Electronic Supplementary Information

Highly Efficient Copper(I) Catalyst for 1,3-Dipolar Cycloaddition of Azides with Terminal and 1-Iodoalkynes in Water: Regioselective Synthesis of 1,4-Disubstituted and 1,4,5-Trisubstituted-1,2,3-Triazoles

Joaquín García-Álvarez,* Josefina Díez, and José Gimeno

Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain

Table of Contents

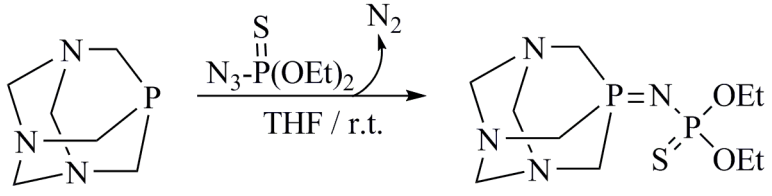
Experimental Section

General Methods. The conductivities were measured at room temperature, in ca. 10^{-3} mol dm^{-3} water solutions, with a Jenway PCM3 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (^{1}H), 282.4 MHz (^{19}F) or 75.4 MHz (^{13}C) using $SiMe_4$, C_6F_6 or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported in this paper. Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; bs, broad signal; m, multiplet.

Preparation and characterization of the hydrosoluble iminophosphorane ligand 2 and its Cu(I) complex 3.

Synthetic procedures were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds PTA[1a] and $N_3P(=S)(OEt)_2$,[2] which were prepared by following the method reported in the literature.

Synthesis of the *N*-thiophosphorylated iminophosphorane ligand 2.



1 **2**

Scheme ESI-1. Synthesis of the *N*-thiophosphorylated iminophosphorane ligand **2**

A solution of the commercially available phosphine ligand PTA (0.314 g, 2 mmol) in 40 mL of THF was treated, at room temperature, with the *N*-thiophosphorylated azide $N_3P=S(OEt)_2$ (2.1 mmol) for 4 h.[1b] Then, the solvent was evaporated to dryness to give a colorless oil which was dissolved in *ca*. 5 mL of CH_2Cl_2. The addition of diethyl ether (*ca.* 50 mL) precipitated a white microcrystalline solid, which was washed with diethyl ether (3 x 10 mL) and dried in vacuo. Yield 78% (0.506 g). Anal. Calcd for

$C_{10}H_{22}N_4O_2P_2S$: C, 37.03; H, 6.84; N, 17.28. Found: C, 37.19; H, 6.79; N, 17.33. IR (KBr, cm^{-1}): *v* 588, 751, 791, 837, 1025, 1097, 1165, 1206, 1238, 1275, 1368. $^{31}P\{^1H\}$ NMR (D_2O): δ -27.92 (d, $^2J_{PP}$ = 8.9 Hz, P=N), 62.38 (d, $^2J_{PP}$ = 8.9 Hz, P=S) ppm. ^1H NMR (D_2O): δ 1.39 (m, 6H, OCH_2CH_3), 4.10 (m, 4H, OCH_2CH_3), 4.37 (dd, 6H, $^2J_{HP}$ = 9.6 Hz, $^4J_{HP}$ = 2.9 Hz, PCH_2N), 4.43 and 4.54 (AB spin system, 3H each, $J_{HA,HB}$ = 13.7 Hz, NCH_2N) ppm. $^{13}C\{^1H\}$ NMR (D_2O): δ 15.37 (d, $^3J_{CP}$ = 8.2 Hz, OCH_2CH_3), 51.91 (dd, $^1J_{CP}$ = 53.0 Hz, $^3J_{CP}$ = 4.1 Hz, PCH_2N), 62.93 (d, $^2J_{CP}$ = 5.8 Hz, OCH_2CH_3), 70.20 (d, $^3J_{CP}$ = 9.3 Hz, NCH_2N).

Synthesis of Cu(I) complex 3. A solution of the iminophosphorane ligand **2** (2 mmol) in 30 mL of CH_2Cl_2 was treated with $[Cu(NCCH_3)_4][PF_6]$ (0.372 g, 1 mmol) and stirred at room temperature for 1 h to yield a pale-yellow clear solution. The solvent was then concentrated (*ca.* 1 mL) in vacuo and the addition of diethyl ether (*ca.* 50 mL) precipitated a white solid, which washed with diethyl ether (3 x 10 mL) and dried in vacuo. **3:** Yield 81% (0.695 g). Anal. Calcd for $CuC_{20}H_{44}F_6N_8P_5O_4S_2$: C, 28.02; H, 5.17; N, 13.07. Found: C, 28.10; H, 5.15; N 13.15. Conductivity (water, 20 °C): 117 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr, cm^{-1}): *v* 559, 943, 956, 973, 1010, 1029, 1207, 1238, 1277, 1288. $^{31}P\{^1H\}$ NMR ($(CD_3)_2C=O$): δ –144.04 (sept, J_{PF} = 707.2 Hz, PF_6), -34.73 (bs, P=N), 59.96 (bs, P=S) ppm. ^1H NMR ($(CD_3)_2C=O$): δ 1.23 (t, 6H, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 3.94 (m, 4H, OCH_2CH_3), 4.23 (d, 6H, $^2J_{HP}$ = 9.4 Hz, PCH_2N), 4.32 and 4.41 (AB spin system, 3H each, $J_{HA,HB}$ = 13.2 Hz, NCH_2N) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2C=O$): δ 15.99 (d, $^3J_{CP}$ = 8.5 Hz, OCH_2CH_3), 54.10 (dd, $^1J_{CP}$ = 51.7 Hz, $^3J_{CP}$ = 2.9 Hz, PCH_2N), 62.64 (d, $^2J_{CP}$ = 6.4 Hz, OCH_2CH_3), 72.10 (d, $^3J_{CP}$ = 9.5 Hz, NCH_2N) ppm.

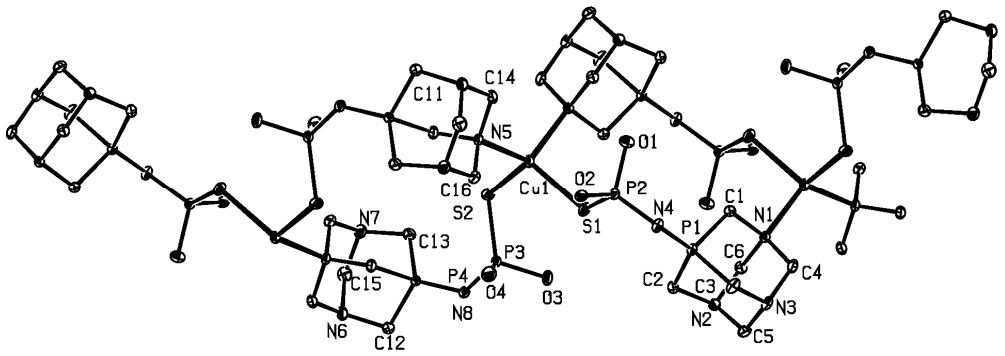
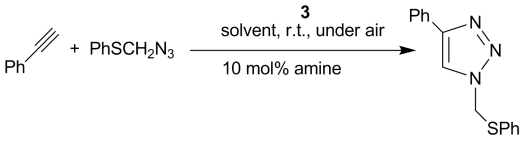


Figure ESI-1. ORTEP-type view of the structure of compound **3** showing the crystallographic labelling scheme. Hydrogen atoms, ethyl groups and PF_6^- anions have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å): Cu(1)-S(1) = 2.314(1); Cu(1)-S(2) = 2.320(1); Cu(1)-N(1) = 2.1576(3); Cu(1)-N(5) = 2.131(4). Selected bond angles (º): N(5)-Cu(1)-N(1) = 117.92(11); N(5)-Cu(1)-S(1) = 114.77(9); N(1)-Cu(1)-S(1) = 103.77(8); N(5)-Cu(1)-S(2) = 105.16(8); N(1)-Cu(1)-S(2) = 103.02(8); S(1)-Cu(1)-S(2) = 111.71(4).

General procedure for the synthesis of 1,2,3-triazoles

All reagents were obtained from commercial suppliers and used without further purification with the exception of compound *p*-NC(C_6H_4)C≡CH, which was prepared by following the method reported in the literature.[3] Typical procedure for the synthesis of 1,2,3-triazoles; synthesis of diphenyl(1-(phenylthiomethyl)-1*H*-1,2,3-triazol-4-yl)methanol (**4f**): 0.0042 g (0.5 mol%) of catalyst **3** were dissolved in 2 mL of H_2O under air. 1,1-diphenyl-2-propyn-1-ol (1mmol, 0.208 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) were added in the presence of 0.012 mL (10 mol%) of 2,6-lutidine. The course of the reaction was monitored by regular sampling and analysis by NMR and GC The reaction was stirred at room temperature for 4h, after which time a yellow powder had formed. The crude of the reaction was washed with CH_2Cl_2 (3x10mL) and the combined organic fractions were concentrated by evaporation to give **4f** as a white solid (0.354 g, 95%). Table S.I-1 summarizes the optimization studies of the CuAAC using **3** as catalyst.

Table ESI-1. Optimization studies of the CuAAC using **3** as catalyst[a]



entry	solvent	amine	mol % of **3**	Time[h]	Yield[%][b]
1	THF	2,6-lutidine	0.5	18	94
2	water	2,6-lutidine	0.5	6	95
3	water	-	0.5	-	0
4	water	NEt_3	0.5	9	97
5	water	pyridine	0.5	8	93
6	water	TMEDA	0.5	11	98
7	water	1,10-Phen	0.5	10	97
8	water	2,6-lutidine	0.25	24	93

[a] General Conditions: amine (10 mol%), PhCCH (1mmol), $PhSCH_2N_3$ (1mmol), 2 mL of solvent, under air, r.t. [b] isolated yields

The identity of the 1,2,3-triazoles **4a**,[4a] **4e**,[4b] **5a**,[4c] **5b**,[4d] **5c**,[4e] **5e**,[4e] **5g**,[4f] **6a**,[4g] **6e**,[4h] **6g**,[4g] was assessed by comparison of their ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data with those previously reported in the literature and by their fragmentation in GC/MS.

4-butyl-1-(phenylthiomethyl)-1H-1,2,3-triazole (4b) Synthesized from 1-hexyne (1mmol, 0.116 mL) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.232 g, 94%, brown oil; Anal. Calcd for $C_{13}H_{17}N_3S$: C, 63.12; H, 6.93; N, 16.99. Found: C, 63.20; H, 6.89; N 17.02. IR (cm^{-1}): ν 690, 741, 1025, 1223, 1439, 2925. ^1H NMR ($CDCl_3$): δ 0.94 (t, 3H, J = 7.4 Hz), 1.34 and 1.63 (m, 2H each), 2.71 (t, 2H, J = 7.4 Hz), 5.61 (s, 2H), 7.30 (s, 1H), 7.32 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.79, 22.18, 25.27, 31.41, 53.73, 120.19, 128.63, 129.44, 132.03, 132.25, 135.65, 148.99 ppm.

4-cyclohexenyl-1-(phenylthiomethyl)-1*H*-1,2,3-triazole (4c) Synthesized from 1-ethynylcyclohexene (1mmol, 0.117 mL) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.252 g, 93%, white solid; Anal. Calcd for $C_{15}H_{17}N_3S$: C, 66.39; H, 6.31; N, 15.48. Found: C, 66.47; H, 6.34; N 15.43. IR (cm^{-1}): ν 892, 1024, 1226, 1439, 1482, 1582, 1661, 1718, 2928. ^1H NMR ($CDCl_3$): δ 1.66 (m, 4H), 2.14 (m, 2H), 2.28 (m, 2H), 5.54 (s, 2H), 6.45 (m, 1H), 7.26 (m, 5H), 7.37 (1H, m) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.07, 22.32, 25.17, 26.18, 53.54, 117.81, 125.20, 126.94, 128.43, 129.33, 131.98, 132.08, 149.80 ppm.

diphenyl(1-(phenylthiomethyl)-1*H*-1,2,3-triazol-4-yl)methanol (4d) Synthesized from 1,1-diphenyl-2-propyn-1-ol (1mmol, 0.208 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.354 g, 95%, white solid; Anal. Calcd for $C_{22}H_{19}N_3OS$: C, 70.75; H, 5.13; N, 11.25. Found: C, 70.68; H, 5.17; N 11.21. IR (cm^{-1}): *v* 694, 750, 794, 890, 1016, 1048, 1125, 1172, 1231, 1363, 1447, 3023, 3399. ^1H NMR (CD_2Cl_2): δ 4.02 (s, 1H), 5.59 (s, 2H), 7.09 (s, 1H), 7.35 (m, 15H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 54.08, 76.51, 122.44, 127.09, 127.48, 127.98, 128.94, 129.45, 131.55, 133.09, 145.78, 154.22 ppm.

4-(1-(phenylthiomethyl)-1H-1,2,3-triazol-4-yl)benzonitrile (4f) Synthesized from 4-ethynylbenzonitrile (1mmol, 0.127 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.283 g, 97%, white solid; Anal. Calcd for $C_{16}H_{12}N_4S$: C, 65.73; H, 4.14; N, 19.16. Found: C, 65.68; H, 4.13; N 19.22. IR (cm^{-1}): *v* 492, 554, 689, 754, 834, 1045, 1071, 1277, 1449, 1612, 2228, 3094. ^1H NMR ($CDCl_3$): δ 5.69 (s, 2H), 7.33 (m, 5H), 7.66 (m, 2H), 7.90 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 54.11, 111.52, 118.76, 120.48, 126.11, 128.88, 129.61, 132.23, 132.73, 134.74 ppm.

ethyl 1-(phenylthiomethyl)-1H-1,2,3-triazole-4-carboxylate (4g) Synthesized from ethyl propiolate (1mmol, 0.102 mL) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.260 g, 99%, yellow oil; Anal. Calcd for $C_{12}H_{13}N_3O_2S$: C, 54.74; H, 4.98; N, 15.96. Found: C, 54.67; H, 4.95; N 15.91. IR (cm^{-1}): *v* 492, 692, 757, 1024, 1046, 1212, 1382, 1472, 1728, 2981, 3123. ^1H NMR (CD_2Cl_2): δ 1.38 (t, 3H, *J* = 7.1 Hz), 4.39 (q, 2H, *J* = 7.1 Hz), 5.66 (s, 2H), 7.28 (bs, 5H), 8.12 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 14.28, 54.24, 61.37, 127.03, 129.00, 129.66, 132.33, 140.61, 160.51 ppm.

(1-benzyl-1H-1,2,3-triazol-4-yl)diphenylmethanol (5d) Synthesized from 1,1-diphenyl-2-propyn-1-ol (1mmol, 0.208 g) and benzylazide (1 mmol, 0.125 mL) using general procedure, 0.321 g, 94%, white solid; Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.49; H, 5.56; N 12.40. IR (cm^{-1}): *v* 694, 758, 1016, 1231, 1446, 3398. ^1H NMR (CD_2Cl_2): δ 3.97 (s, 1H), 5.49 (s, 2H), 7.13 (s, 1H), 7.32 (m, 15H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 54.12, 76.78, 122.47, 127.23, 127.51, 127.89, 128.05, 128.73, 129.13, 134.64, 145.72, 154.46 ppm.

4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzonitrile (5f) Synthesized from 4-ethynylbenzonitrile (1mmol, 0.127 g) and benzylazide (1 mmol, 0.125 mL) using general procedure, 0.252 g, 97%, white solid; Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.74; H, 4.70; N 21.60. IR (cm^{-1}): *v* 556, 719, 832, 871, 971,

1048, 1176, 1238, 1461, 1609, 2223, 3018. ^{1}H NMR ($CDCl_3$): δ 5.59 (s, 2H), 7.36 (m, 5H), 7.64 (m, 2H), 7.85 (s, 1H), 7.90 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 54.39, 111.37, 118.79, 120.93, 126.05, 128.07, 128.16, 128.98, 129.26, 132.66, 134.34, 134.98, 146.30 ppm.

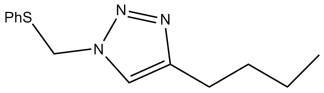
1-adamantyl-4-butyl-1H-1,2,3-triazole (6b) Synthesized from 1-hexyne (1mmol, 0.116 mL) and 1-azidoadamantane (1 mmol, 0.177 g) using general procedure, 0.243 g, 94%, white solid; Anal. Calcd for $C_{16}H_{25}N_3$: C, 74.09; H, 9.71; N, 16.20. Found: C, 74.17; H, 9.65; N 16.25. IR (cm^{-1}): ν 677, 814, 843, 1057, 1102, 1248, 1453, 2852, 2912. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, J = 6.9 Hz), 1.36 and 1.62 (m, 2H each), 1.76 (bs, 6H), 2.20 (bs, 9H), 2.68 (t, 2H, J = 6.9 Hz), 7.31 (s, 1H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 13.79, 22.18, 25.27, 31.41, 53.73, 120.19, 128.63, 129.44, 132.03, 132.25, 135.65, 148.99 ppm.

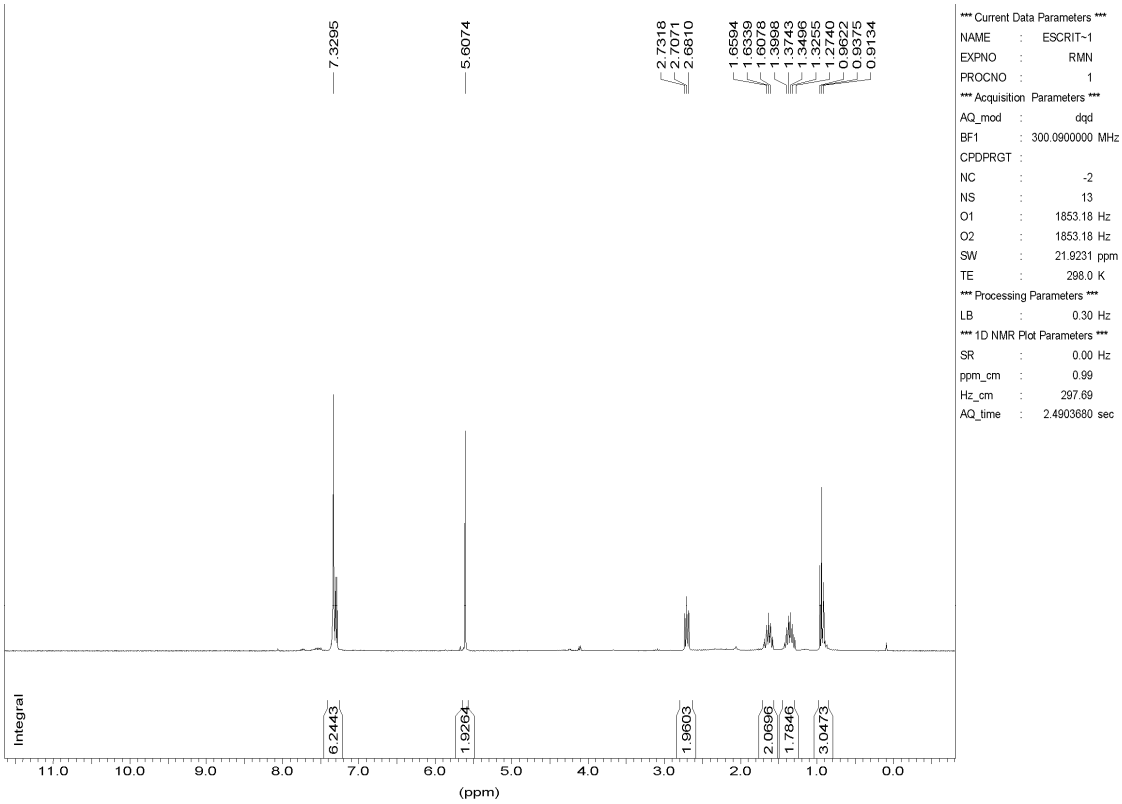
1-adamantyl-4-cyclohexenyl-1H-1,2,3-triazole (6c) Synthesized from 1-ethynylcyclohexene (1mmol, 0.117 mL) and 1-azidoadamantane (1 mmol, 0.177 g) using general procedure, 0.269 g, 95%, white solid; Anal. Calcd for $C_{18}H_{25}N_3$: C, 76.28; H, 8.89; N, 14.83. Found: C, 76.37; H, 8.81; N 14.85. IR (cm^{-1}): ν 668, 796, 1017, 1053, 1217, 1456, 1653, 2851, 2916. ^{1}H NMR ($CDCl_3$): δ 1.71 (m, 10H), 2.20 (m, 11H), 2.41 (m, 2H), 6.50 (m, 1H), 7.46 (s, 1H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 22.29, 22.54, 25.27, 26.41, 35.95, 42.97, 59.16, 114.67, 124.28, 127.66, 148.42 ppm.

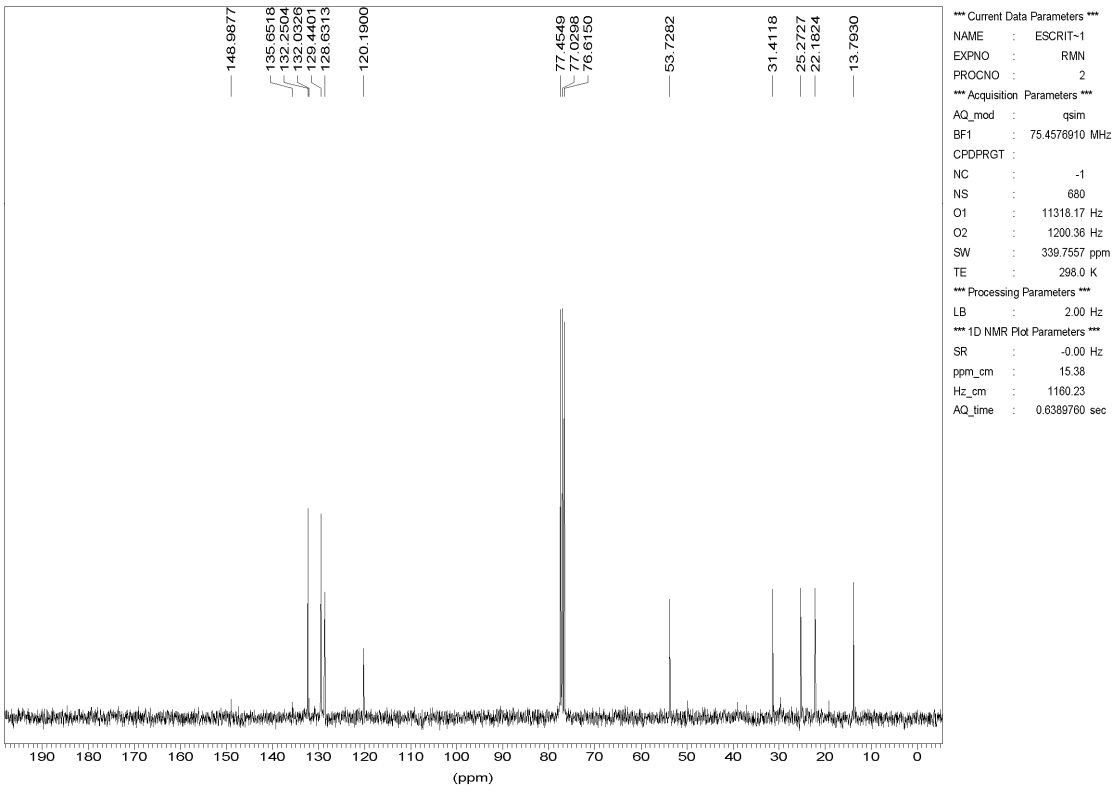
(1-Adamantyl-1H-1,2,3-triazol-4-yl)diphenylmethanol (6d) Synthesized from 1,1-diphenyl-2-propyn-1-ol (1mmol, 0.208 g) and 1-azidoadamantane (1 mmol, 0.177 g) using general procedure, 0.385 g, 99%, white solid; Anal. Calcd for $C_{25}H_{27}N_3O$: C, 77.89; H, 7.06; N, 10.90. Found: C, 77.98; H, 7.11; N 10.97. IR (cm^{-1}): ν 636, 682, 700, 764, 802, 899, 1036, 1061, 1141, 1180, 1360, 1446, 1489, 2849, 2912, 3247. ^{1}H NMR ($CDCl_3$): δ 1.78 (bs, 6H), 2.23 (bs, 9H), 4.24 (s, 1H), 7.21 (s, 1H), 7.33 (m, 10H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 29.44, 35.88, 42.95, 59.71, 67.95, 118.83, 127.29, 127.36, 127.98, 146.09, 152.90 ppm.

