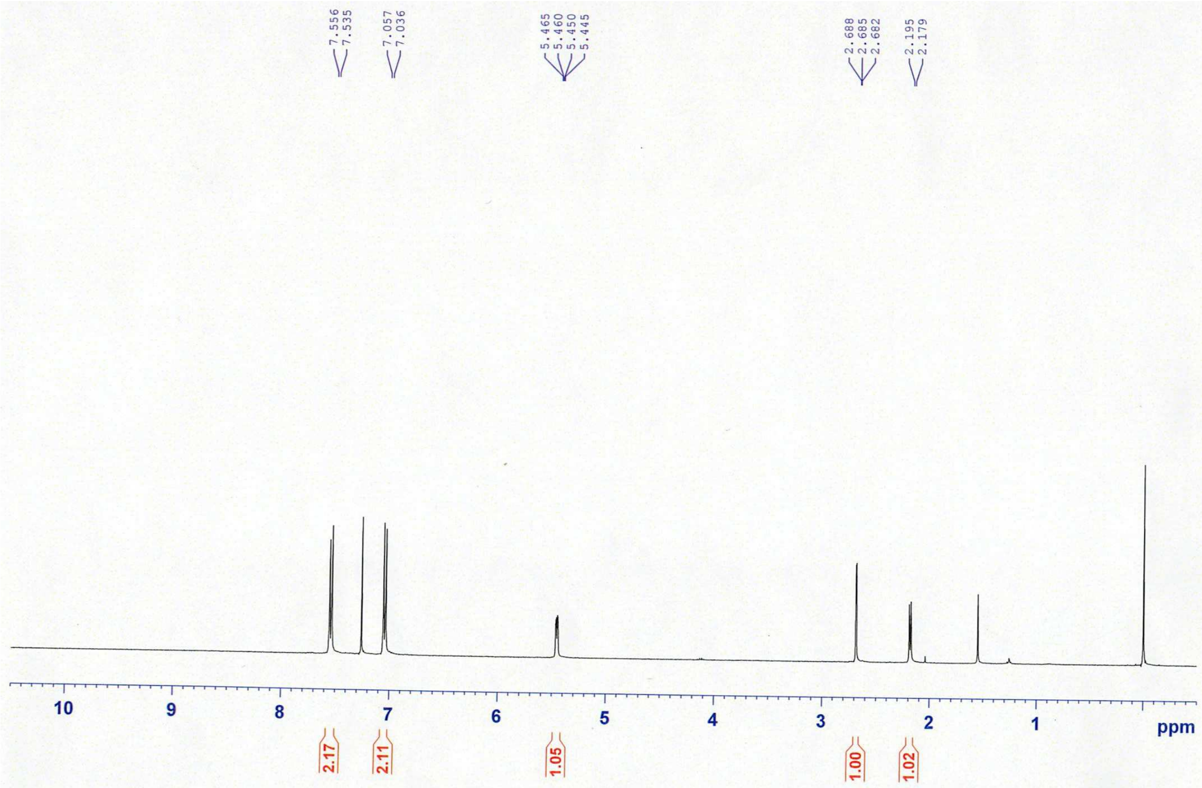


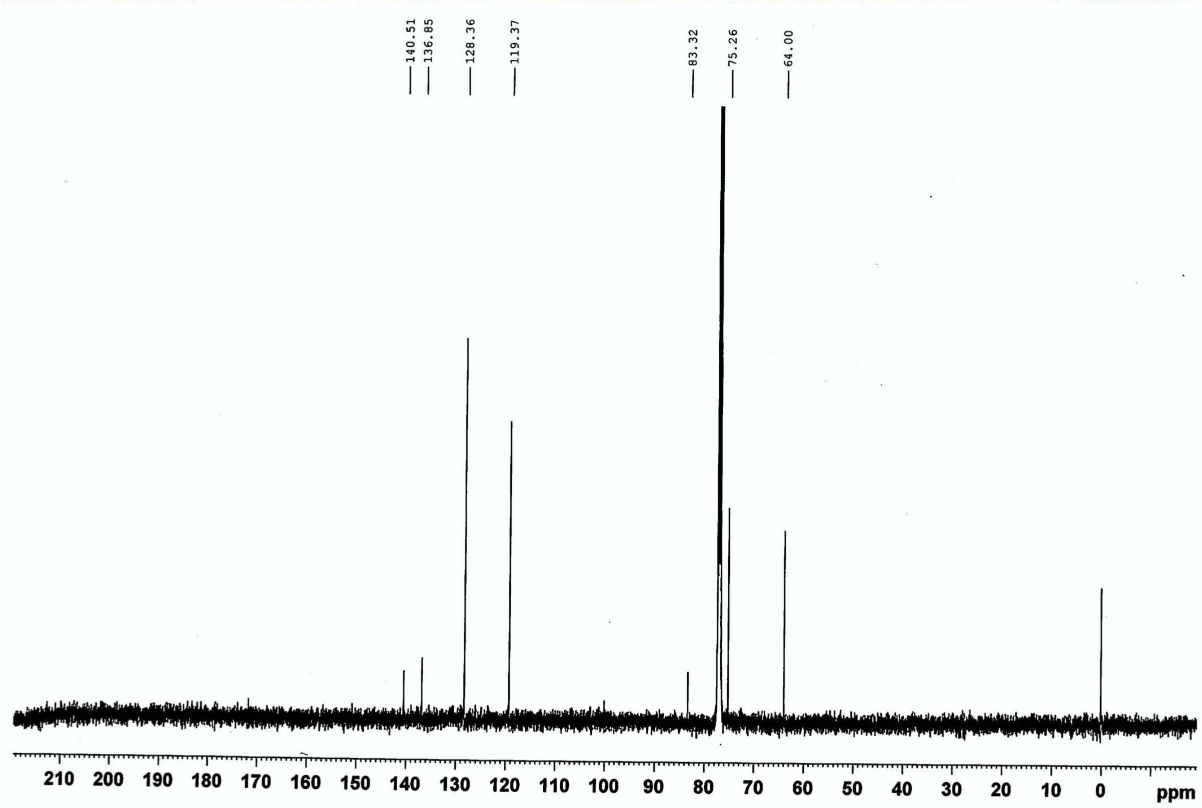
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-azidophenyl-tert-butyl-methylalcohol (**8i**) ($CDCl_3$)



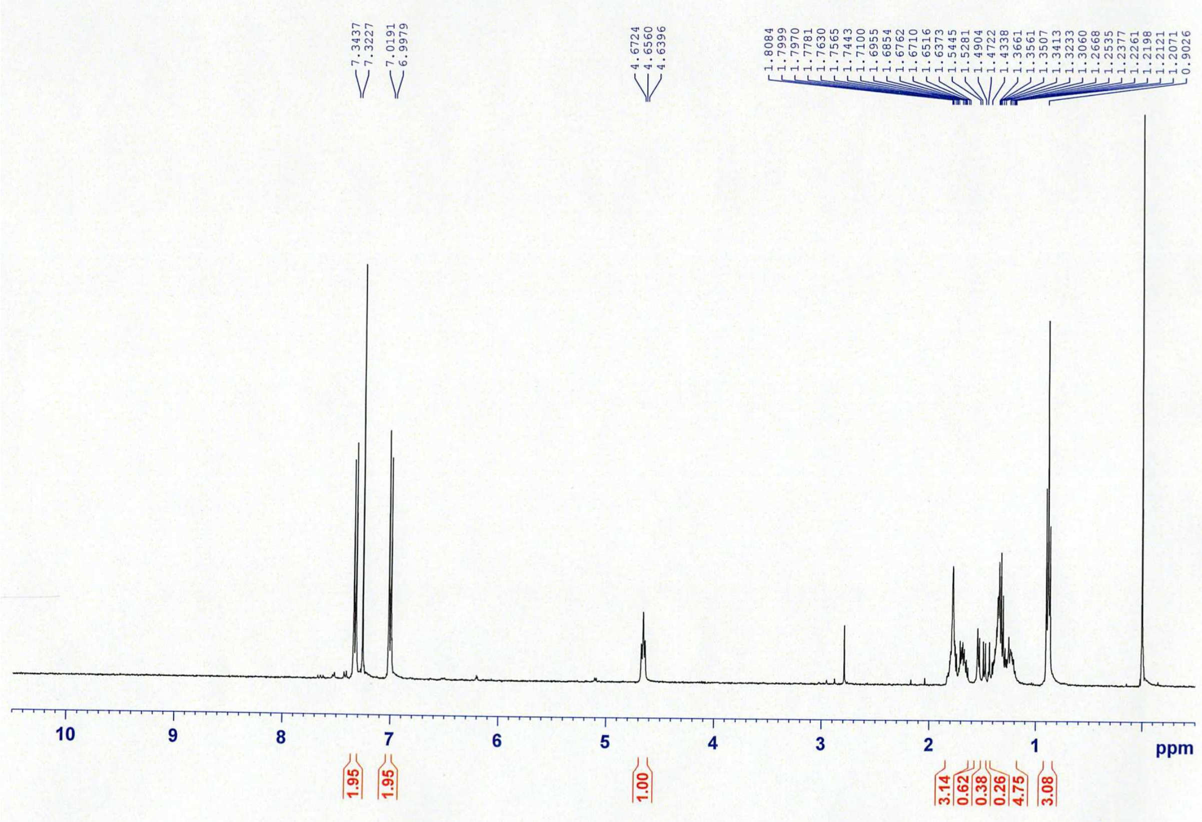


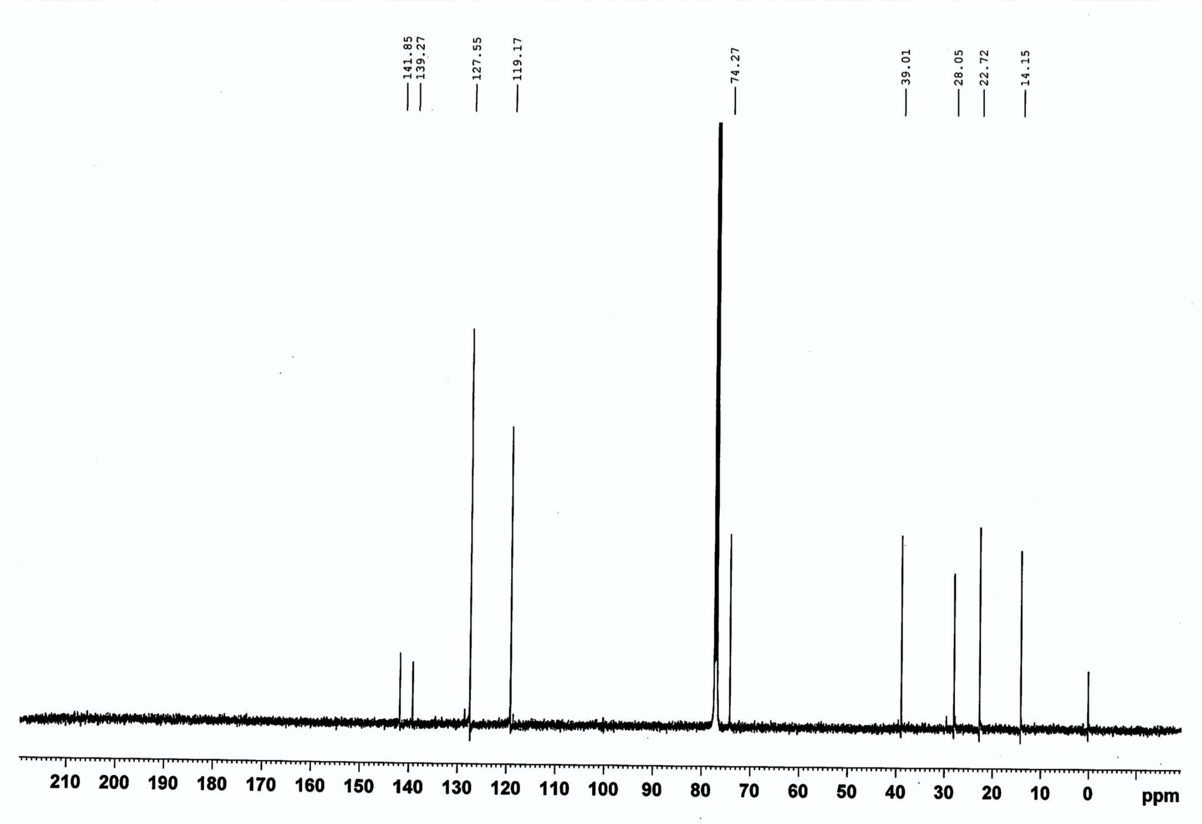
^1H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-azidophenyl)propargyl alcohol (**8j**) ($CDCl_3$)



