

Alpha hydroxy tetrazoles as latent ethynyl moieties: a mechanistic investigation

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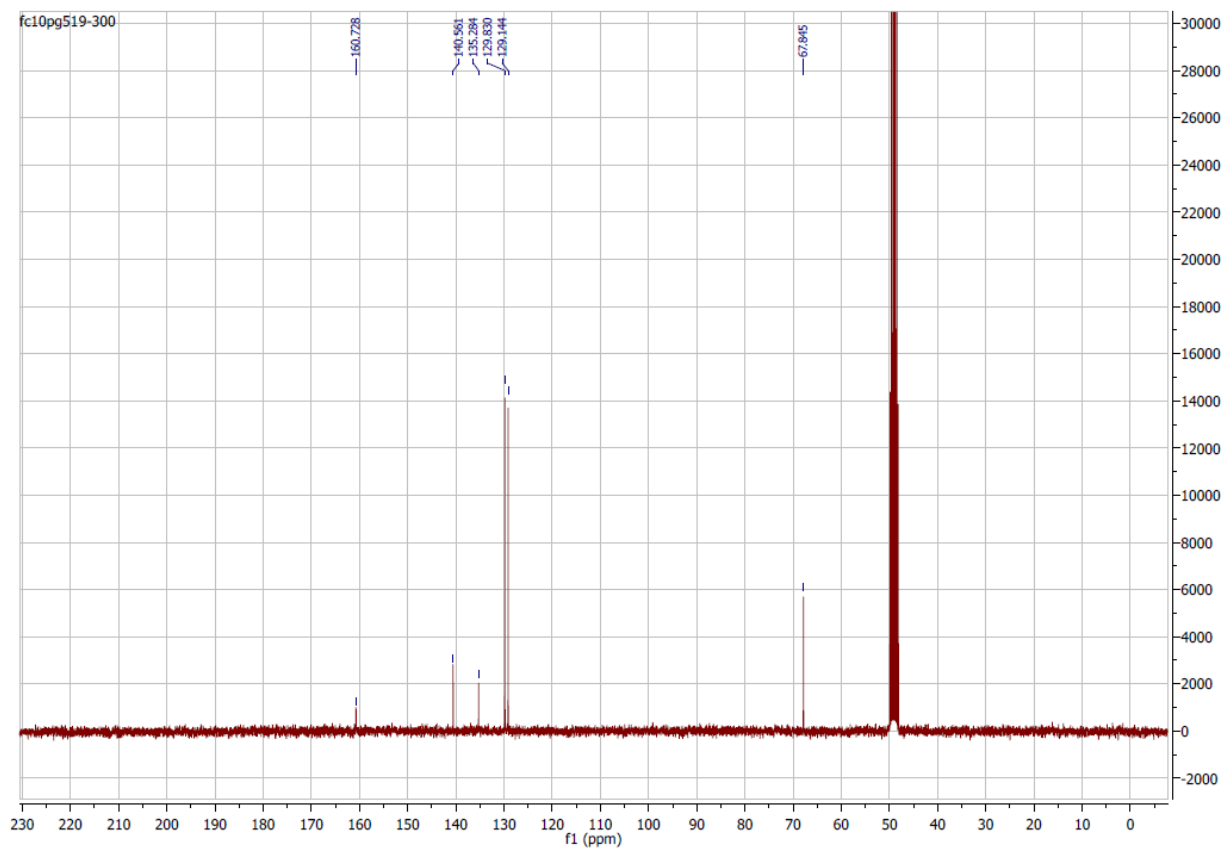
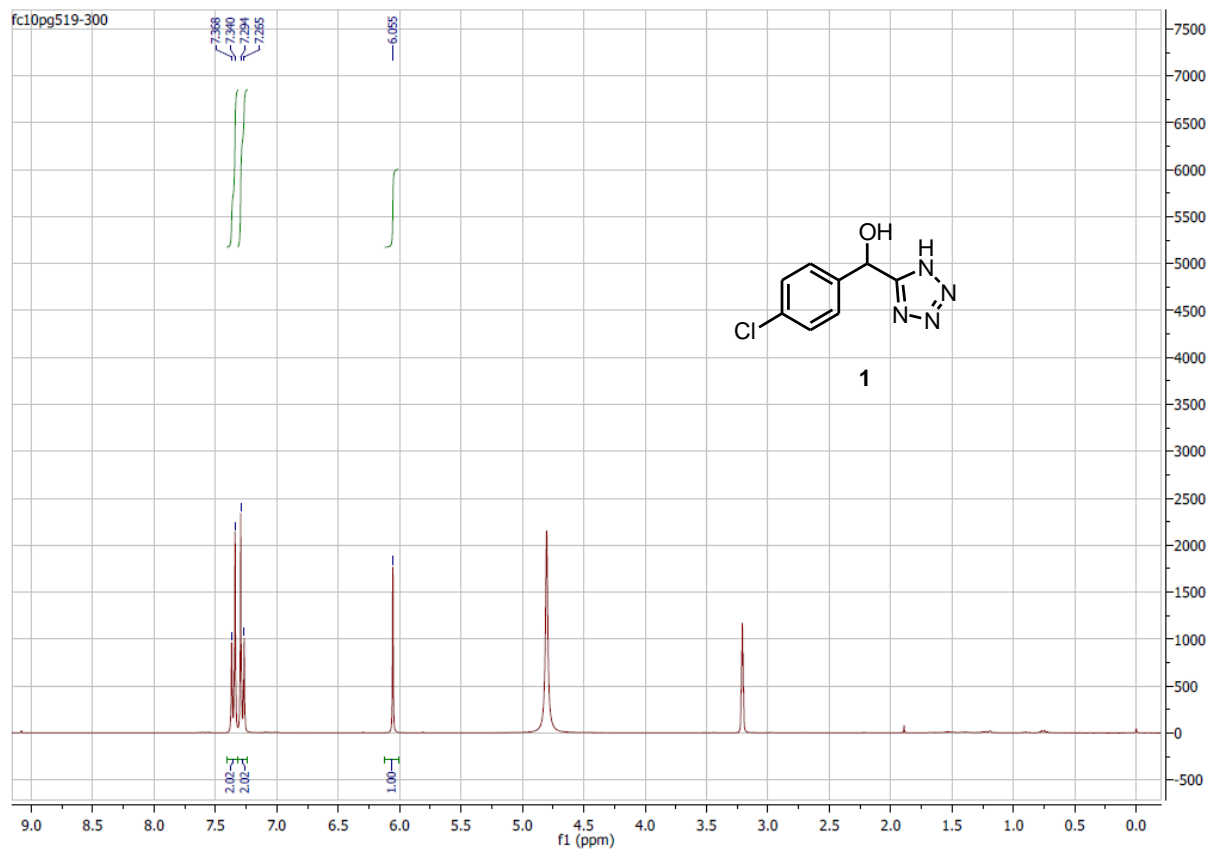
Supporting Information

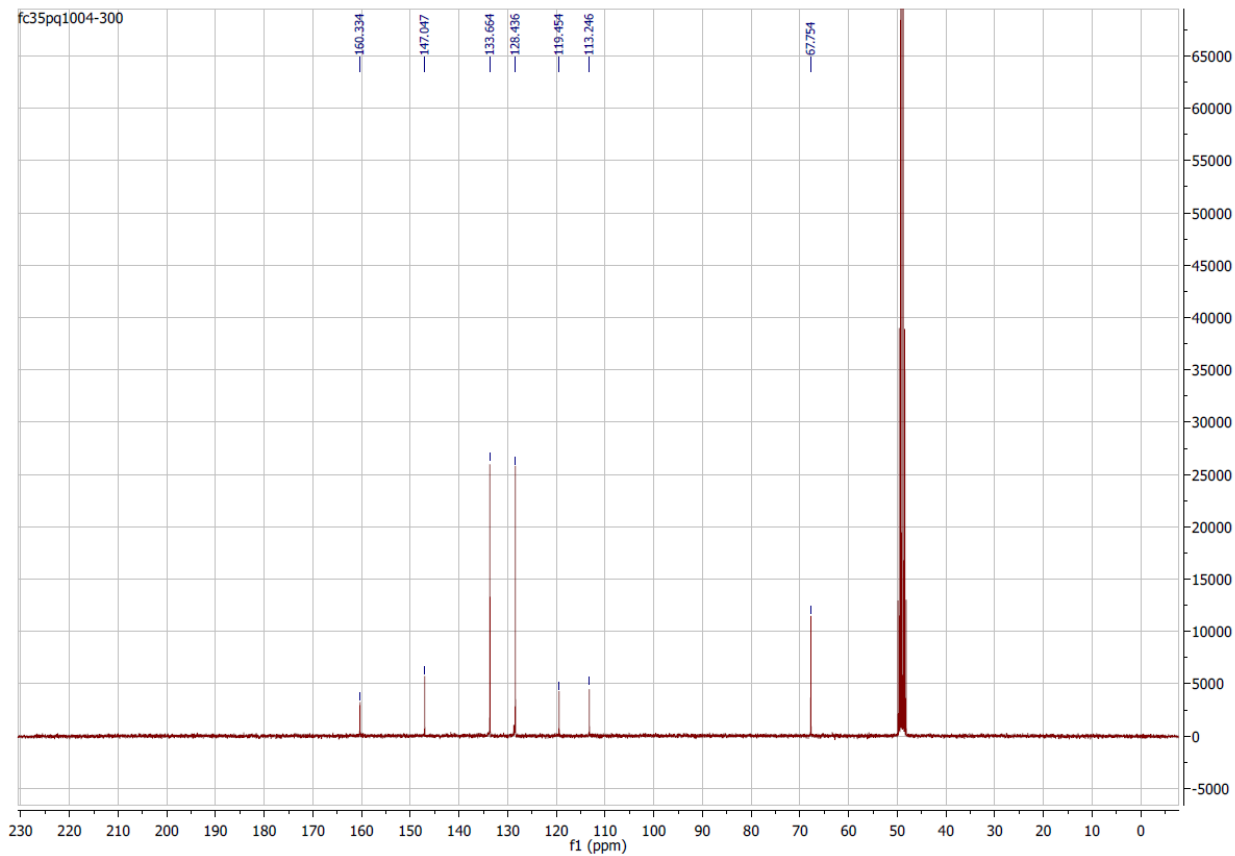
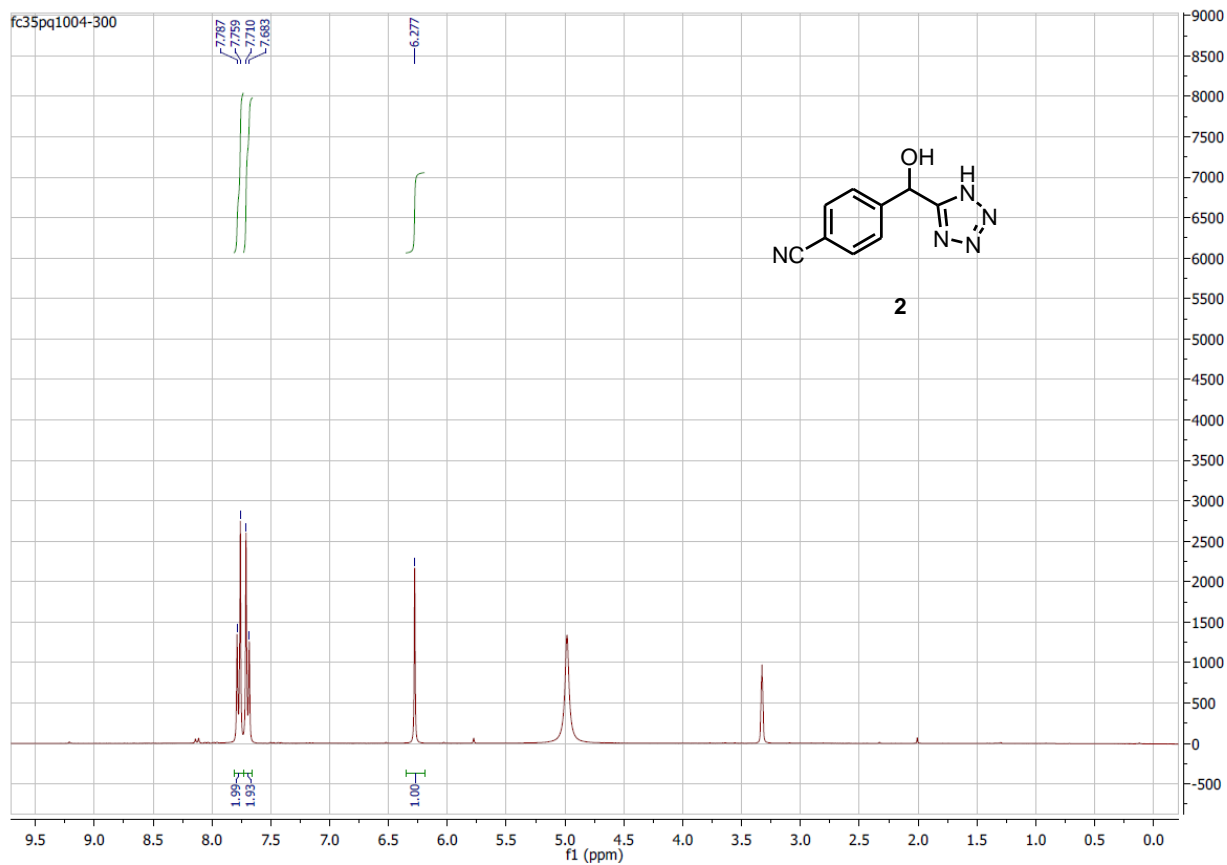
Content

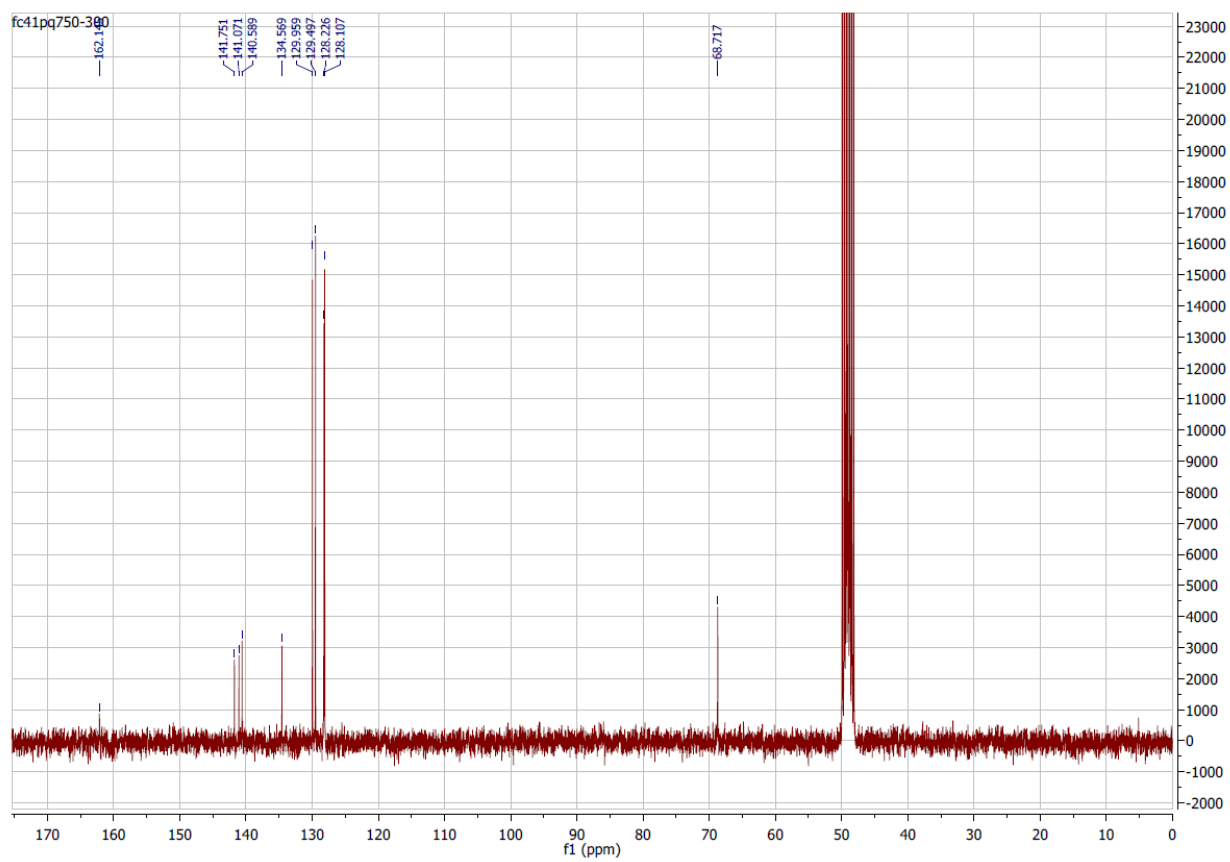
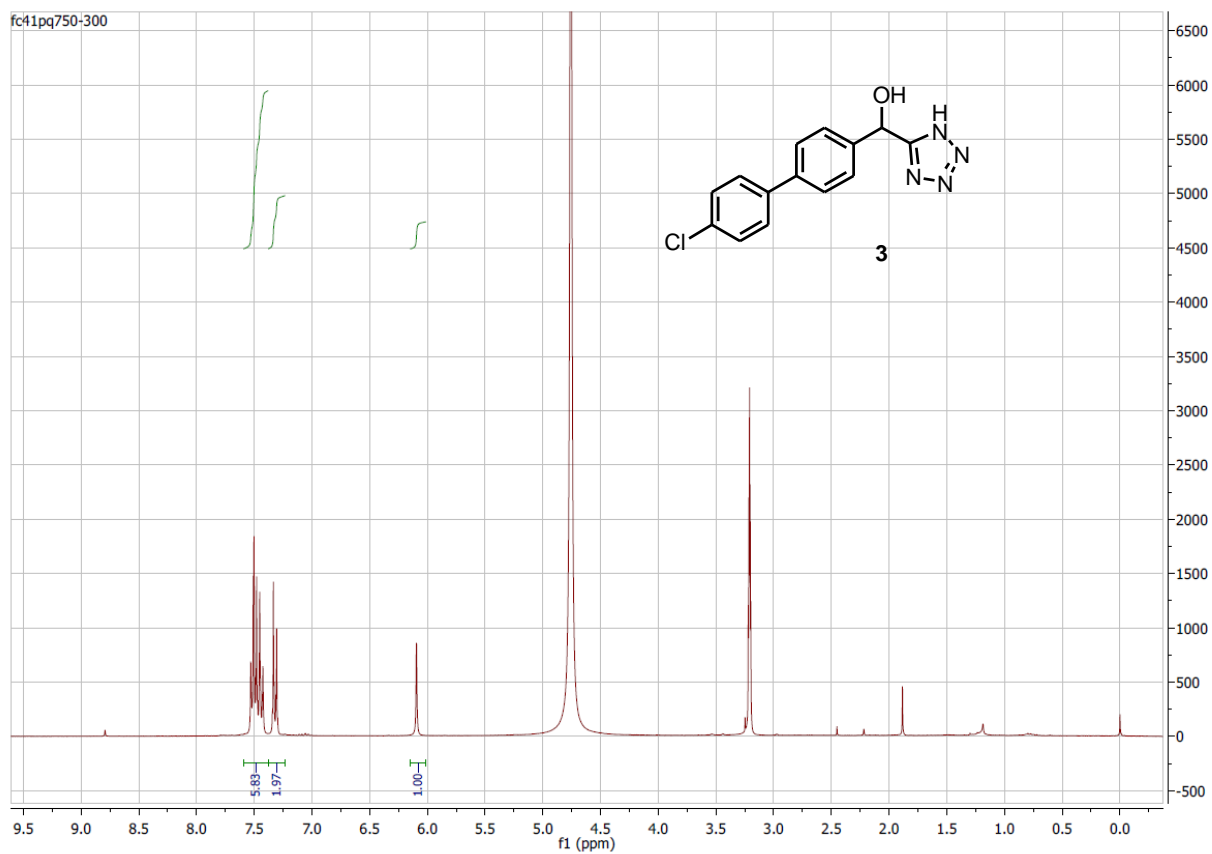
Copies of ¹ H and ¹³ C NMR spectra for all new compounds	S1-S27
Computational details	S28-S30