4-(1-Adamantyl-1H-1,2,3-triazol-4-yl)benzonitrile (6f) Synthesized from 4-ethynylbenzonitrile (1mmol, 0.127 g) and 1-azidoadamantane (1 mmol, 0.177 g) using general procedure, 0.286 g, 94%, white solid; Anal. Calcd for $C_{19}H_{20}N_4$: C, 74.97; H, 6.62; N, 18.41. Found: C, 74.87; H, 6.67; N 18.47. IR (cm^{-1}): ν 558, 841, 851, 1015, 1093, 1237, 1307, 1434, 1611, 2223, 2851, 2907. ^{1}H NMR ($CDCl_3$): δ 1.81 (bs, 6H), 2.28 (bs, 9H), 7.67 (m, 2H), 7.96 (m, 3H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 29.43, 35.81, 42.98, 60.09, 111.01, 117.52, 125.94, 132.63, 135.58, 144.90 ppm.

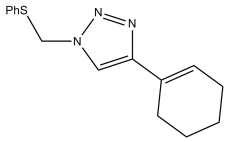
4-butyl-1-(phenylthiomethyl)-1H-1,2,3-triazole (4b)

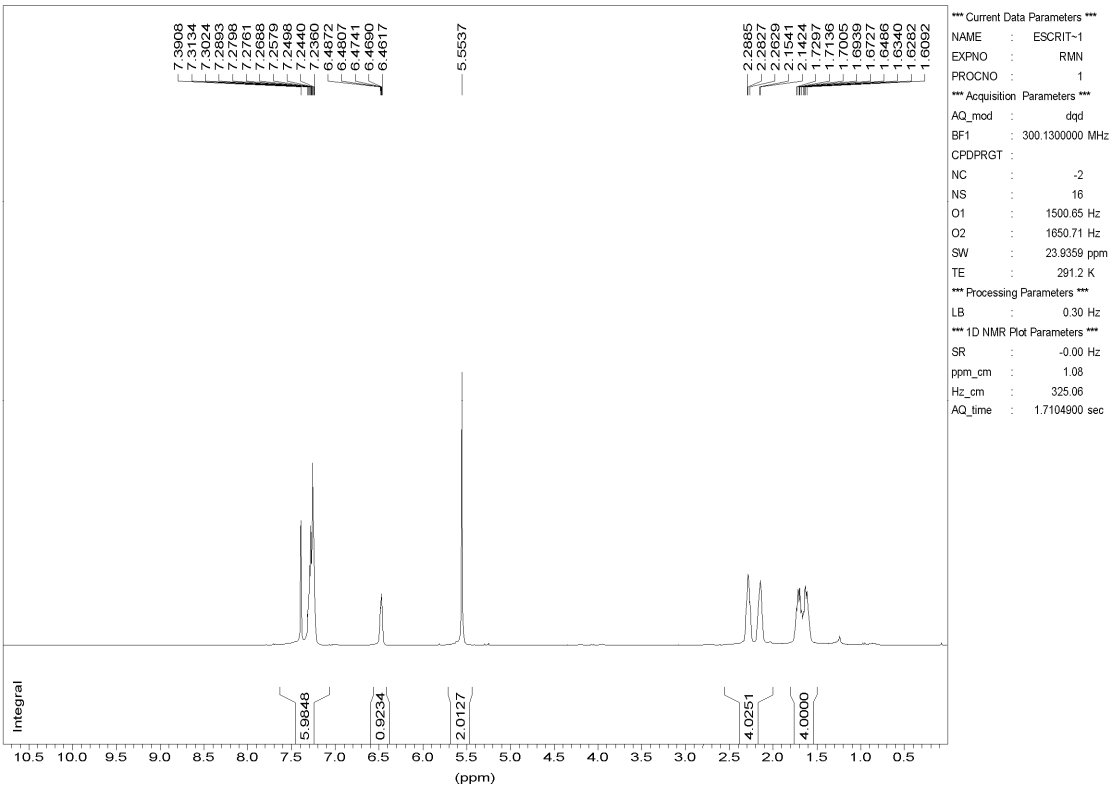




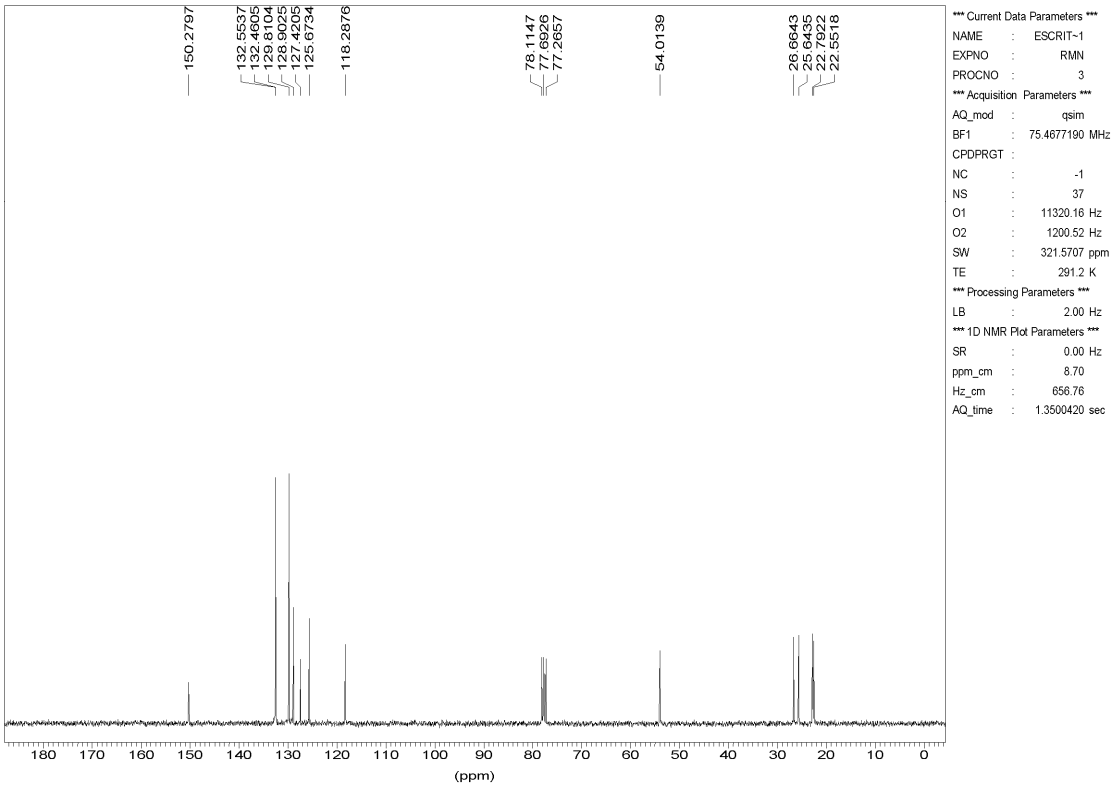


4-cyclohexenyl-1-(phenylthiomethyl)-1*H*-1,2,3-triazole (4c)



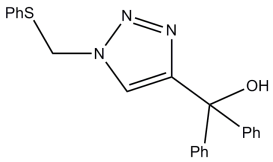


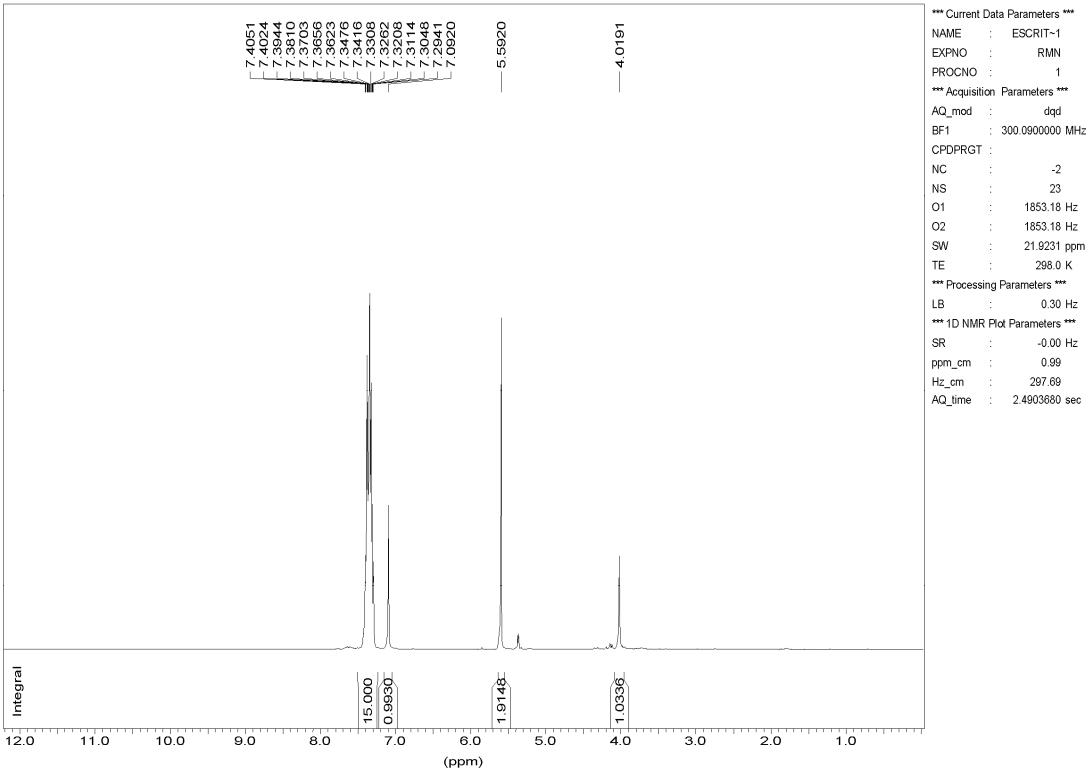

```
*** Current Data Parameters ***
NAME      :  ESCRIT~1
EXPNO     :  RMN
PROCNO    :  1
*** Acquisition Parameters ***
AQ_mod    :  dqd
BF1       :  300.1300000 MHz
CPDPRGT   :
NC        :  -2
NS        :  16
O1        :  1500.65 Hz
O2        :  1650.71 Hz
SW        :  23.9359 ppm
TE        :  291.2 K
*** Processing Parameters ***
LB        :  0.30 Hz
*** 1D NMR Plot Parameters ***
SR        :  -0.00 Hz
ppm_cm    :  1.08
Hz_cm     :  325.06
AQ_time   :  1.7104900 sec
```

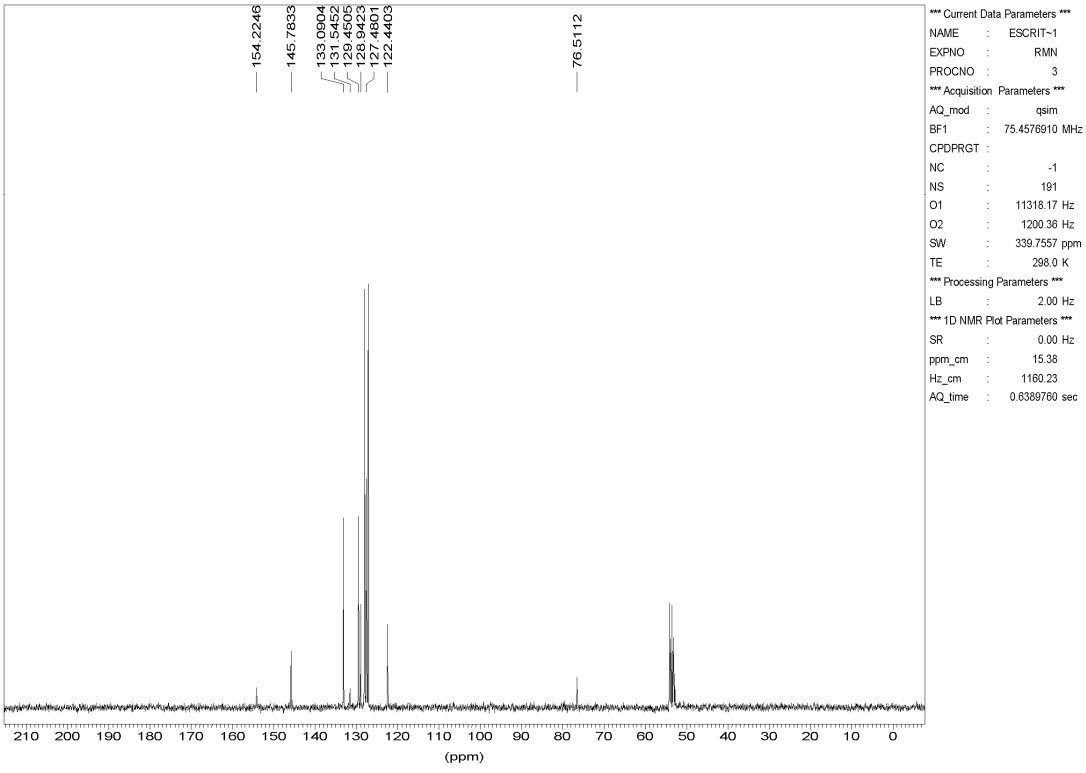



```
*** Current Data Parameters ***
NAME      :  ESCRIT~1
EXPNO     :  RMN
PROCNO    :  3
*** Acquisition Parameters ***
AQ_mod    :  qsim
BF1       :  75.4677190 MHz
CPDPRGT   :
NC        :  -1
NS        :  37
O1        :  11320.16 Hz
O2        :  1200.52 Hz
SW        :  321.5707 ppm
TE        :  291.2 K
*** Processing Parameters ***
LB        :  2.00 Hz
*** 1D NMR Plot Parameters ***
SR        :  0.00 Hz
ppm_cm    :  8.70
Hz_cm     :  656.76
AQ_time   :  1.3500420 sec
```

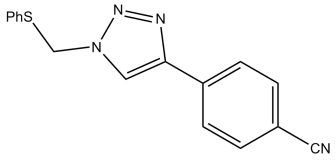
diphenyl(1-(phenylthiomethyl)-1*H*-1,2,3-triazol-4-yl)methanol (4d)

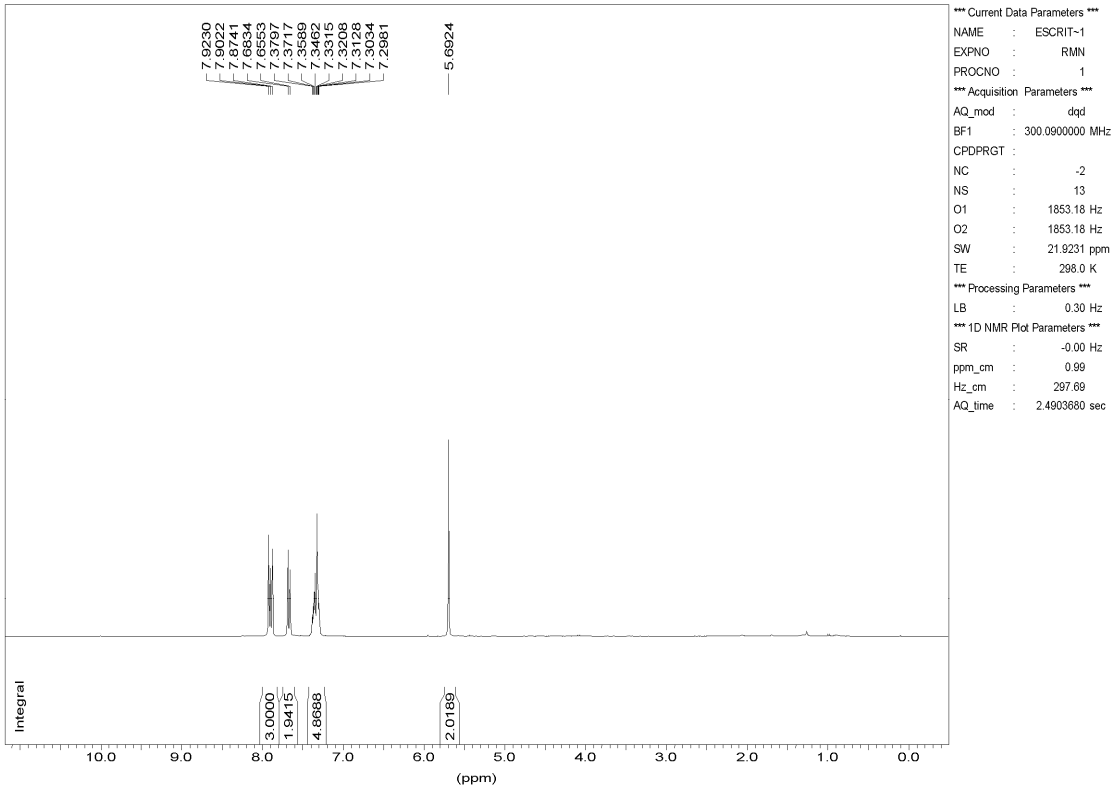




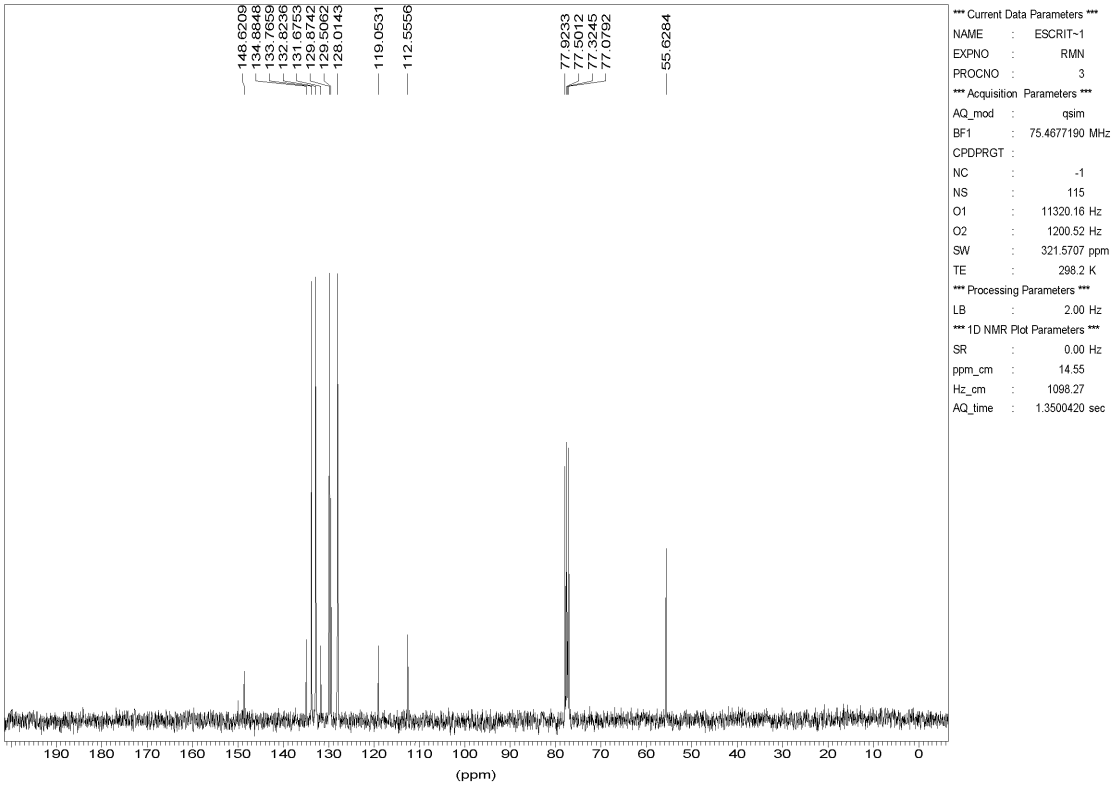


4-(1-(phenylthiomethyl)-1H-1,2,3-triazol-4-yl)benzonitrile (4f)