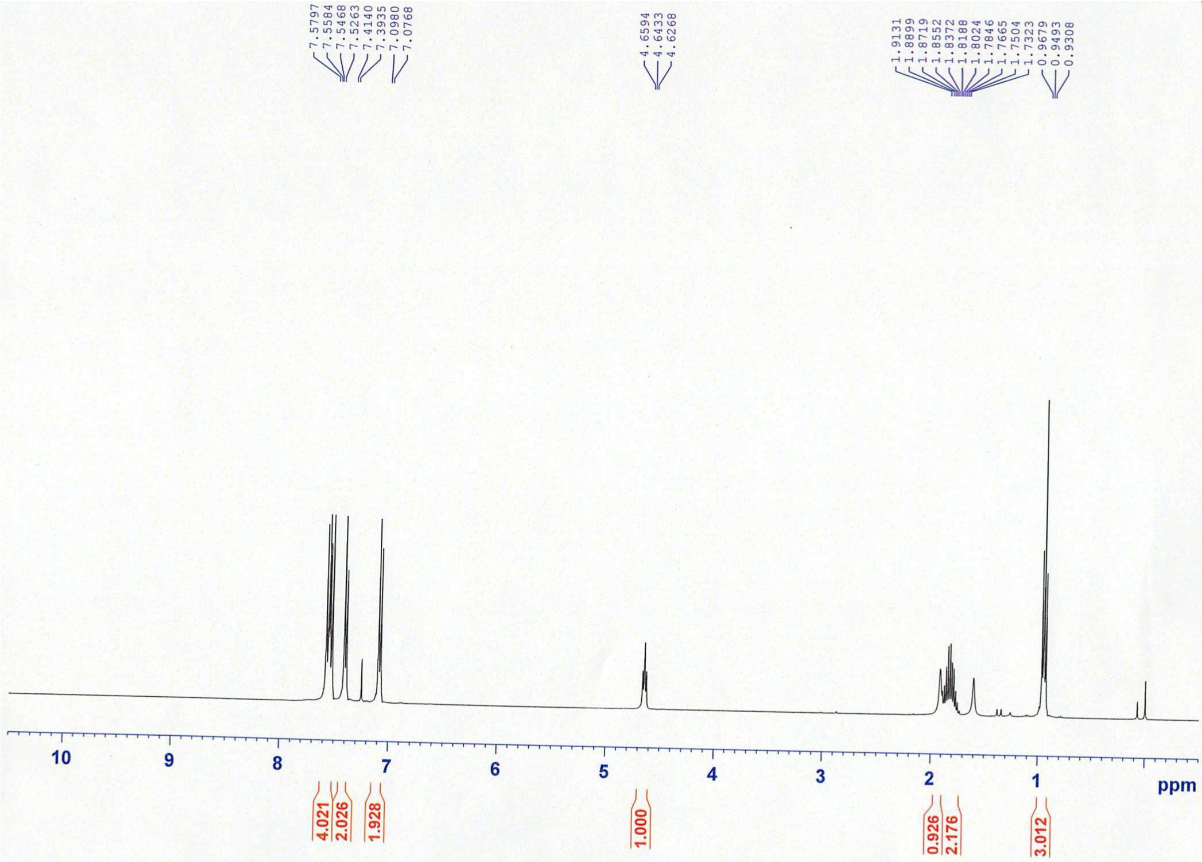


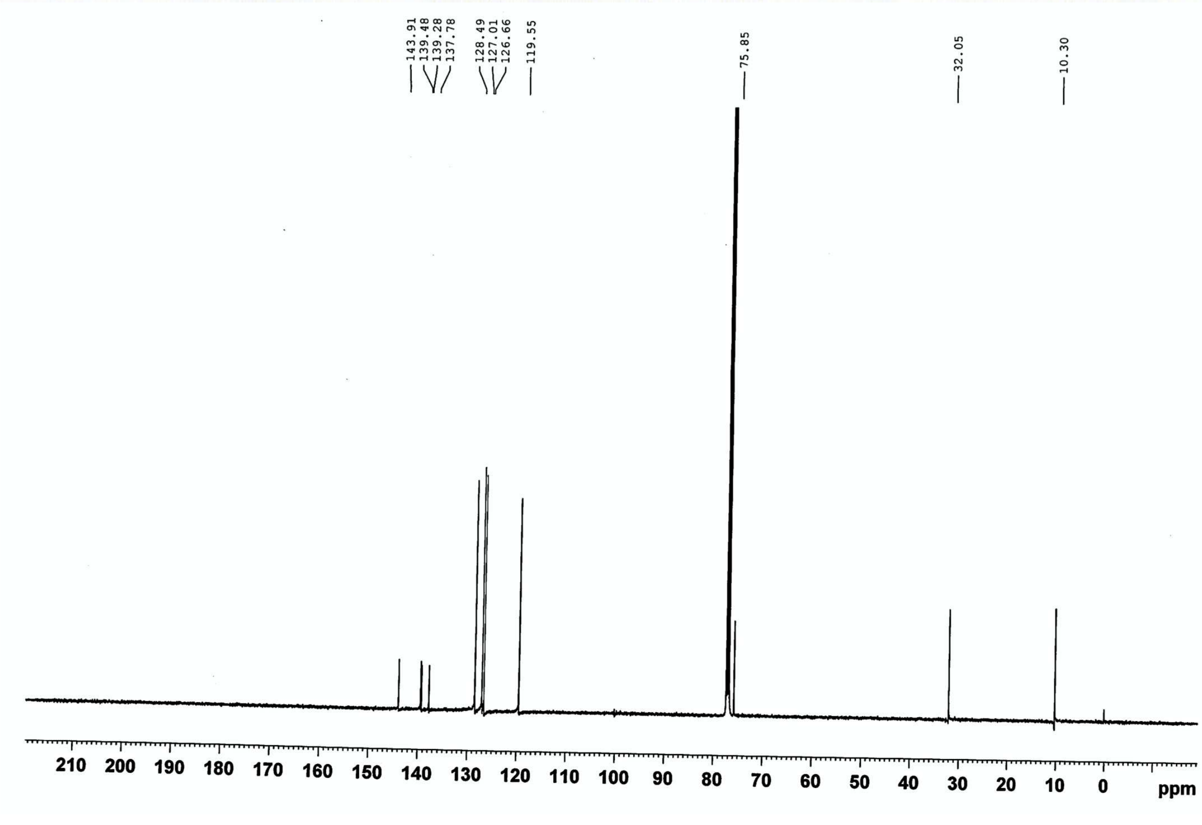
^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-azidophenyl)-1-pentanol (**8k**) ($CDCl_3$)