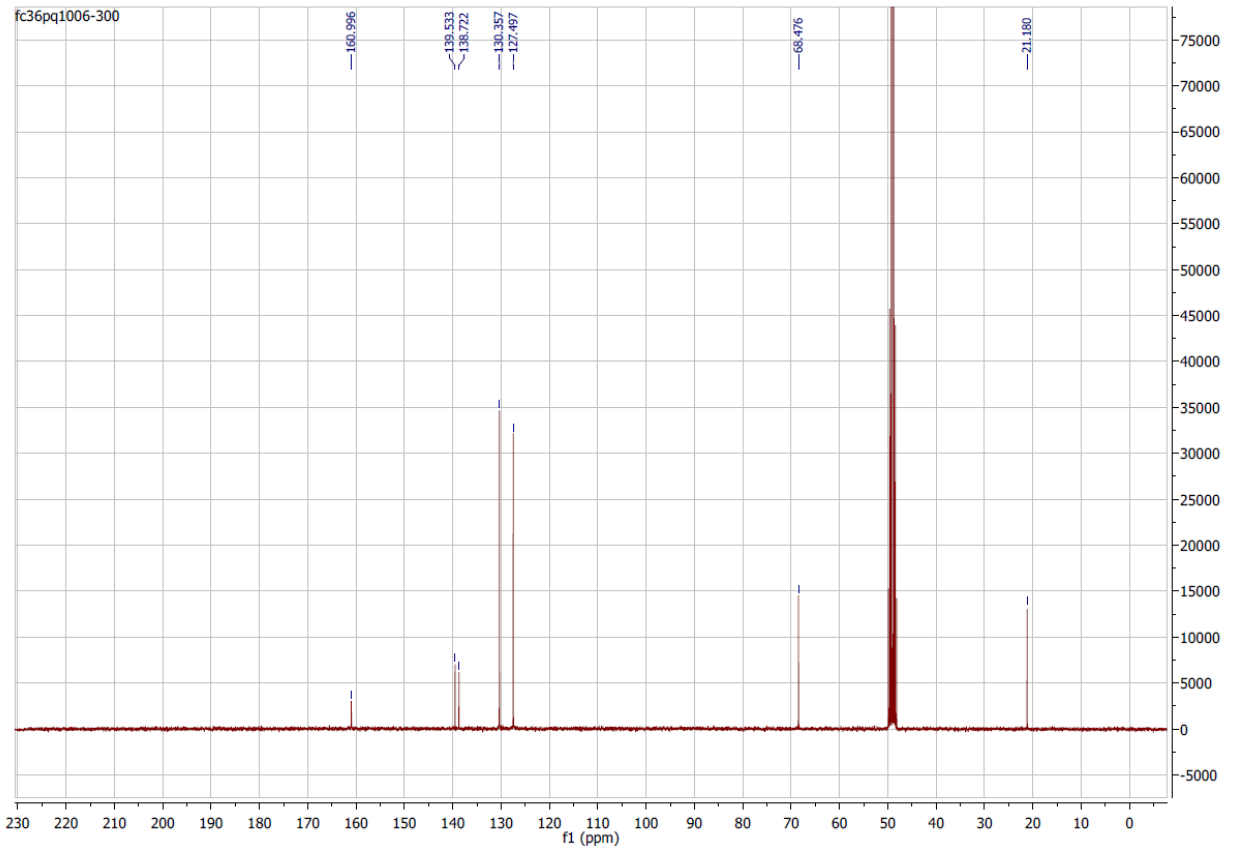
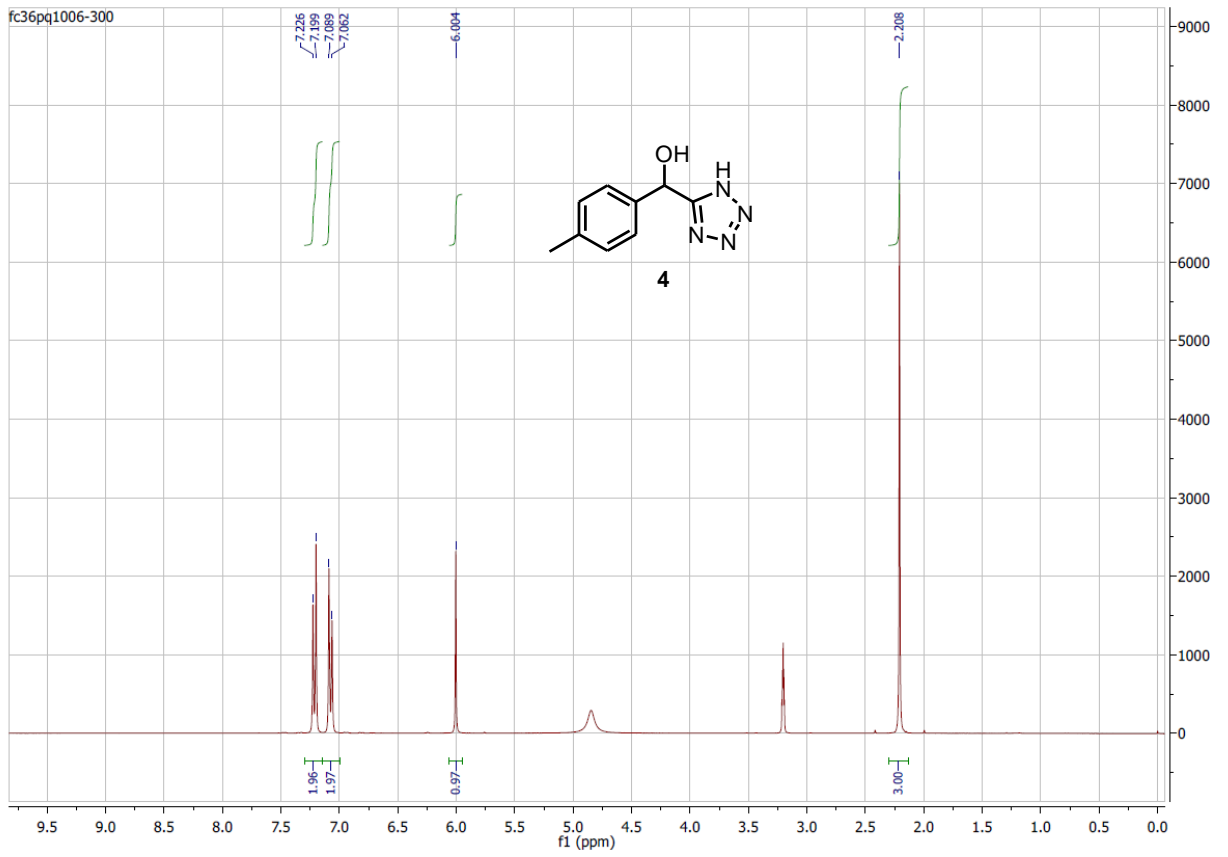
^1H and ^{13}C spectra for unreported compounds.

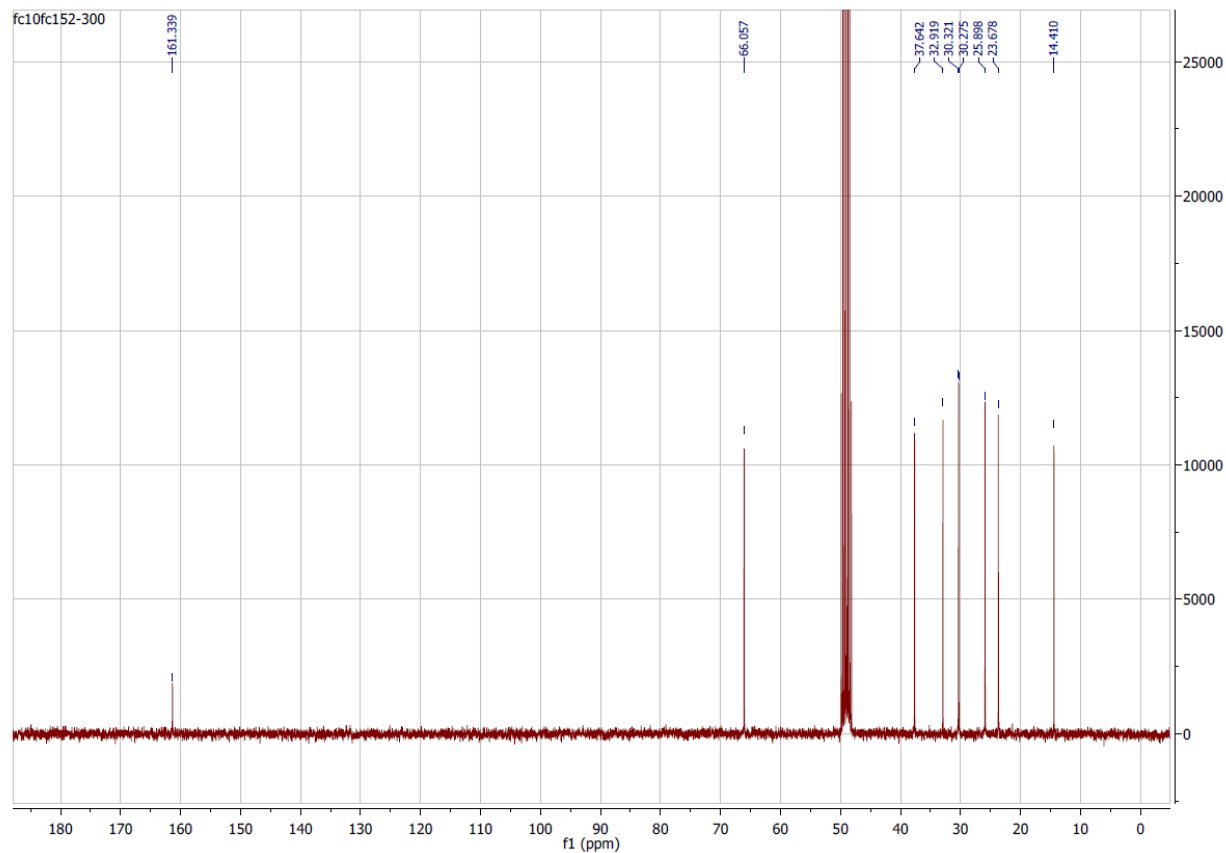
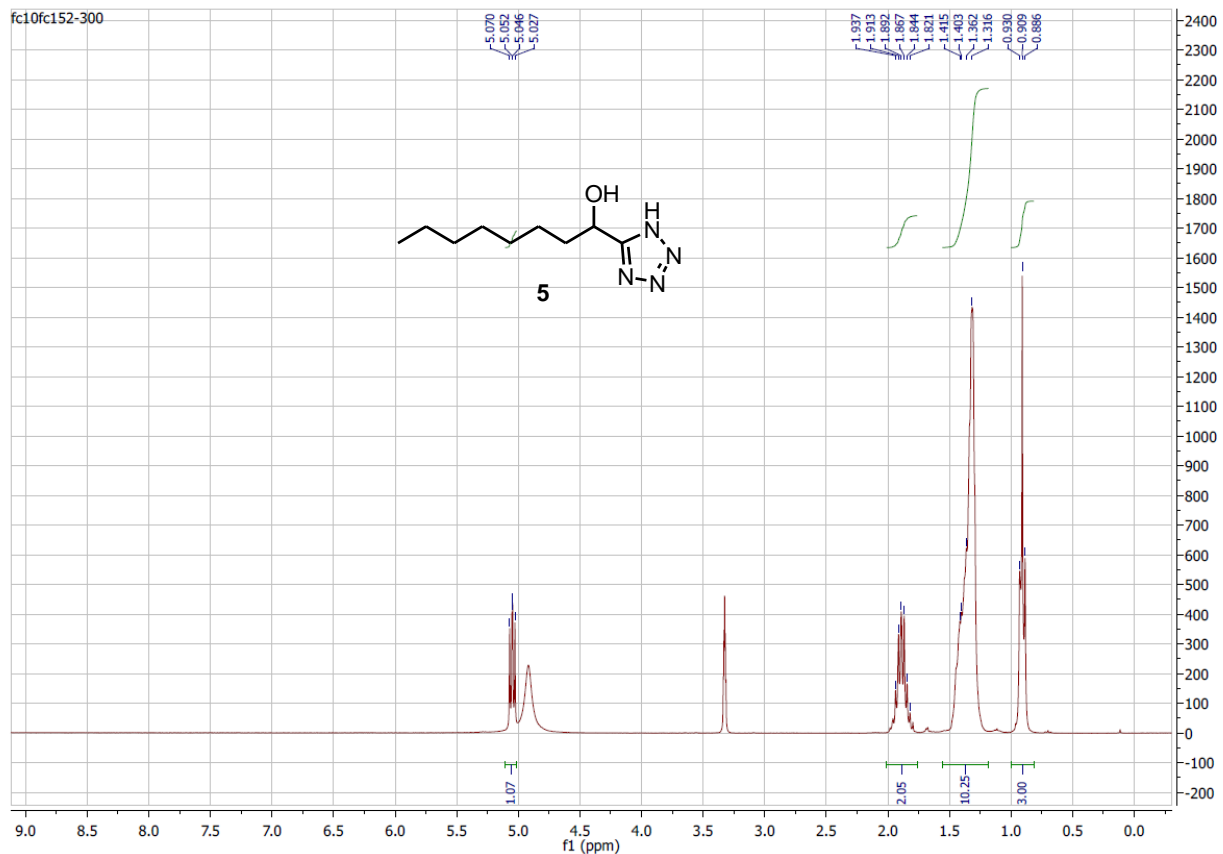
Unless otherwise stated, spectra were recorded at 300 MHz for ^1H data and 75 MHz for ^{13}C data, in CDCl_3 .

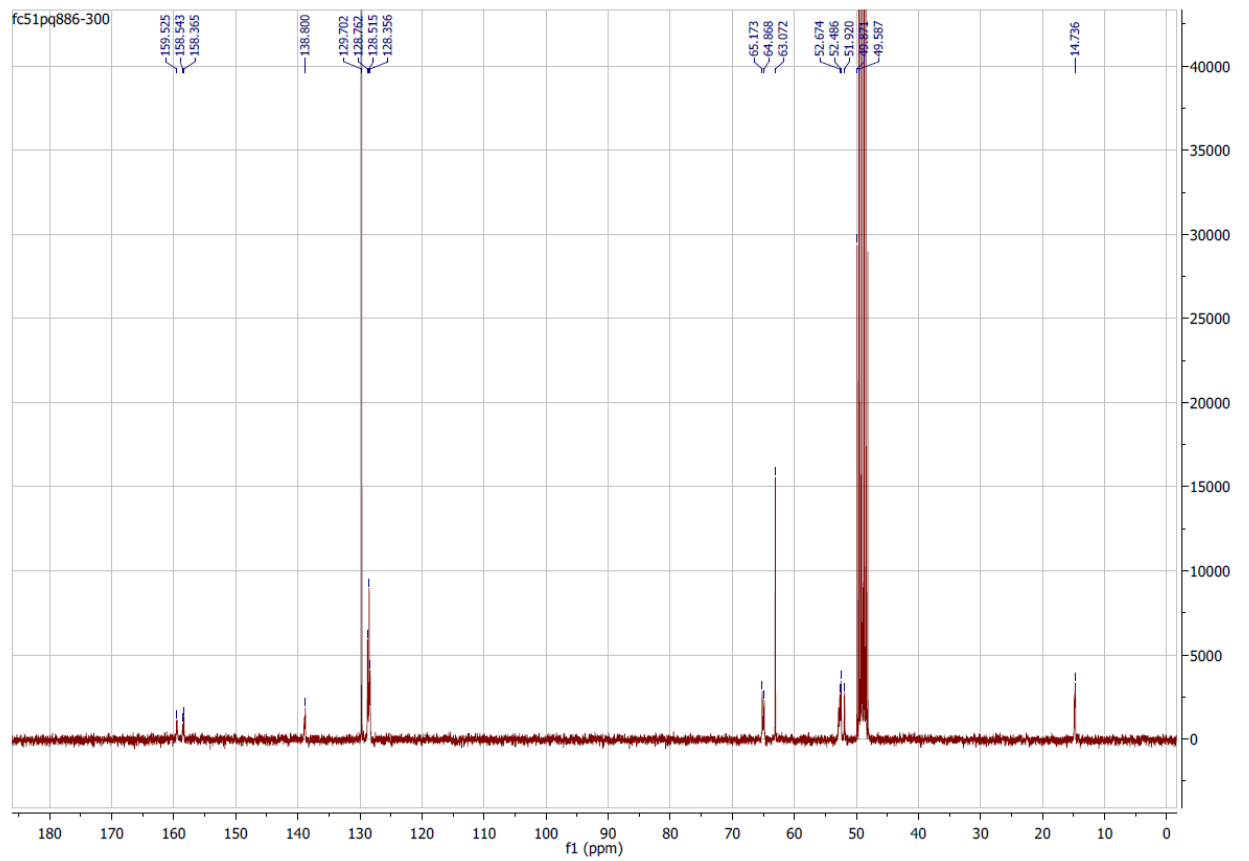
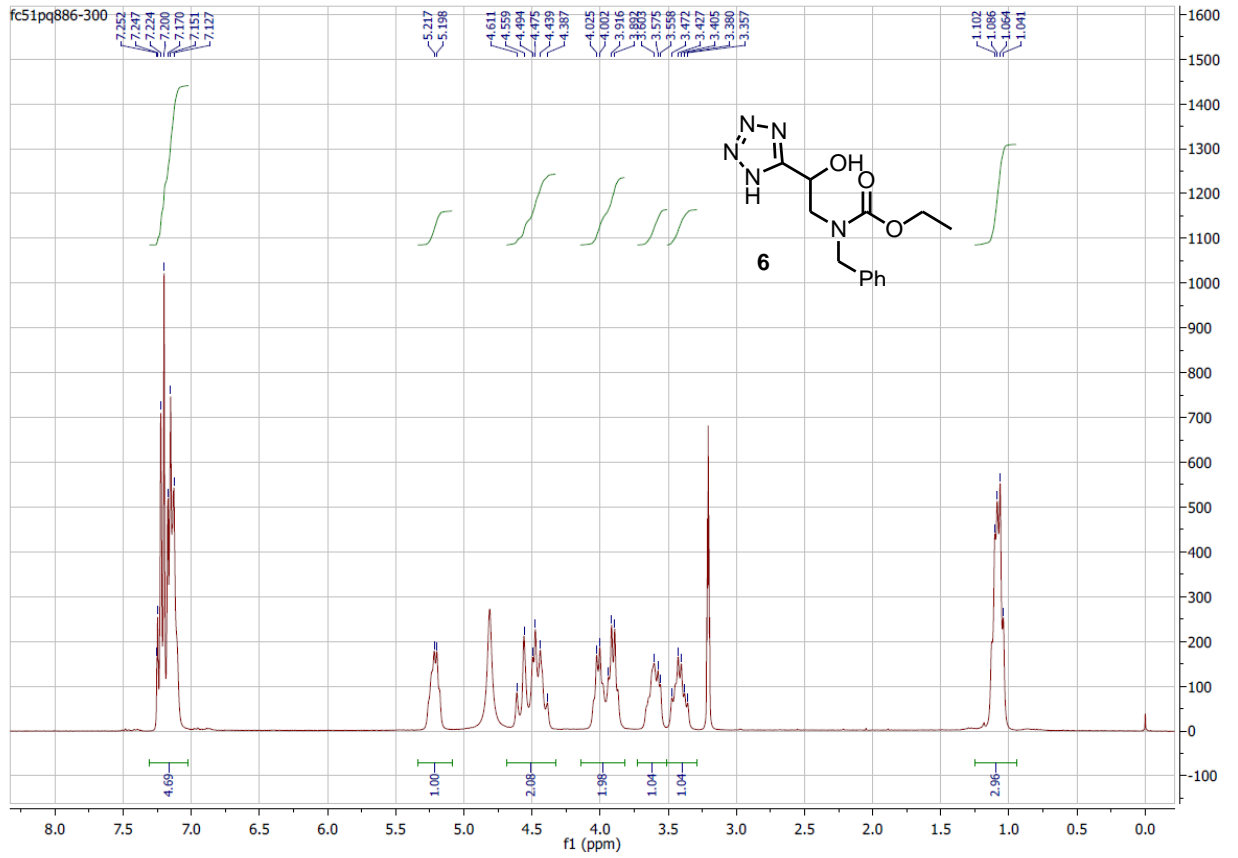


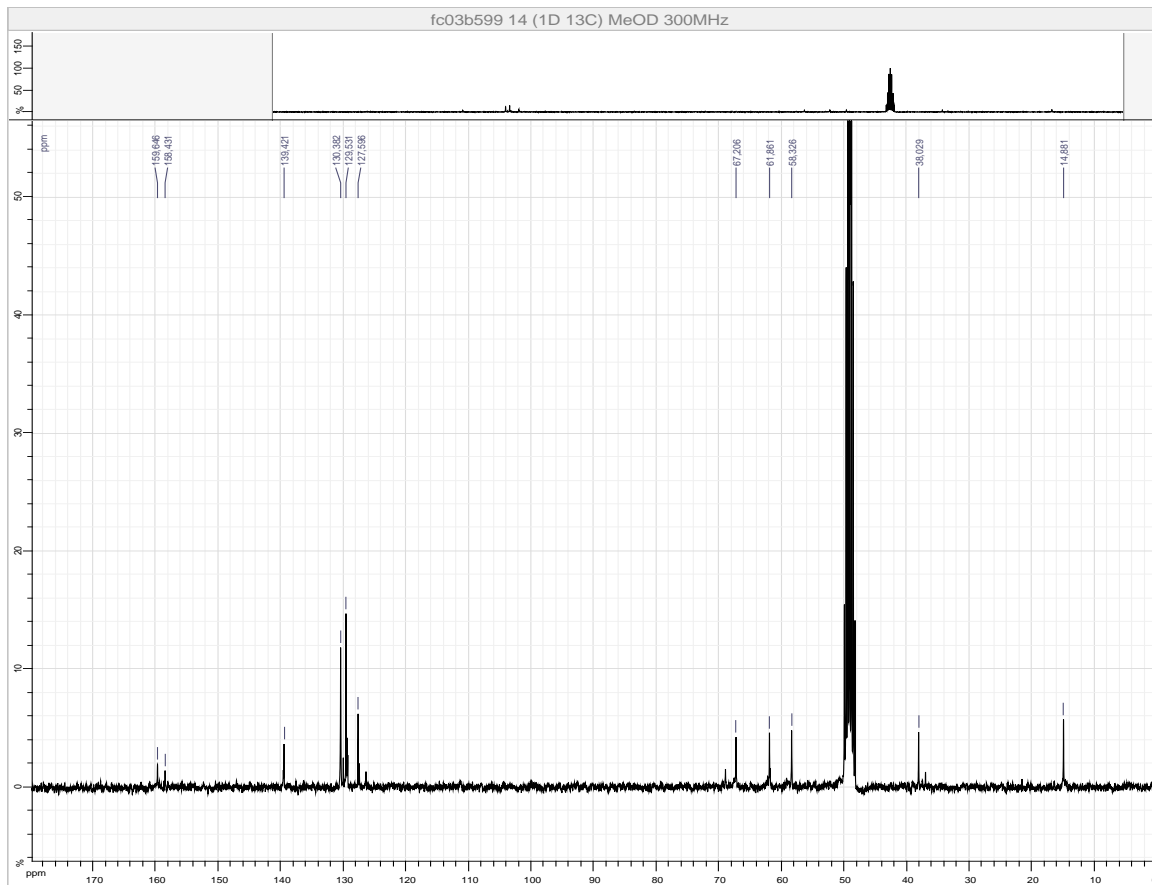
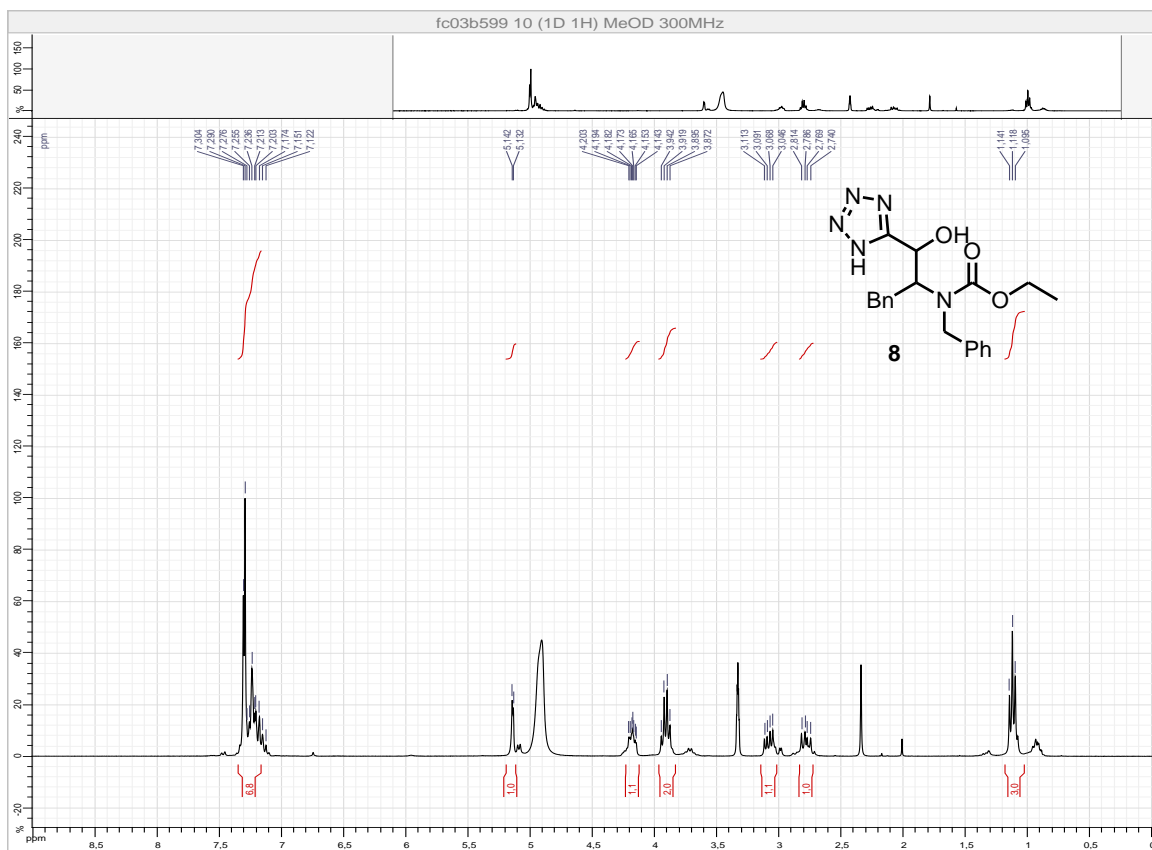