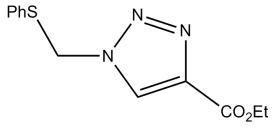


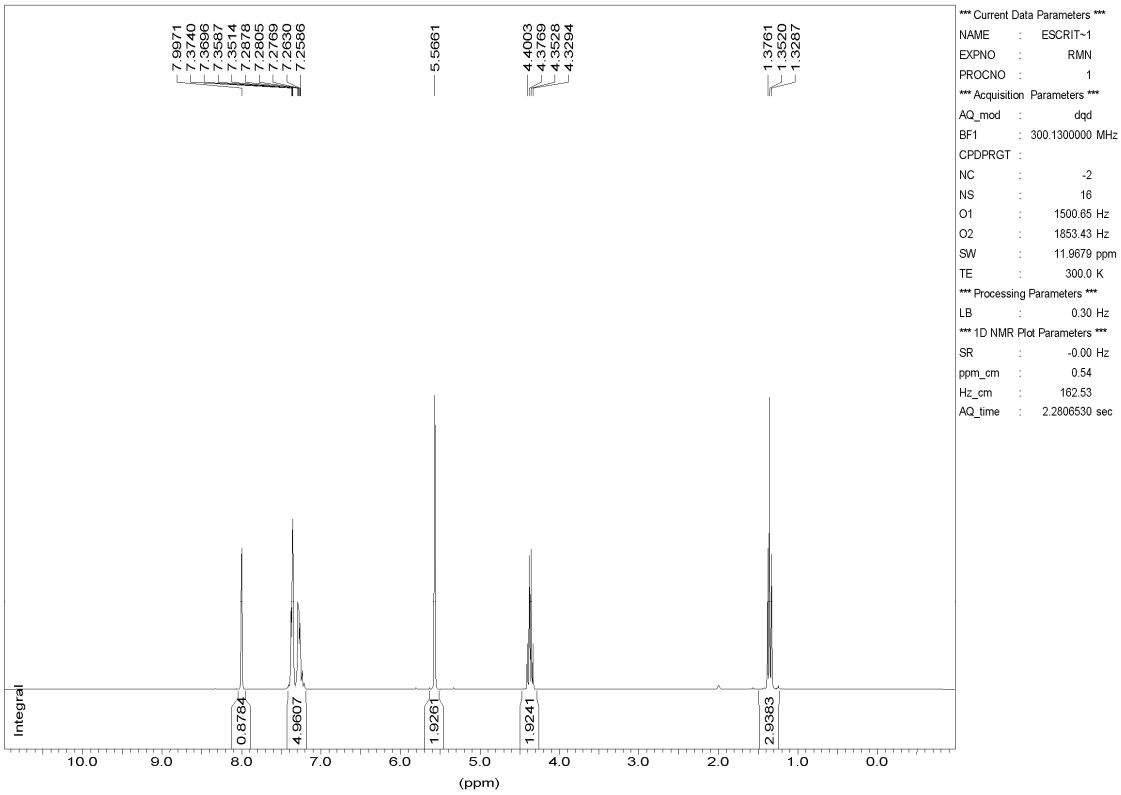
*** Current Data Parameters ***
NAME : ESCRIT~1
EXPNO : RMN
PROCNO : 1
*** Acquisition Parameters ***
AQ_mod : dqd
BF1 : 300.0900000 MHz
CPDPRGT :
NC : -2
NS : 13
O1 : 1853.18 Hz
O2 : 1853.18 Hz
SW : 21.9231 ppm
TE : 298.0 K
*** Processing Parameters ***
LB : 0.30 Hz
*** 1D NMR Plot Parameters ***
SR : -0.00 Hz
ppm_cm : 0.99
Hz_cm : 297.69
AQ_time : 2.4903680 sec

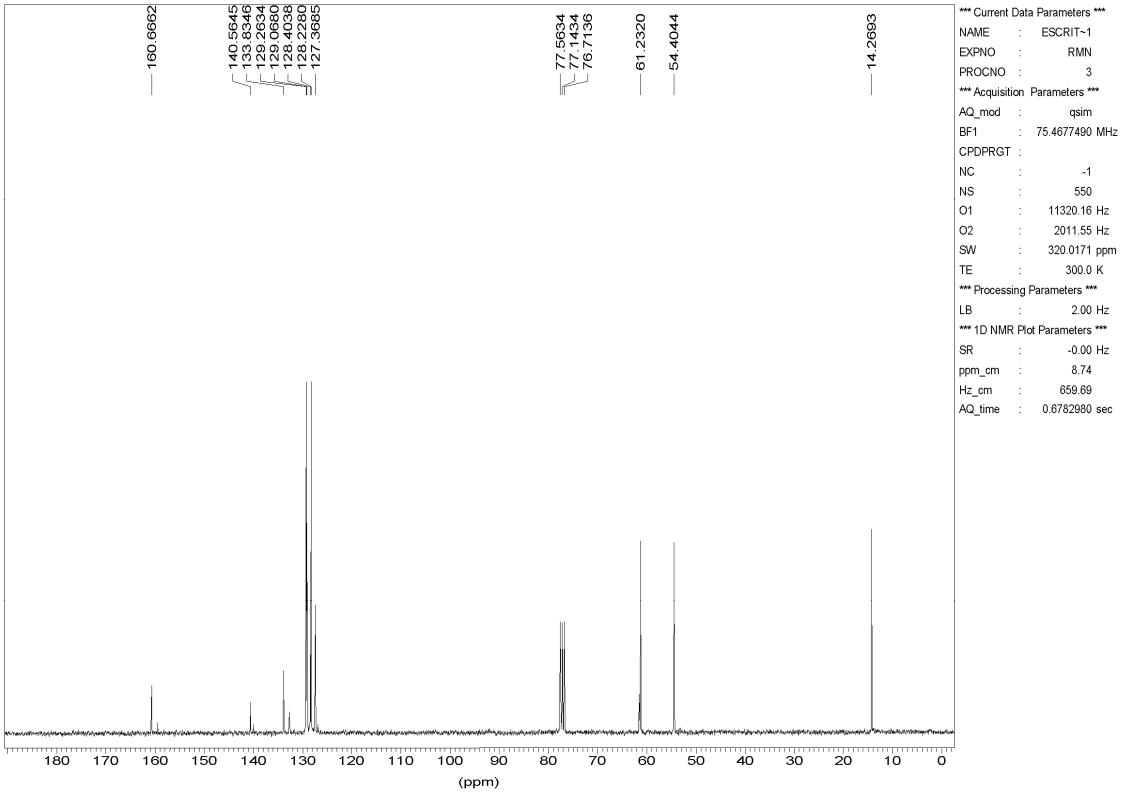


*** Current Data Parameters ***
NAME : ESCRIT~1
EXPNO : RMN
PROCNO : 3
*** Acquisition Parameters ***
AQ_mod : qsim
BF1 : 75.4677190 MHz
CPDPRGT :
NC : -1
NS : 115
O1 : 11320.16 Hz
O2 : 1200.52 Hz
SW : 321.5707 ppm
TE : 298.2 K
*** Processing Parameters ***
LB : 2.00 Hz
*** 1D NMR Plot Parameters ***
SR : 0.00 Hz
ppm_cm : 14.55
Hz_cm : 1098.27
AQ_time : 1.3500420 sec

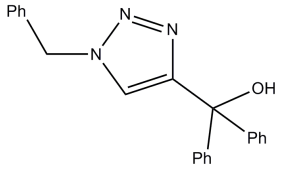
ethyl 1-(phenylthiomethyl)-1H-1,2,3-triazole-4-carboxylate (4g)

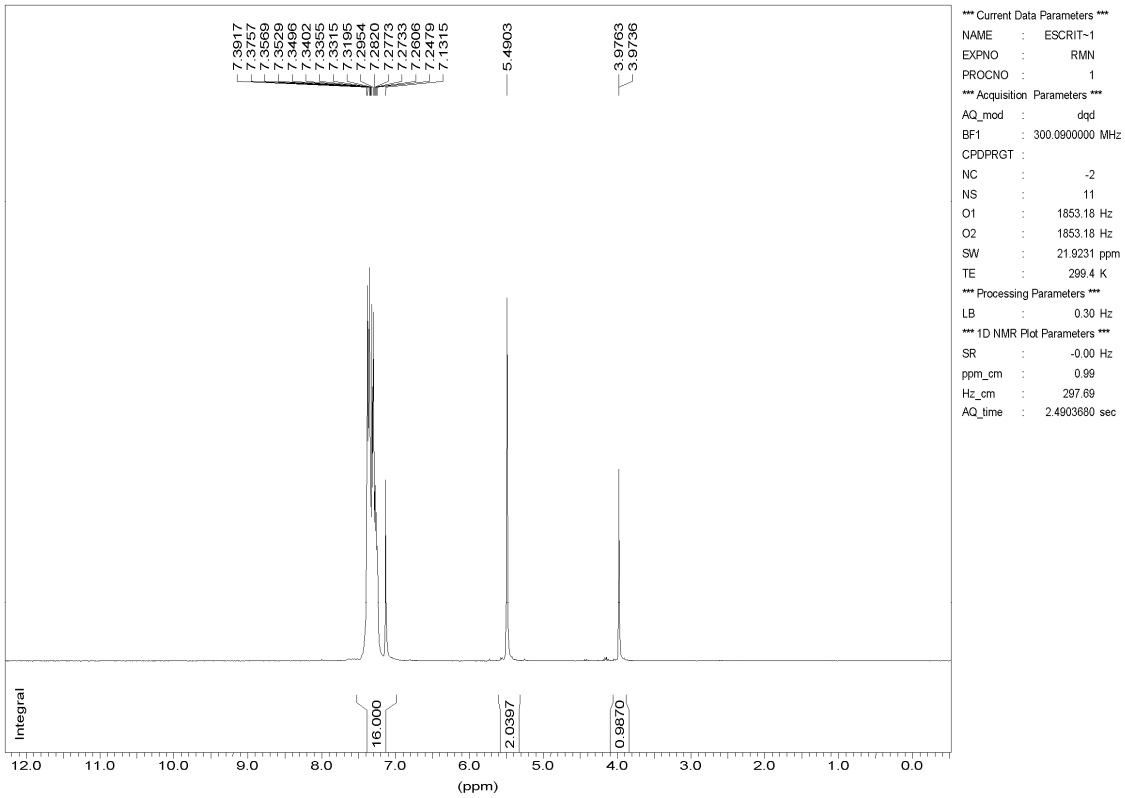


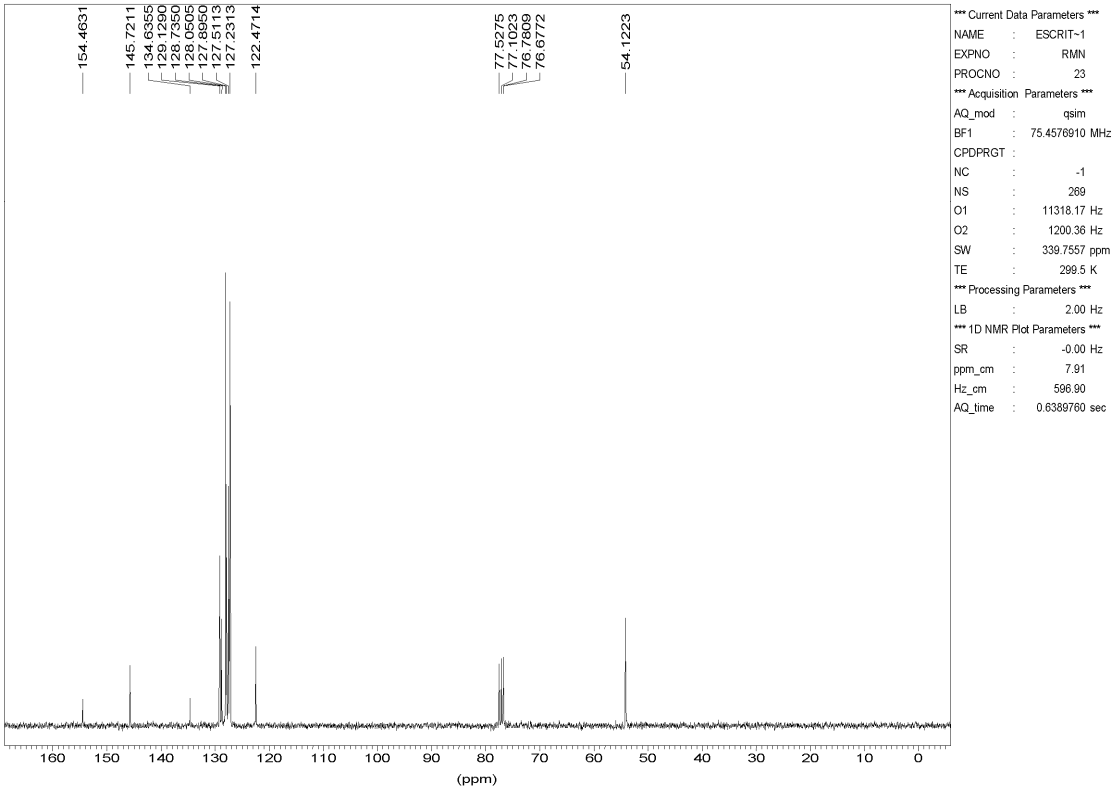




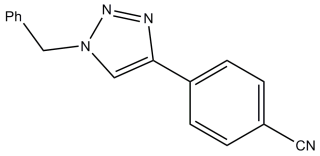
(1-benzyl-1H-1,2,3-triazol-4-yl)diphenylmethanol (5d)

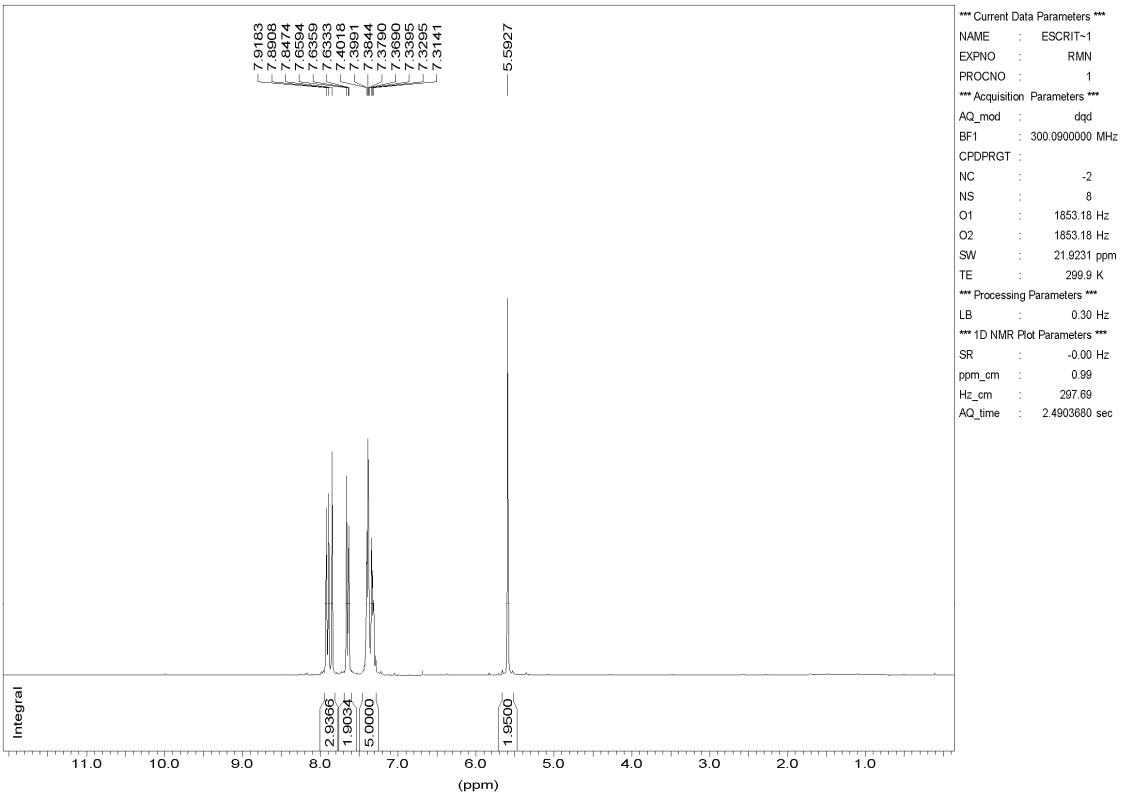


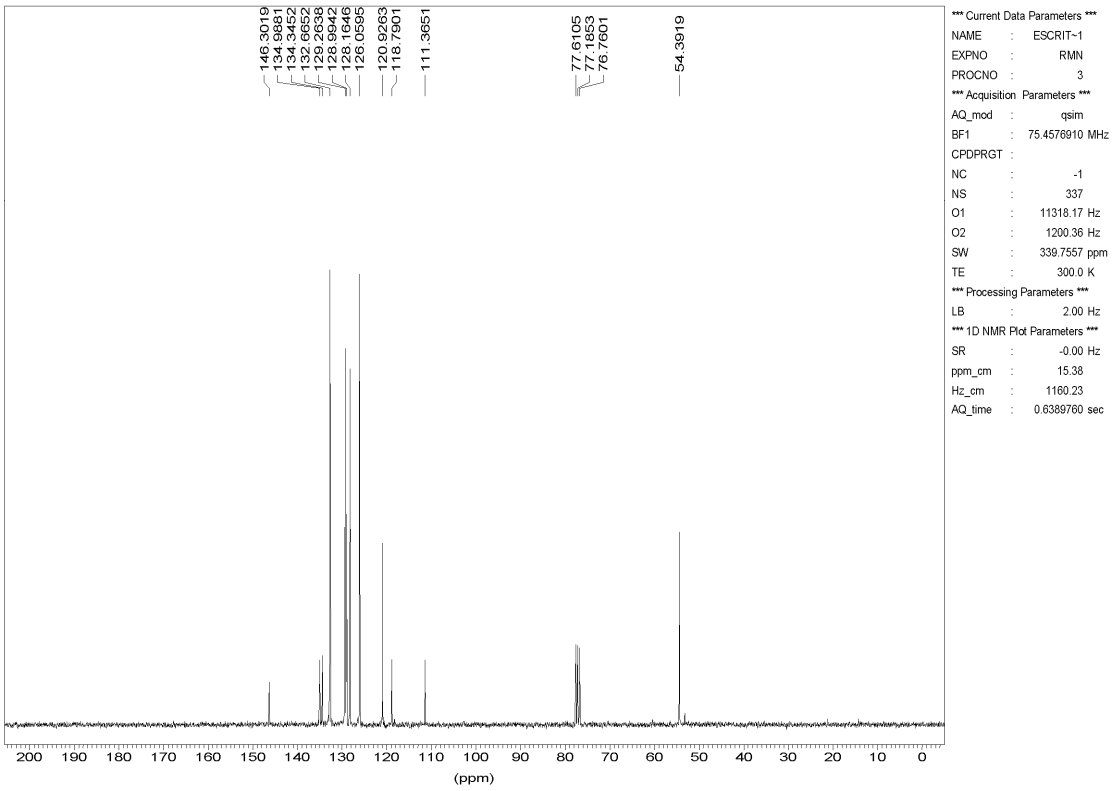




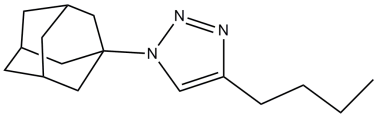
4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzonitrile (5f)

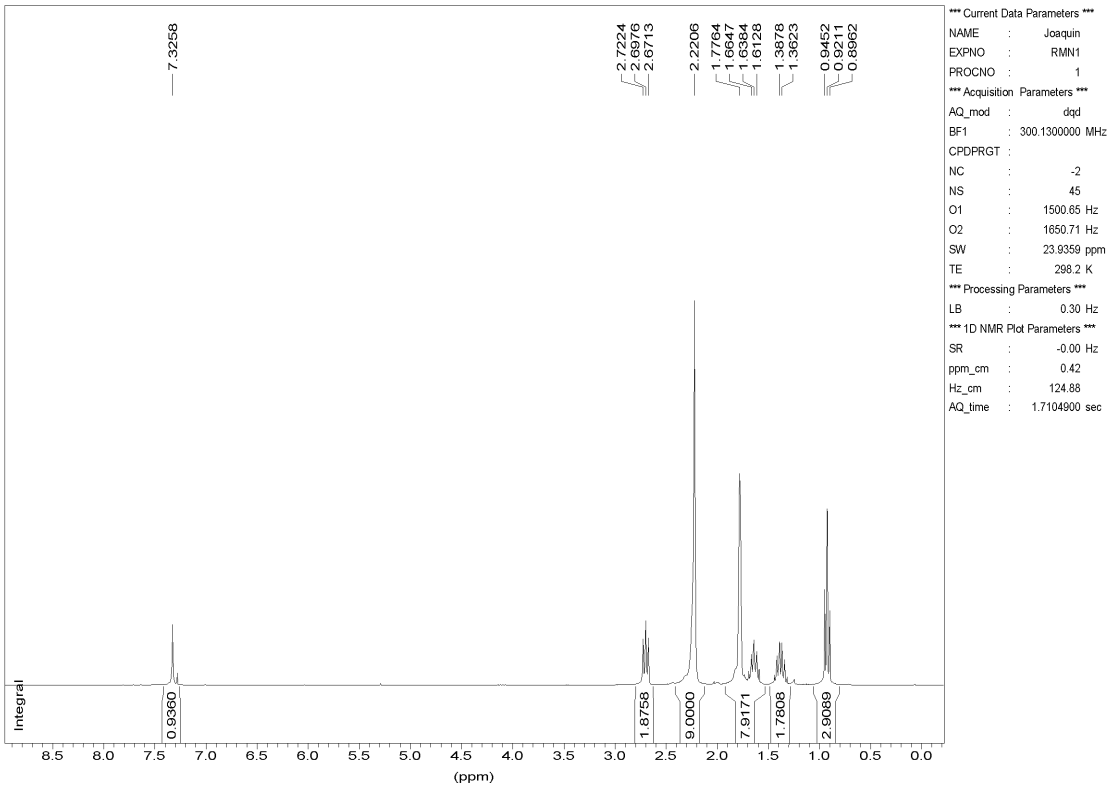


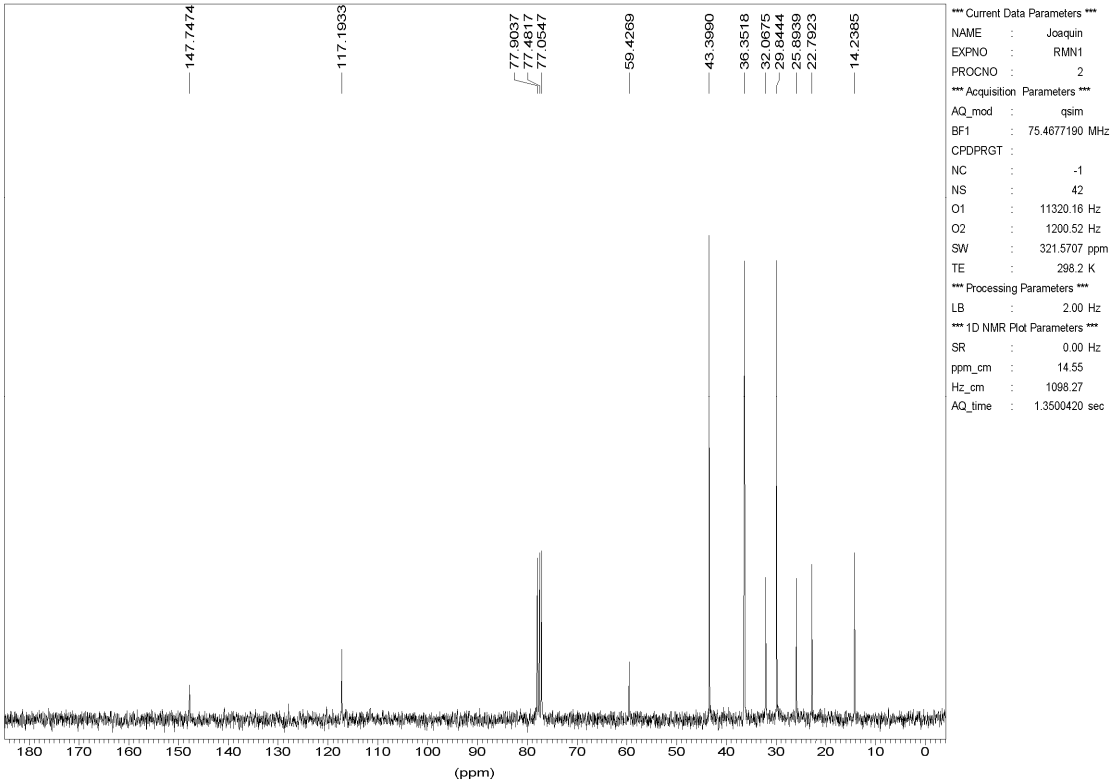




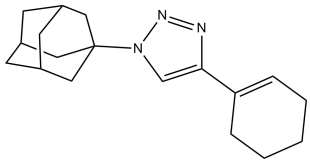
1-adamantyl-4-butyl-1H-1,2,3-triazole (6b)