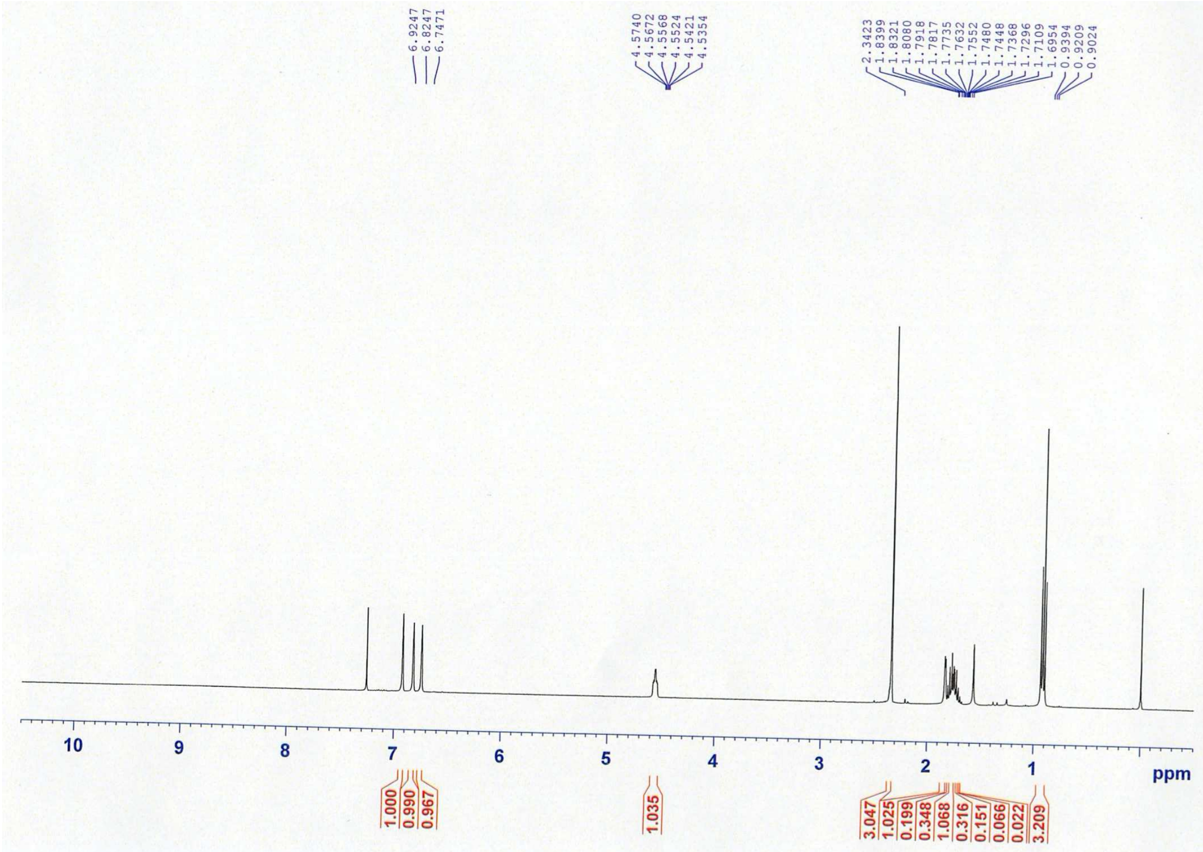


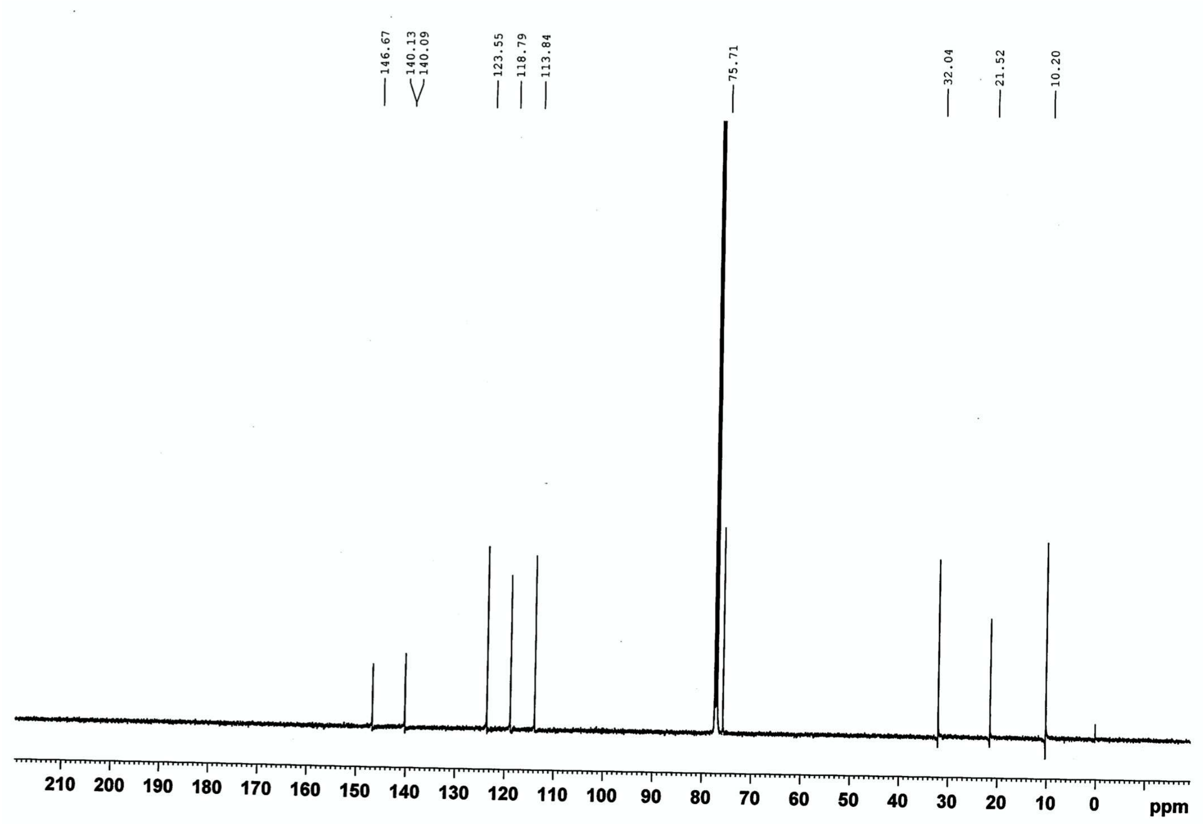
[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of 1-(4-azidobiphenyl)-1-propanol (**8l**) ($CDCl_3$)



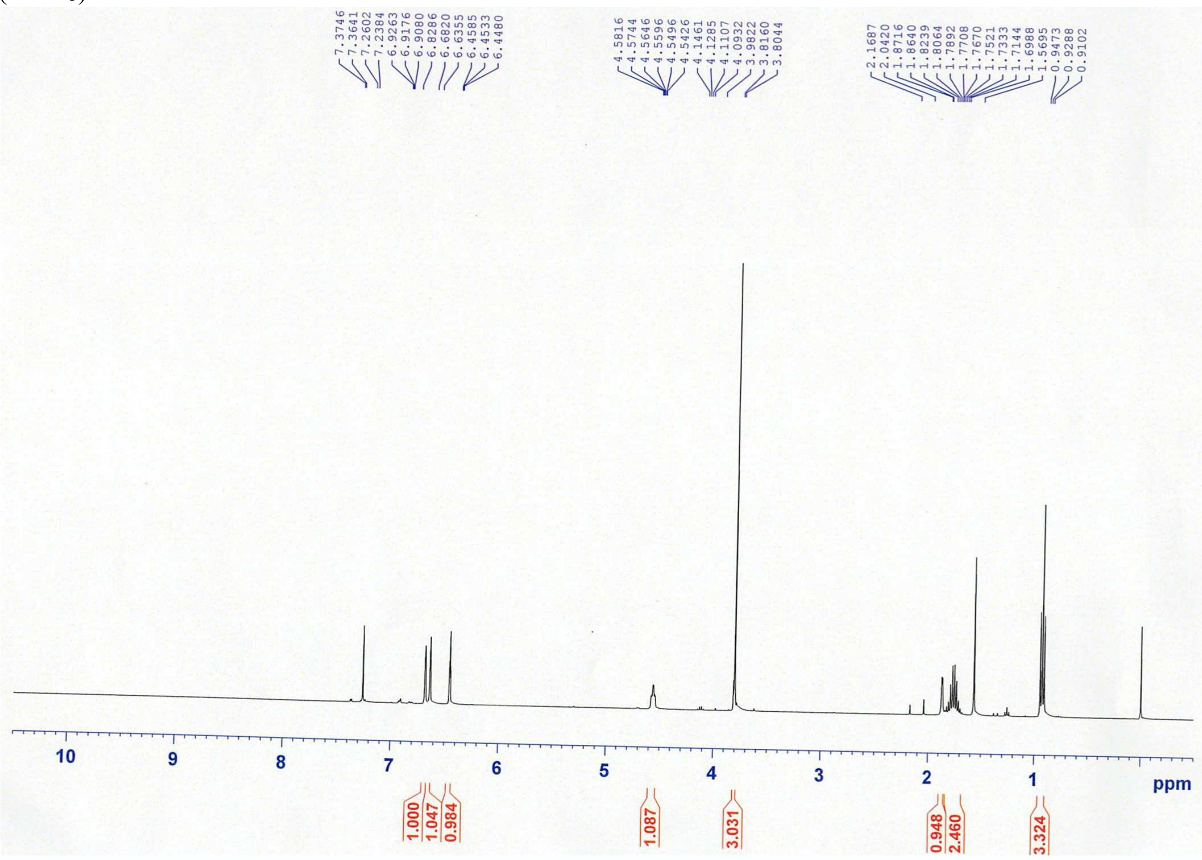


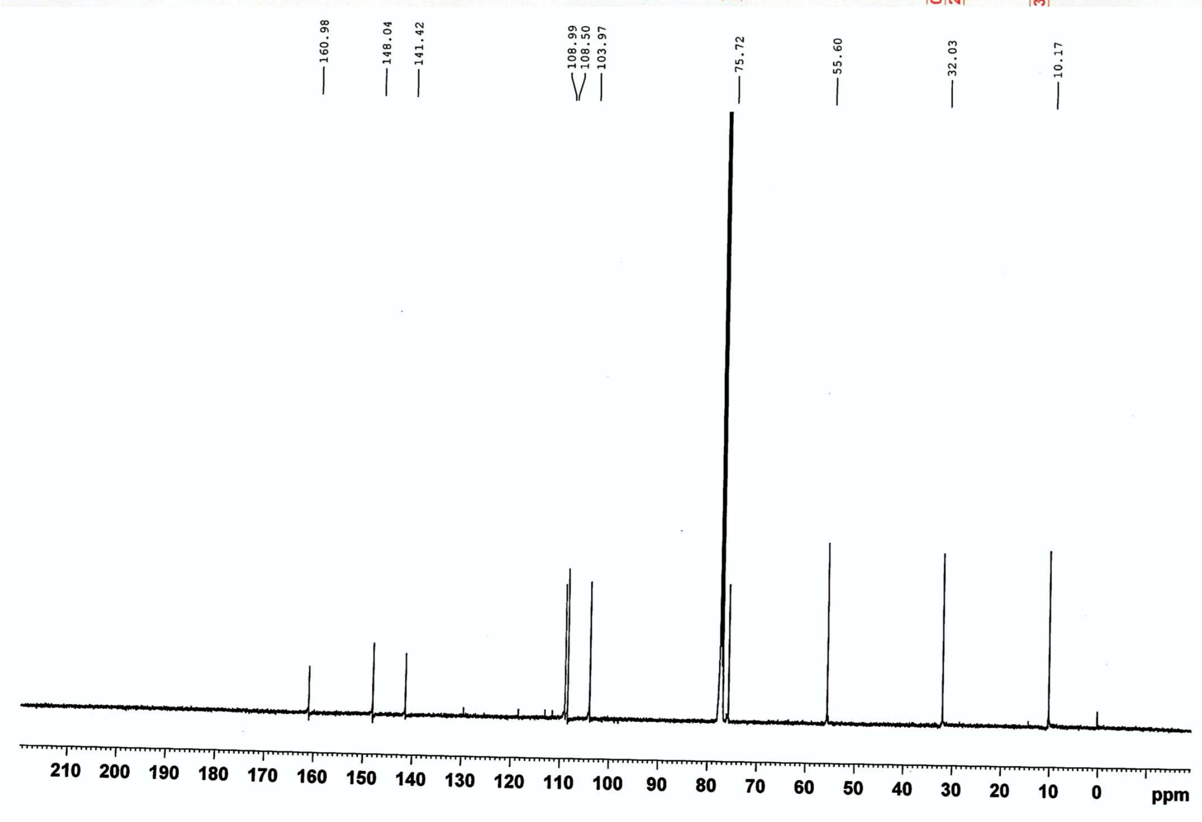
^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(3-azido-5-methylphenyl)-1-propanol (**8m**) ($CDCl_3$)