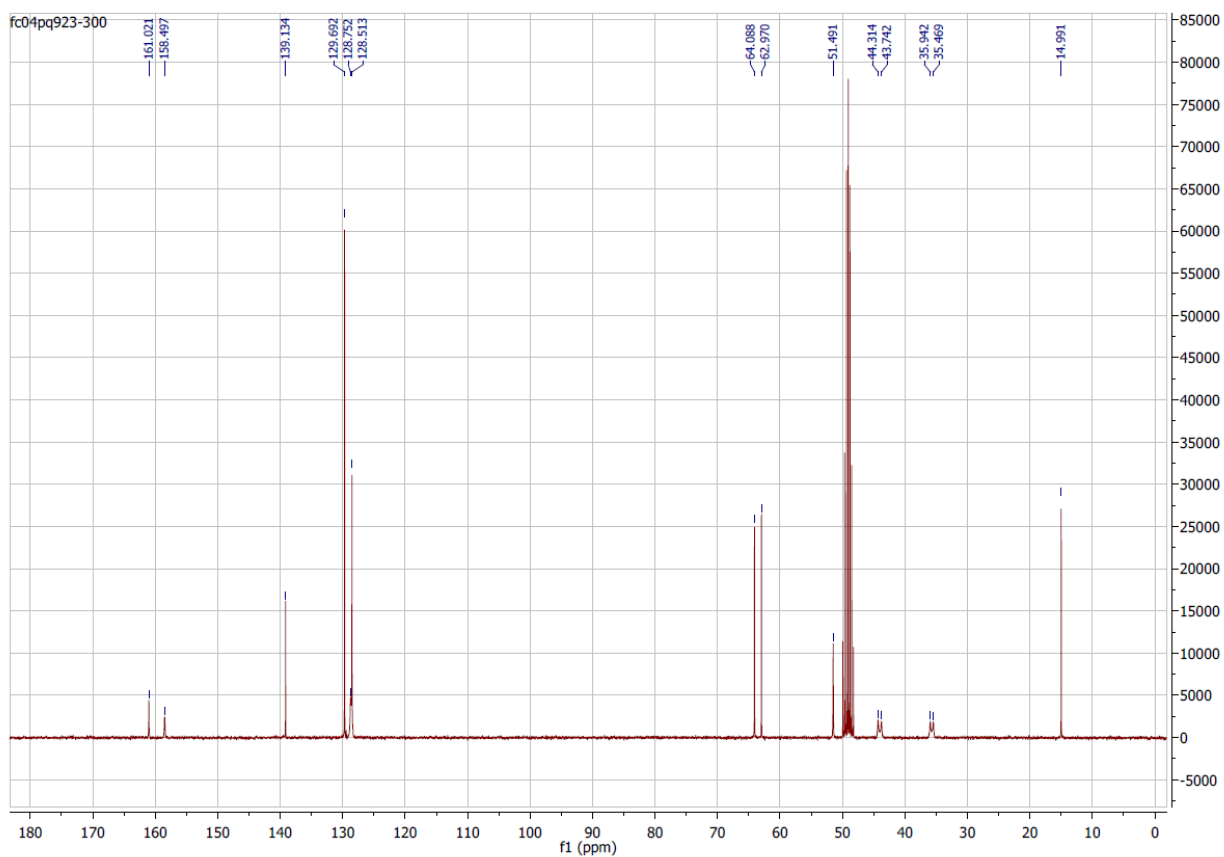
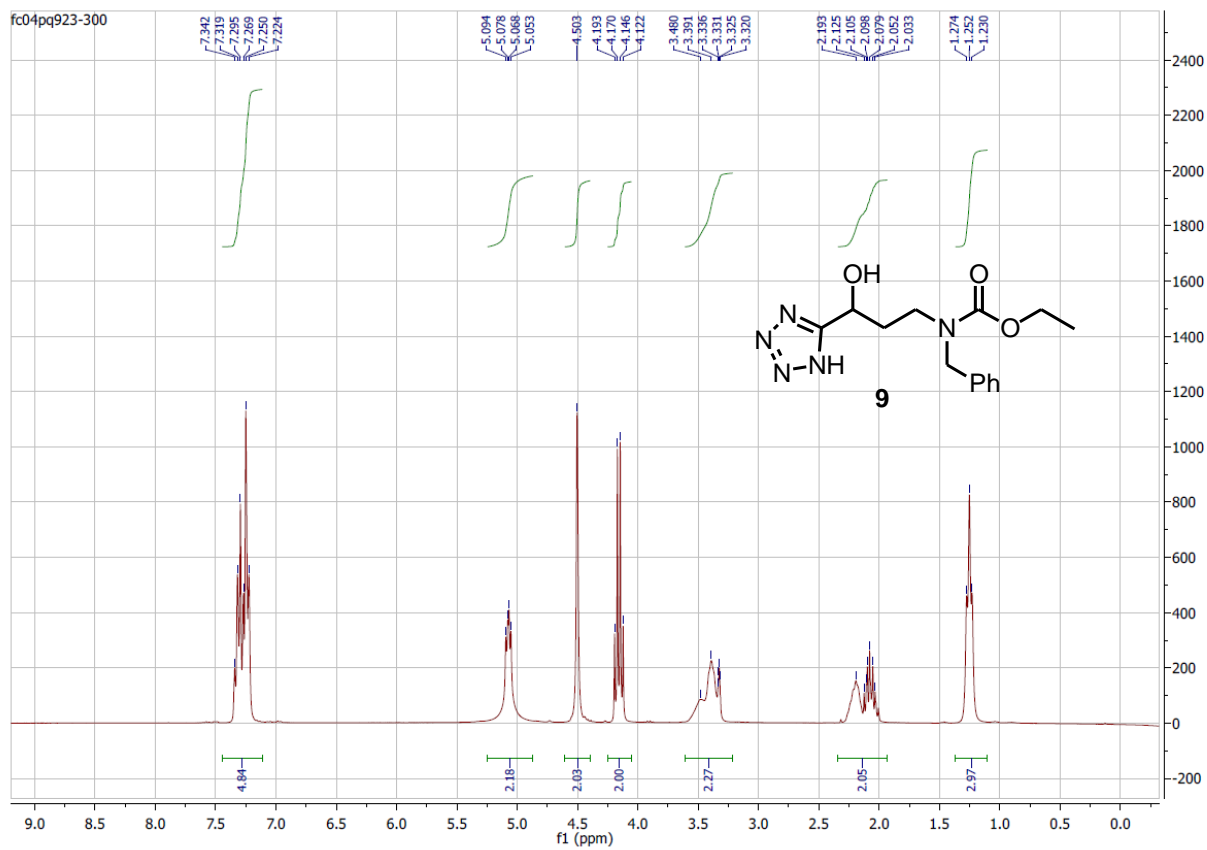


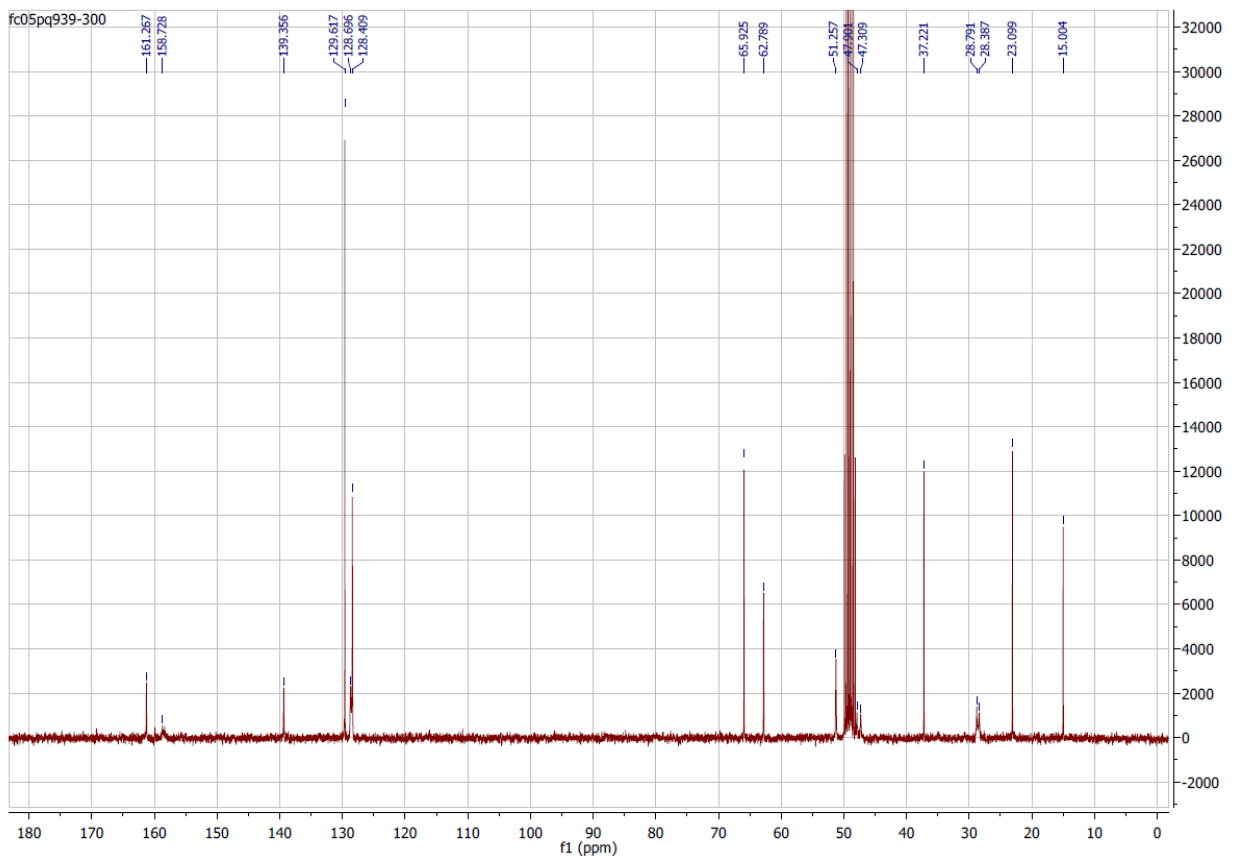
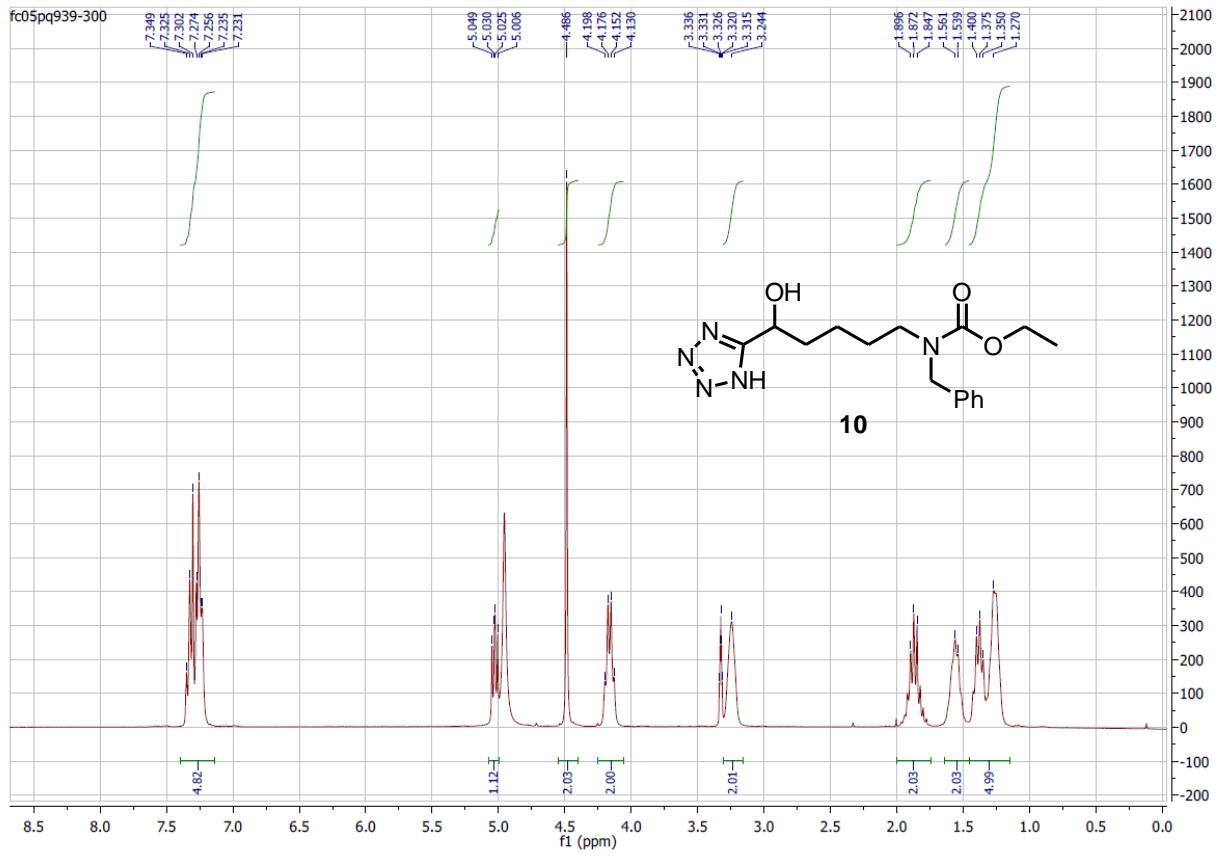


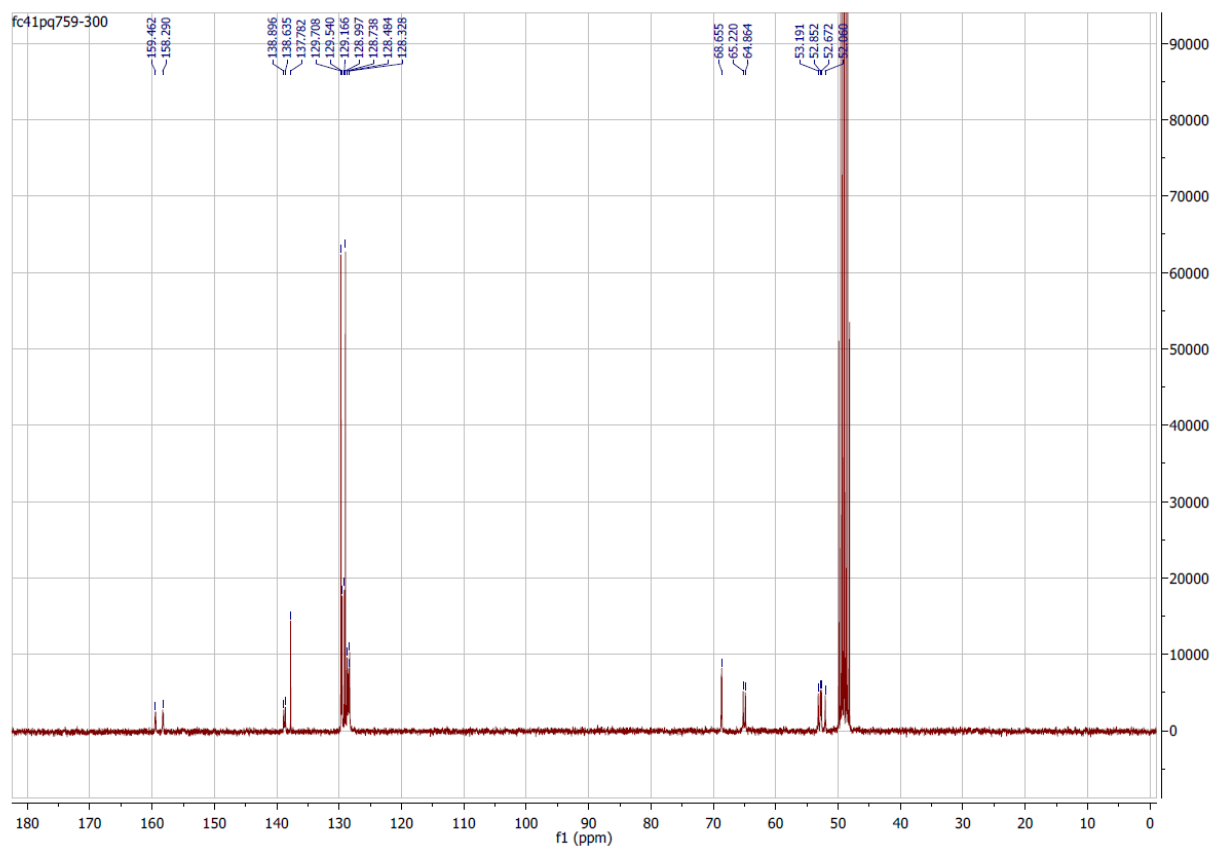
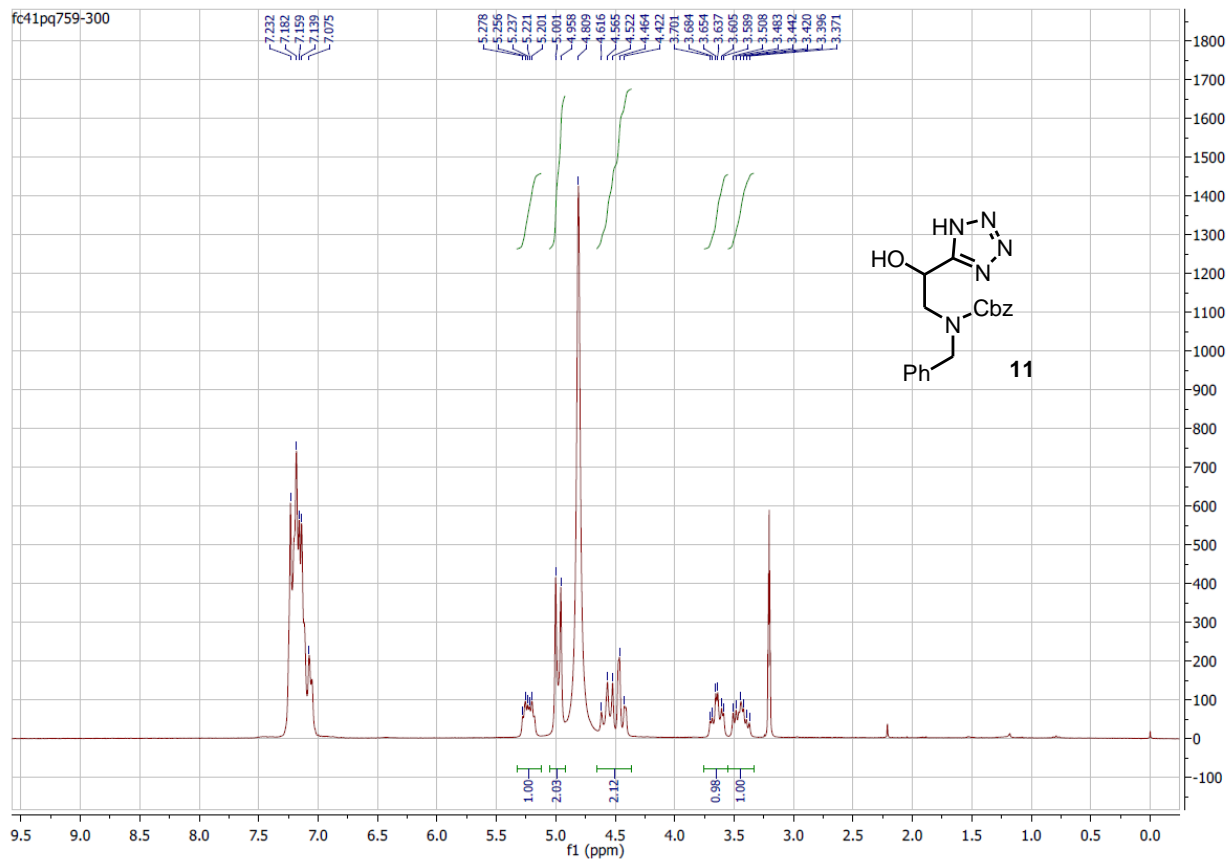