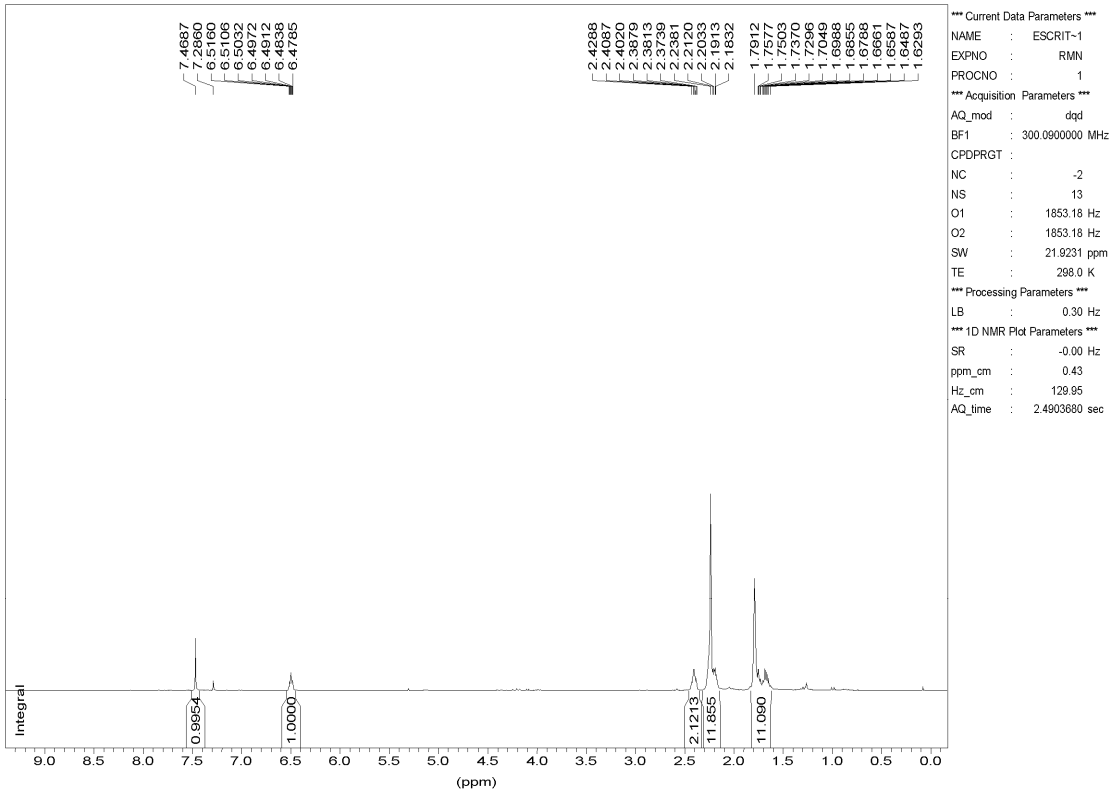


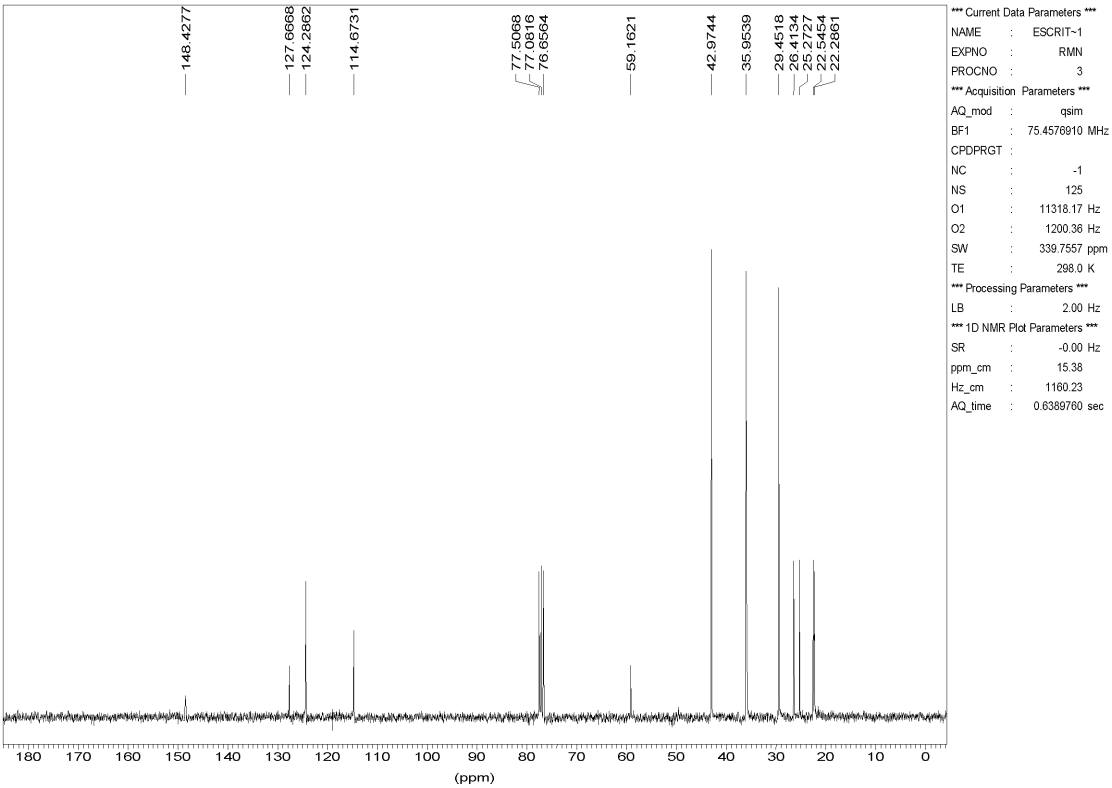




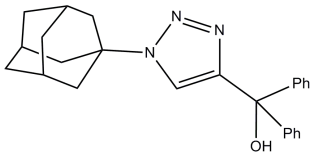
1-adamantyl-4-cyclohexenyl-1H-1,2,3-triazole (6c)

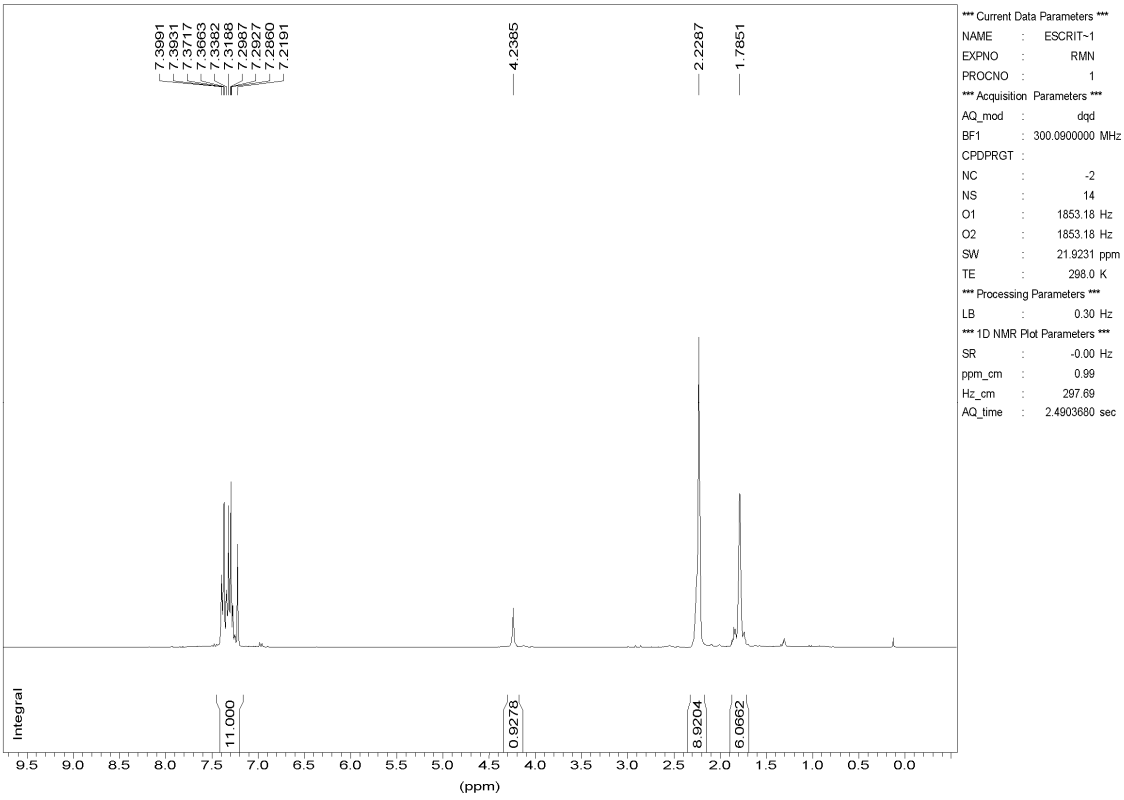


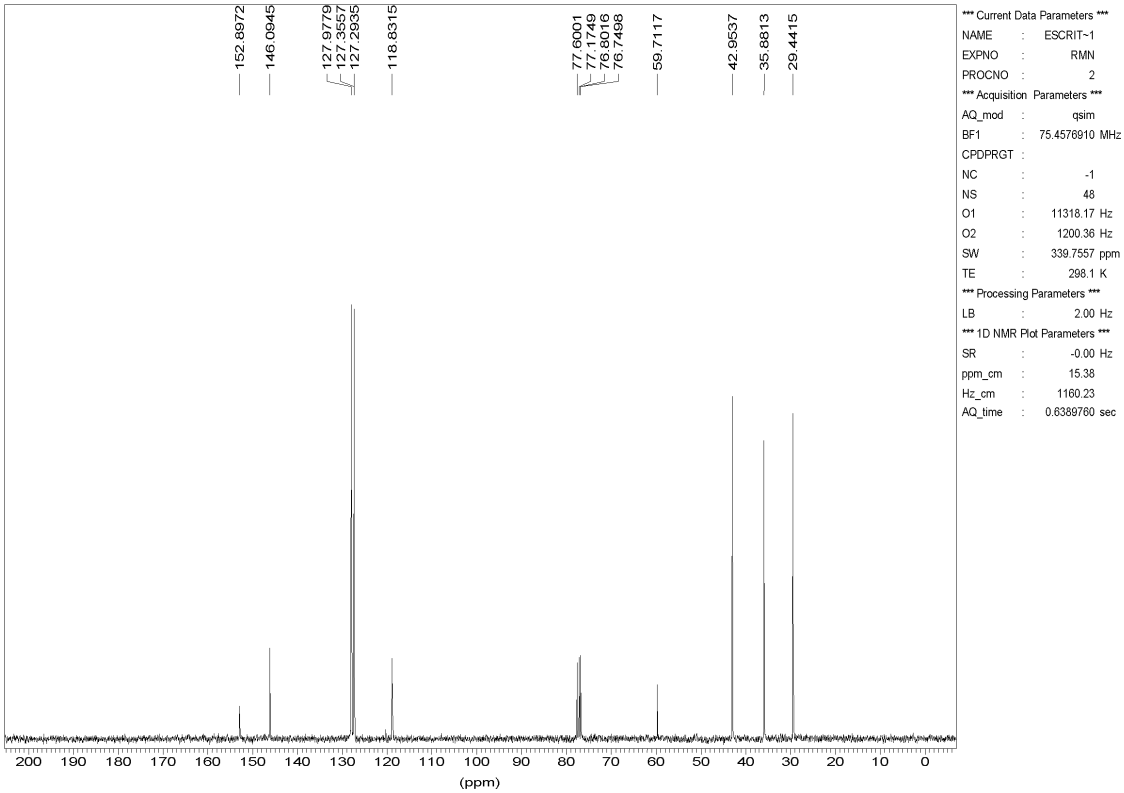




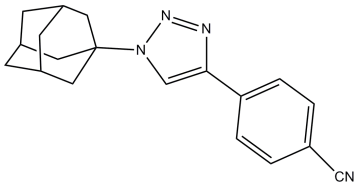
(1-Adamantyl-1H-1,2,3-triazol-4-yl)diphenylmethanol (6d)

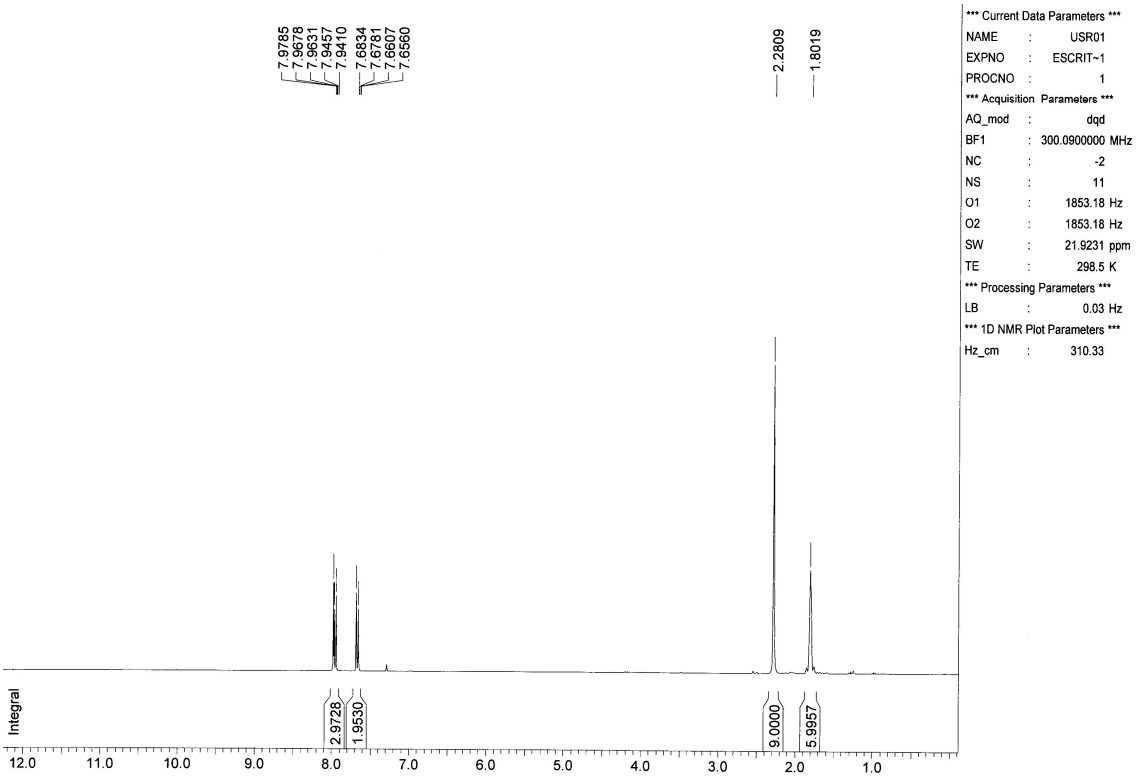




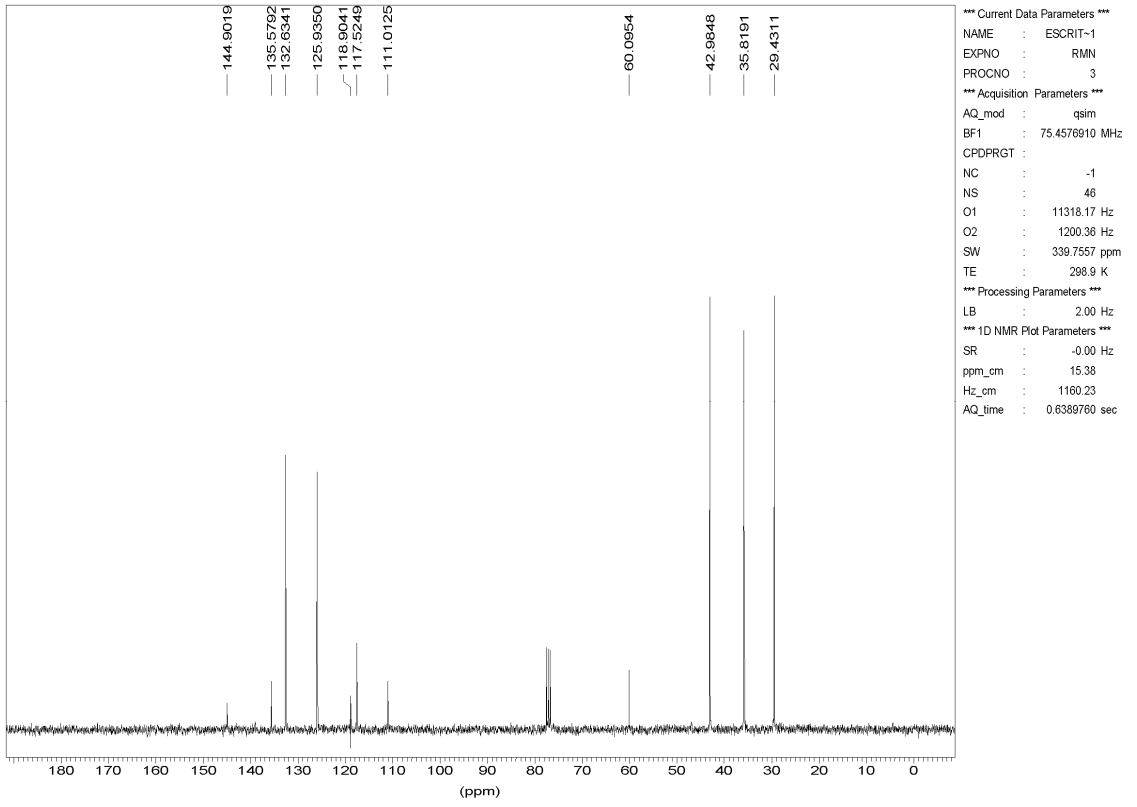


4-(1-Adamantyl-1H-1,2,3-triazol-4-yl)benzonitrile (6f)






```
*** Current Data Parameters ***
NAME      :      USR01
EXPNO     :      ESCRIT~1
PROCNO    :      1
*** Acquisition  Parameters ***
AQ_mod    :      dqd
BF1       :      300.0900000 MHz
NC        :      -2
NS        :      11
O1        :      1853.18 Hz
O2        :      1853.18 Hz
SW        :      21.9231 ppm
TE        :      298.5 K
*** Processing Parameters ***
LB        :      0.03 Hz
*** 1D NMR Plot Parameters ***
Hz_cm     :      310.33
```




```
*** Current Data Parameters ***
NAME      :      ESCRIT~1
EXPNO     :      RMN
PROCNO    :      3
*** Acquisition  Parameters ***
AQ_mod    :      qsim
BF1       :      75.4576910 MHz
CPDPRGT   :
NC        :      -1
NS        :      46
O1        :      11318.17 Hz
O2        :      1200.36 Hz
SW        :      339.7557 ppm
TE        :      298.9 K
*** Processing Parameters ***
LB        :      2.00 Hz
*** 1D NMR Plot Parameters ***
SR        :      -0.00 Hz
ppm_cm    :      15.38
Hz_cm     :      1160.23
AQ_time   :      0.6389760 sec
```

General procedure for the synthesis of 5-iodo-1,2,3-triazoles

All reagents were obtained from commercial suppliers and used without further purification with the exception of 1-iodoalkynes, which were prepared by following the method reported in the literature.[5] For the synthesis of 5-iodo-1,2,3-triazoles; synthesis of 5-iodo-4-phenyl-1-(phenylthiomethyl)-1*H*-1,2,3-triazole (**7a**): 0.0168 g (2 mol%) of catalyst **3** were dissolved in 2 mL of H_2O under air. 1-iodo-phenylacetylene (1mmol, 0.228 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) were added in the presence of 0.012 mL (10 mol%) of 2,6-lutidine. The reaction was stirred at room temperature for 8h, after which time a yellow powder had formed. The crude of the reaction was washed with CH_2Cl_2 (3x10mL) and the combined organic fractions were concentrated by evaporation to give **7a** as a white solid (0.377 g, 96%).

The identity of the 5-iodo-1,2,3-triazoles **8a**,[5a] **8b**,[4d] **8e**,[6] and **9a**[5a] was assessed by comparison of their ^{1}H a ^{13}C{^{1}H} NMR spectroscopic data with those previously reported in the literature and by their fragmentation in GC/MS.

We note that these reactions can be performed in a preparative scale. Representative example **7a**: 0.336 g of catalyst **3** were dissolved in 40 mL of H_2O under air. 1-iodo-phenylacetylene (20 mmol, 4.560 g) and (azidomethyl)(phenyl)sulfane (20 mmol, 2.84 mL) were added in the presence of 0.24 mL of 2,6-lutidine. The reaction was stirred at room temperature for 12h, after which time a yellow powder had formed. The crude of the reaction was washed with CH_2Cl_2 (3x40mL) and the combined organic fractions were concentrated by evaporation to give **7a** as a white solid (6.99 g, 89%).

5-iodo-4-phenyl-1-(phenylthiomethyl)-1H-1,2,3-triazole (7a) Synthesized from 1-iodo-phenylacetylene (1mmol, 0.228 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.377 g, 96%, white solid; Anal. Calcd for $C_{15}H_{12}IN_3S$: C, 45.81; H, 3.08; N, 10.69. Found: C, 45.90; H, 3.04; N 10.65. IR (cm^{-1}): ν 687, 742, 765, 982, 1065, 1234, 1418, 1467, 2998. ^{1}H NMR ($CDCl_3$): δ 5.74 (s, 2H), 7.42 (m, 8H), 7.97 (m, 2H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 55.04, 75.87, 127.45, 128.60, 128.75, 128.96, 129.41, 130.06, 131.56, 133.37, 150.30 ppm.