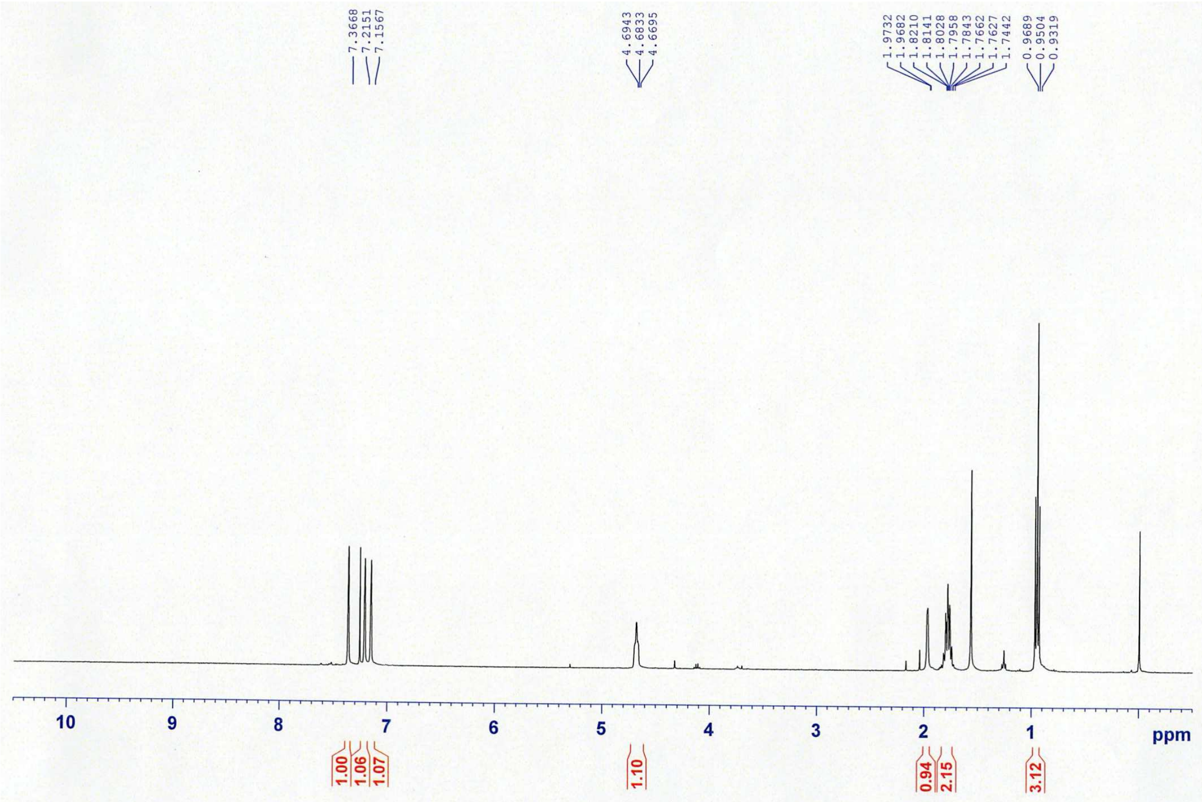


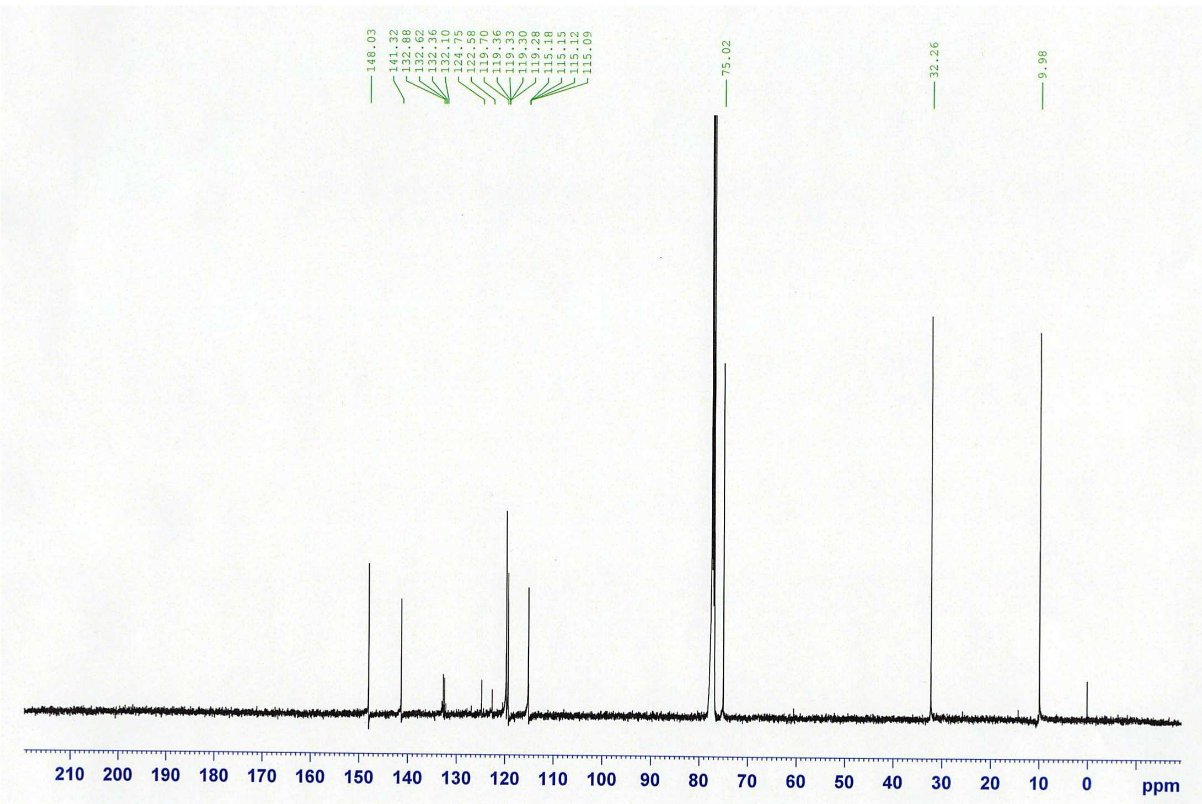
[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of 1-(3-azido-5-methoxyphenyl)-1-propanol (**8n**) ($CDCl_3$)



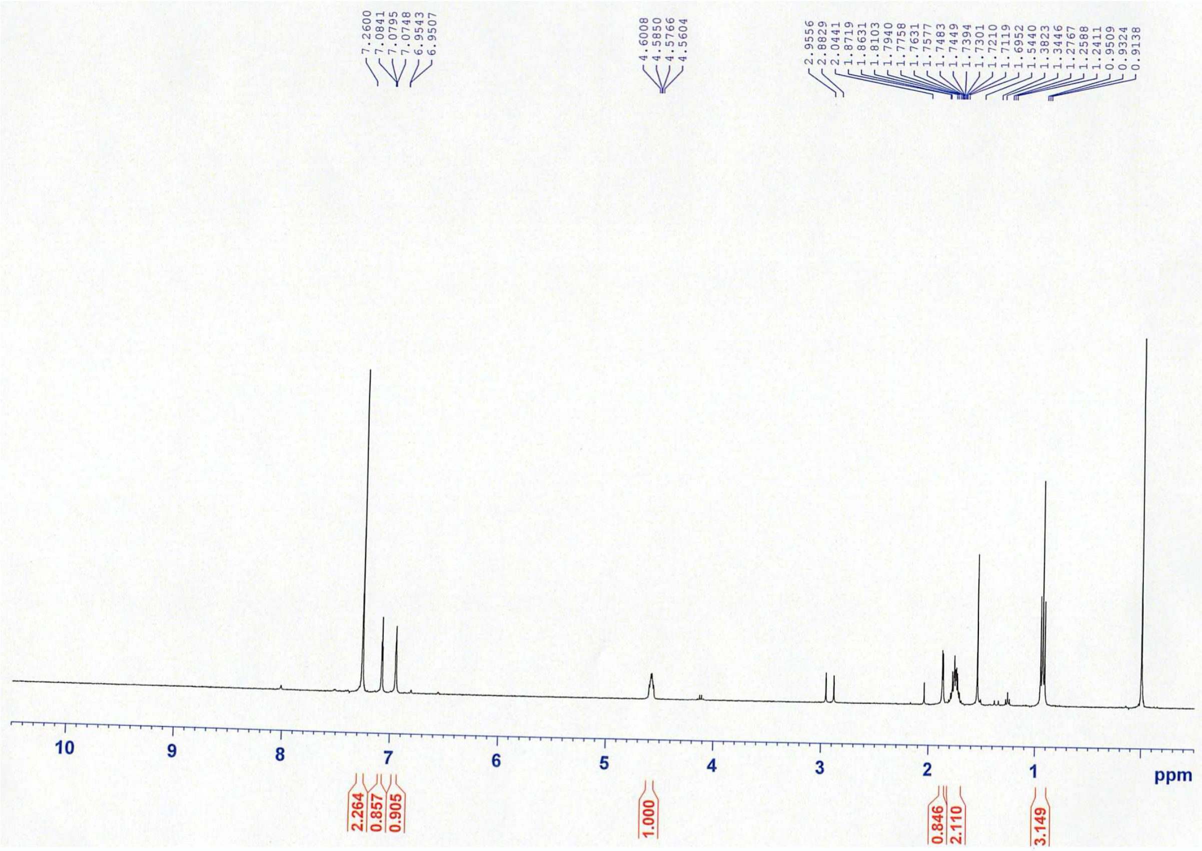


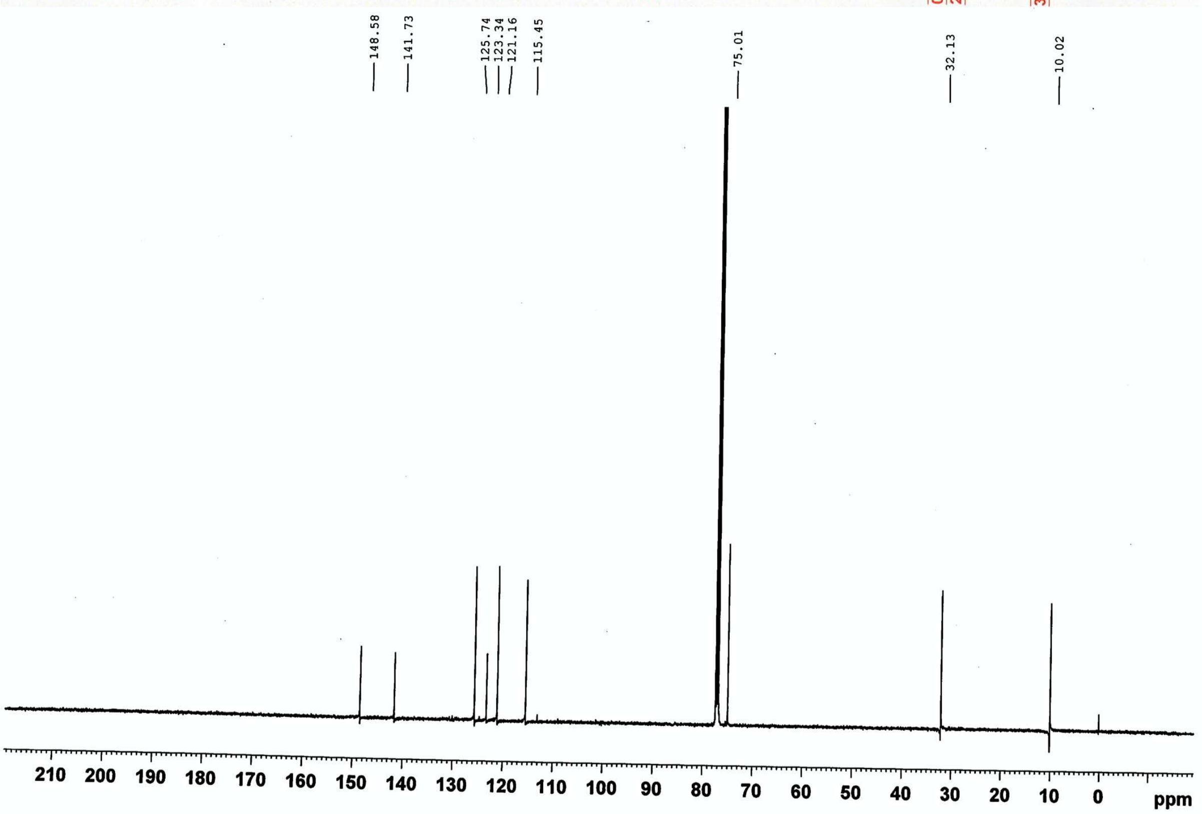
[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of 1-(3-azido-5-trifluoromethylphenyl)-1-propanol (**8o**) ($CDCl_3$)