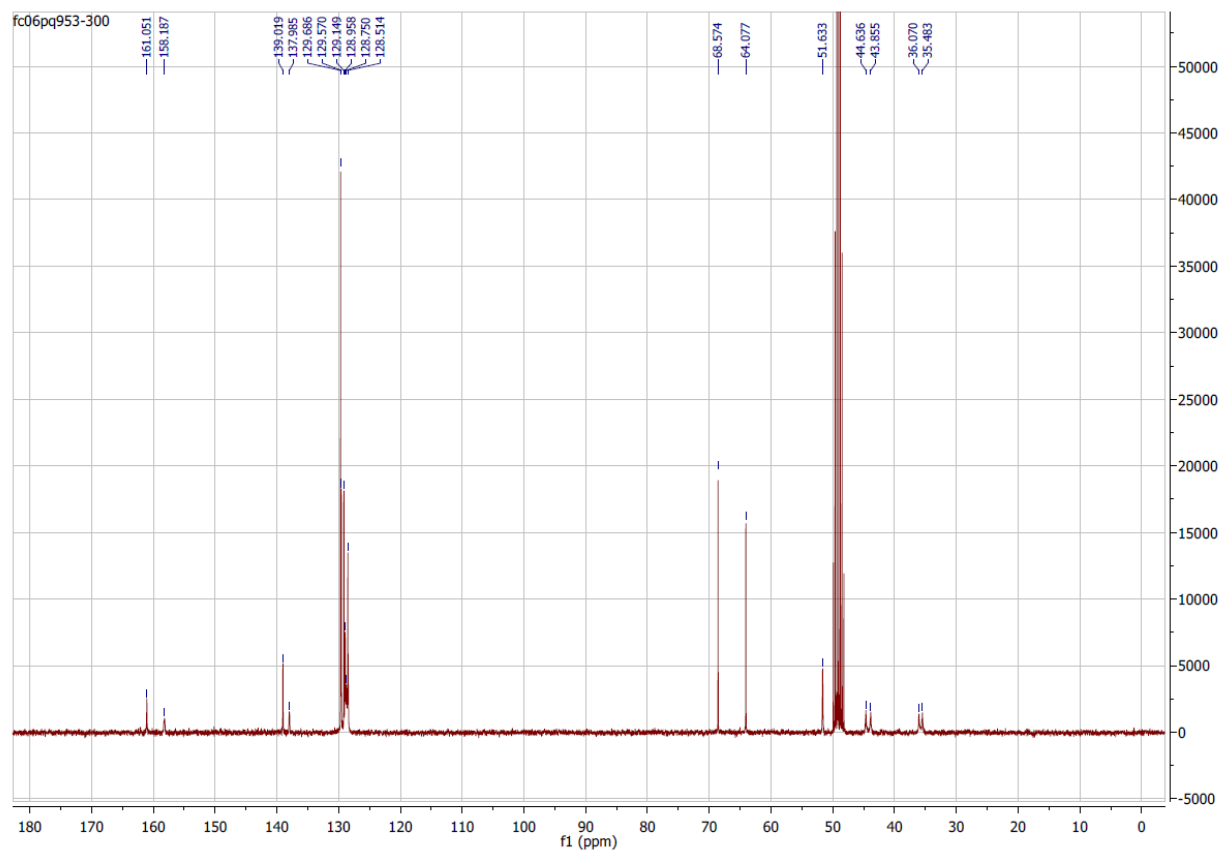
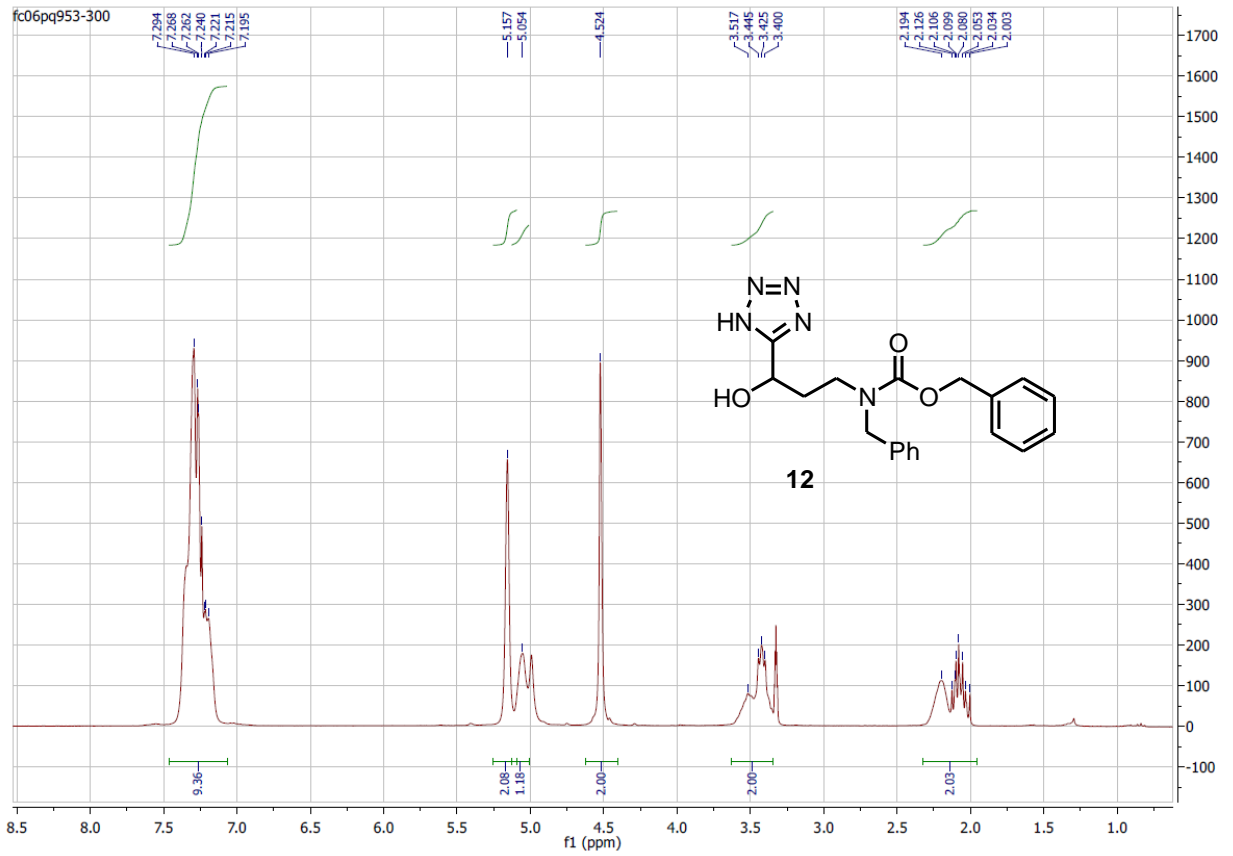


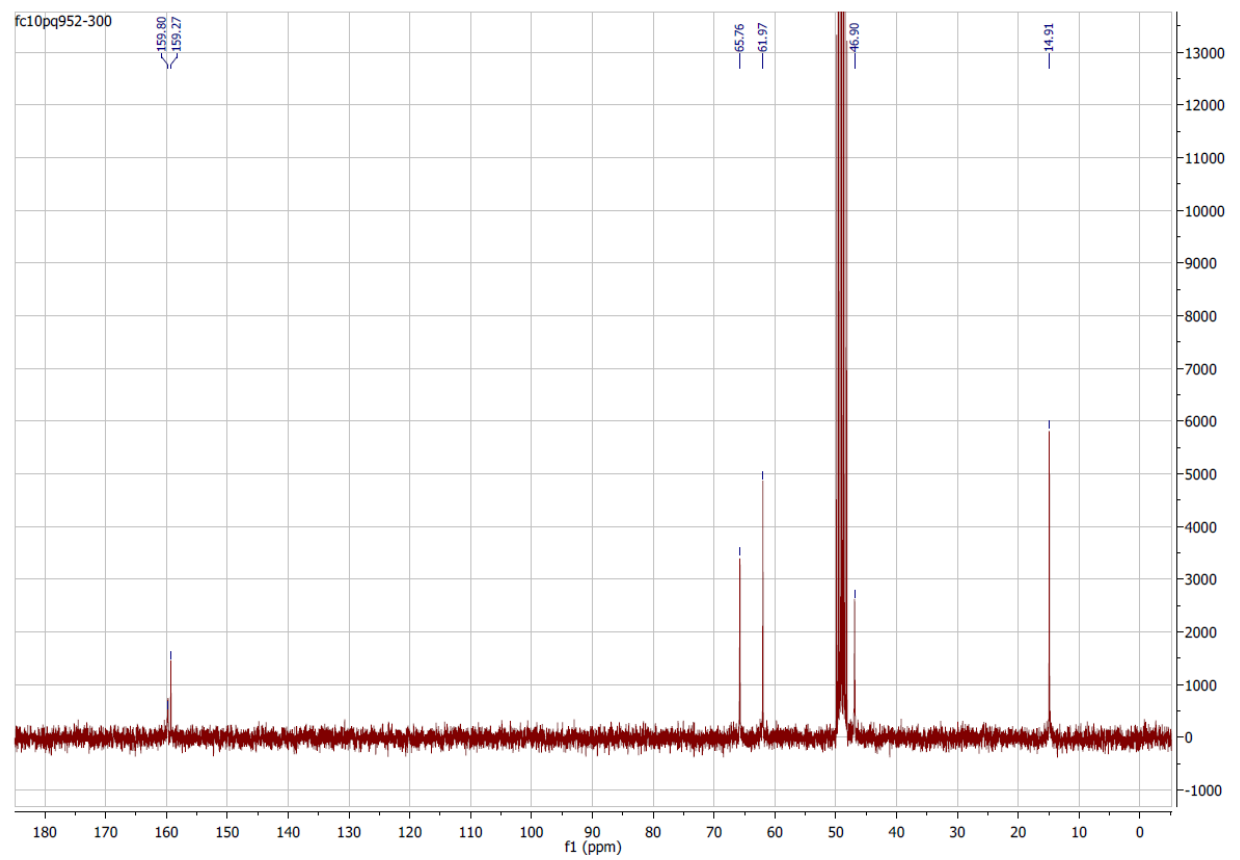
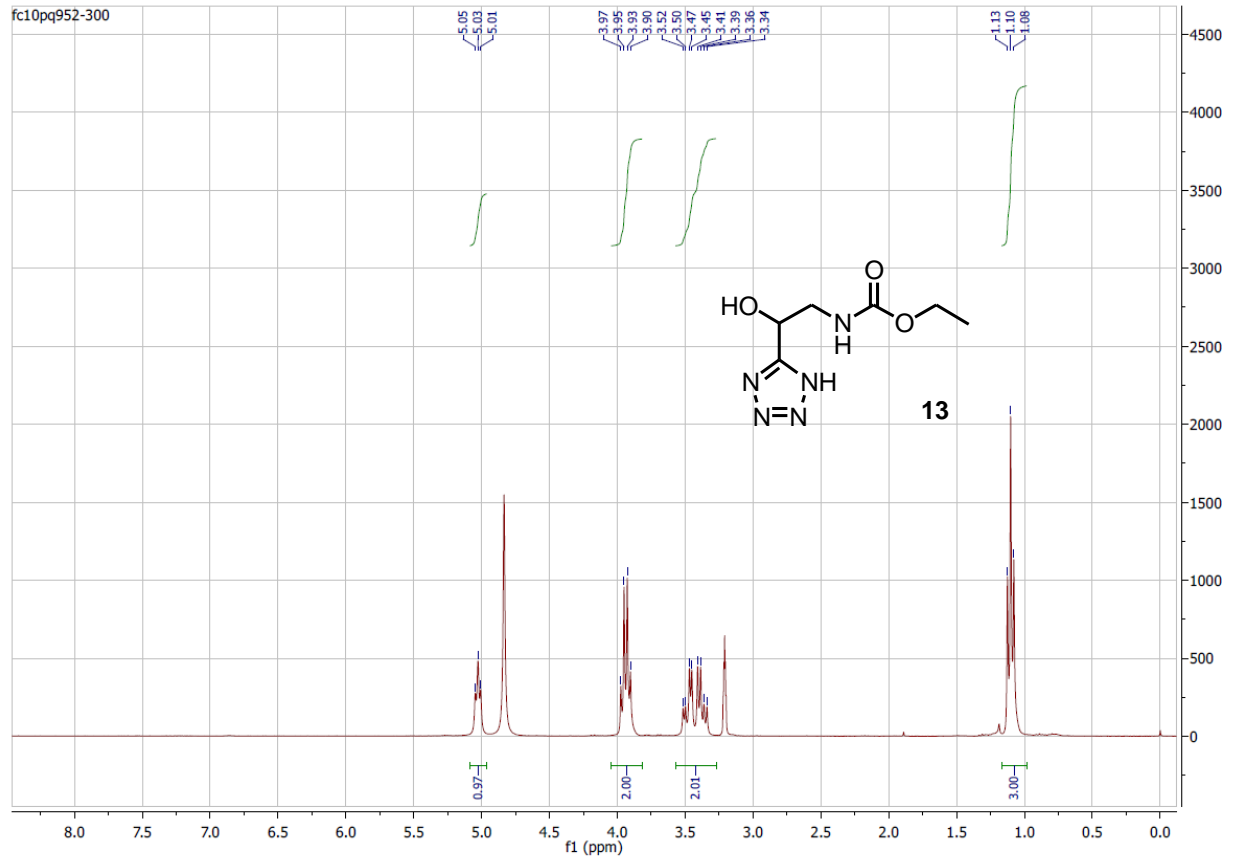


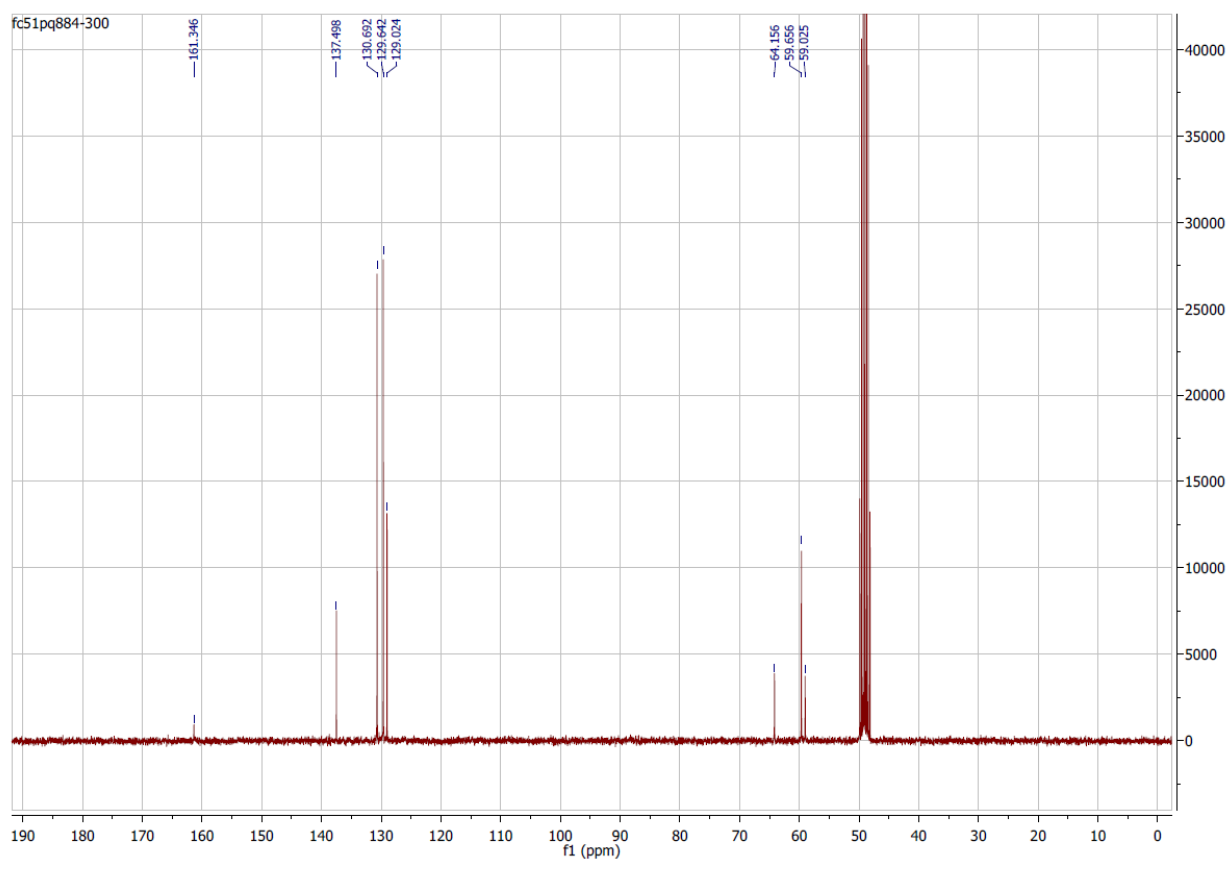
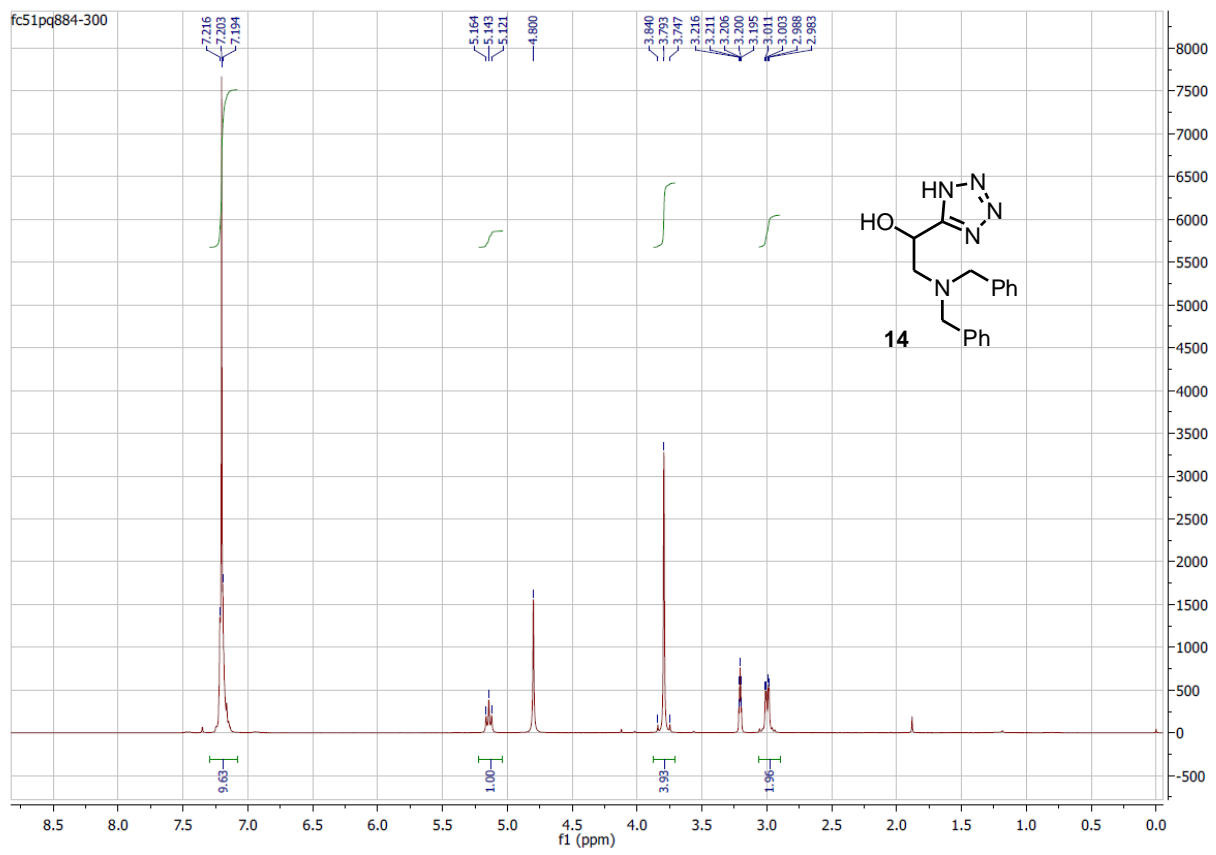


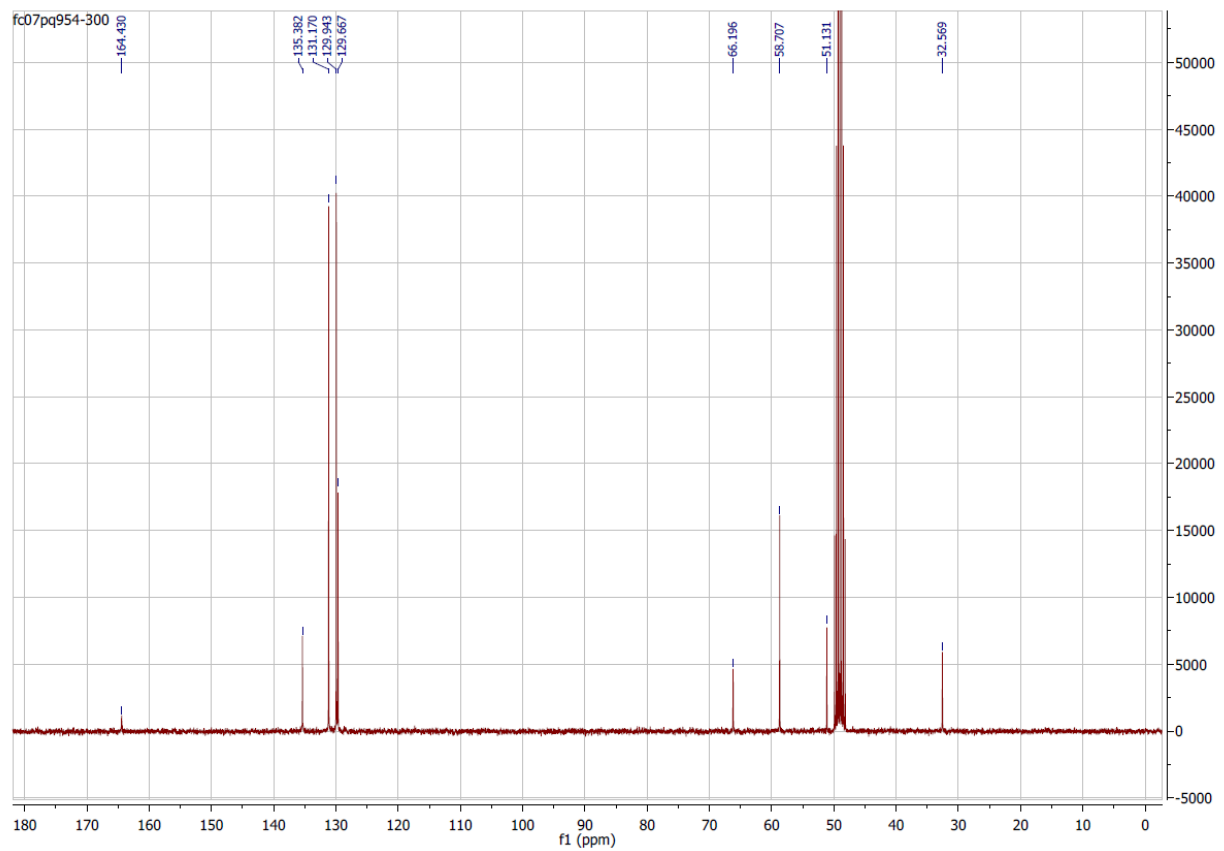
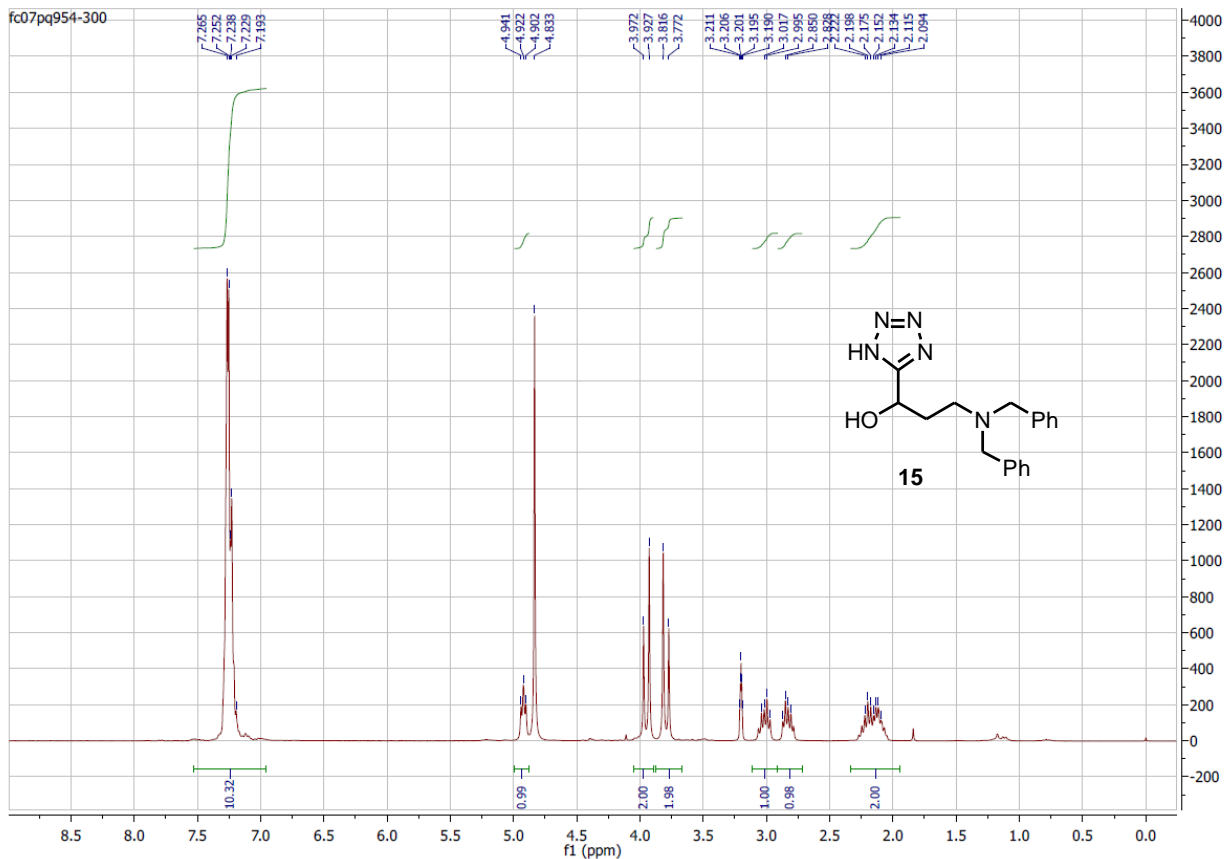