4-butyl-5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazole (7b) Synthesized from 1-iodo-hexyne (1mmol, 0.208 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.347 g, 93%, white solid; Anal. Calcd for $C_{13}H_{16}IN_3S$: C, 41.83; H, 4.32; N, 11.26. Found: C, 41.91; H, 4.28; N 11.30. IR (cm^{-1}): *v* 496, 690, 740, 1059, 1216, 1437, 2972, 2951. ^1H NMR ($CDCl_3$): δ 0.95 (m, 3H), 1.37 and 1.67 (m, 2H each), 2.65 (m, 2H), 5.61 (s, 2H), 7.32 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.84, 22.21, 25.73, 30.99, 54.56, 77.75, 128.85, 129.31, 131.58, 133.38, 152.63 ppm.

4-cyclohexenyl-5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazole (7c) Synthesized from 1-(iodoethynyl)cyclohex-1-ene (1mmol, 0.232 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.373 g, 94%, white solid; Anal. Calcd for $C_{15}H_{16}IN_3S$: C, 45.35; H, 4.06; N, 10.58. Found: C, 45.28; H, 4.01; N 10.63. IR (cm^{-1}): *v* 485, 684, 738, 764, 842, 920, 1066, 1231, 1287, 1419, 2929. ^1H NMR ($CDCl_3$): δ 1.73 (m, 4H), 2.23 (m, 2H), 2.55 (m, 2H), 5.54 (s, 2H), 6.47 (m, 1H), 7.34 (m, 5H), ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.89, 22.61, 25.46, 27.20, 54.75, 74.54, 127.90, 128.74, 128.79, 129.32, 131.83, 133.11, 151.70 ppm.

(5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazol-4-yl)diphenylmethanol (7d) Synthesized from 3-iodo-1,1-diphenylprop-2-yn-1-ol (1mmol, 0.334 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.464 g, 93%, white solid; Anal. Calcd for $C_{22}H_{18}IN_3OS$: C, 52.91; H, 3.63; N, 8.41. Found: C, 53.01; H, 3.59; N 8.47. IR (cm^{-1}): 697, 764, 907, 1011, 1159, 1298, 1441, 1492, 3552. ^1H NMR (CD_2Cl_2): δ 4.10 (s, 1H), 5.69 (s, 2H), 7.33 (m, 15H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 54.97, 77.64, 78.20, 127.83, 127.97, 128.08, 129.11, 129.34, 131.16, 133.93, 144.27, 154.89 ppm.

4-(4-fluorophenyl)-5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazole (7e) Synthesized from 1-fluoro-4-(iodoethynyl)benzene (1mmol, 0.246 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.399 g, 97%, white solid; Anal. Calcd for $C_{15}H_{11}FIN_3S$: C, 43.81; H, 2.70; N, 10.22. Found: C, 43.90; H, 2.68; N 10.26. IR (cm^{-1}): *v* 499, 696, 752, 839, 987, 1093, 1157, 1255, 1279, 1470, 1540. ^1H NMR ($CDCl_3$): δ 5.74 (s, 2H), 7.18 (m, 2H), 7.33 (m, 3H), 7.43 (m, 2H), 7.94 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 55.07, 75,73, 115.65 (d, J = 21.9 Hz), 126.20 (d, J = 3.1 Hz), 128.97, 129.33 (d, J = 8.6 Hz), 129.42, 149.55, 162.99 (d, J = 249.8 Hz) ppm. ^{19}F NMR ($CDCl_3$): -112.30 ppm.

4-(5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazol-4-yl)benzonitrile (7f) Synthesized from 4-(iodoethynyl)benzonitrile (1mmol, 0.253 g) and (azidomethyl)(phenyl)sulfane (1

mmol, 0.142 mL) using general procedure, 0.396 g, 95%, white solid; Anal. Calcd for $C_{16}H_{11}IN_4S$: C, 45.95; H, 2.65; N, 13.40. Found: C, 45.91; H, 2.63; N 13.43. IR (cm^{-1}): *v* 549, 696, 723, 843, 985, 1235, 1338, 1445, 1612, 2230. ^1H NMR ($CDCl_3$): δ 5.73 (s, 2H), 7.35 (m, 5H), 8.11 (m, 2H), 8.13 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 55.15, 76.85, 112.08, 118.58, 127.54, 129.03, 129.40, 131.20, 132.35, 132.29, 134.41, 148.14 ppm.

ethyl 5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazole-4-carboxylate (7g) Synthesized from ethyl 3-iodopropiolate (1mmol, 0.224 g) and (azidomethyl)(phenyl)sulfane (1 mmol, 0.142 mL) using general procedure, 0.373 g, 96%, yellow solid; Anal. Calcd for $C_{12}H_{12}IN_3O_2S$: C, 37.03; H, 3.11; N, 10.80 . Found: C, 37.10; H, 3.15; N 10.85. IR (cm^{-1}): *v* 474, 687, 766, 1032, 1046, 1250, 1388, 1491, 1734, 2942, 3133. ^1H NMR ($CDCl_3$): δ 1.45 (t, 3H, *J* = 7.2 Hz), 4.46 (q, 2H, *J* = 7.2 Hz), 5.70 (s, 2H), 7.33 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 13.76, 54.87, 61.16, 83.71, 128.80, 129.04, 130.41, 133.23, 141.87, 159.66 ppm.

1-benzyl-4-cyclohexenyl-5-iodo-1H-1,2,3-triazole (8c) Synthesized from 1-(iodoethynyl)cyclohex-1-ene (1mmol, 0.232 g) and (benzylazide (1 mmol, 0.125 mL) using general procedure, 0.347 g, 95%, white solid; Anal. Calcd for $C_{15}H_{16}IN_3$: C, 49.33; H, 4.42; N, 11.51. Found: C, 49.21; H, 4.44; N 11.55. IR (cm^{-1}): *v* 689, 720, 918, 1065, 1233, 1432, 1497, 2934. ^1H NMR ($CDCl_3$): δ 1.73 (m, 4H), 2.21 (m, 2H), 2.57 (m, 2H), 5.60 (s, 2H), 6.46 (m, 1H), 7.30 (m, 5H), ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.92, 22.63, 25.44, 27.22, 54.13, 75.11, 127.73, 128.05, 128.35, 128.52, 128.82, 134.58, 151.58 ppm.

(1-benzyl-5-iodo-1H-1,2,3-triazol-4-yl)diphenylmethanol (8d) 3-iodo-1,1-diphenylprop-2-yn-1-ol (1mmol, 0.334 g) and benzylazide (1 mmol, 0.125 mL) using general procedure, 0.444 g, 95%, white solid; Anal. Calcd for $C_{22}H_{18}IN_3O$: C, 56.54; H, 3.88; N, 8.99. Found: C, 56.59; H, 3.84; N 8.97. IR (cm^{-1}): 628, 698, 723, 763, 1009, 1161, 1447, 3551. ^1H NMR (CD_2Cl_2): δ 4.25 (s, 1H), 5.62 (s, 2H), 7.44 (m, 15H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 54.35, 77.80, 78.51, 126.15, 127.75, 127.86, 128.06, 128.21, 128.40, 128.51, 128.95, 134.32, 144.17, 154.92 ppm.

4-(1-benzyl-5-iodo-1H-1,2,3-triazol-4-yl)benzonitrile (8f) Synthesized from 4-(iodoethynyl)benzonitrile (1mmol, 0.253 g) and benzylazide (1 mmol, 0.125 mL) using general procedure, 0.355 g, 92%, white solid; Anal. Calcd for $C_{16}H_{11}IN_4$: C, 49.76; H, 2.87; N, 14.51. Found: C, 49.69; H, 2.91; N 13.54. IR (cm^{-1}): *v* 555, 686, 732, 845, 981, 1235, 1409, 1611, 2229. ^1H NMR ($CDCl_3$): δ 5.71 (s, 2H), 7.35 (m, 5H), 7.75 (m, 2H),

8.14 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 54.50, 77.19, 111.97, 118.60, 127.55, 127.79, 128.63, 128.94, 132.30, 133.84, 134.61, 148.10, ppm

ethyl 1-benzyl-5-iodo-1H-1,2,3-triazole-4-carboxylate (8g) Synthesized from ethyl 3-iodopropiolate (1mmol, 0.224 g) and benzylazide (1 mmol, 0.125 mL) using general procedure, 0.336 g, 94%, yellow solid; Anal. Calcd for $C_{12}H_{12}IN_3O_2$: C, 40.36; H, 3.39; N, 11.77. Found: C, 40.40; H, 3.34; N 11.81. IR (cm^{-1}): ν 488, 686, 743, 1053, 1126, 1222, 1518, 1719. ^{1}H NMR ($CDCl_3$): δ 1.43 (m, 3H), 4.44 (m, 2H), 5.67 (s, 2H), 7.31 (m, 5H) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 14.18, 54.43, 61.50, 84.56, 127.76, 128.65, 128.90, 133.53, 142.24, 160.17 ppm.

1-adamantyl-4-butyl-5-iodo-1H-1,2,3-triazole (9b) Synthesized from 1-iodo-hexyne (1mmol, 0.208 g) and 1-azidoadamantane (1 mmol, 0.177 g) using general procedure, 0.377 g, 98%, white solid; Anal. Calcd for $C_{16}H_{24}IN_3$: C, 49.88; H, 6.28; N, 10.91. Found: C, 49.81; H, 6.33; N 10.87. IR (cm^{-1}): ν 698, 760, 816, 837, 1016, 1148, 1232, 1310, 1356, 1450, 1464, 1517, 2912. ^{1}H NMR ($CDCl_3$): δ 0.95 (t, 3H, J = 7.4 Hz), 1.40 and 1.66 (m, 2H each), 1.78 (bs, 6H), 2.27 (bs, 3H), 2.52 (bs, 6H), 2.66 (t, 2H, J = 7.7 Hz) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 13.37, 21.93, 25.22, 29.30, 30.64, 35.44, 40.95, 62.87, 69.92, 152.49 ppm.

1-adamantyl-4-cyclohexenyl-5-iodo-1H-1,2,3-triazole (9c) Synthesized from 1-(iodoethynyl)cyclohex-1-ene (1mmol, 0.232 g) and 1-azidoadamantane (1 mmol, 0.177 g) using general procedure, 0.380 g, 93%, white solid; Anal. Calcd for $C_{18}H_{24}IN_3$: C, 52.82; H, 5.91; N, 10.27. Found: C, 52.75; H, 5.85; N 10.30. IR (cm^{-1}): ν 687, 713, 801, 848, 920, 1017, 1145, 1240, 1308, 1357, 2904. ^{1}H NMR ($CDCl_3$): δ 1.71 (m, 10H), 2.23 (m, 5H), 2.44 (m, 2H), 2.54 (6H), 6.18 (m, 1H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 21.42, 22.24, 24.97, 27.62, 29.35, 35.43, 40.98, 63.38, 68.12, 127.84, 129.57, 152.98 ppm.

(1-Adamantyl-5-iodo-1-1H-1,2,3-triazol-4-yl)diphenylmethanol (9d) Synthesized from 3-iodo-1,1-diphenylprop-2-yn-1-ol (1mmol, 0.334 g) and 1-azidoadamantane (1 mmol, 0.177 g) using general procedure, 0.496 g, 97%, white solid; Anal. Calcd for $C_{25}H_{26}IN_3O$: C, 58.72; H, 5.12; N, 8.22. Found: C, 58.79; H, 5.07; N 8.26. IR (cm^{-1}): ν 634, 697, 758, 887, 1006, 1017, 1140, 1235, 1357, 1446, 2851, 2903, 3539. ^{1}H NMR ($CDCl_3$): δ 1.78 (bs, 6H), 2.28 (bs, 3H), 2.58 (bs, 6H), 4.26 (s, 1H), 7.31 (m, 10H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 28.85, 34.84, 40.41, 63.90, 69.43, 77.04, 126.67, 126.90, 127.22, 143.40, 154.10 ppm.

1-adamantyl-4-(4-fluorophenyl)-5-iodo-1H-1,2,3-triazole (9e) Synthesized from 1-fluoro-4-(iodoethynyl)benzene (1mmol, 0.246 g) and 1-azidoadamantane (1 mmol,

0.177 g) using general procedure, 0.393 g, 97%, white solid; Anal. Calcd for Chemical Formula: $C_{18}H_{19}FIN_3$: C, 51.08; H, 4.52; N, 9.93. Found: C, 51.01; H, 4.59; N 9.90. IR (cm^{-1}): *v* 531, 611, 811, 840, 1015, 1092, 1155, 1188, 1234, 1308, 1494, 1555, 2853, 2908. ^1H NMR ($CDCl_3$): δ 1.81 (bs, 6H), 2.29 (bs, 9H), 7.10 (m, 2H), 7.81 (m, 2H), ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.99, 35.44, 42.55, 59.20, 76.80, 115.23 (d, J = 21.4 Hz), 126.84, 126.79, 145.43, 162.03 (d, J = 247.1 Hz) ppm. ^{19}F NMR ($CDCl_3$): -114.17 ppm.

4-(1-adamantyl-5-iodo-1H-1,2,3-triazol-4-yl)benzonitrile (9f) Synthesized from 4-(iodoethynyl)benzonitrile (1mmol, 0.253 g) and 1-azidoadamantane (1 mmol, 0.177 g) using general procedure, 0.400 g, 93%, white solid; Anal. Calcd for $C_{19}H_{19}IN_4$: C, 53.04; H, 4.45; N, 13.02. Found: C, 53.12; H, 4.51; N 13.07. IR (cm^{-1}): *v* 589, 751, 884, 948, 1025, 1113, 1287, 1374, 1456, 1712, 2228,. ^1H NMR ($CDCl_3$): δ 1.68 (bs, 6H), 2.15 (bs, 9H), 6.96 (m, 2H), 7.69 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.60, 35.34, 42.51, 59.62, 76.88, 110.53, 117.05, 125.45, 132.15, 135.10, 144.43 ppm.

ethyl 1-adamantyl-5-iodo-1H-1,2,3-triazole-4-carboxylate (9g) Synthesized from ethyl 3-iodopropiolate (1mmol, 0.224 g) and 1-azidoadamantane (1 mmol, 0.177 g) using general procedure, 0.369 g, 92%, yellow solid; Anal. Calcd for $C_{15}H_{20}IN_3O_2$: C, 44.90; H, 5.02; N, 10.47. Found: C, 44.84; H, 5.09; N 10.41 IR (cm^{-1}): *v* 560, 812, 1308, 1358, 1553, 1640, 2984. ^1H NMR ($CDCl_3$): δ 1.64 (bs, 9H), 1.94 (bs, 6H), 2.03 (bs, 3H), 3.48 (bs, 2H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 28.90, 35.76, 41.04, 76.79, 140.55, 167.84 ppm.

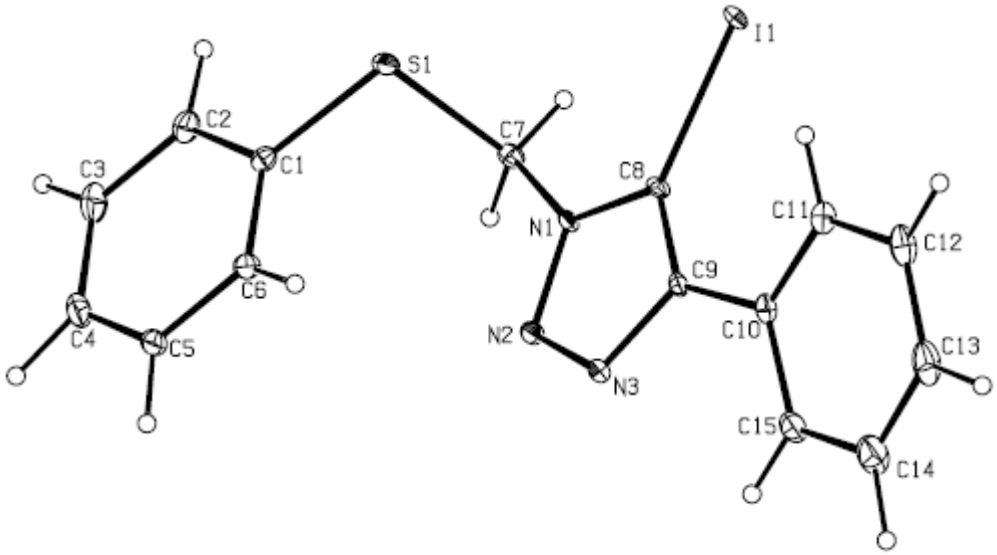
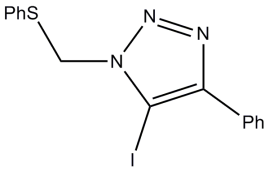
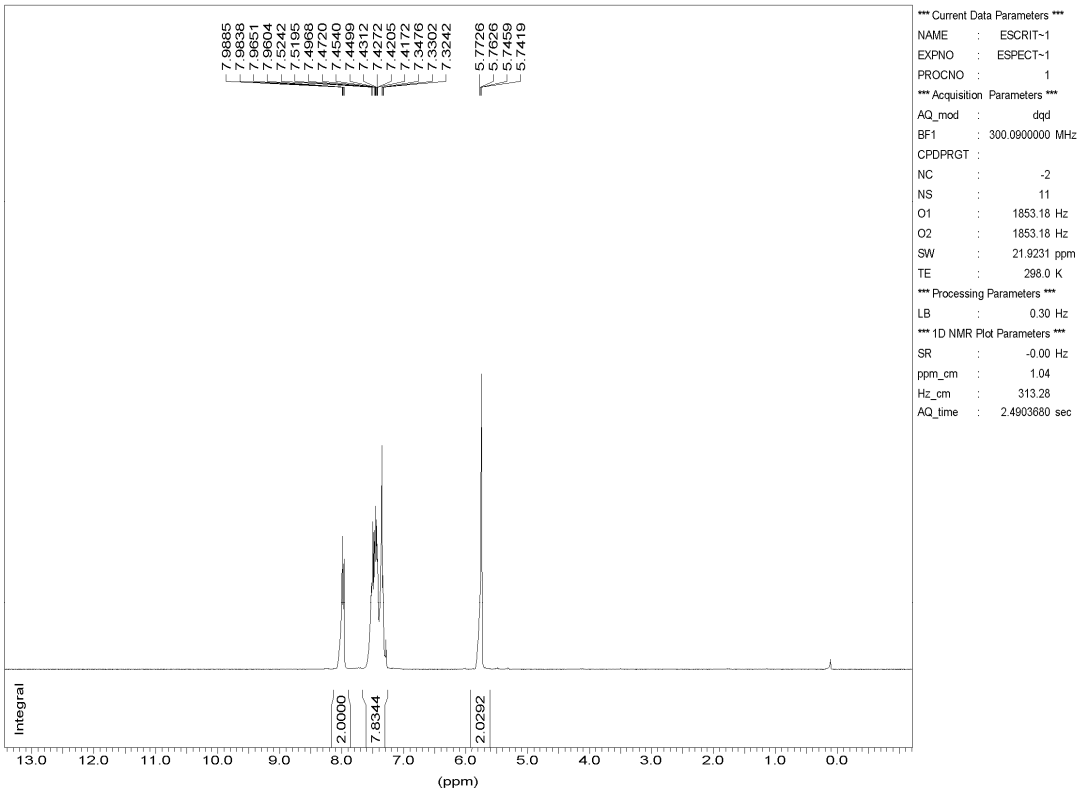


Figure ESI-2. ORTEP-type view of the structure of compound **7a** showing the crystallographic labelling scheme. Thermal ellipsoids are drawn at 20% probability level. Selected bond lengths (Å): N(1)-N(2) = 1.346(3); N(2)-N(3) = 1.311(4); N(3)-C(9) = 1.364(5); C(9)-C(8) = 1.373(5); C(8)-N(1) = 1.356(4); C(8)-I(1) = 2.094(4). Selected bond angles (º): N(1)-N(2)-N(3) = 106.7(2); N(2)-N(3)-C(9) = 110.3(3); N(3)-C(9)-C(8) = 106.9(3); C(9)-C(8)-N(1) = 105.5(3); C(9)-C(8)-I(1) = 134.0(3); N(1)-C(8)-I(1) = 120.6(3).