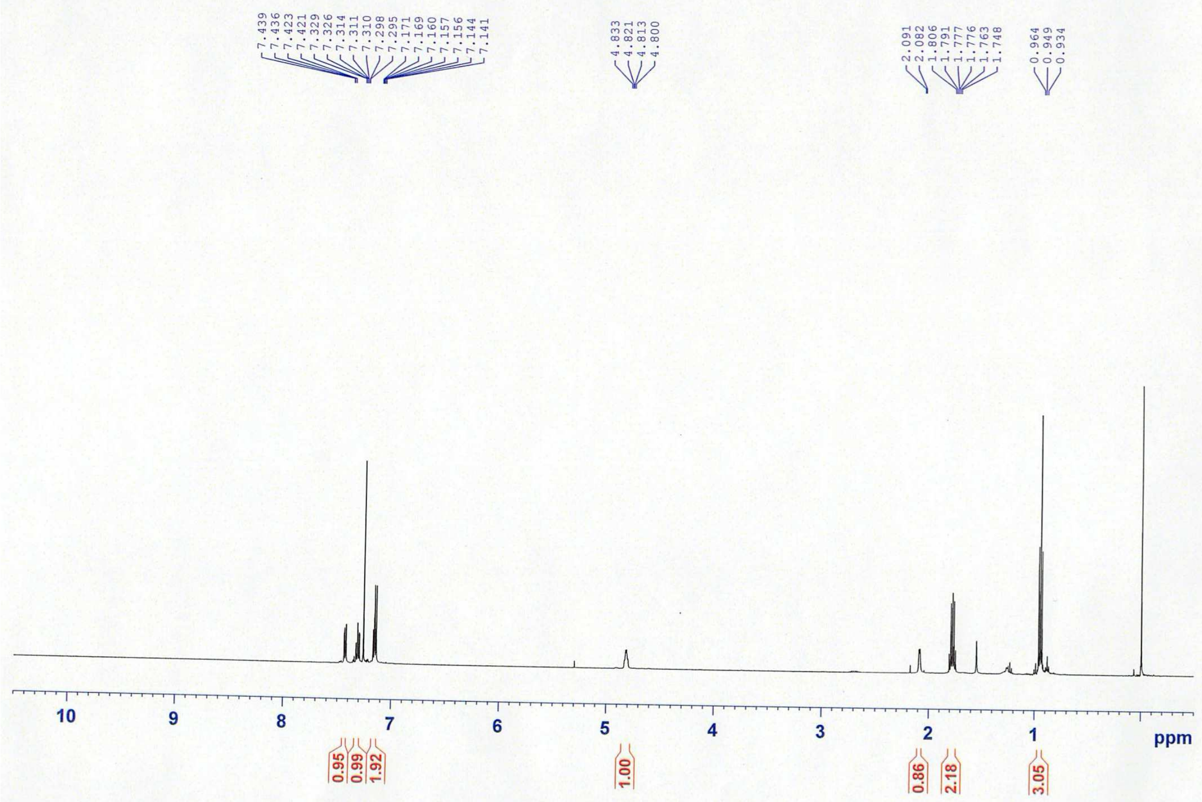


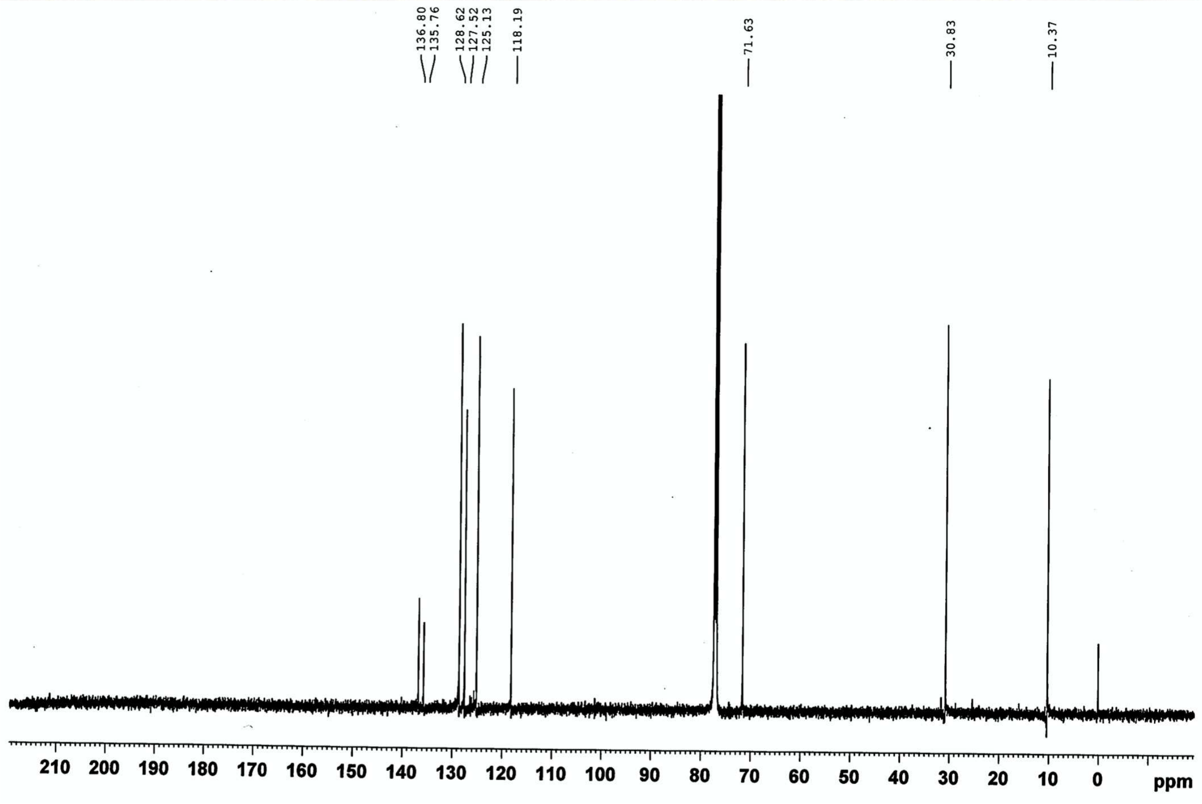
[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of 1-(3-azido-5-bromophenyl)-1-propanol (**8p**) ($CDCl_3$)



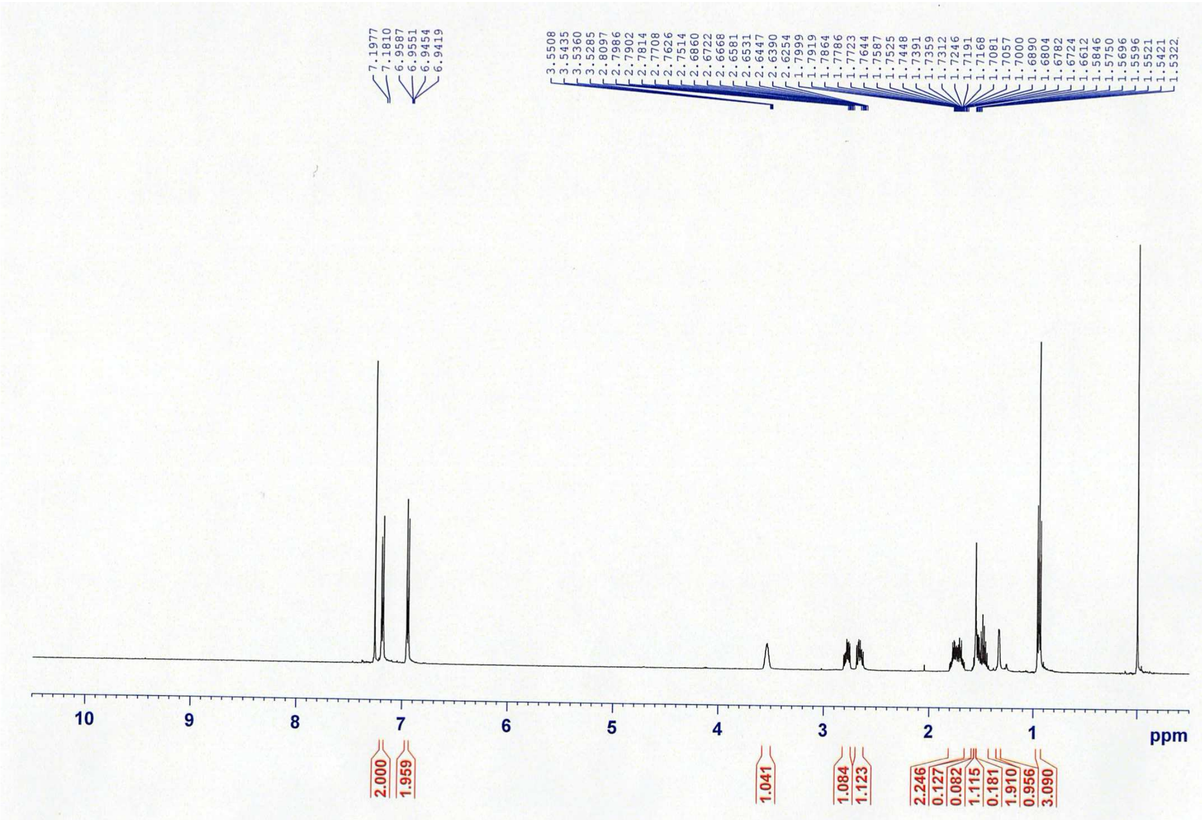


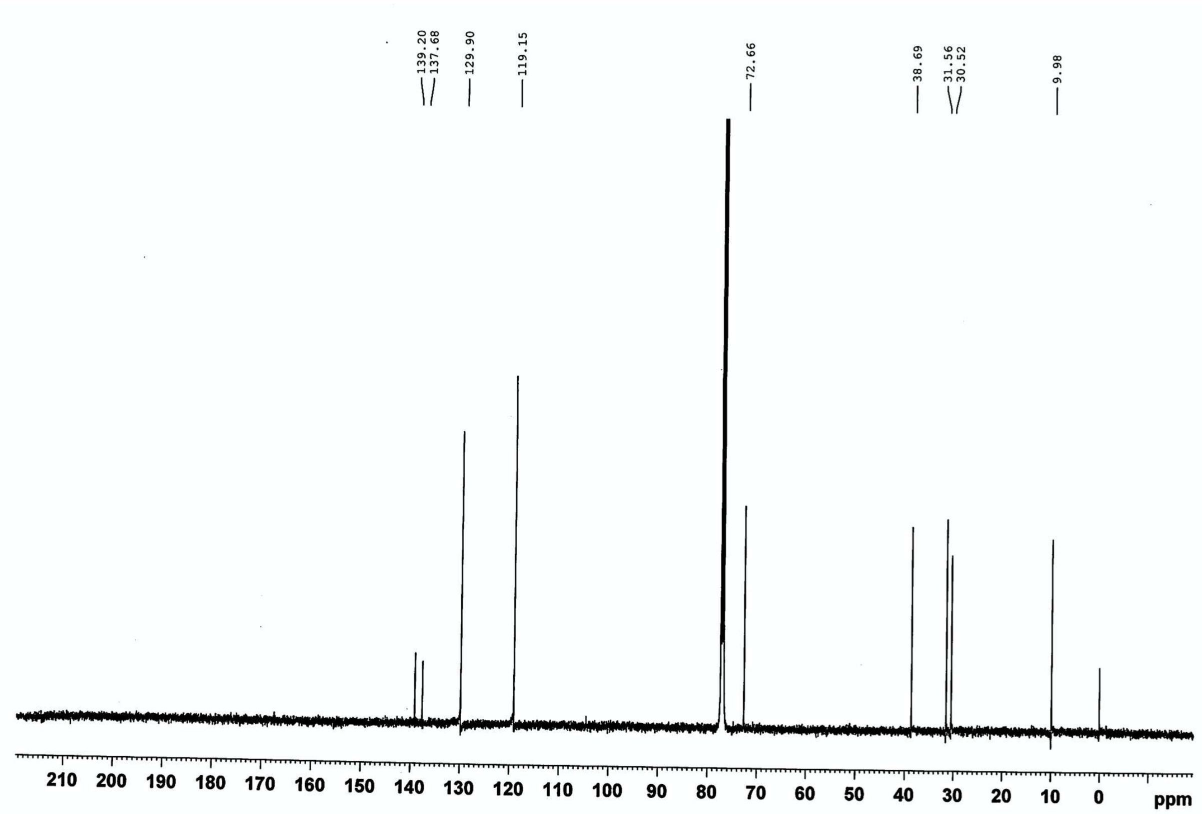
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(2-azidophenyl)-1-propanol (**8q**) ($CDCl_3$)