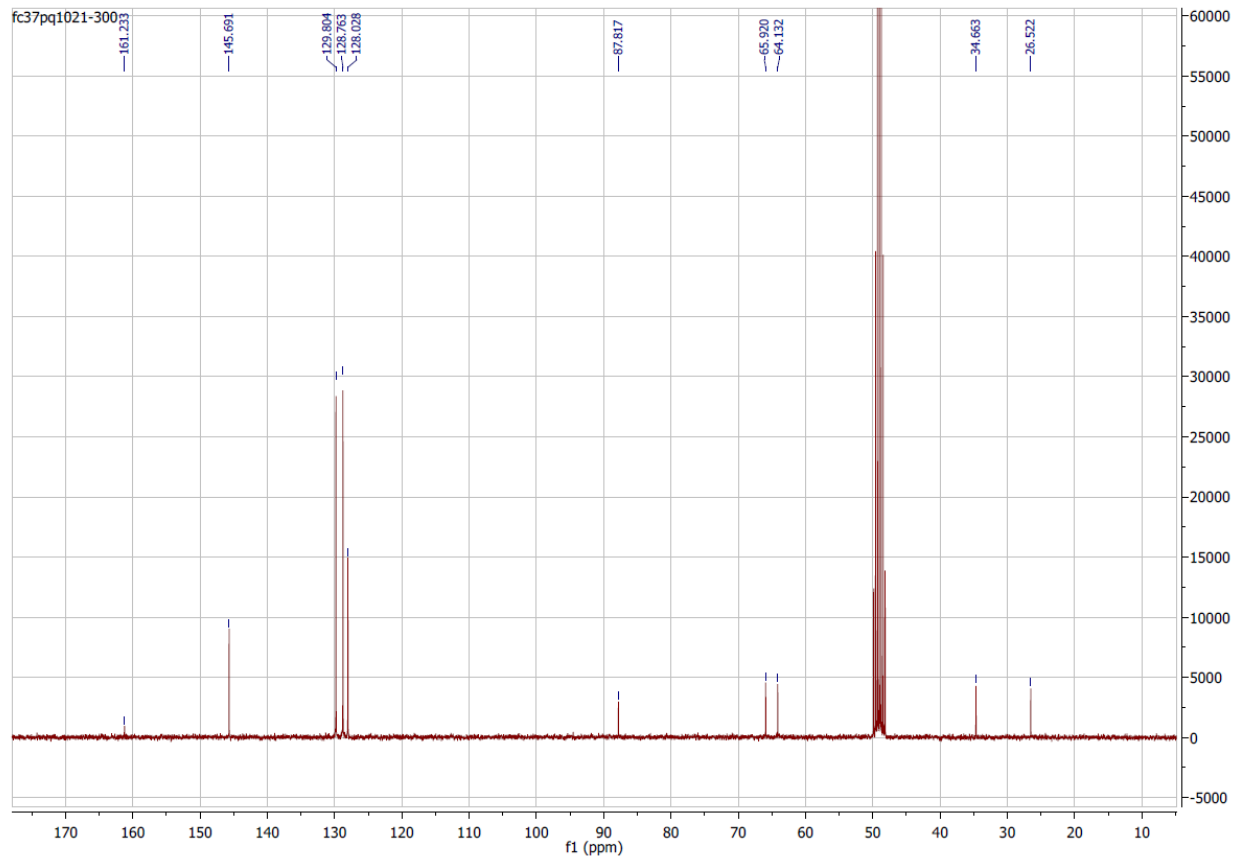
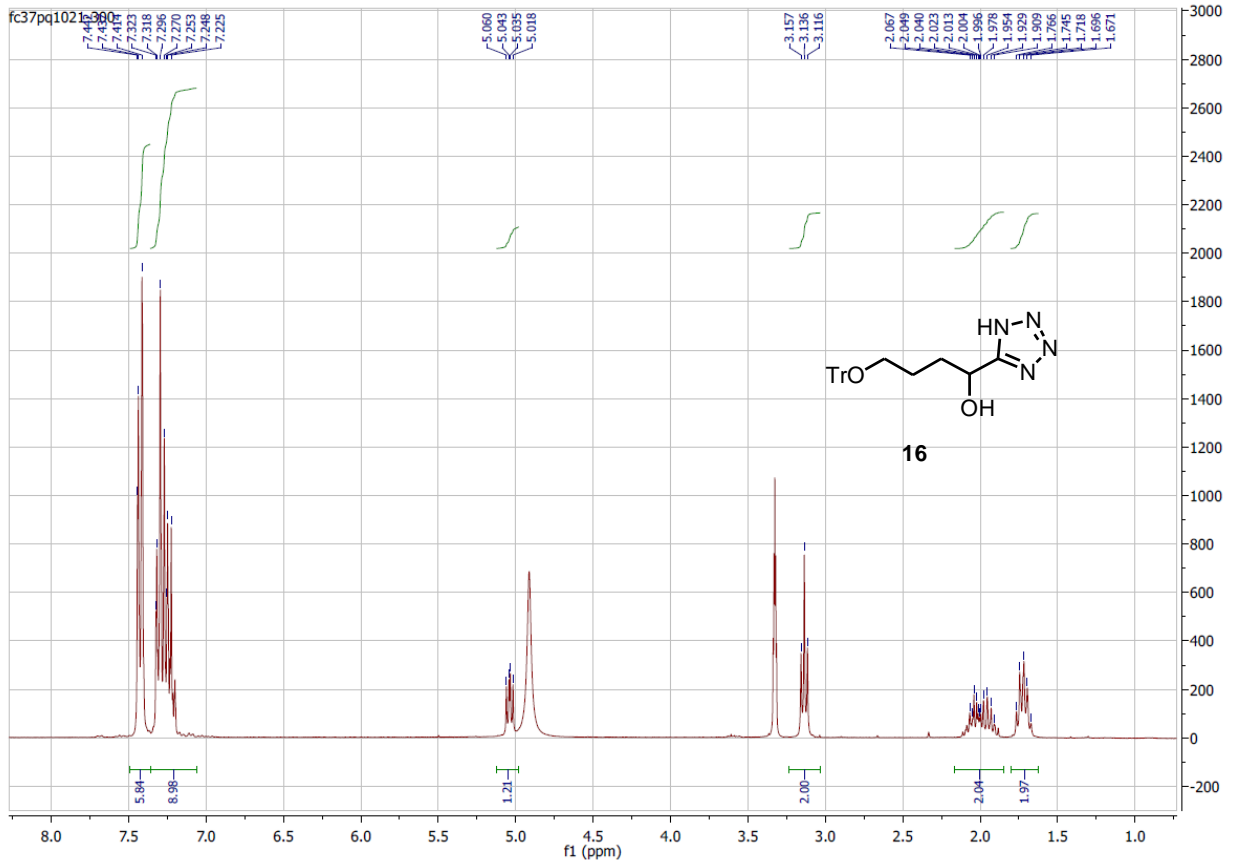


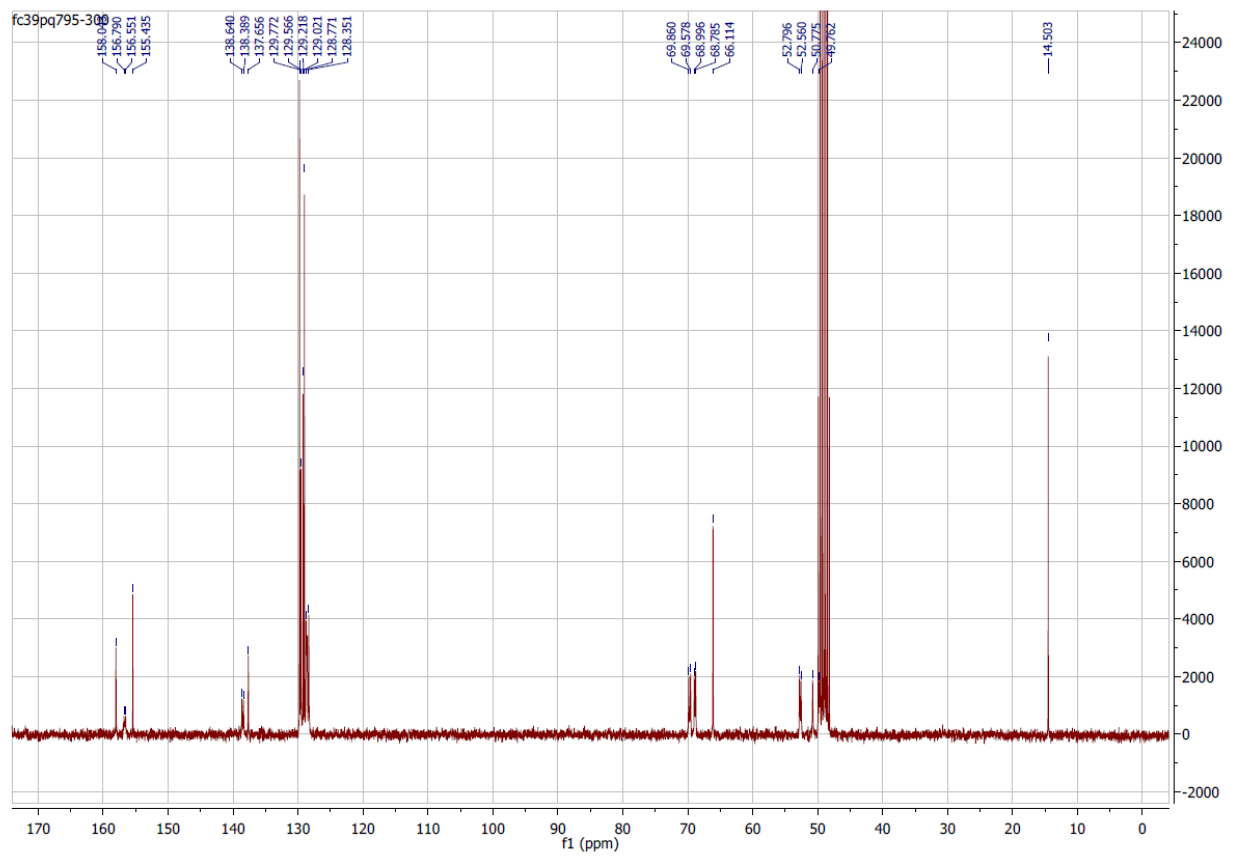
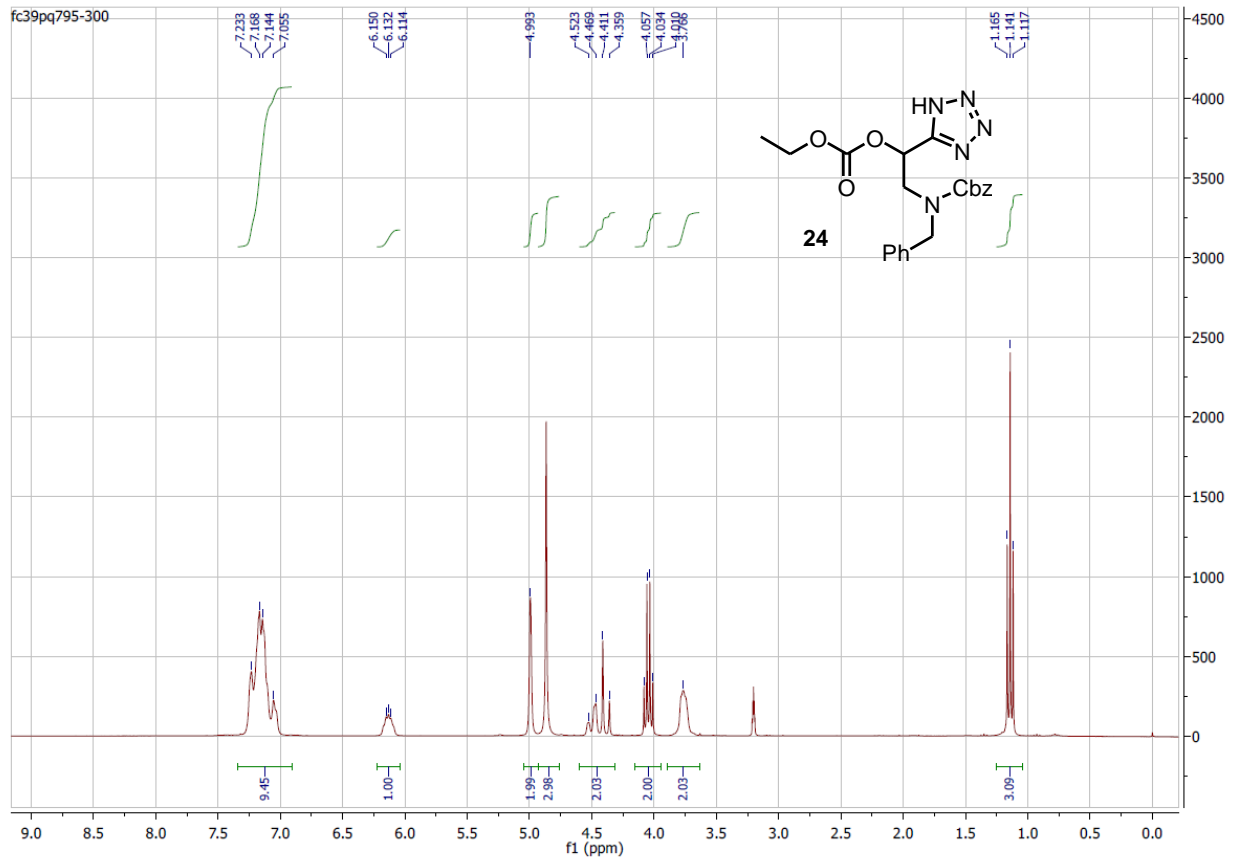


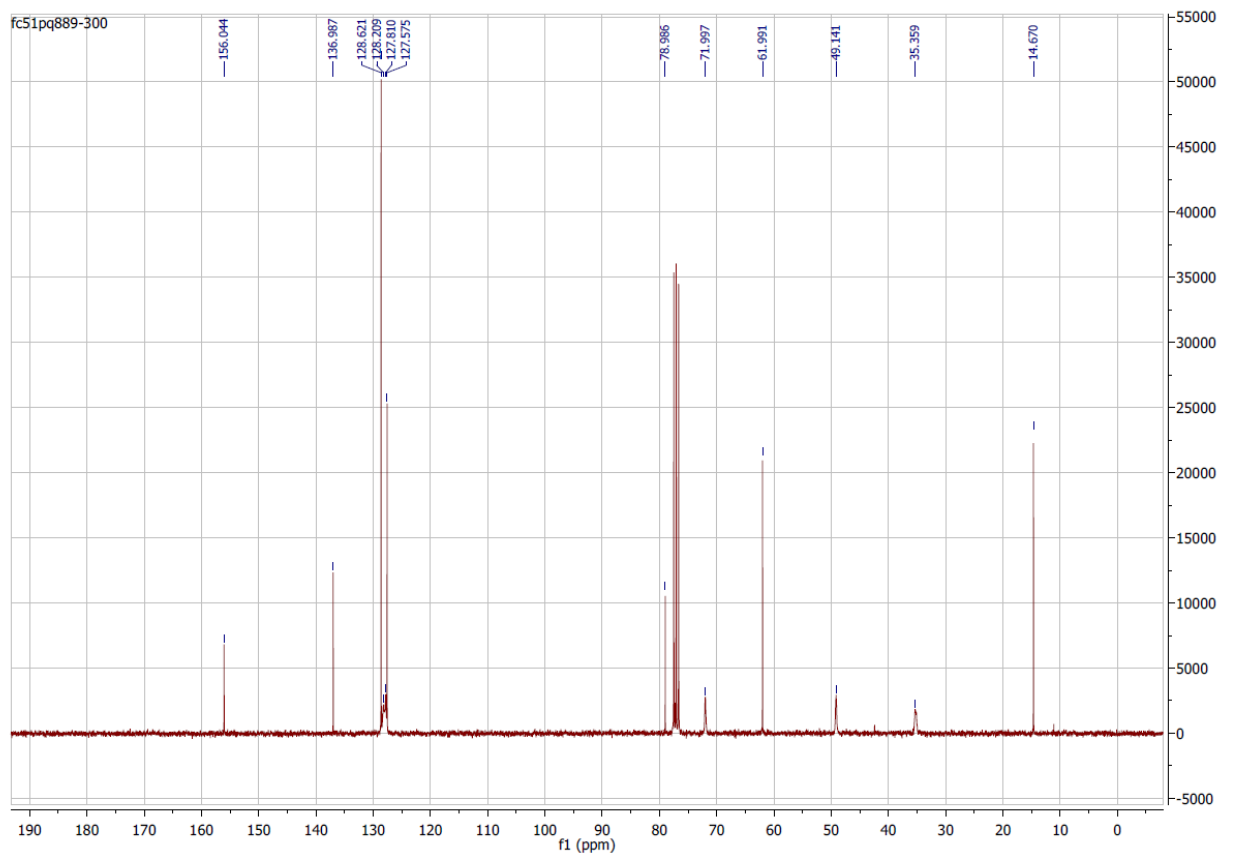
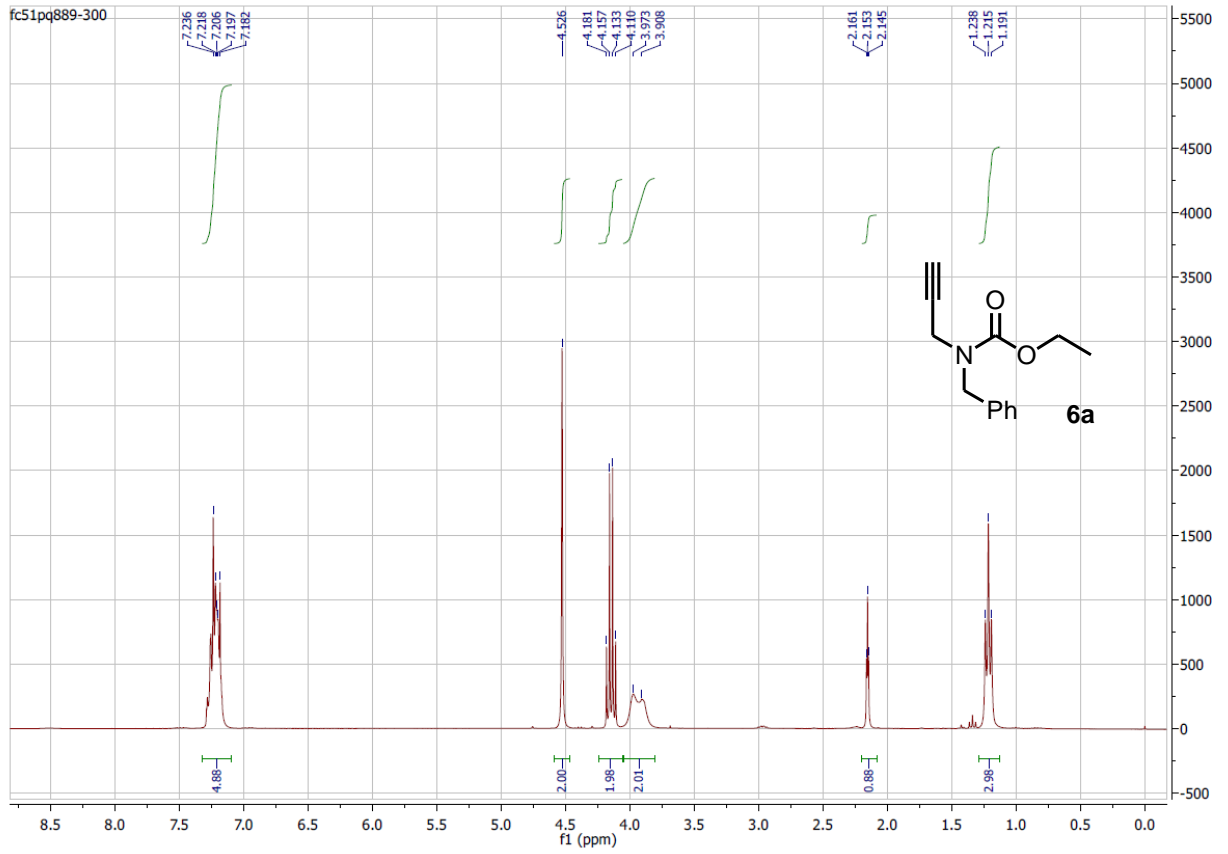