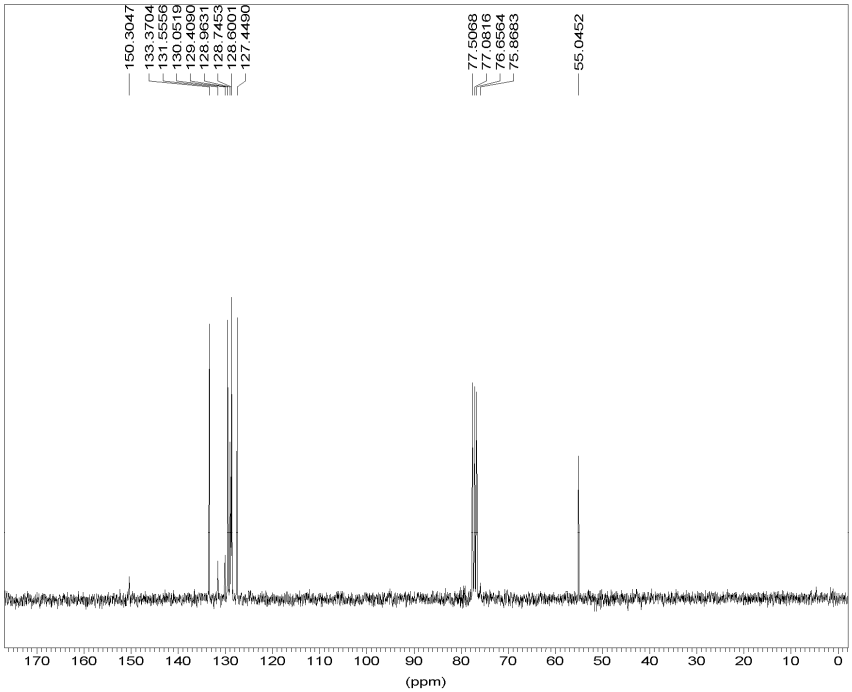
5-iodo-4-phenyl-1-(phenylthiomethyl)-1H-1,2,3-triazole (7a)





*** Current Data Parameters ***
NAME : ESCRIT~1
EXPNO : ESPECT~1
PROCNO : 1
*** Acquisition Parameters ***
AQ_mod : dqd
BF1 : 300.0900000 MHz
CPDPRGT :
NC : -2
NS : 11
O1 : 1853.18 Hz
O2 : 1853.18 Hz
SW : 21.9231 ppm
TE : 298.0 K
*** Processing Parameters ***
LB : 0.30 Hz
*** 1D NMR Plot Parameters ***
SR : -0.00 Hz
ppm_cm : 1.04
Hz_cm : 313.28
AQ_time : 2.4903680 sec

C13 CPD AV300



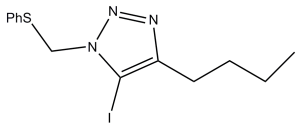
*** Current Data Parameters ***
NAME : ESCRIT~1
EXPNO : ESPECT~1
PROCNO 3

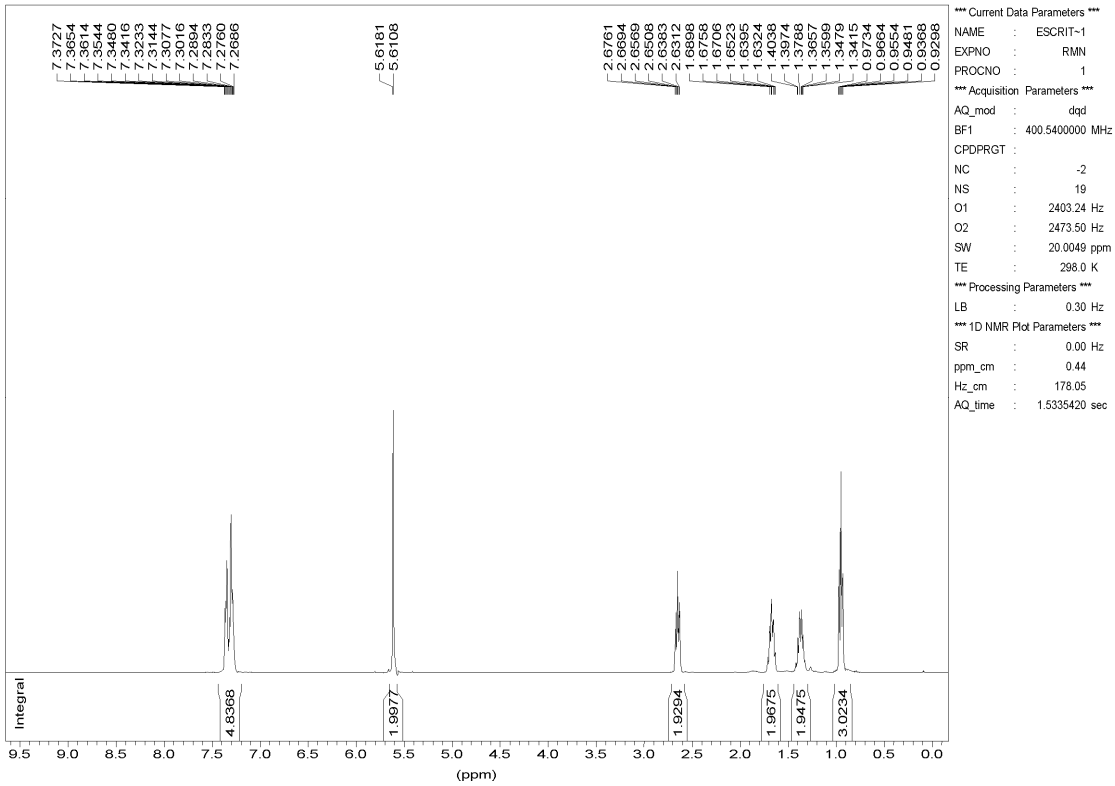
*** Acquisition Parameters ***
AQ_mod : qsim
BF1 : 75.4576910 MHz
CPDPRGT
NC : -1
NS : 239
O1 : 11318.17 Hz
O2 : 1200.36 Hz
SW : 339.7557 ppm
TE : 298.1 K

*** Processing Parameters ***
LB : 2.00 Hz

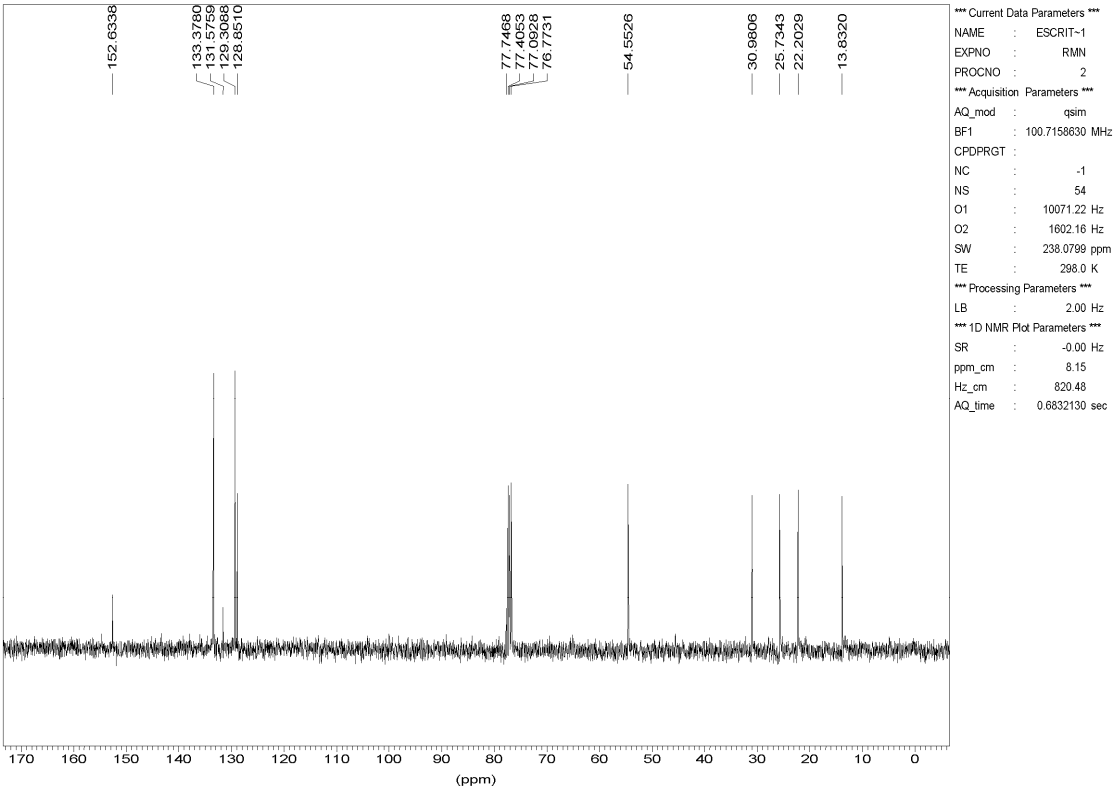
*** 1D NMR Plot Parameters ***
SR : 0.00 Hz
ppm_cm : 8.10
Hz_cm : 611.13
AQ_time : 0.6389760 sec

4-butyl-5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazole (7b)



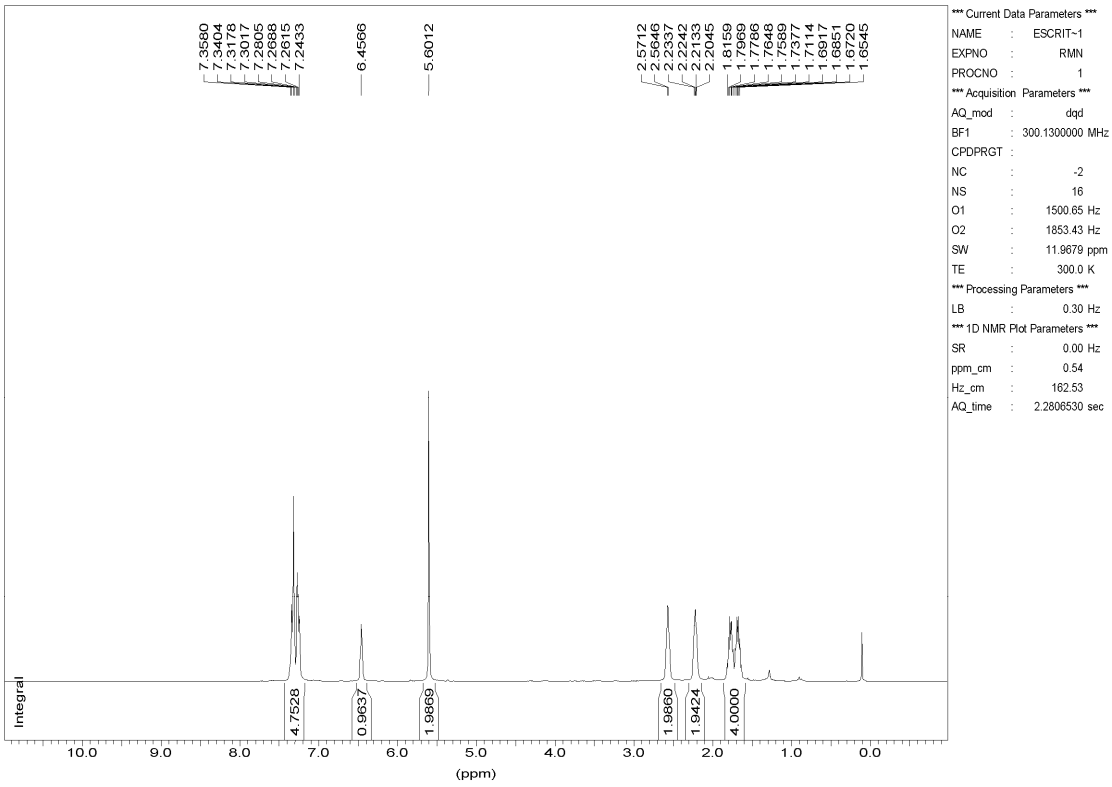


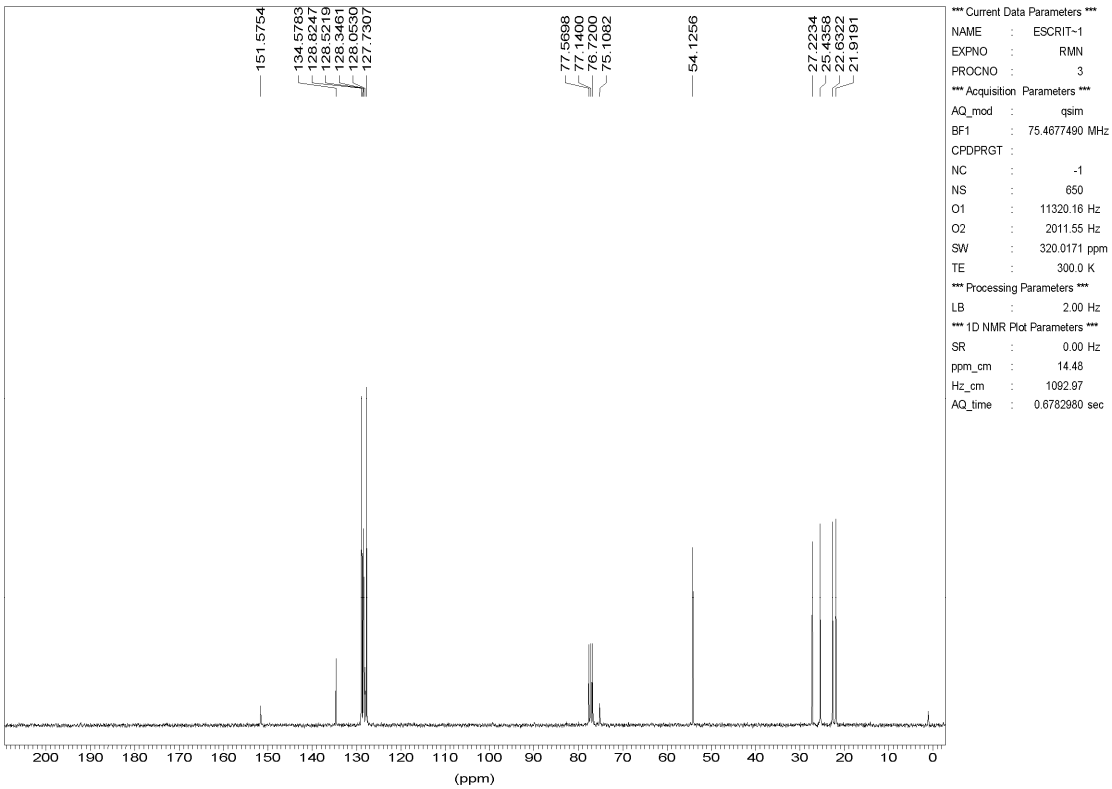
*** Current Data Parameters ***
NAME : ESCRIT~1
EXPNO : RMN
PROCNO : 1
*** Acquisition Parameters ***
AQ_mod : dqd
BF1 : 400.5400000 MHz
CPDPRGT :
NC : -2
NS : 19
O1 : 2403.24 Hz
O2 : 2473.50 Hz
SW : 20.0049 ppm
TE : 298.0 K
*** Processing Parameters ***
LB : 0.30 Hz
*** 1D NMR Plot Parameters ***
SR : 0.00 Hz
ppm_cm : 0.44
Hz_cm : 178.05
AQ_time : 1.5335420 sec



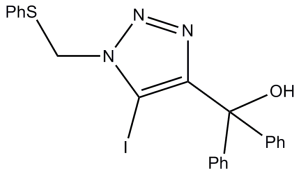
*** Current Data Parameters ***
NAME : ESCRIT~1
EXPNO : RMN
PROCNO : 2
*** Acquisition Parameters ***
AQ_mod : qsim
BF1 : 100.7158630 MHz
CPDPRGT :
NC : -1
NS : 54
O1 : 10071.22 Hz
O2 : 1602.16 Hz
SW : 238.0799 ppm
TE : 298.0 K
*** Processing Parameters ***
LB : 2.00 Hz
*** 1D NMR Plot Parameters ***
SR : -0.00 Hz
ppm_cm : 8.15
Hz_cm : 820.48
AQ_time : 0.6832130 sec

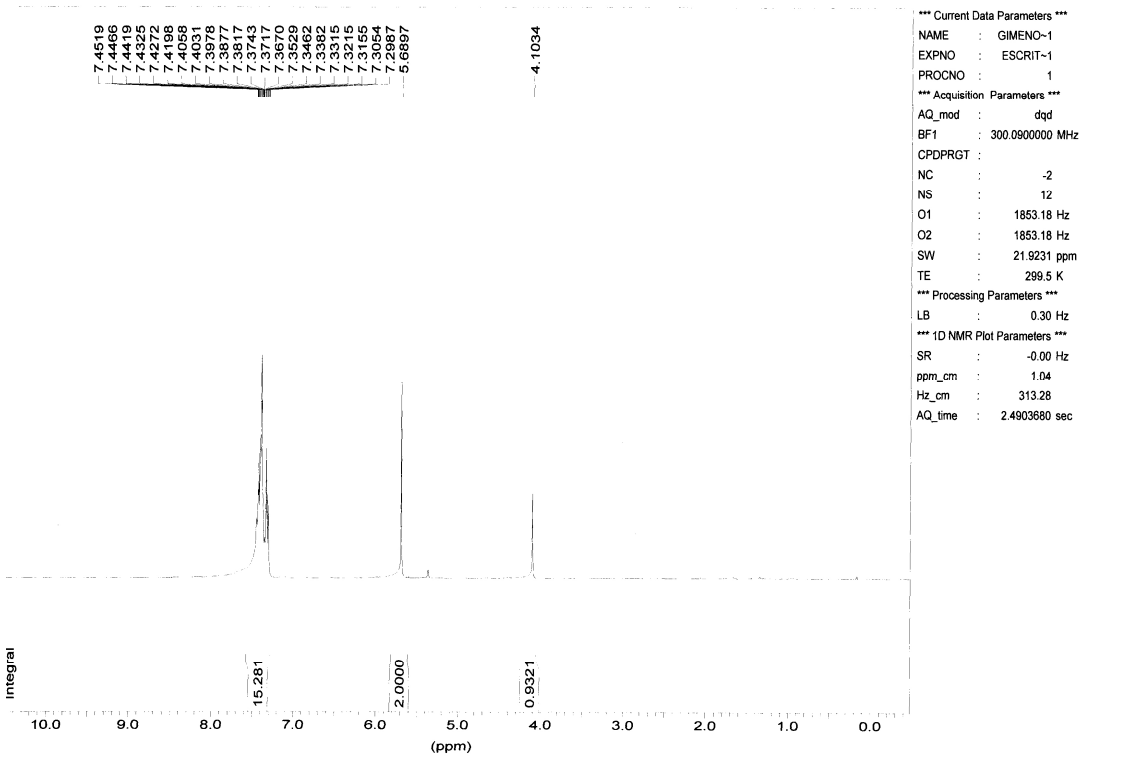
4-cyclohexenyl-5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazole (7c)



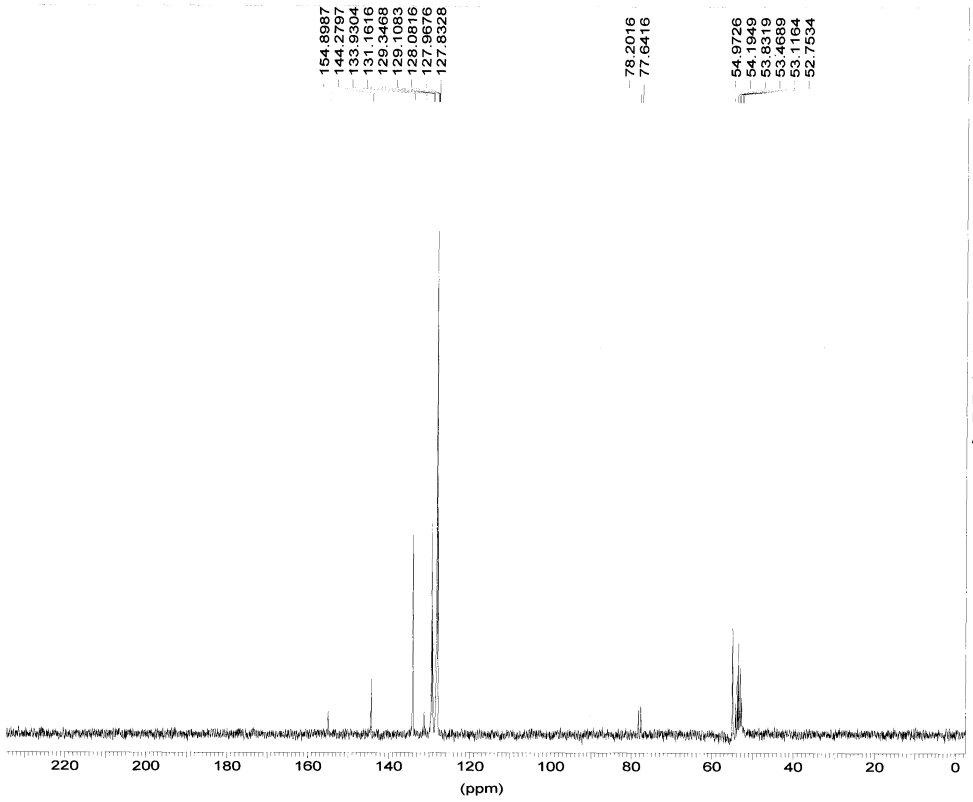


(5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazol-4-yl)diphenylmethanol (7d)



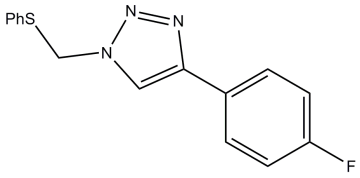


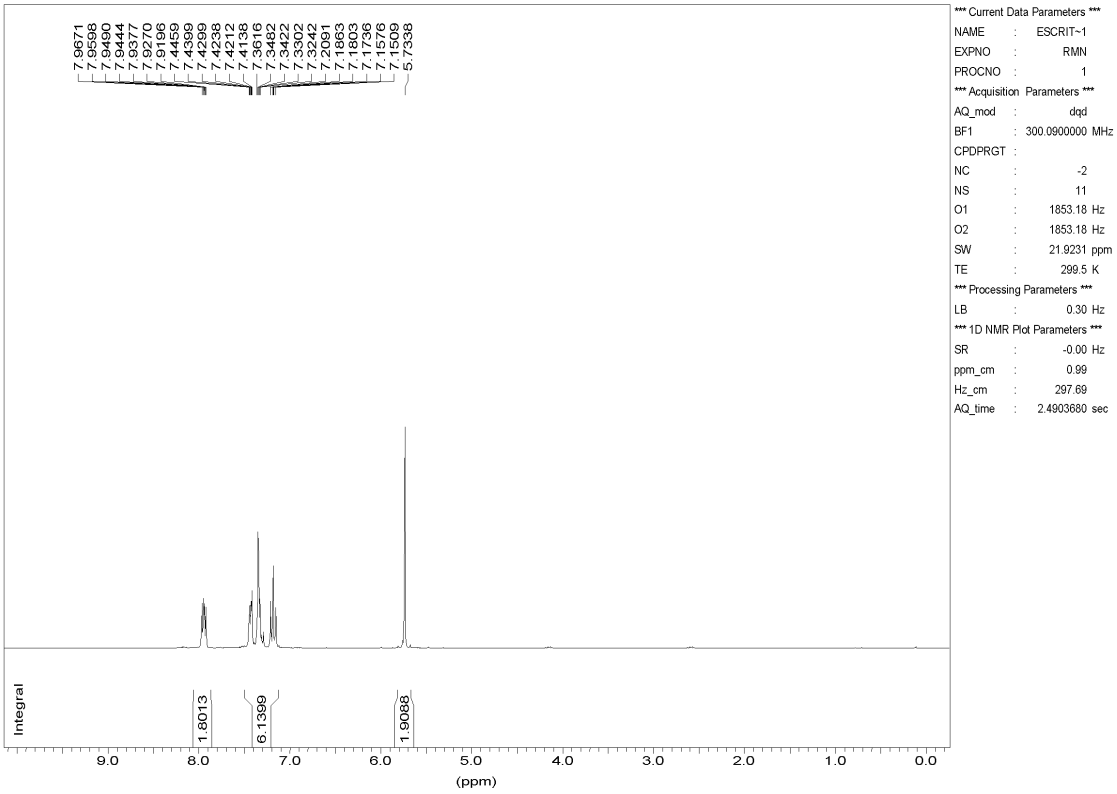
*** Current Data Parameters ***
NAME : GIMENO~1
EXPNO : ESCRIT~1
PROCNO : 1
*** Acquisition Parameters ***
AQ_mod : dqd
BF1 : 300.0900000 MHz
CPDPRGT :
NC : -2
NS : 12
O1 : 1853.18 Hz
O2 : 1853.18 Hz
SW : 21.9231 ppm
TE : 299.5 K
*** Processing Parameters ***
LB : 0.30 Hz
*** 1D NMR Plot Parameters ***
SR : -0.00 Hz
ppm_cm : 1.04
Hz_cm : 313.28
AQ_time : 2.4903680 sec