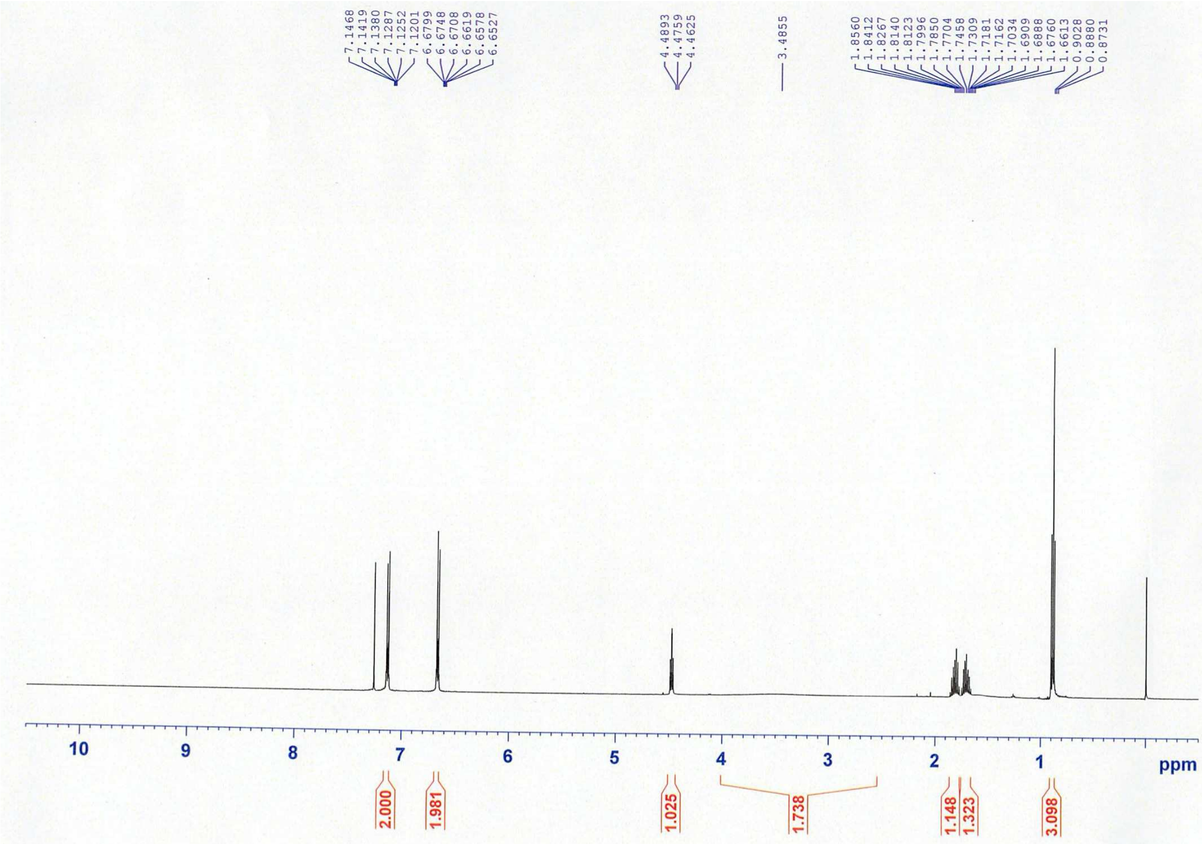


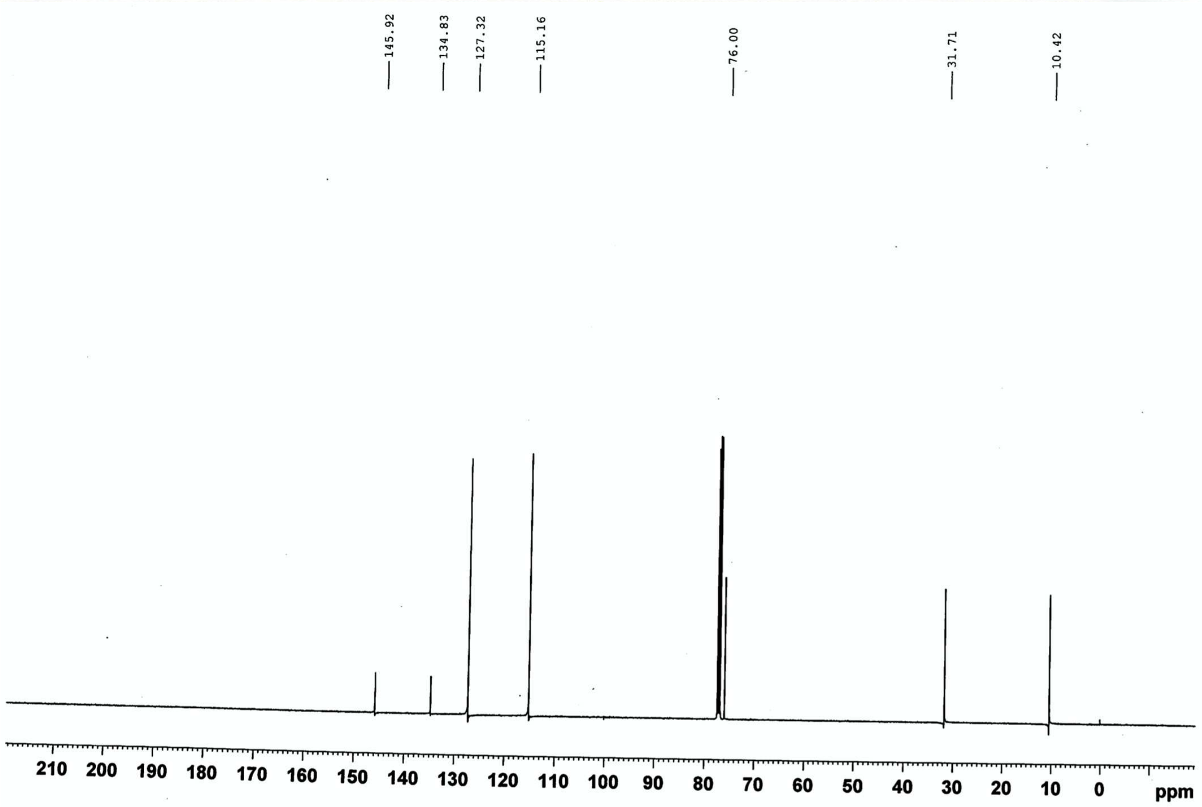
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-azidophenyl)pentan-3-ol (**8r**) ($CDCl_3$)