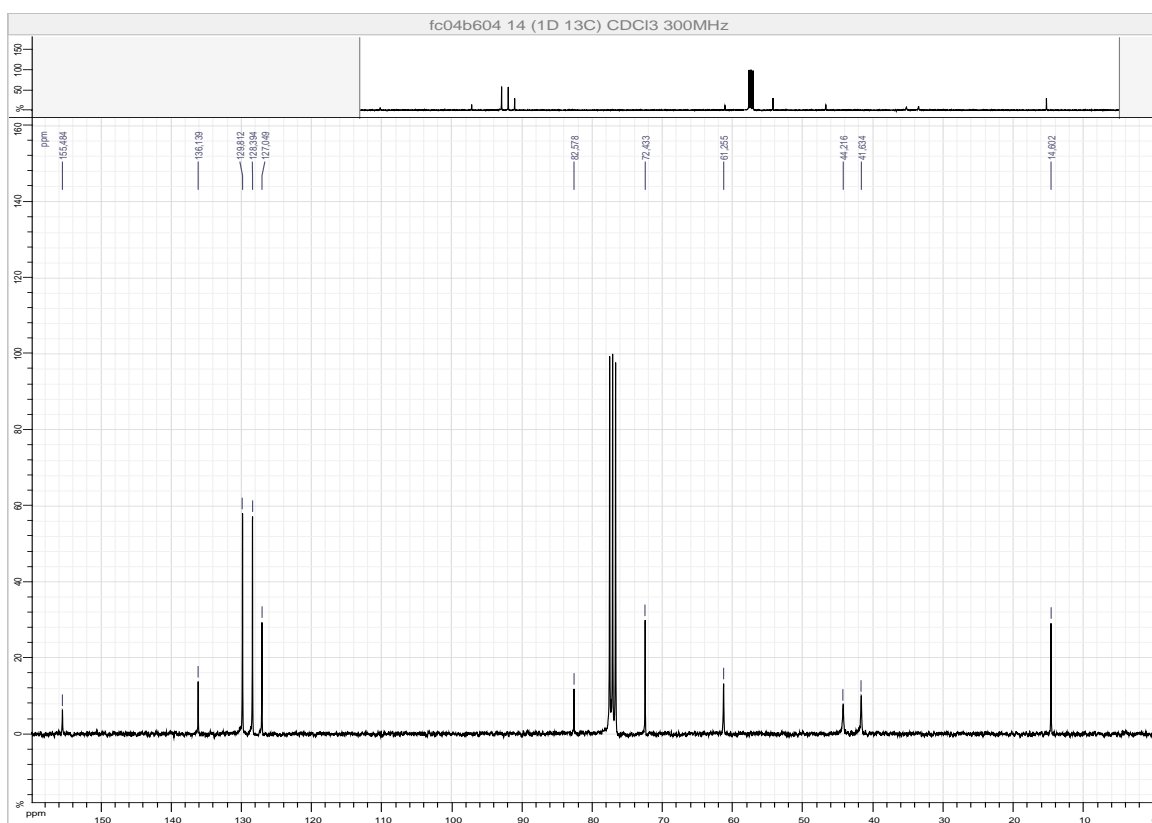
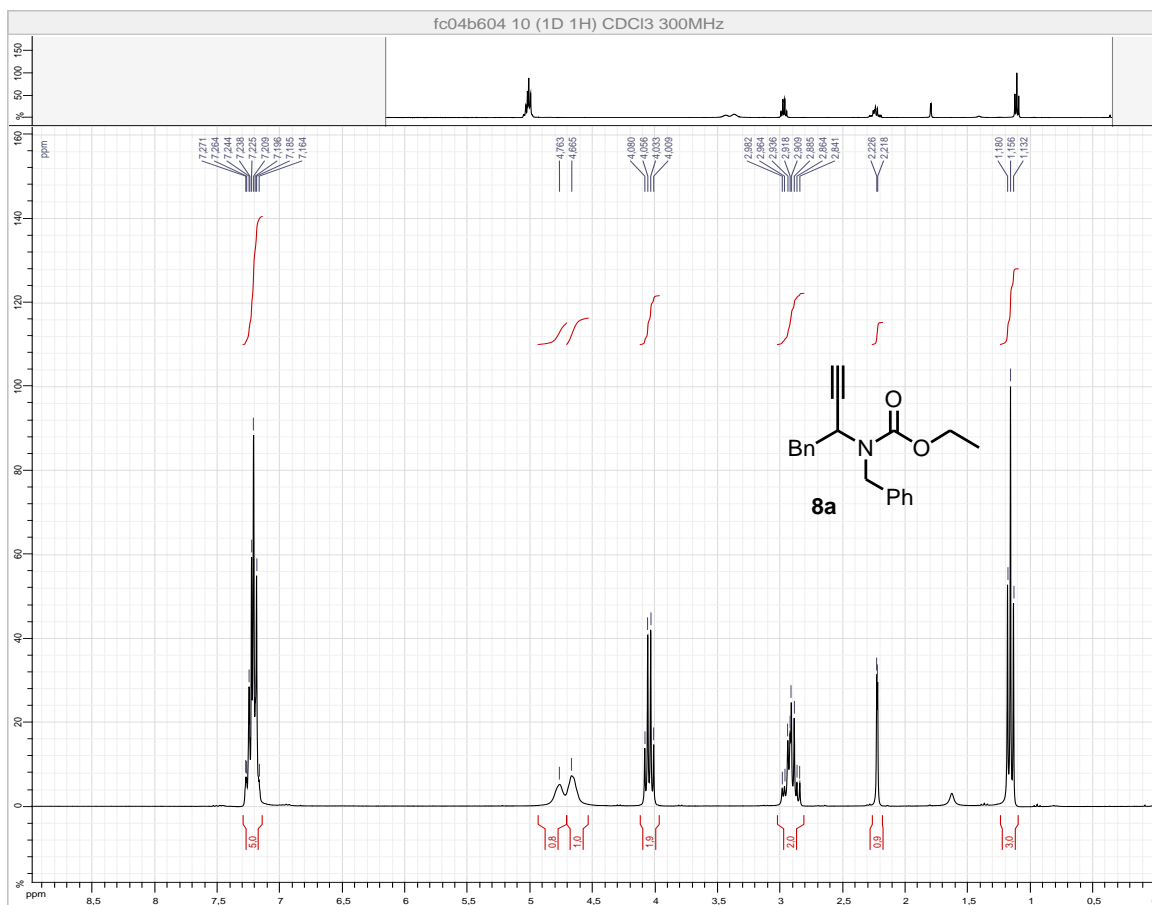


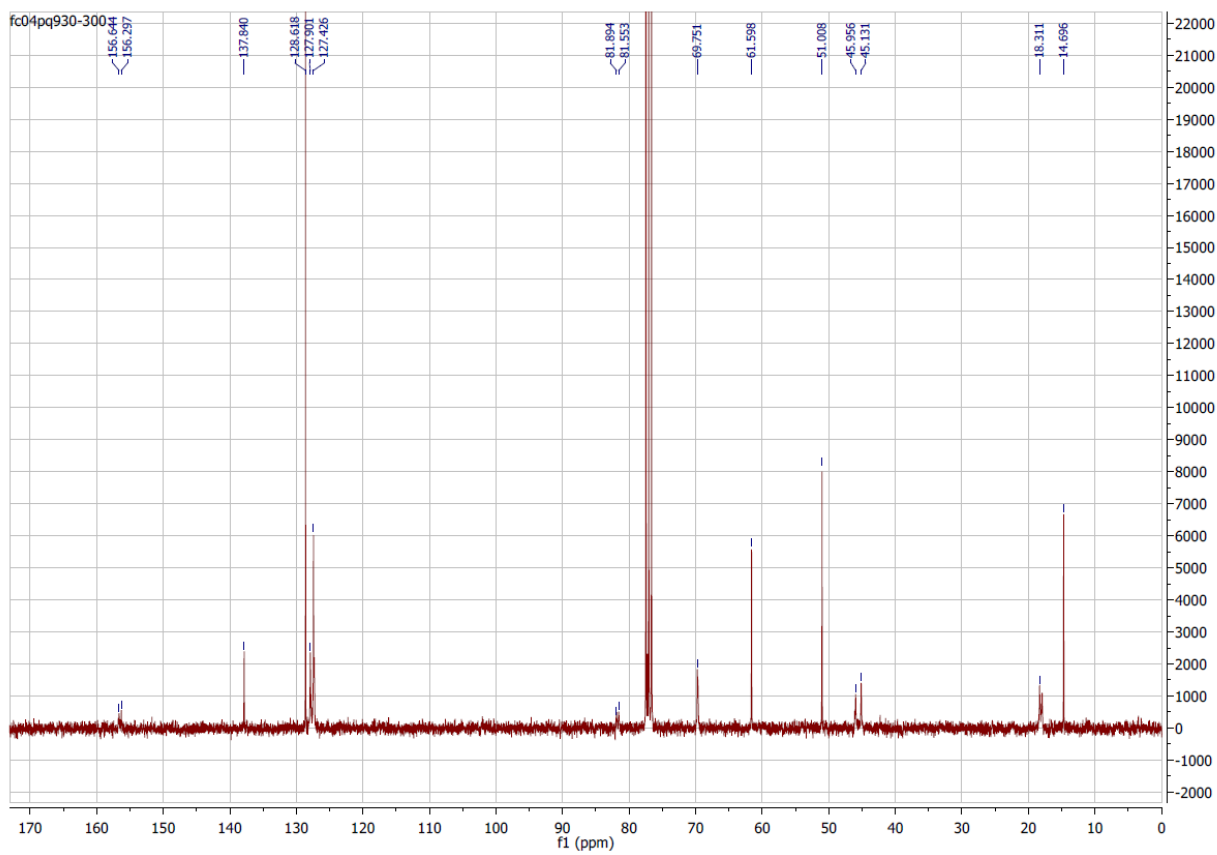
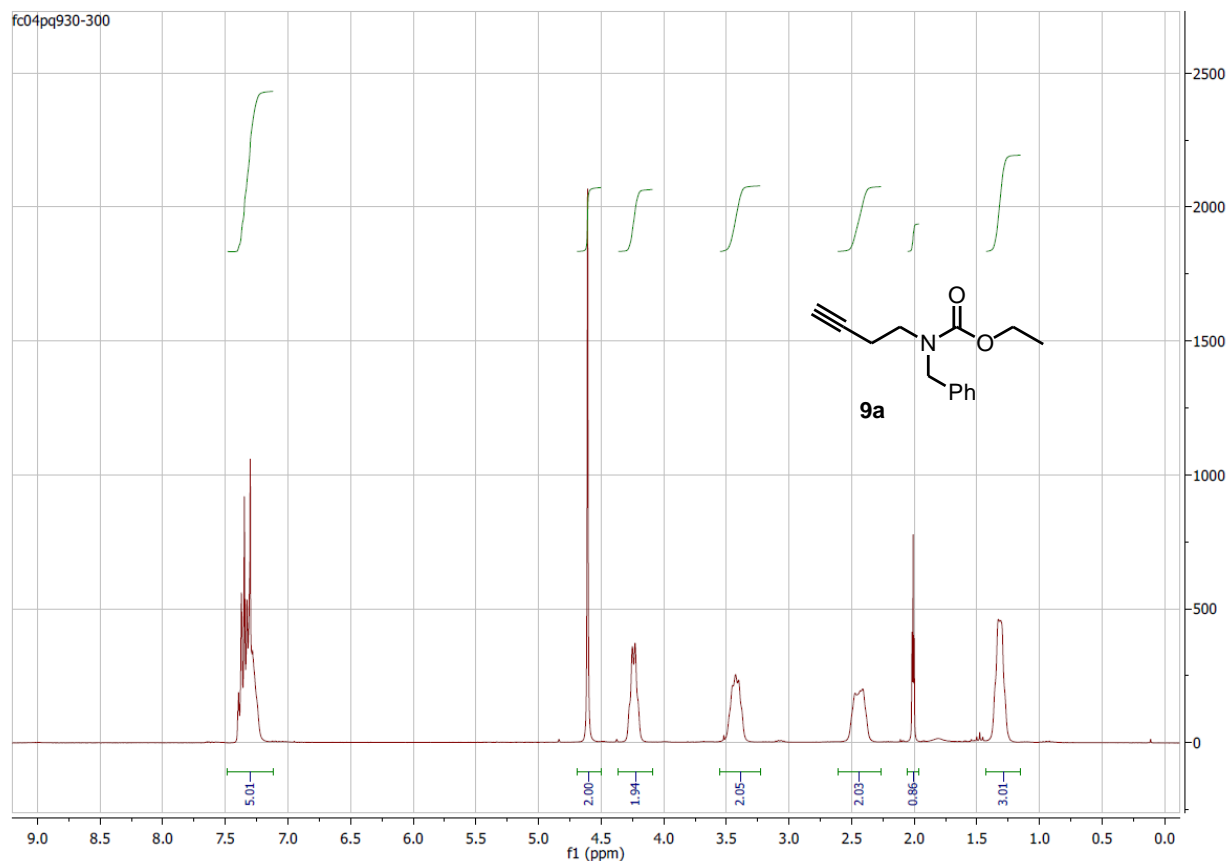


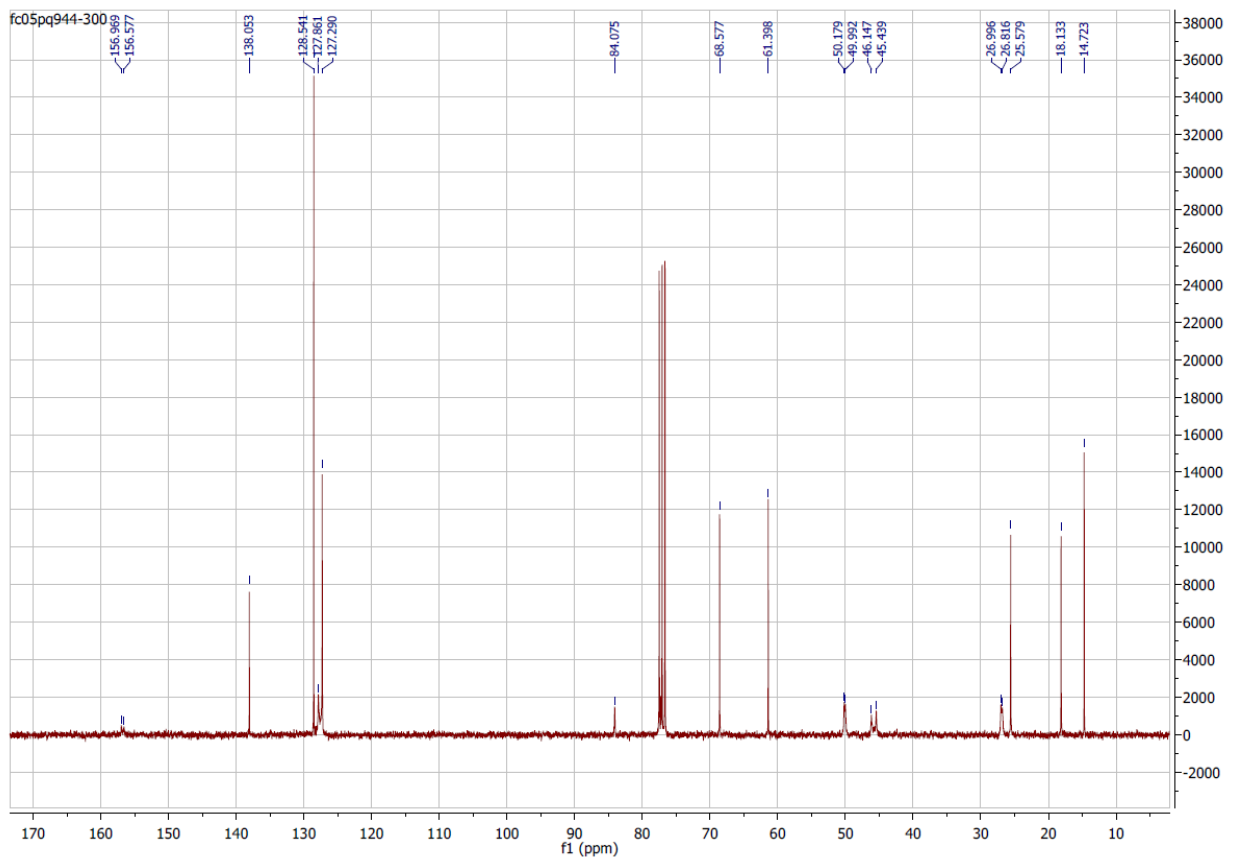
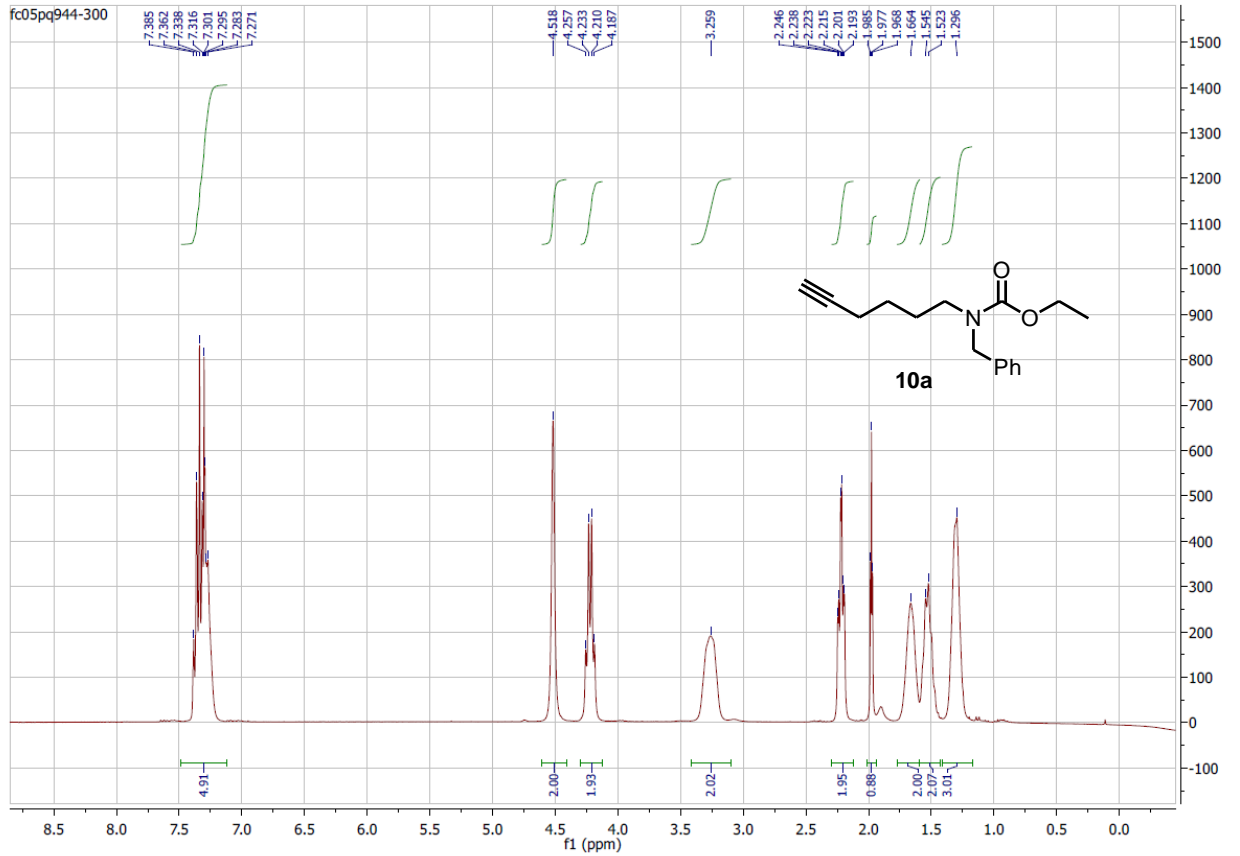