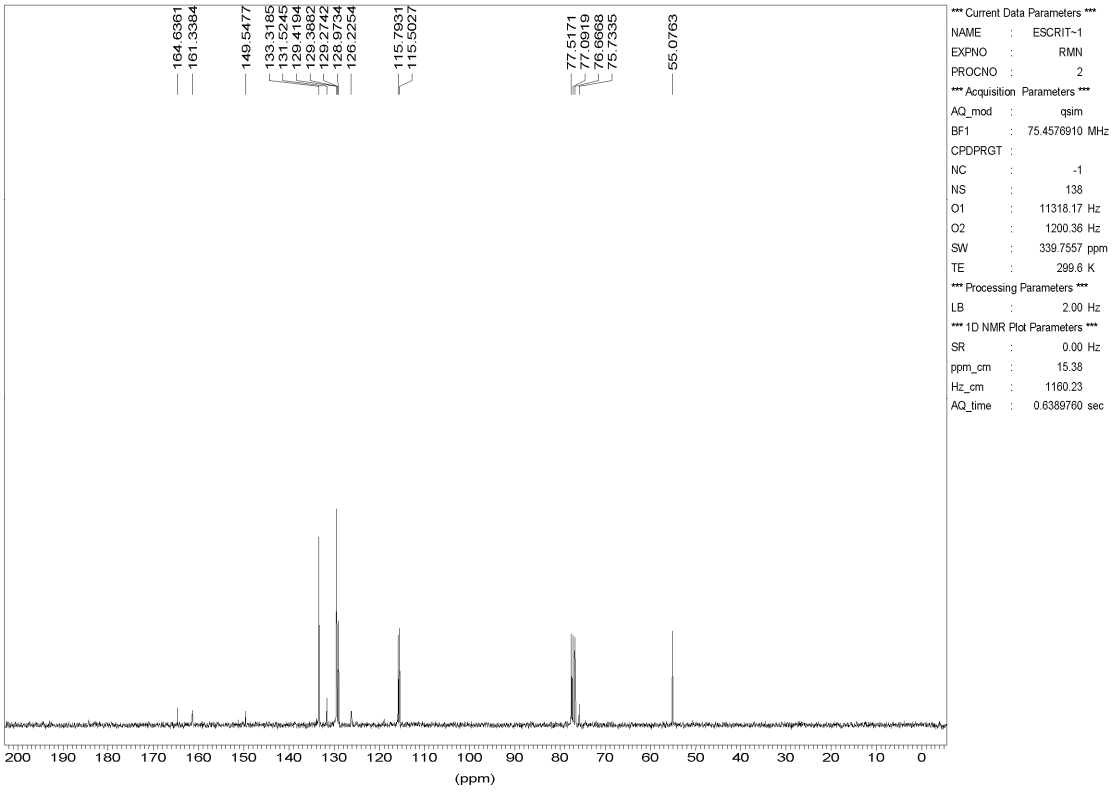


*** Current Data Parameters ***
NAME : GIMENO~1
EXPNO : ESCRIT~1
PROCNO : 2
*** Acquisition Parameters ***
AQ_mod : qsim
BF1 : 75.4576910 MHz
CPDPRGT :
NC : -1
NS : 173
O1 : 11318.17 Hz
O2 : 1200.36 Hz
SW : 339.7557 ppm
TE : 299.5 K
*** Processing Parameters ***
LB : 2.00 Hz
*** 1D NMR Plot Parameters ***
SR : -0.00 Hz
ppm_cm : 16.18
Hz_cm : 1221.00
AQ_time : 0.6389760 sec

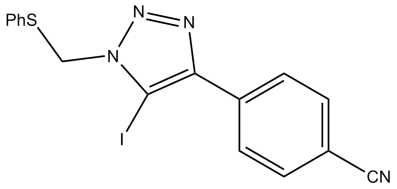
4-(4-fluorophenyl)-5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazole (7e)

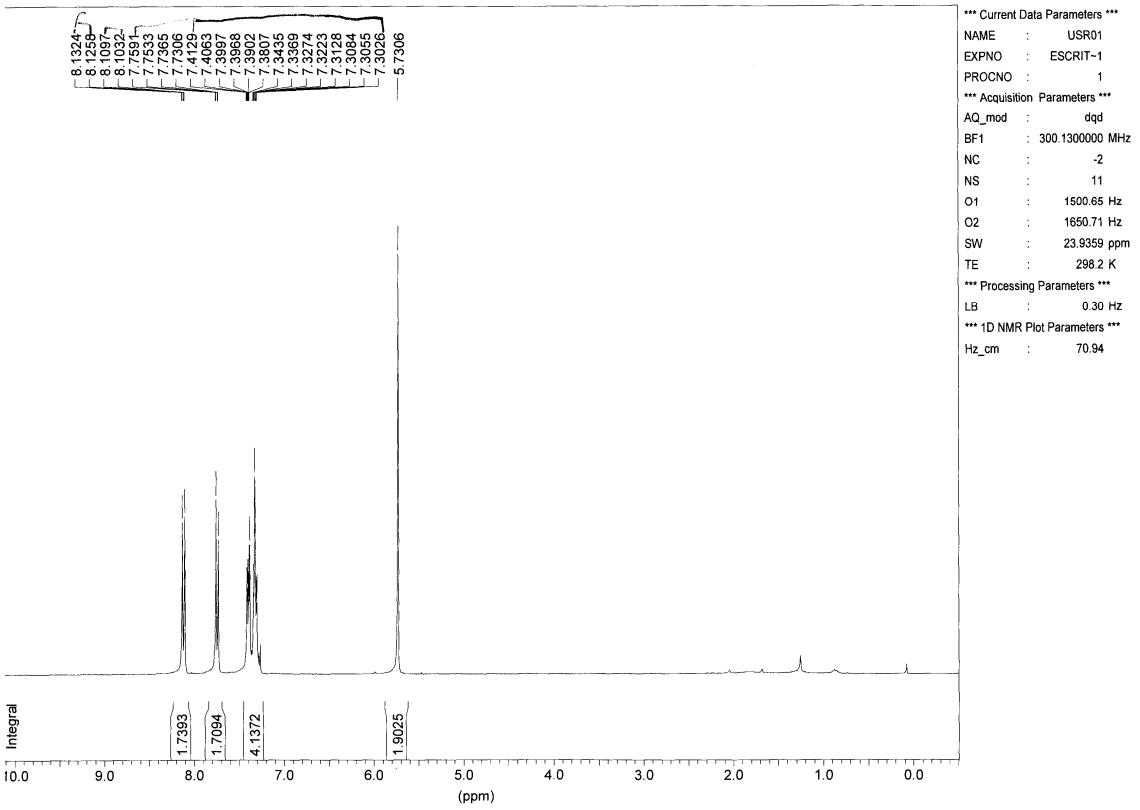


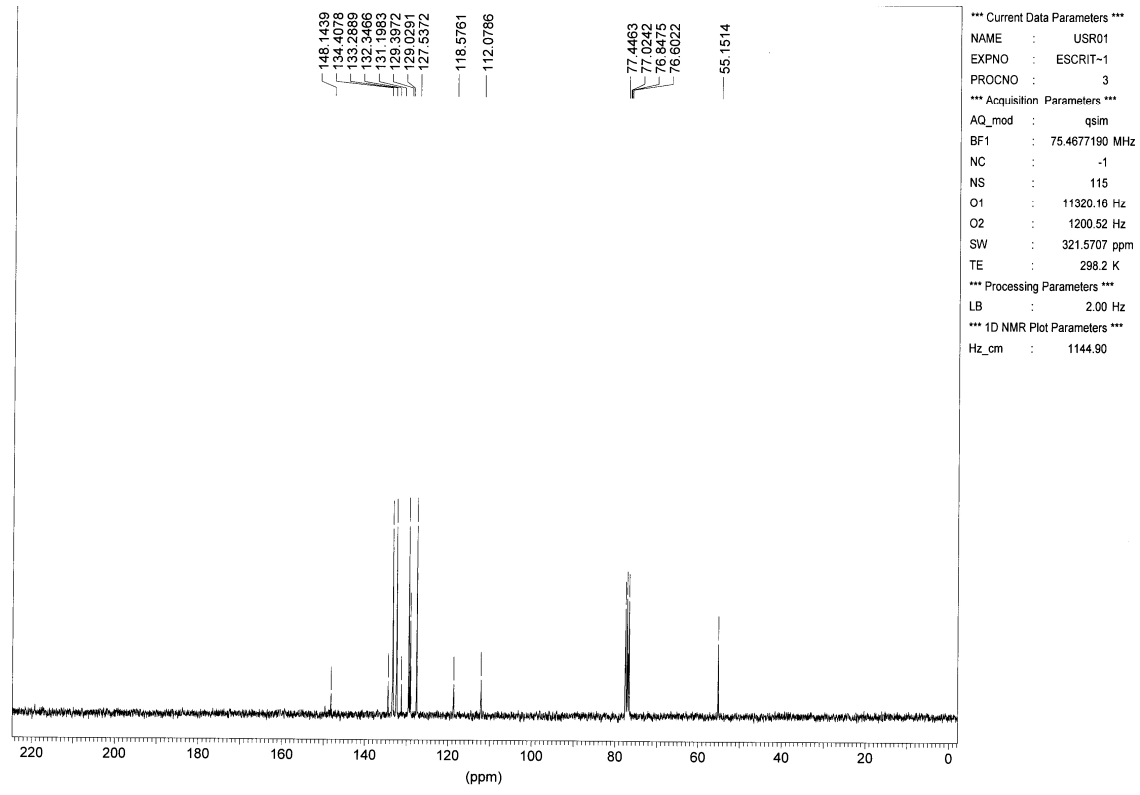




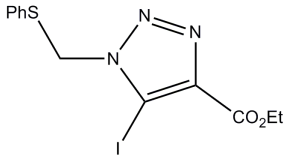
4-(5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazol-4-yl)benzonitrile (7f)

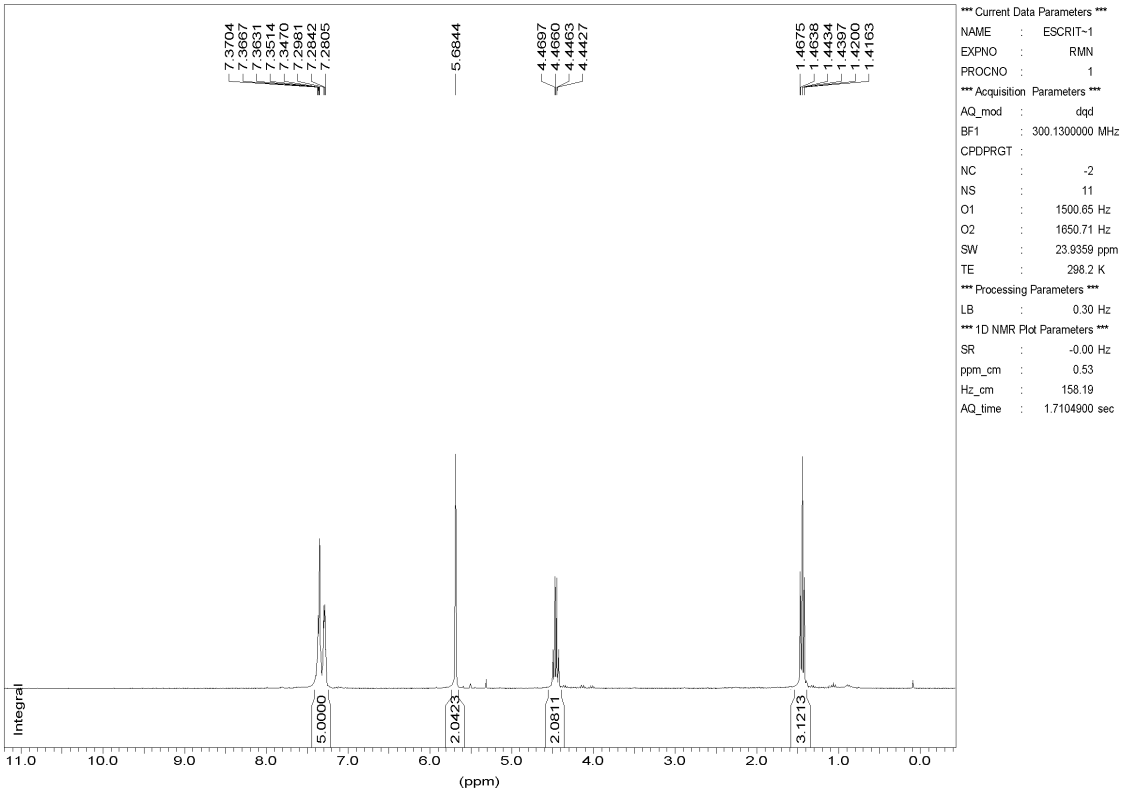


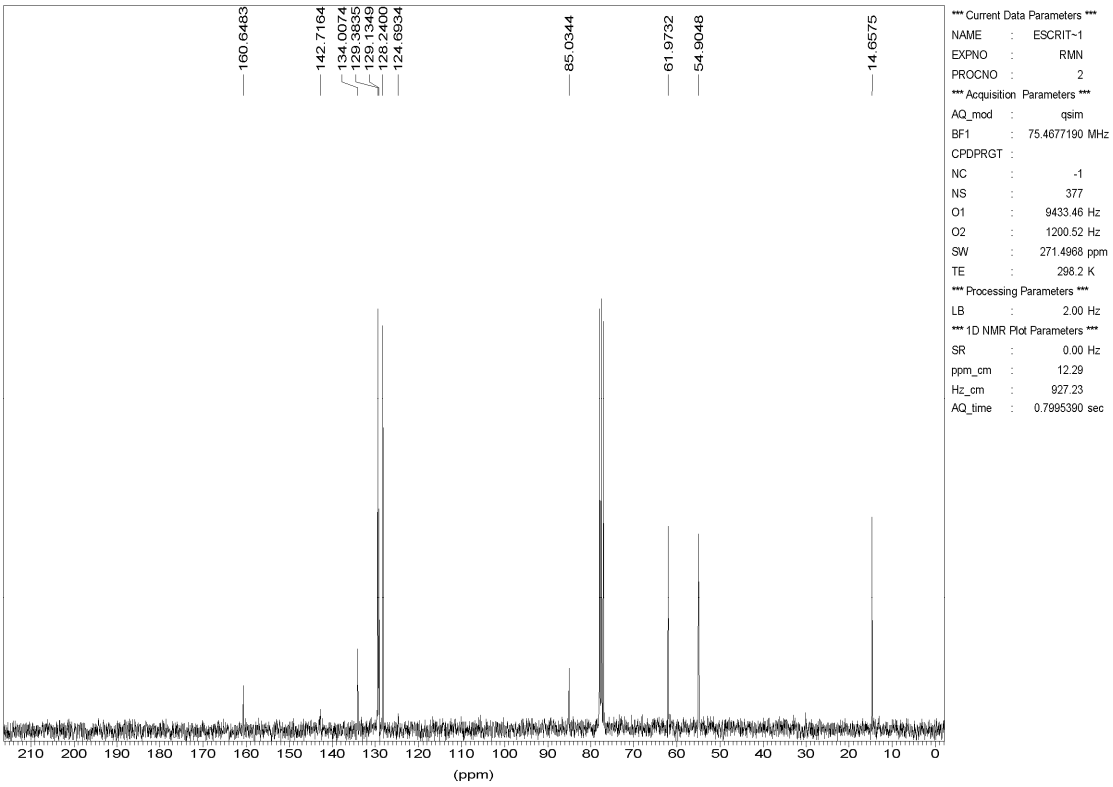




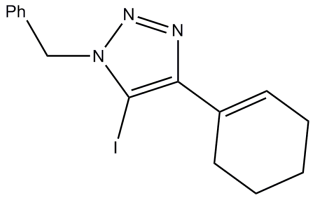
ethyl 5-iodo-1-(phenylthiomethyl)-1H-1,2,3-triazole-4-carboxylate (7g)

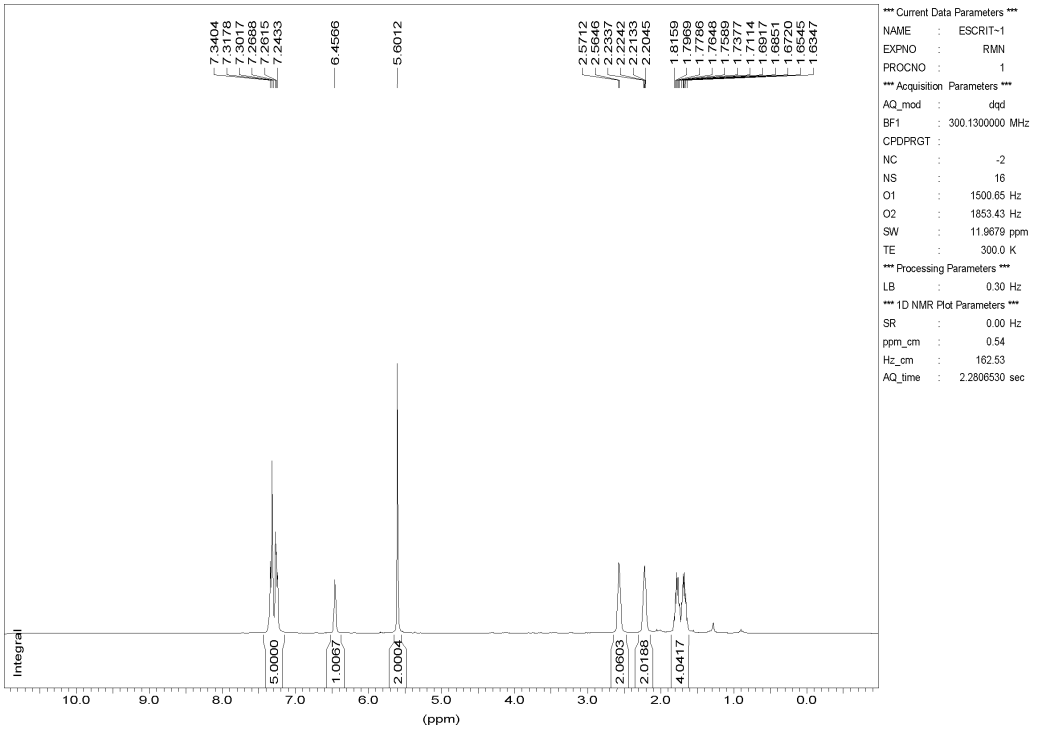


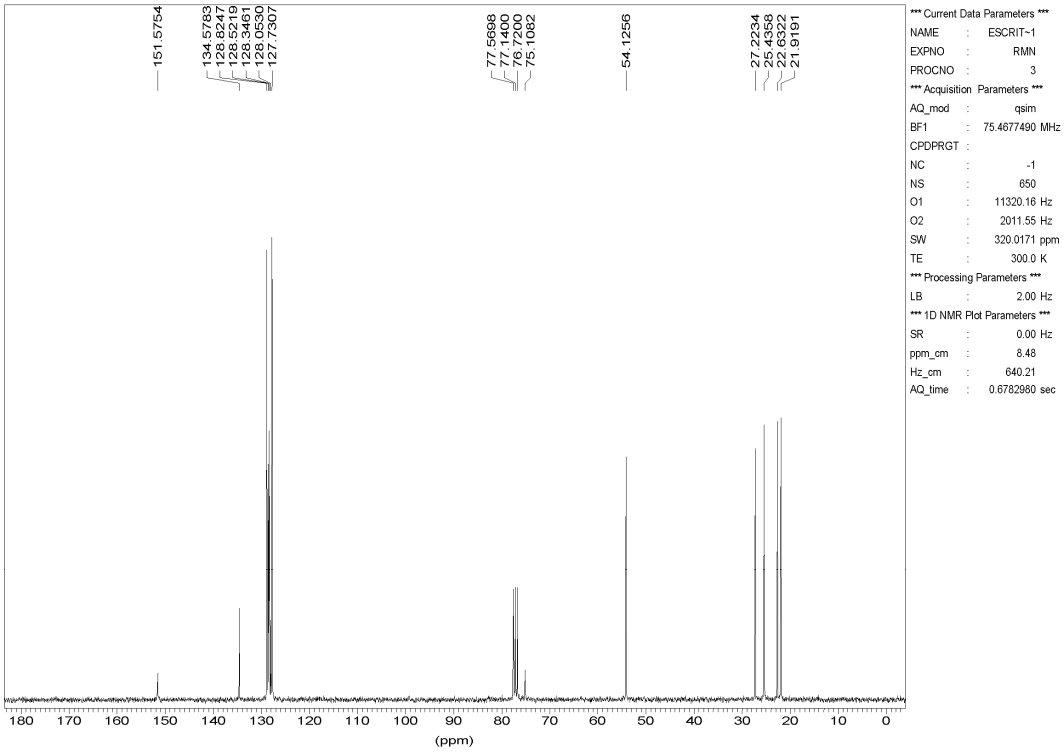




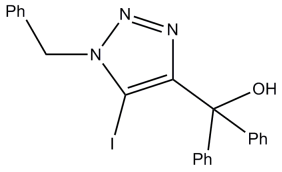
1-benzyl-4-cyclohexenyl-5-iodo-1H-1,2,3-triazole (8c)