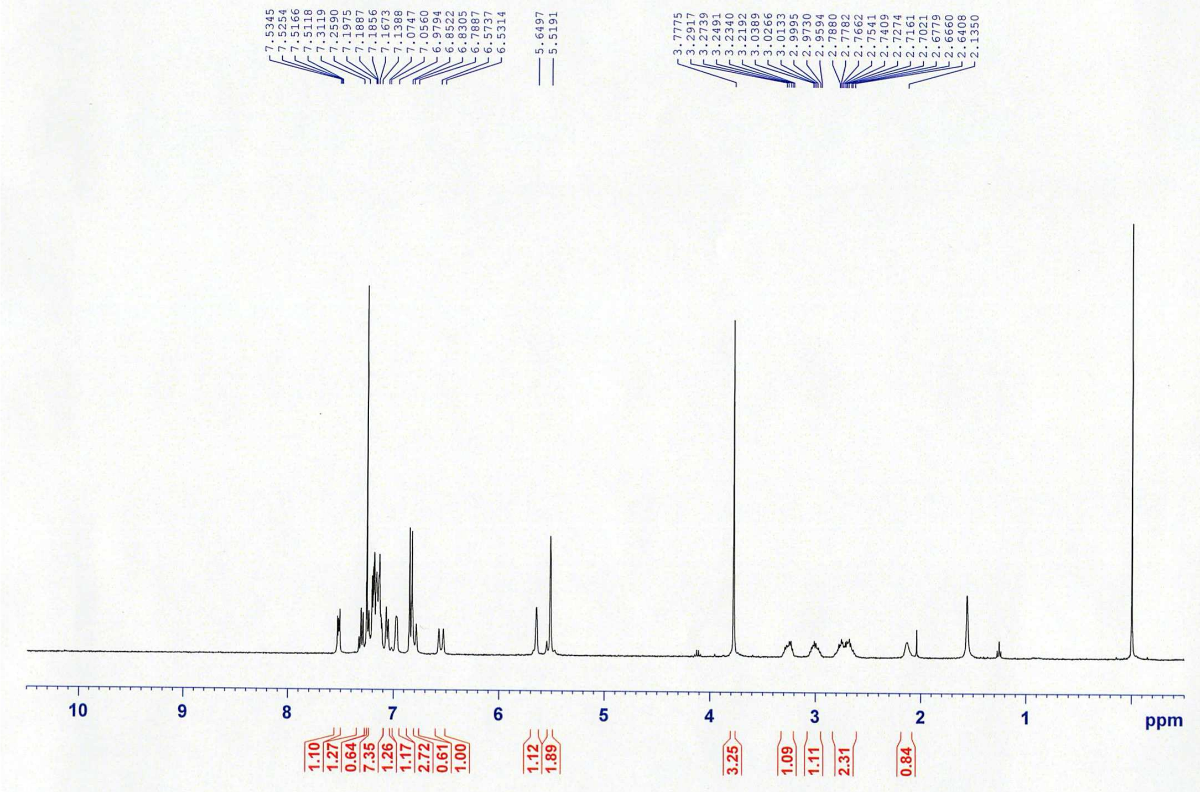


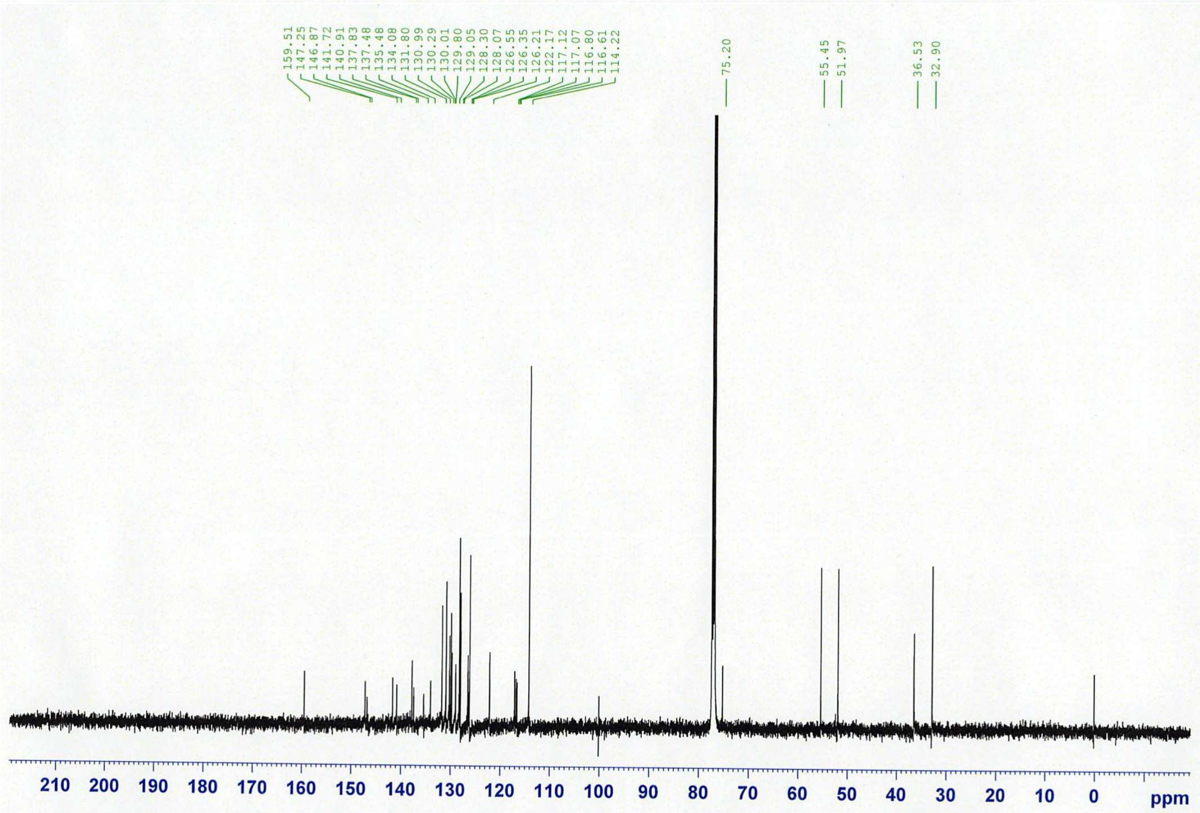
[1]H NMR (500 MHz) and [13]C NMR (126 MHz) spectra of 1-(4-aminophenyl)-1-propanol (**9**) ($CDCl_3$)



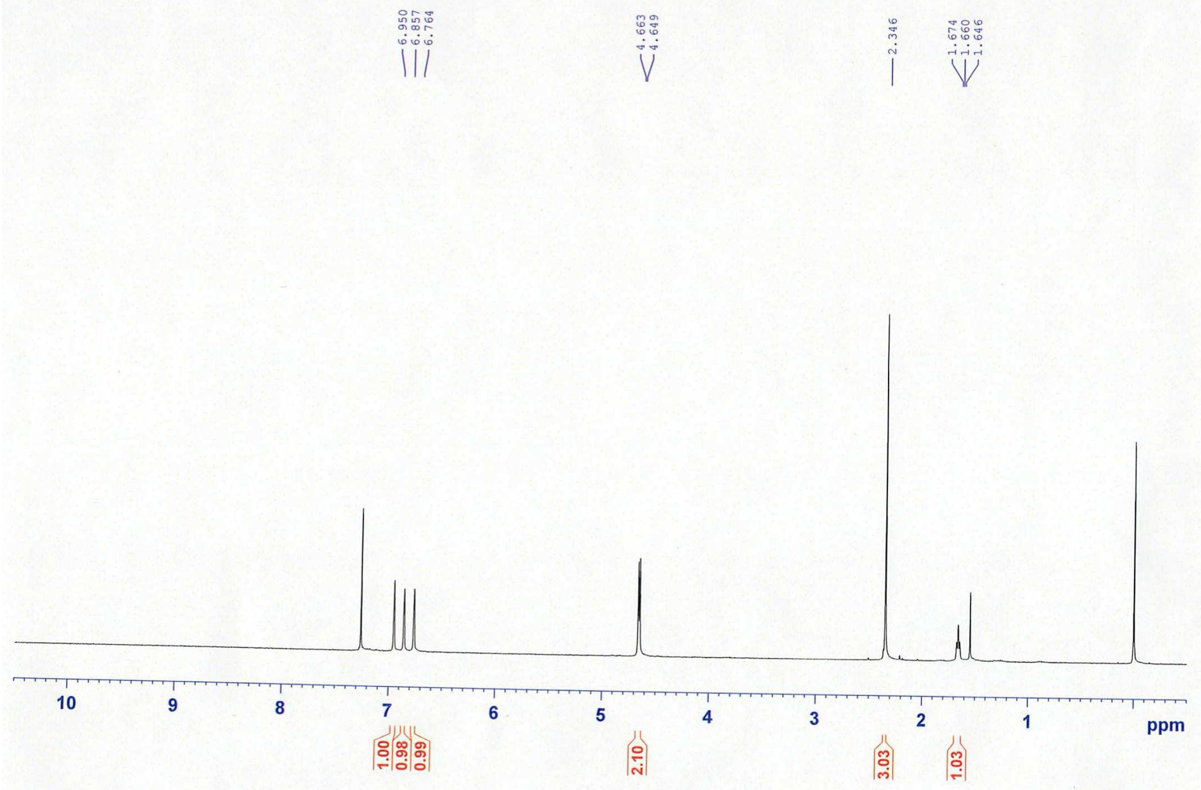


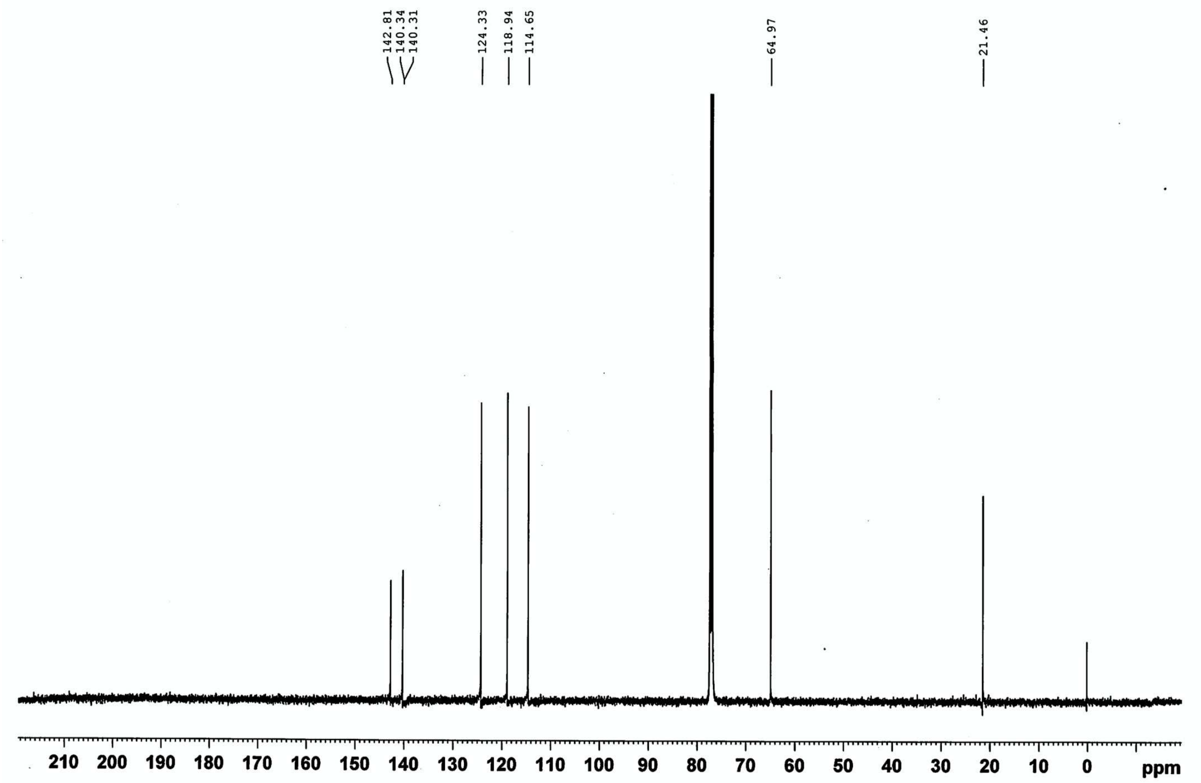
[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of (3-azido-5-((8,9-dihydro-1*H*-dibenzo[3,4:7,8]cycloocta[1,2-*d*][1,2,3]triazol-1-yl)methyl)phenyl)(4-methoxyphenyl)methanol (**14**) ($CDCl_3$)