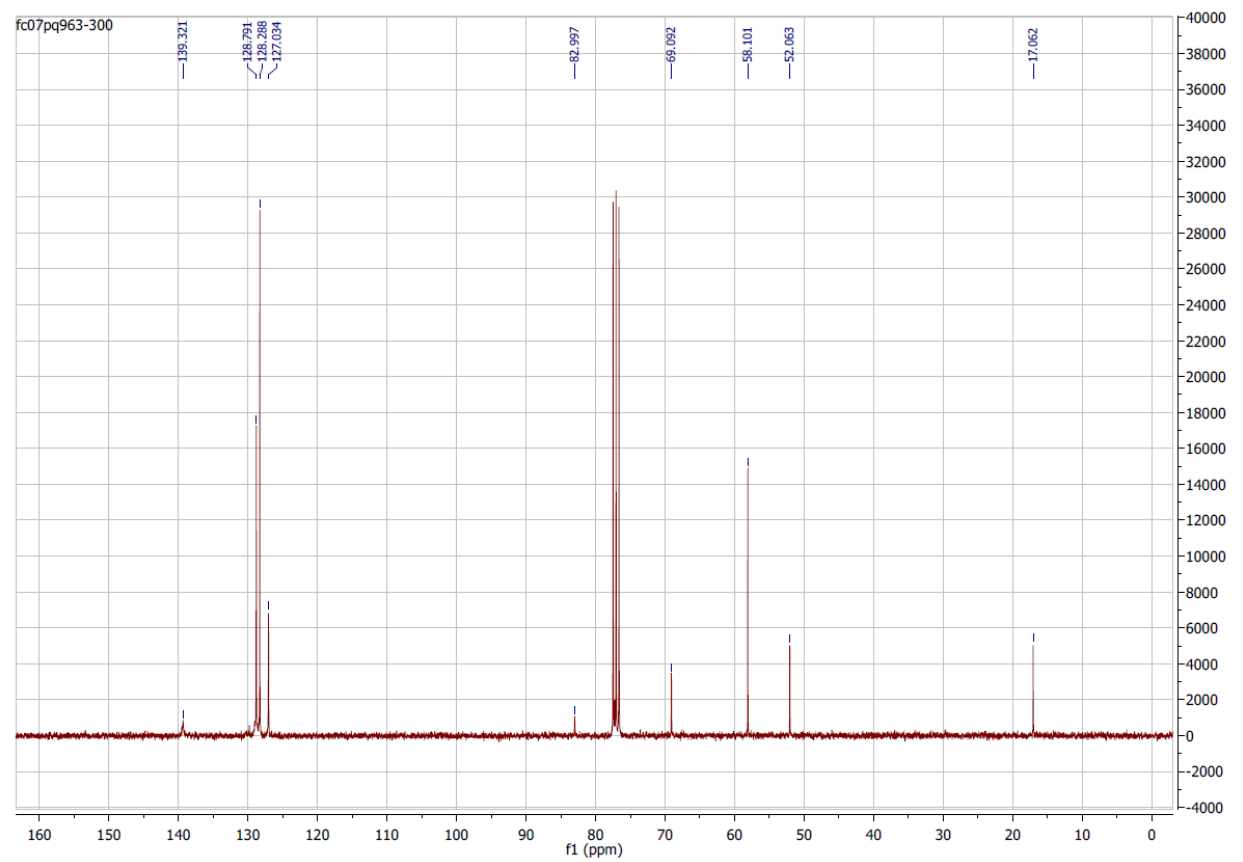
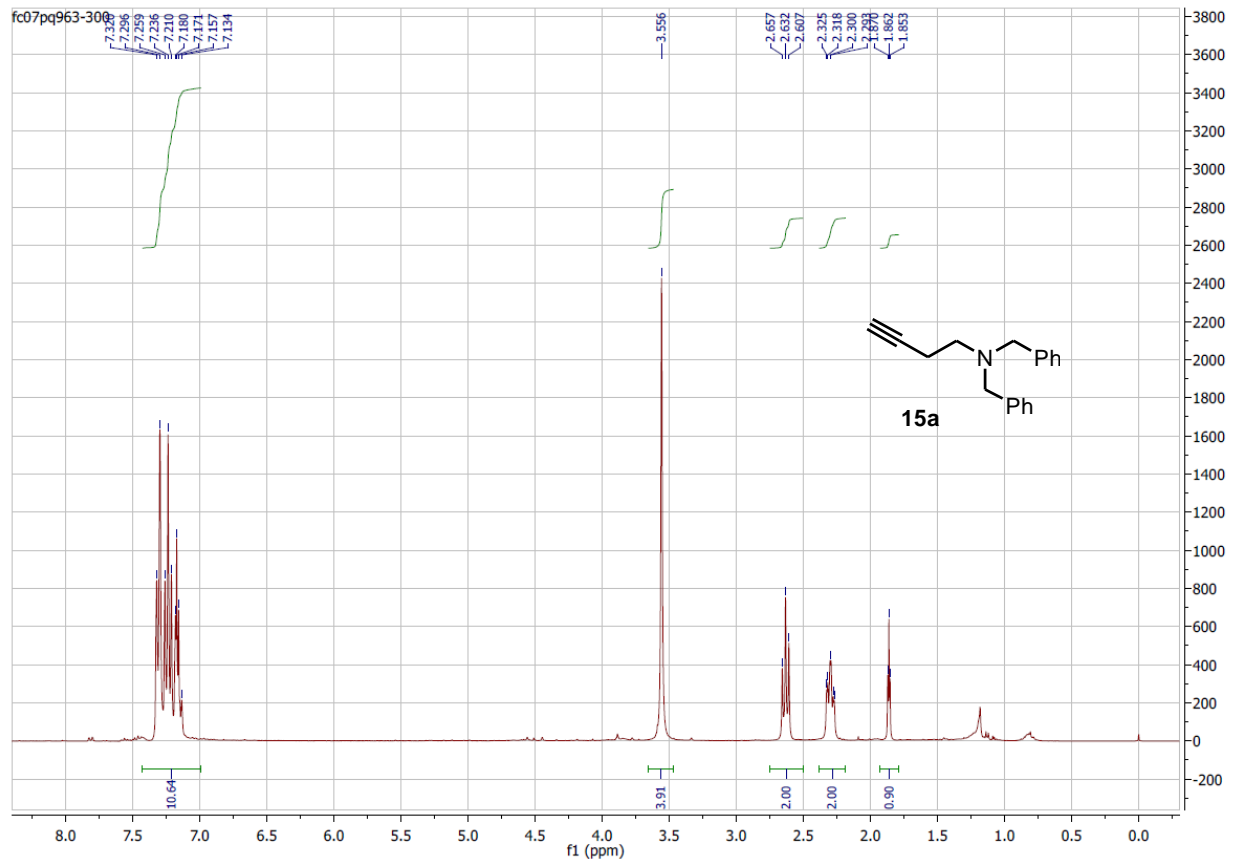


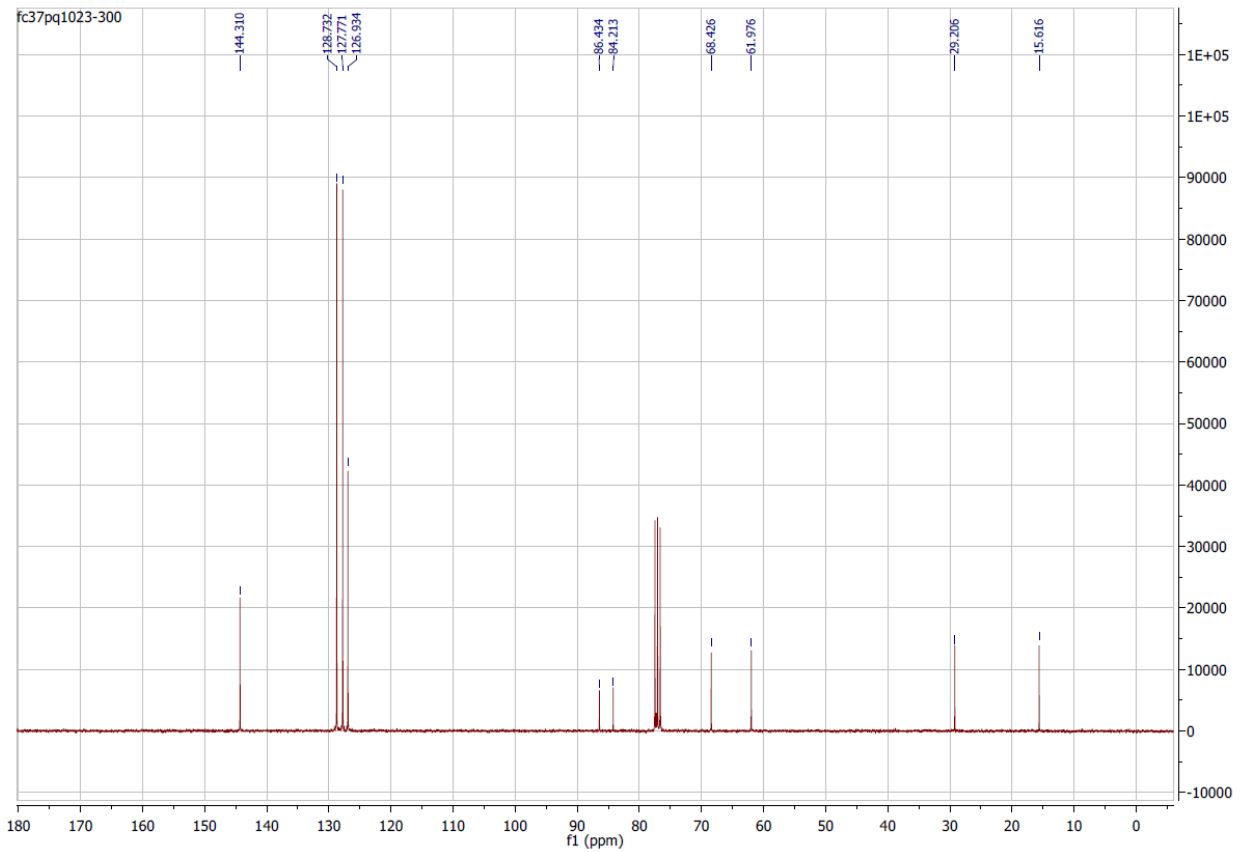
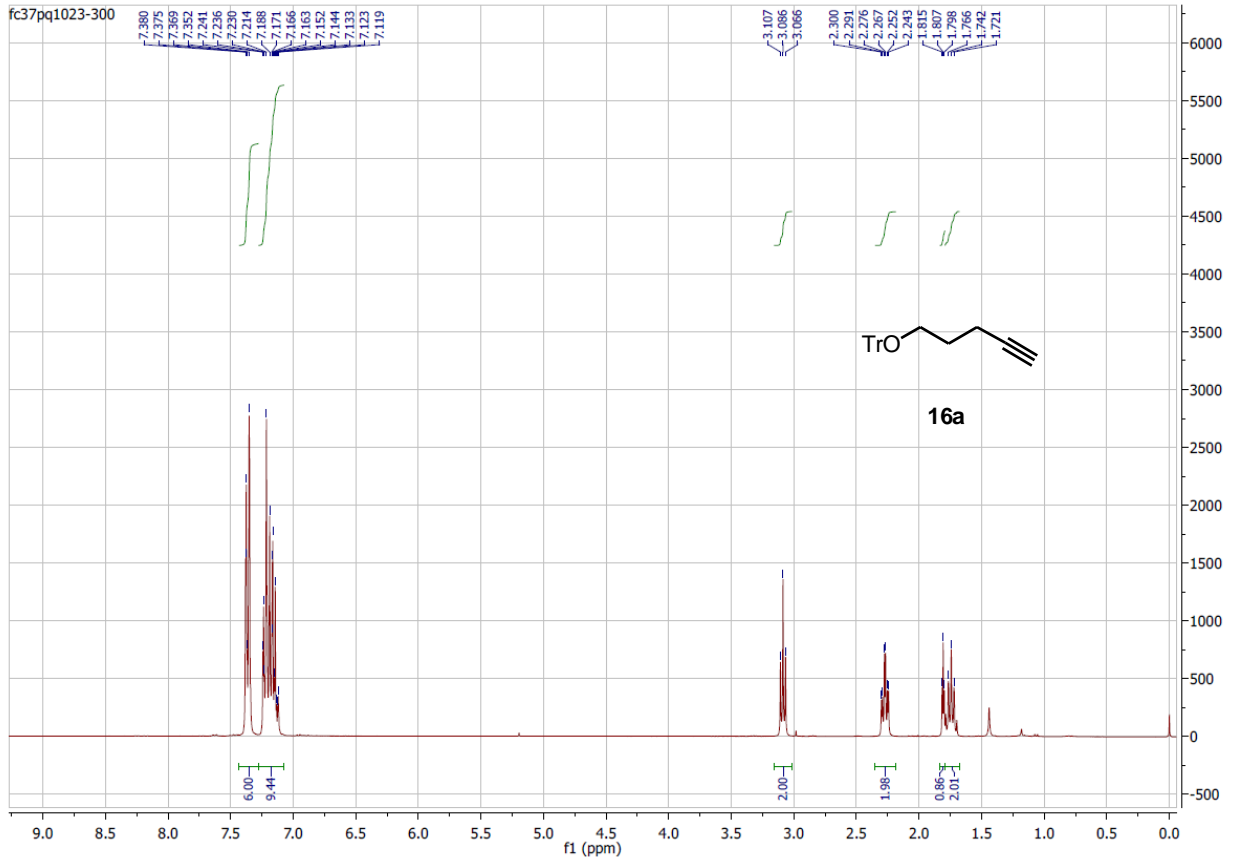


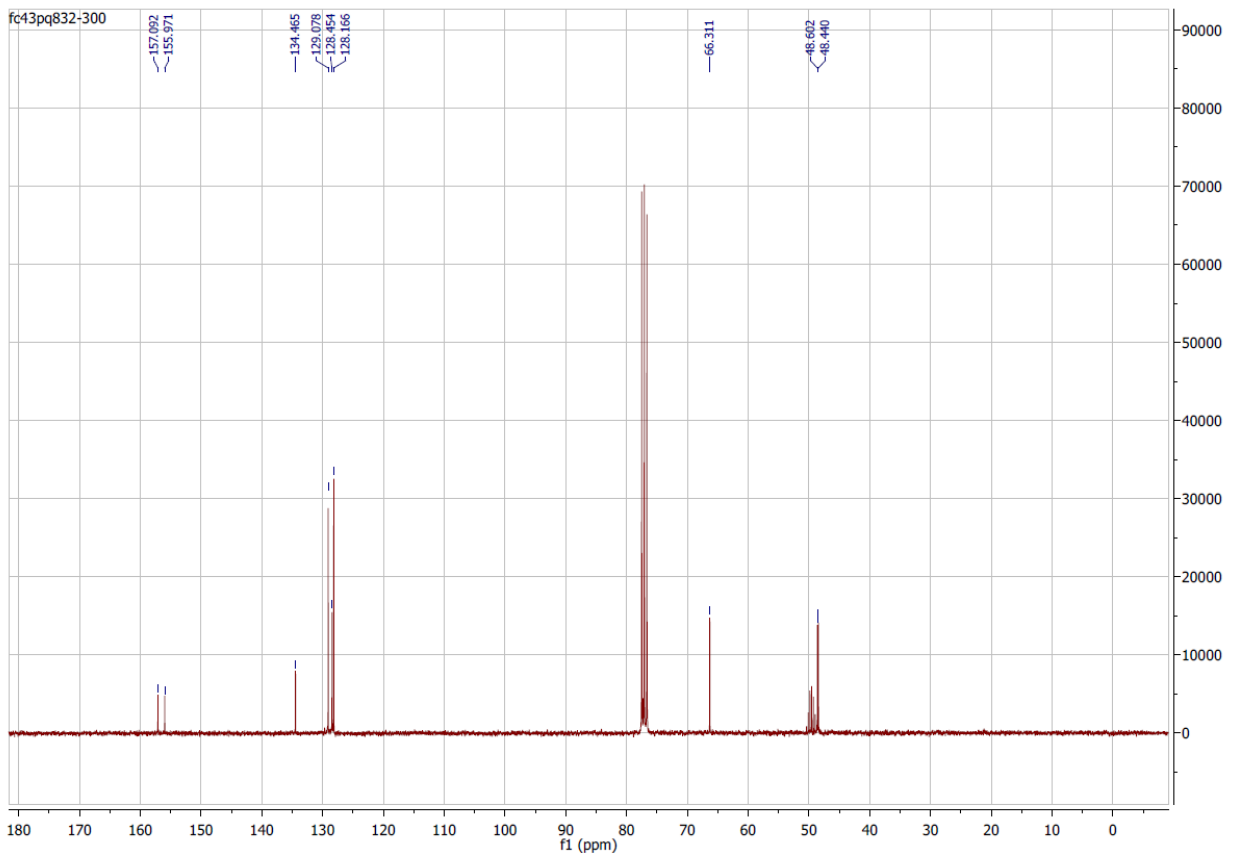
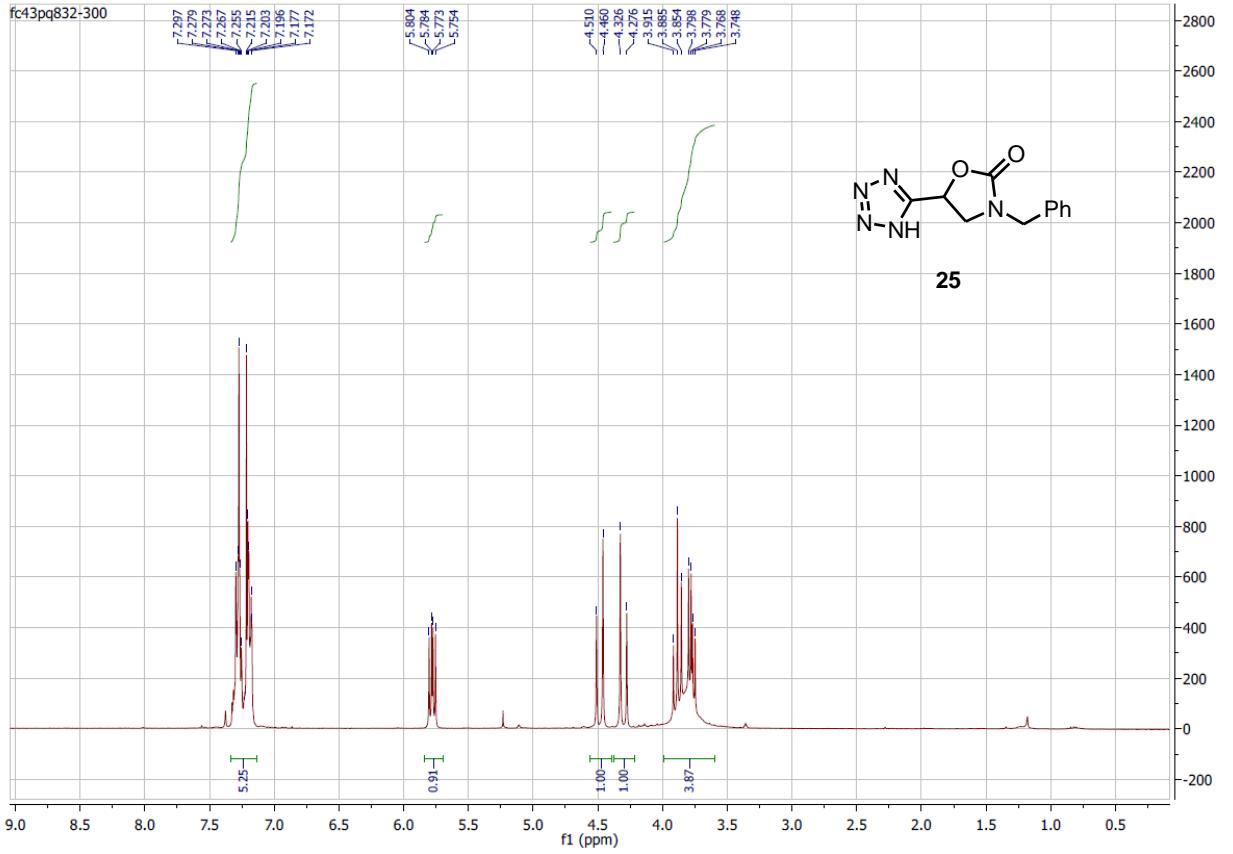


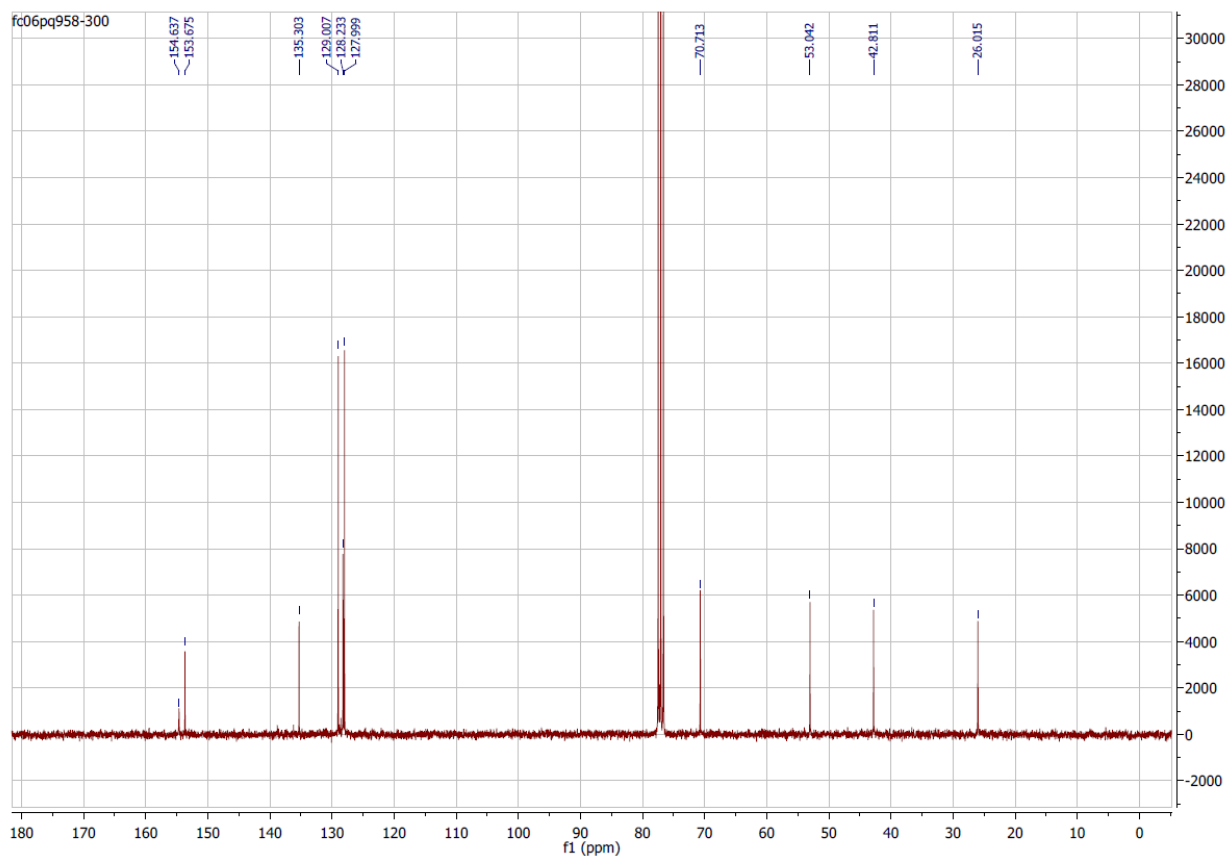
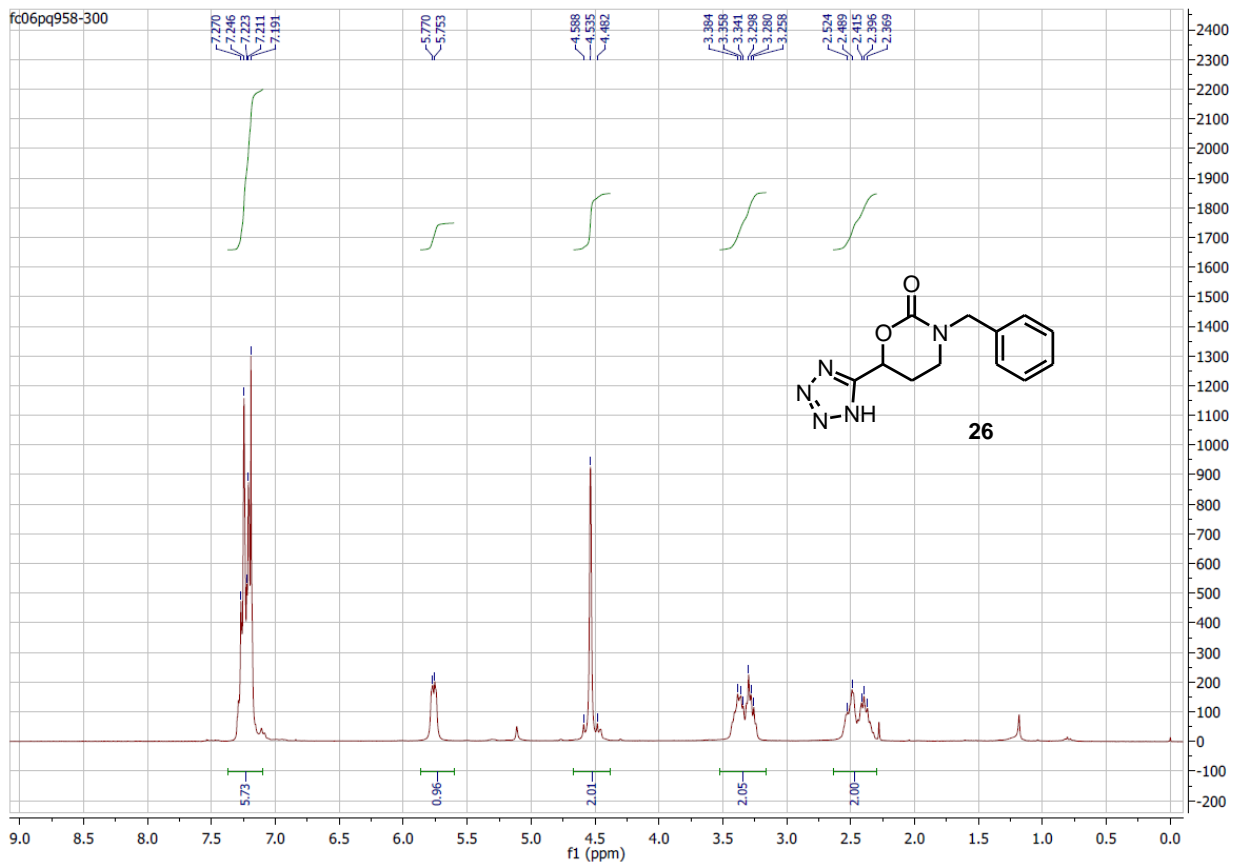