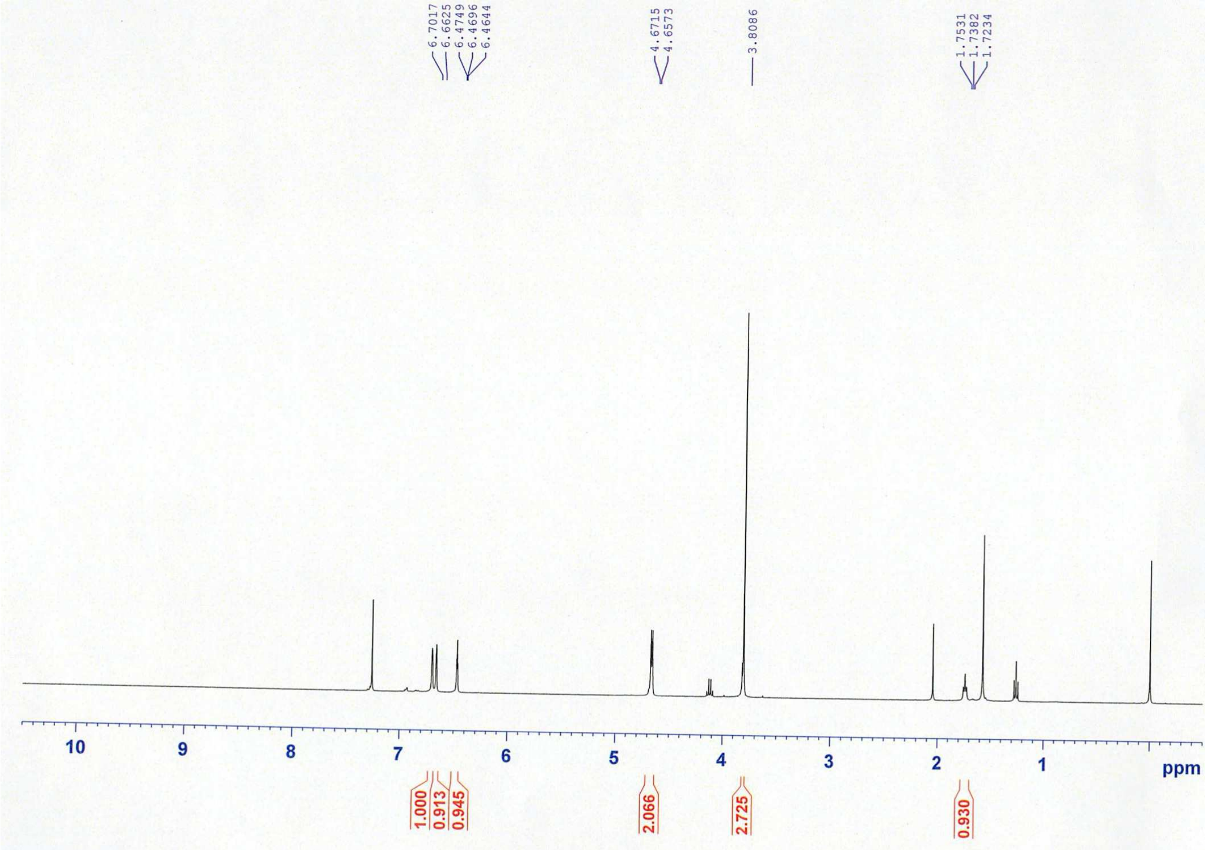


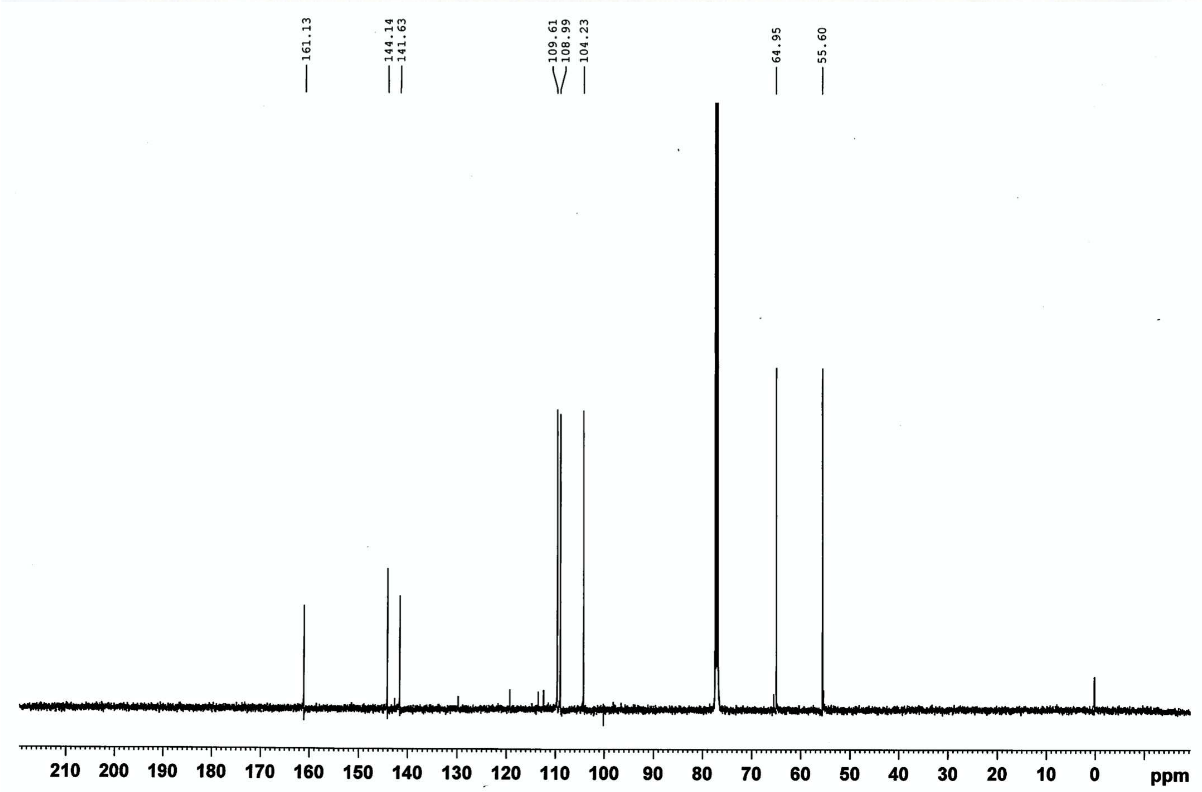
^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 3-azido-5-methylbenzyl alcohol ($CDCl_3$)



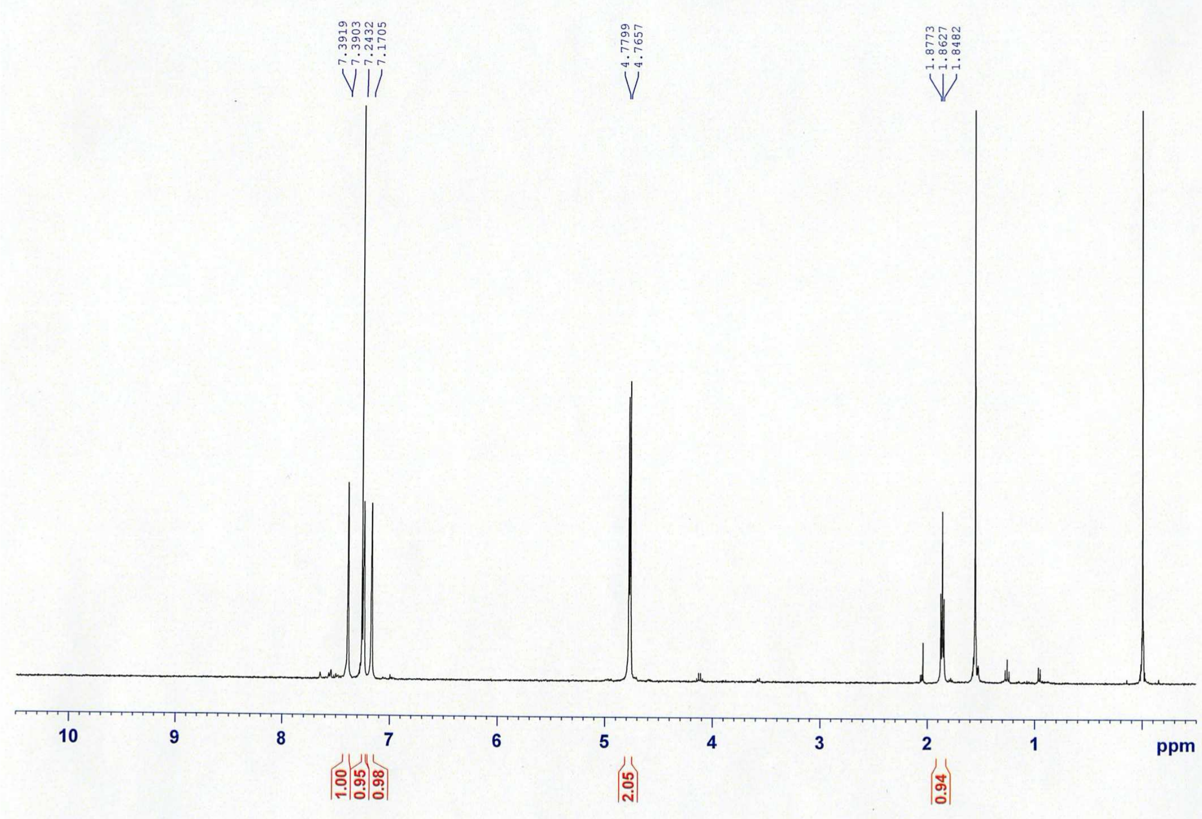


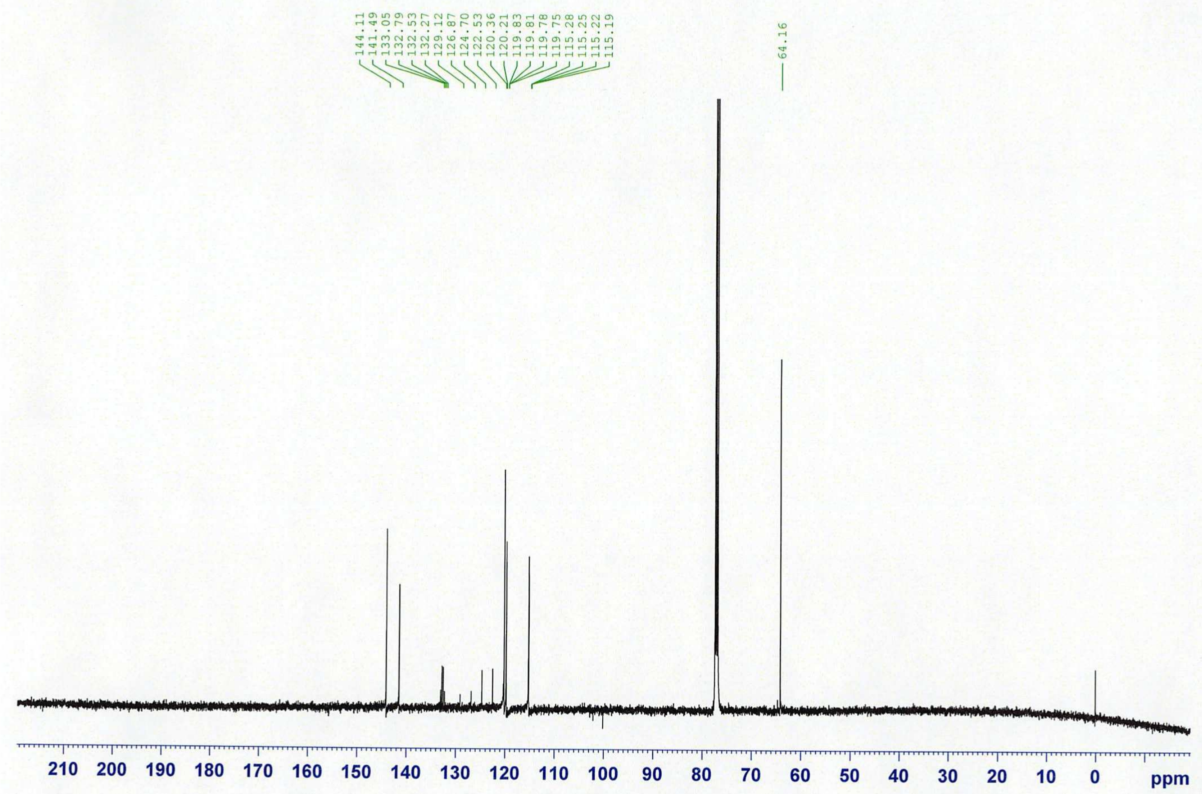
^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 3-azido-5-methoxybenzyl alcohol ($CDCl_3$)





^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectra of 3-azido-5-(trifluoromethyl)benzyl alcohol ($CDCl_3$)





[1]H NMR (400 MHz) and [13]C NMR (126 MHz) spectra of 3-azido-5-bromobenzyl alcohol ($CDCl_3$)