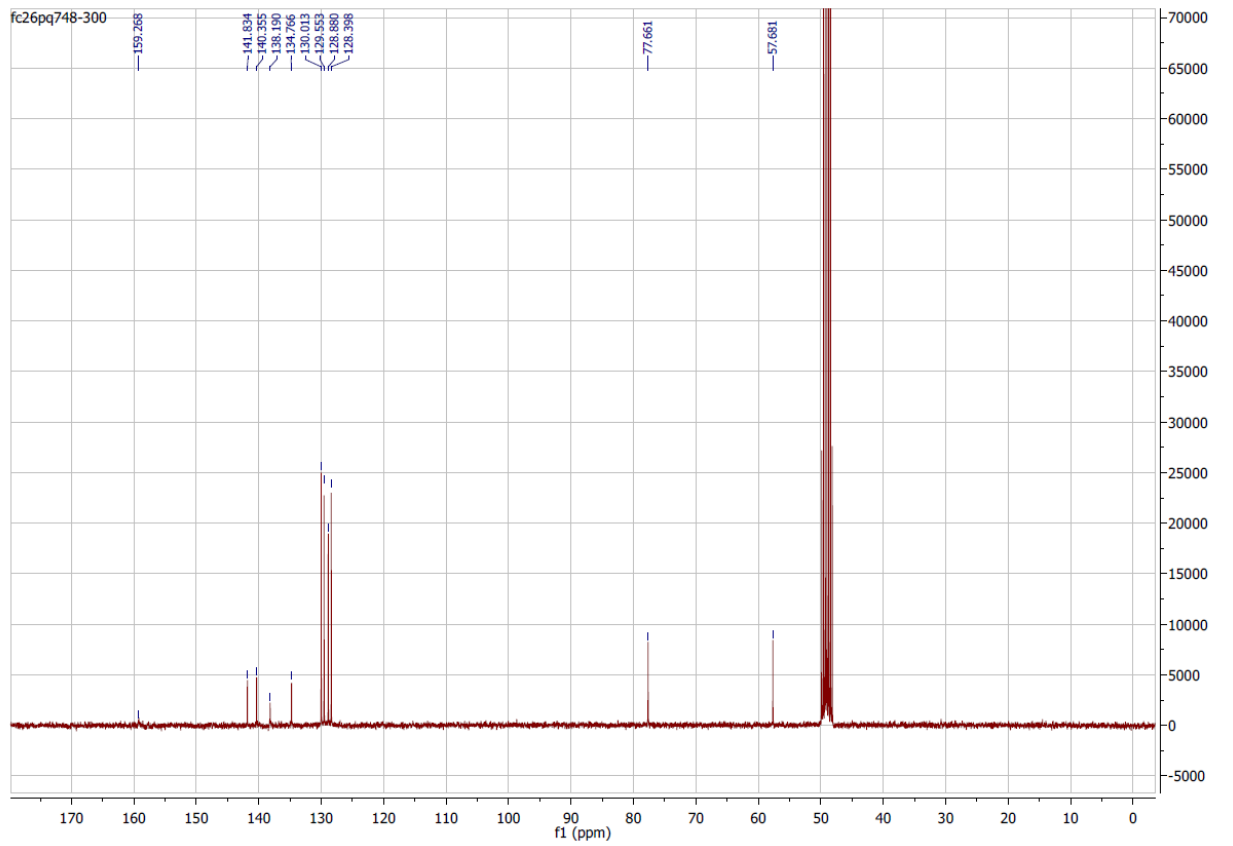
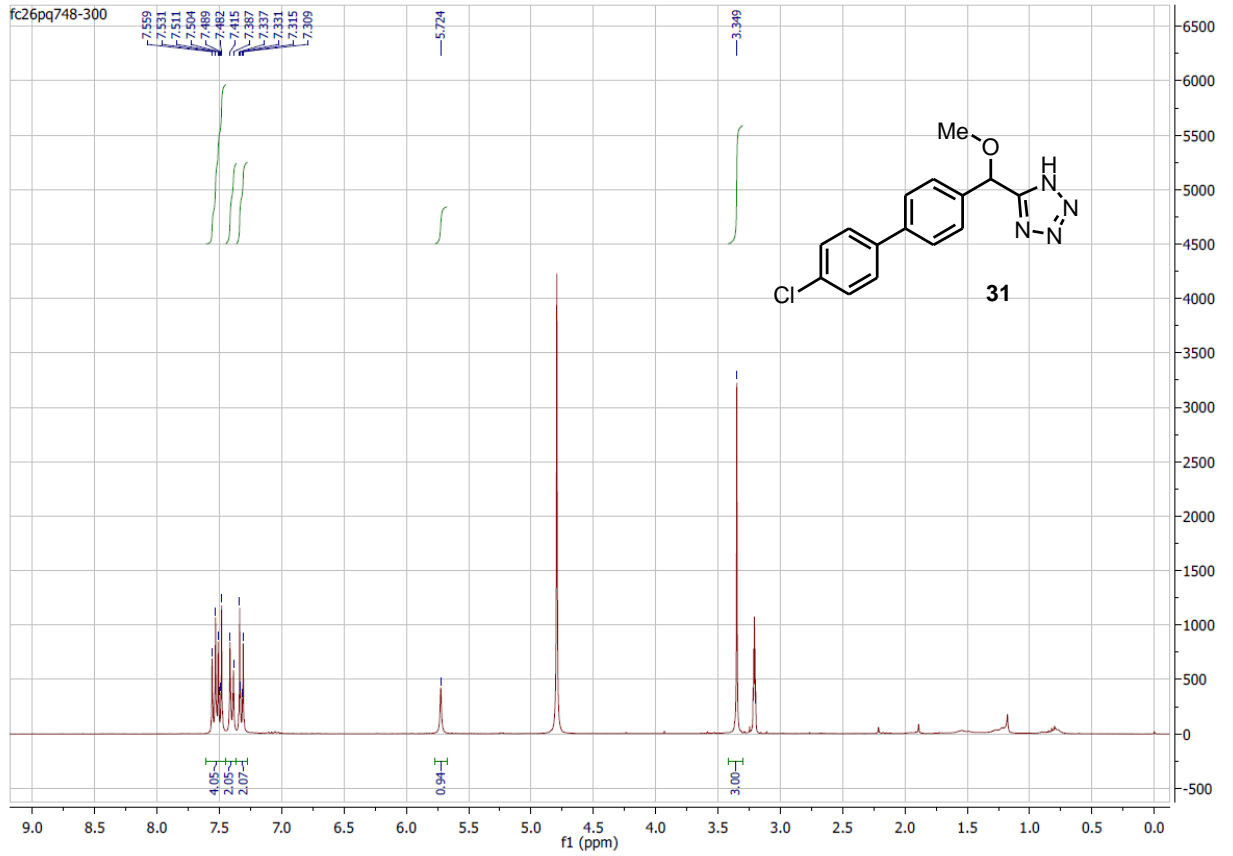


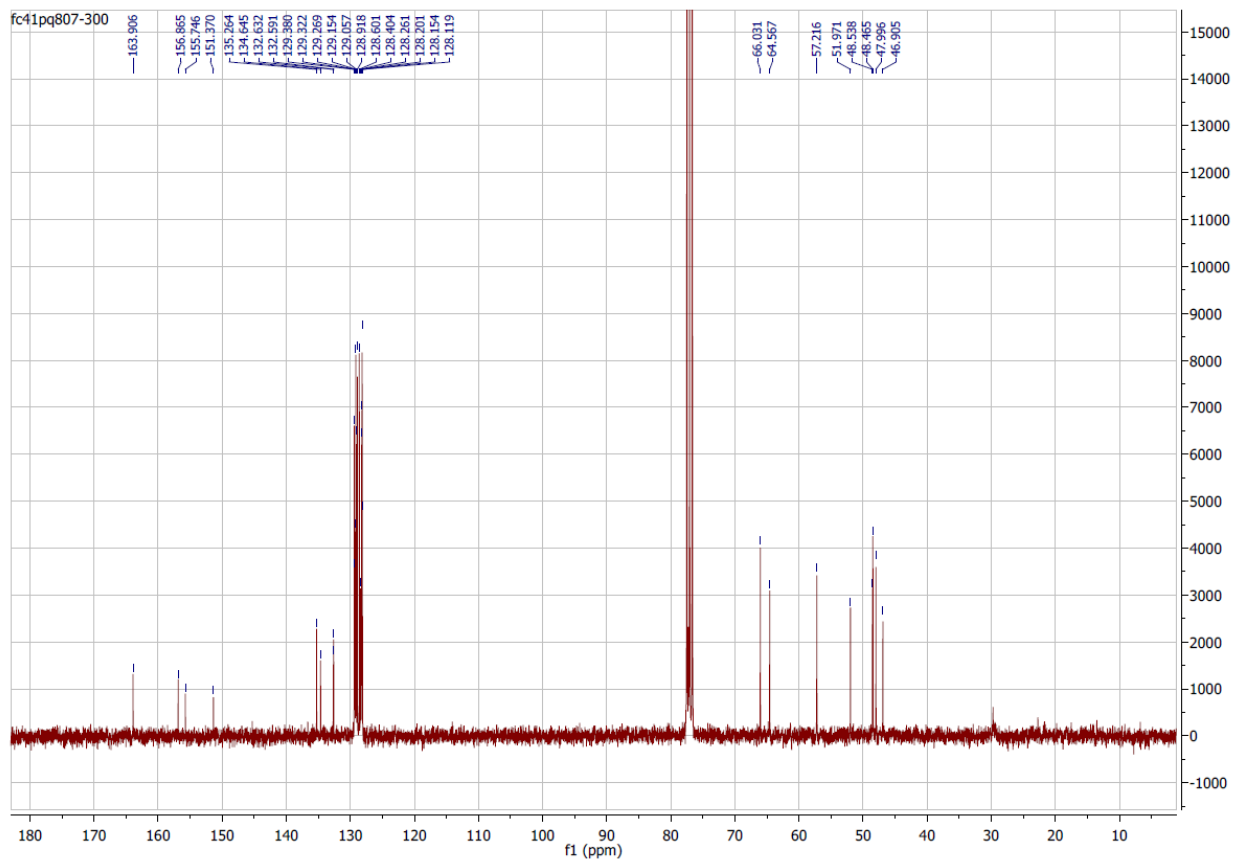
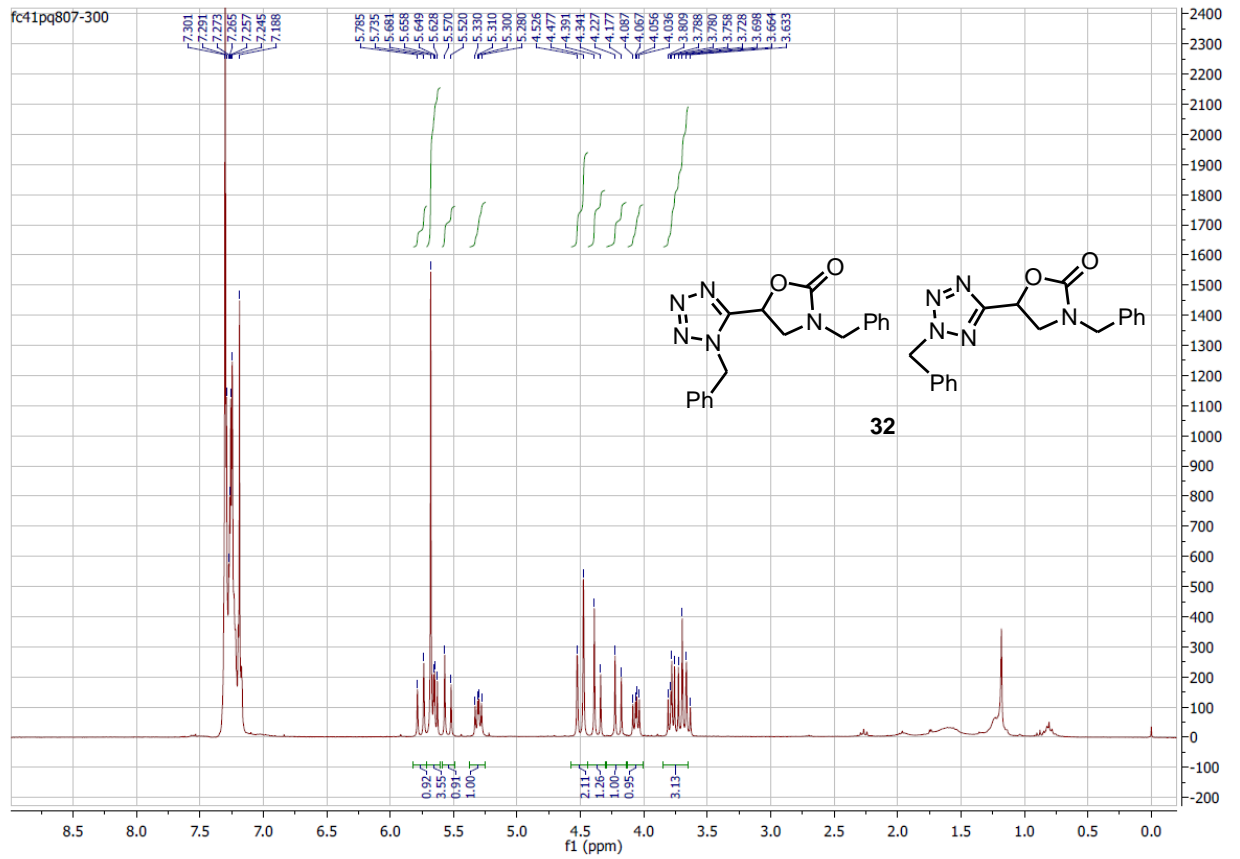












Computational methods

All computations were carried out with Gaussian 09 [S1] program package using DFT methods, employing PBE0 exchange correlation functional [S2, S3] and 6-311+G(d,p) basis set. The stationary points (minima and transition states) on the potential energy surface (PES) were verified by calculating the eigenvalues of the Hessian matrix. The solvent effect was included at the DFT level using the polarizable continuum model (PCM) [S4] within the integral equation formalism (IEFPCM) [S5].

S1. Gaussian 09, Revision A.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

S2. Ernzerhof, M.; Scuseria, G. E. *J.Chem. Phys.***1999**, *111*, 911–915.

S3. Adamo, C.; Scuseria, G. E.; Barone, V. *J. Chem. Phys.***1999**, *111*, 2889–2899.

S4. Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.*, **1997**, *107*, 3210–3221

S5. Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.*, **1997**, *107*, 3032–3041.

Table S1. Geometrical characteristics (optimized Cartesian coordinates X,Y,Z in Å) of stationary points shown in Figure 2. PCM/PBE0/6-31++G(d,p) calculations in dichloromethane. Total energies in a.u.

C ($E_{\text{tot.}}=-599.73101$)				Transition state ($E_{\text{tot.}}=-599.68338$)			
N	1.643357000	0.893421000	0.004689000	N	1.918416000	0.823549000	0.363787000
N	2.788273000	1.252292000	-0.567259000	N	2.724582000	1.445770000	-0.364569000
N	3.578138000	0.211505000	-0.630274000	N	3.692589000	0.509996000	-0.888888000
N	2.968917000	-0.858522000	-0.118525000	N	3.417644000	-0.636942000	-0.468175000
C	1.778945000	-0.407592000	0.265756000	C	2.299351000	-0.512745000	0.345491000
H	-0.076376000	1.089799000	0.214604000	H	-0.336525000	0.817311000	0.253972000
C	0.718397000	-1.215339000	0.913656000	C	1.662222000	-1.511685000	0.984089000
H	1.064484000	-2.233978000	1.073194000	H	2.008589000	-2.532885000	0.875609000
H	0.400744000	-0.782676000	1.865457000	H	0.809280000	-1.308321000	1.615472000
O	-0.464457000	-1.371156000	0.077834000	O	-0.907501000	-1.495640000	-0.093172000
H	-2.668332000	-1.888910000	-0.227094000	H	-3.230100000	-1.800530000	-0.329485000
N	-2.595695000	-0.882223000	-0.248123000	N	-3.066403000	-0.817907000	-0.175131000
C	-1.386188000	-0.425287000	0.051561000	C	-1.728581000	-0.569412000	-0.036037000
N	-1.084771000	0.828874000	0.302576000	N	-1.339264000	0.717828000	0.171659000
C	-3.673877000	-0.144470000	-0.889662000	C	-4.028001000	0.081550000	-0.795392000
H	-3.272773000	0.697300000	-1.452031000	H	-3.554587000	0.710339000	-1.554522000
H	-4.167621000	-0.815638000	-1.591801000	H	-4.790135000	-0.523055000	-1.287640000
H	-4.411154000	0.212411000	-0.168229000	H	-4.528814000	0.724593000	-0.067727000
C	-2.020415000	1.878093000	0.674801000	C	-2.133259000	1.756852000	0.804579000
H	-1.507442000	2.544516000	1.368482000	H	-1.453118000	2.434173000	1.322336000
H	-2.349195000	2.461545000	-0.187478000	H	-2.709453000	2.344257000	0.085063000
H	-2.885380000	1.455024000	1.183968000	H	-2.818464000	1.335811000	1.545136000
D+E							
N	1.790687000	-0.563214000	0.067987000				
N	2.651048000	-1.460160000	0.159301000				
N	3.972079000	-0.836072000	0.147087000				
N	3.831259000	0.398694000	0.048913000				
C	2.462586000	0.658183000	-0.007465000				
H	-0.365654000	-0.616099000	0.044624000				
C	1.873171000	1.859900000	-0.113693000				
H	2.483981000	2.754143000	-0.165796000				
H	0.782752000	1.919730000	-0.145695000				
O	-1.228192000	1.615253000	-0.131573000				
H	-3.580958000	1.655188000	-0.194264000				
N	-3.294278000	0.690516000	-0.137928000				
C	-1.931275000	0.594571000	-0.085131000				
N	-1.378360000	-0.642820000	0.013783000				
C	-4.228845000	-0.203457000	0.528441000				
H	-3.803645000	-0.613349000	1.449051000				
H	-5.116291000	0.371099000	0.795121000				
H	-4.545594000	-1.030472000	-0.111385000				
C	-1.964581000	-1.880184000	-0.470451000				
H	-1.151678000	-2.546470000	-0.762033000				
H	-2.561146000	-2.391630000	0.289573000				
H	-2.589621000	-1.706851000	-1.350815000				

Table S2. Geometrical characteristics (optimized Cartesian coordinates X,Y,Z in Å) of stationary points shown in Figure 3. PCM/PBE0/6-31++G(d,p) calculations in dichloromethane. Total energies in a.u.

D ($E_{\text{tot.}}=-296.05044$)				Transition state 1 ($E_{\text{tot.}}=-296.03011$)			
N	-0.162219000	-1.132700000	-0.000081000	N	0.469640000	-1.294508000	-0.000272000
N	-1.339898000	-0.739731000	0.000061000	N	1.539368000	-0.898113000	0.000328000
N	-1.339896000	0.739743000	0.000030000	N	1.150985000	1.295156000	0.000360000
N	-0.162212000	1.132692000	-0.000060000	N	0.000538000	1.133518000	-0.000371000
C	0.659210000	-0.000015000	0.000004000	C	-0.759339000	0.012113000	-0.000685000
C	1.997864000	0.000004000	0.000053000	C	-2.061104000	-0.189726000	0.000391000
H	2.543543000	0.935928000	0.000005000	H	-2.776295000	0.624478000	0.000832000
H	2.543596000	-0.935889000	0.000008000	H	-2.424769000	-1.211167000	0.000625000
F ($E_{\text{tot.}}=-186.63120$)				N₂ ($E_{\text{tot.}}=-109.43272$)			
N	-1.782114000	0.164797000	0.000004000	N	0.000000000	0.000000000	0.546773000
N	-0.674659000	-0.036033000	-0.000005000	N	0.000000000	0.000000000	-0.546773000
C	0.538815000	-0.555236000	0.000000000				
C	1.626646000	0.225124000	0.000000000				
H	1.595134000	1.314140000	-0.000002000				
H	2.609509000	-0.234819000	0.000009000				
Transition state 2 ($E_{\text{tot.}}=-186.60791$)				G ($E_{\text{tot.}}=-77.18302$)			
N	1.947605000	0.030016000	-0.002488000	C	-0.816648000	-0.000033000	0.000022000
N	0.855168000	0.145441000	0.003120000	C	0.474213000	-0.000006000	-0.000073000
C	-0.831895000	-0.692539000	0.000644000	H	1.027512000	-0.940157000	0.000154000
C	-1.717673000	0.280213000	-0.000829000	H	1.027098000	0.940393000	0.000154000
H	-1.584030000	1.353766000	0.000724000				
H	-2.737971000	-0.108008000	-0.004039000				