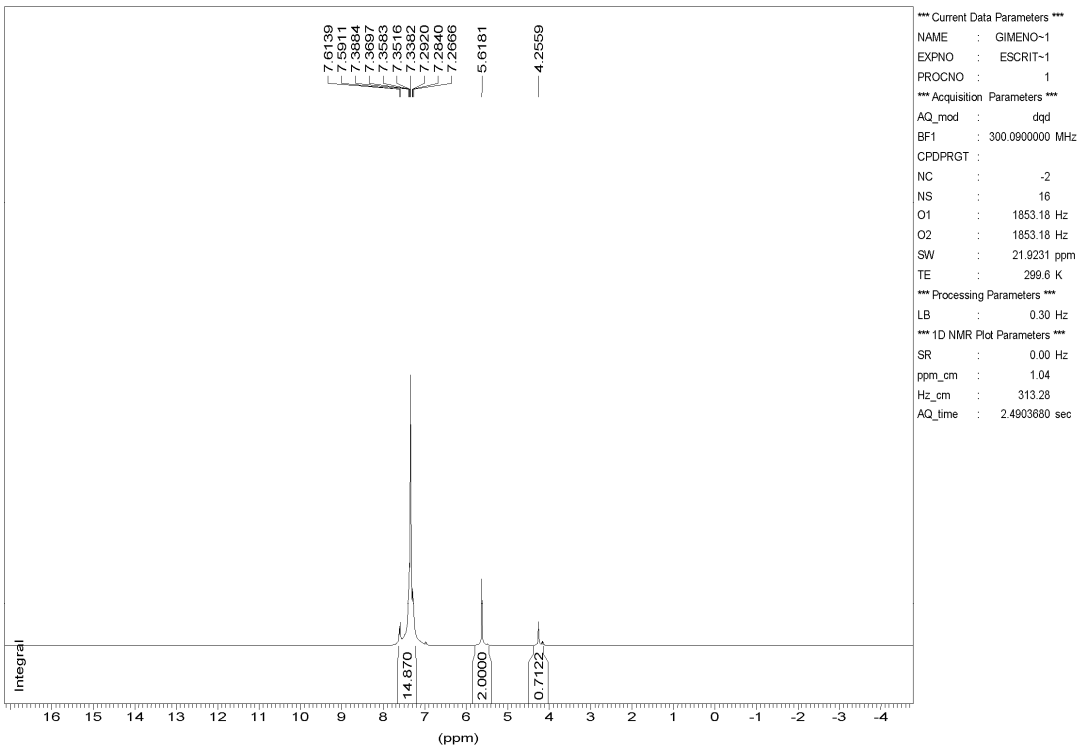


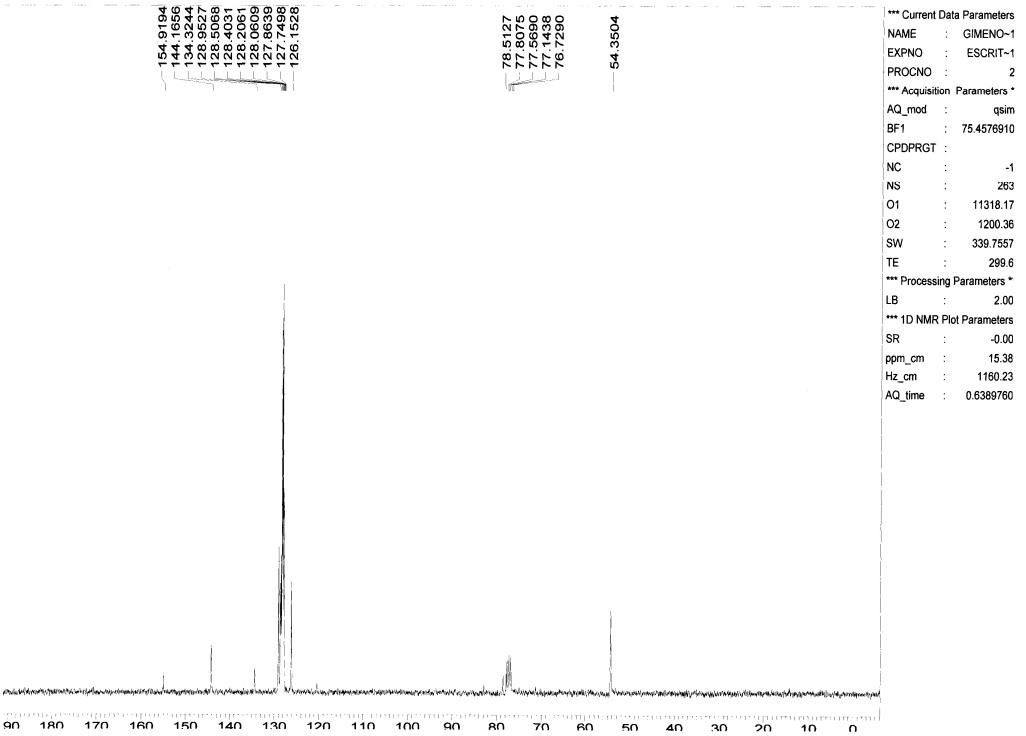




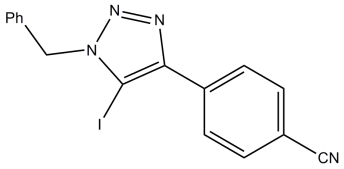
(1-benzyl-5-iodo-1H-1,2,3-triazol-4-yl)diphenylmethanol (8d)

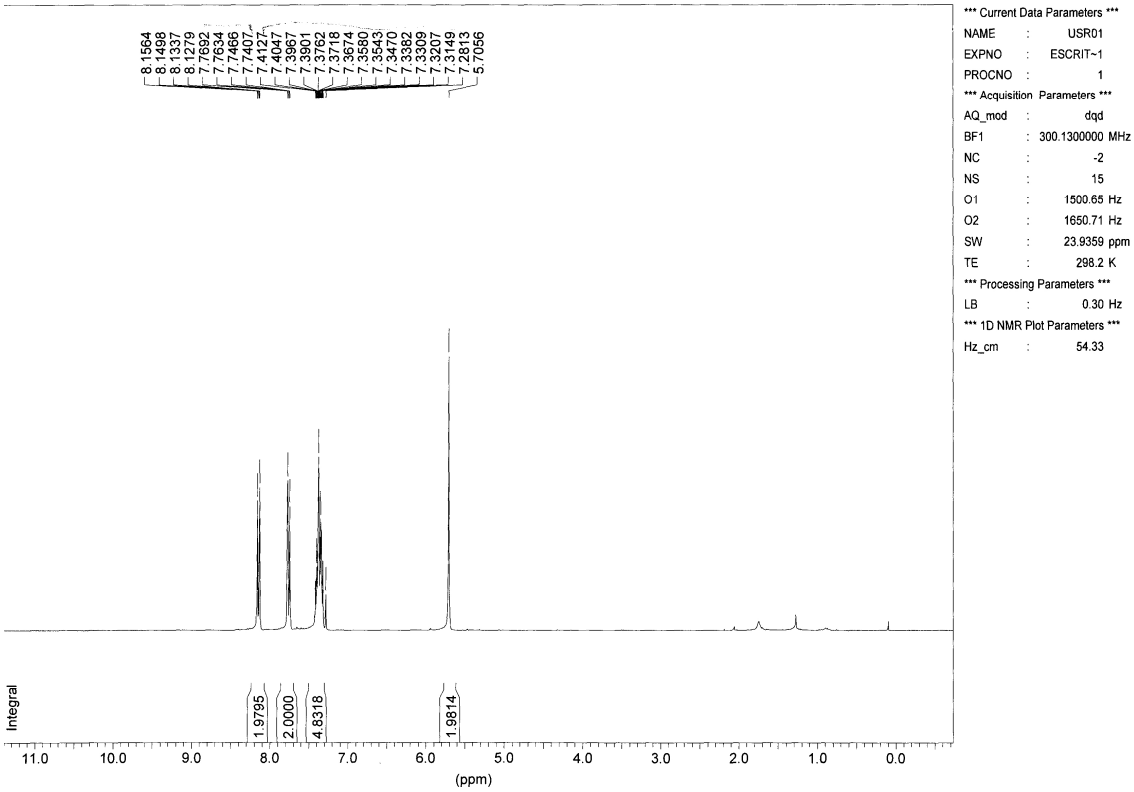


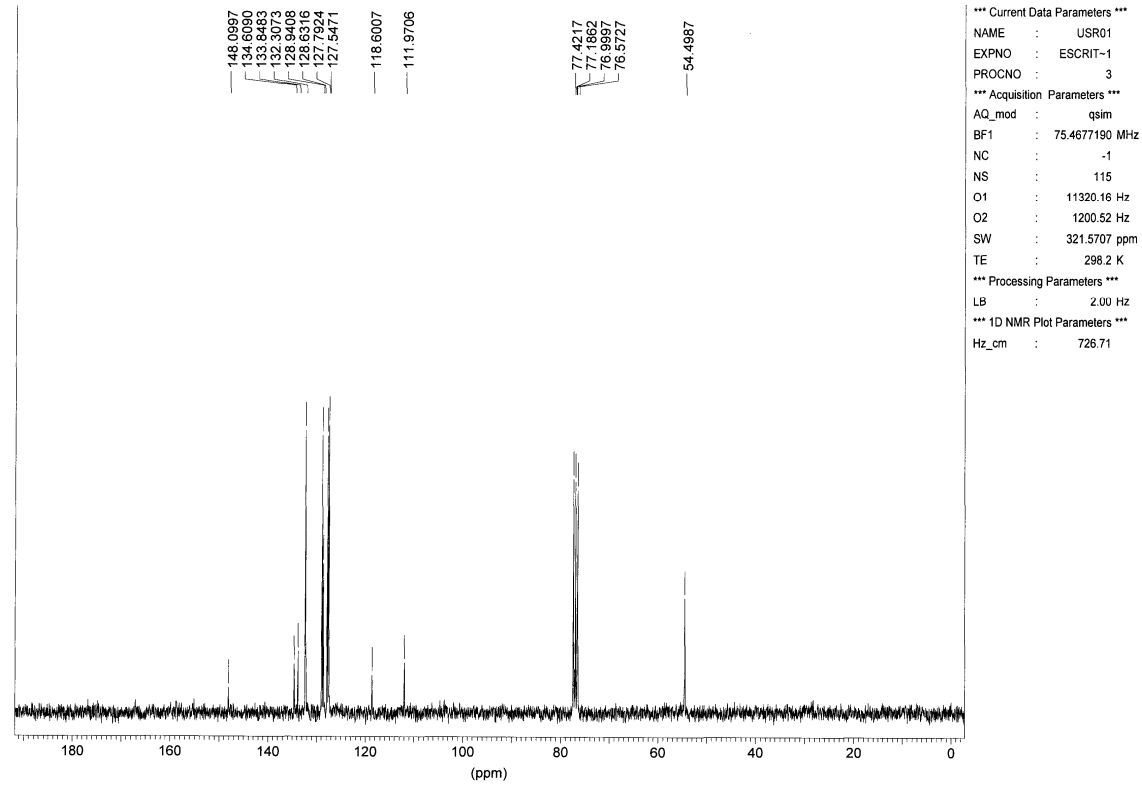




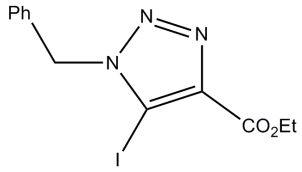
4-(1-benzyl-5-iodo-1H-1,2,3-triazol-4-yl)benzonitrile (8f)

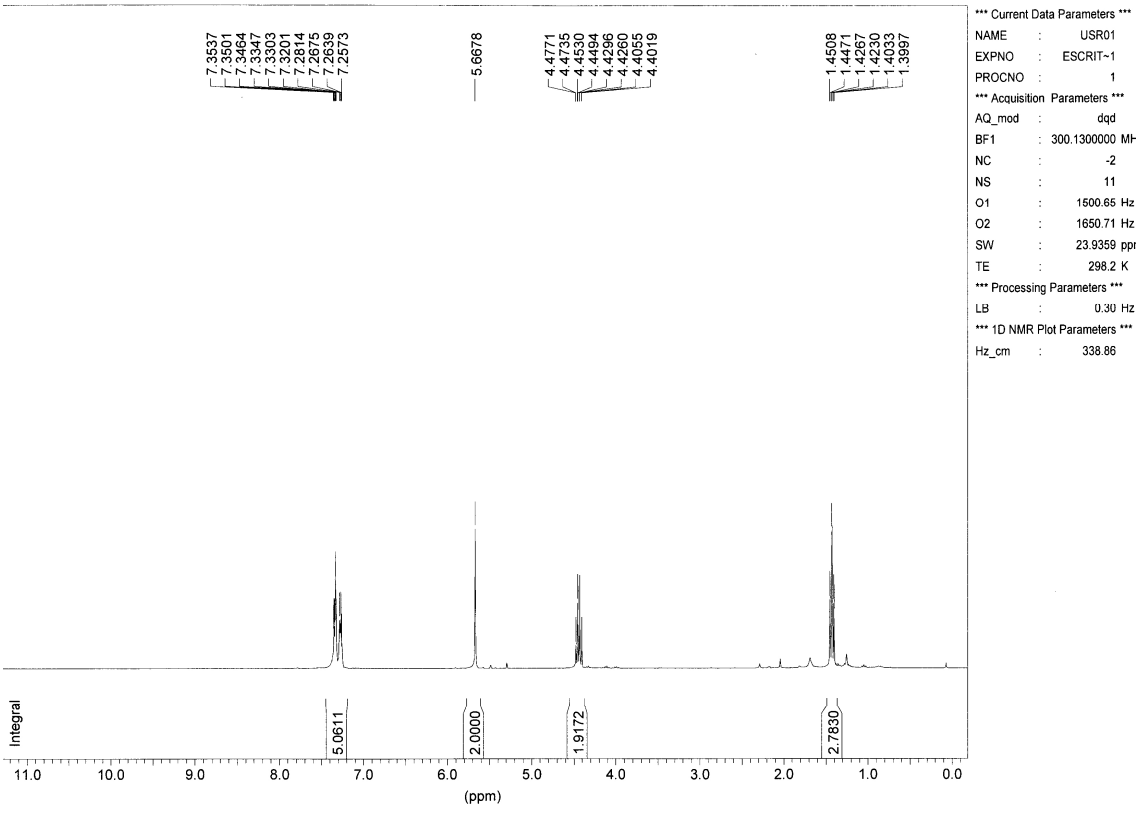




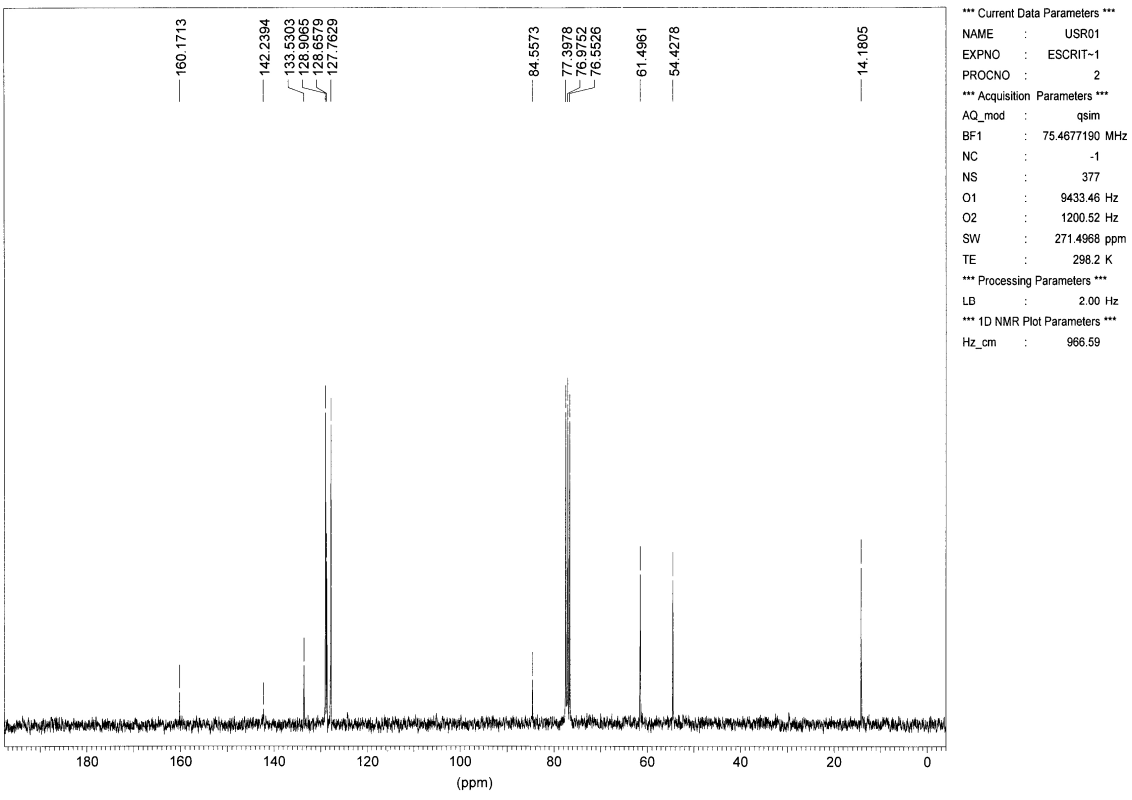


ethyl 1-benzyl-5-iodo-1H-1,2,3-triazole-4-carboxylate (8g)



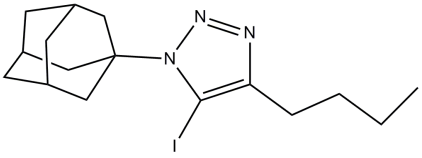


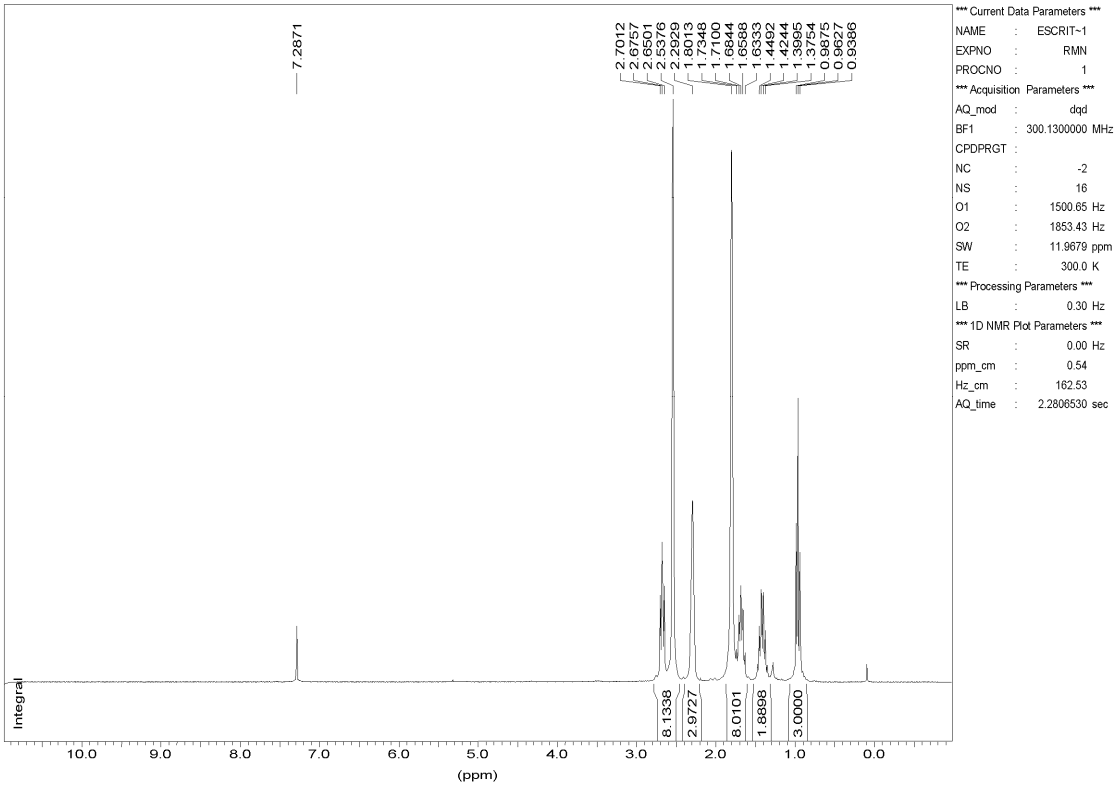
*** Current Data Parameters ***
NAME : USR01
EXPNO : ESCRIT~1
PROCNO : 1
*** Acquisition Parameters ***
AQ_mod : dqd
BF1 : 300.1300000 MH
NC : -2
NS : 11
O1 : 1500.65 Hz
O2 : 1650.71 Hz
SW : 23.9359 ppr
TE : 298.2 K
*** Processing Parameters ***
LB : 0.30 Hz
*** 1D NMR Plot Parameters ***
Hz_cm : 338.86

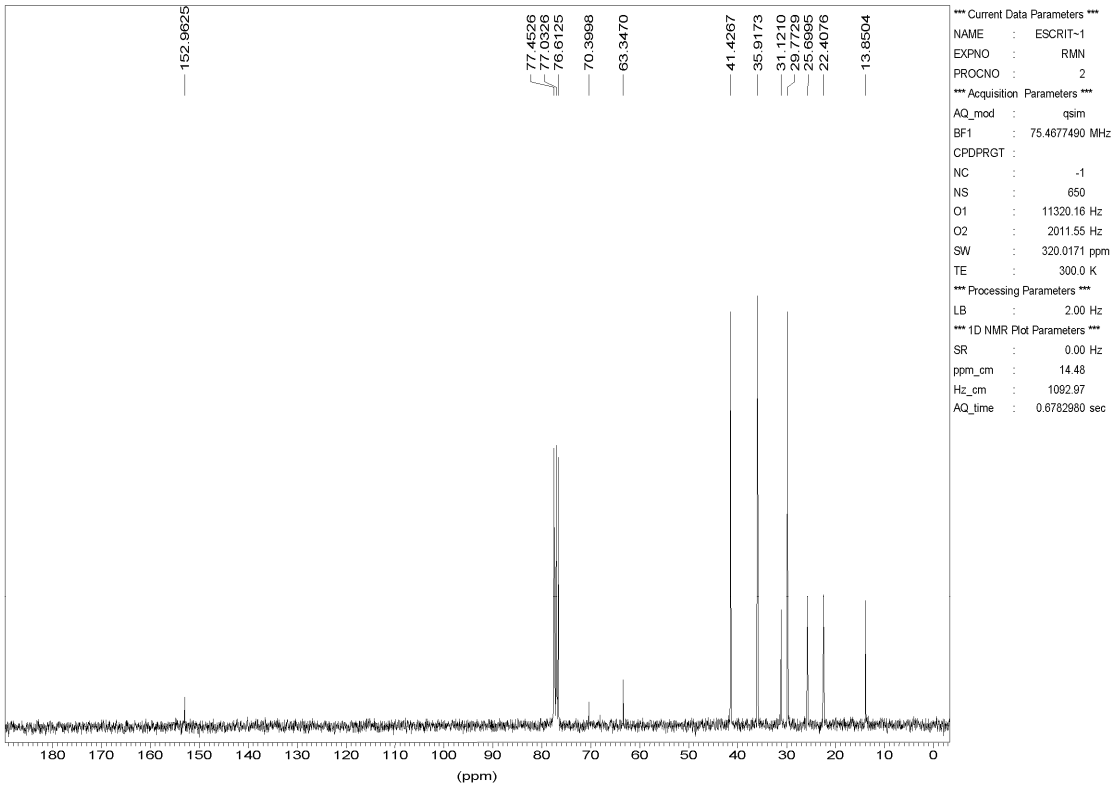


*** Current Data Parameters ***
NAME : USR01
EXPNO : ESCRIT~1
PROCNO : 2
*** Acquisition Parameters ***
AQ_mod : qsim
BF1 : 75.4677190 MHz
NC : -1
NS : 377
O1 : 9433.46 Hz
O2 : 1200.52 Hz
SW : 271.4968 ppm
TE : 298.2 K
*** Processing Parameters ***
LB : 2.00 Hz
*** 1D NMR Plot Parameters ***
Hz_cm : 966.59

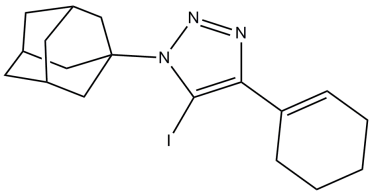
1-adamantyl-4-butyl-5-iodo-1H-1,2,3-triazole (9b)

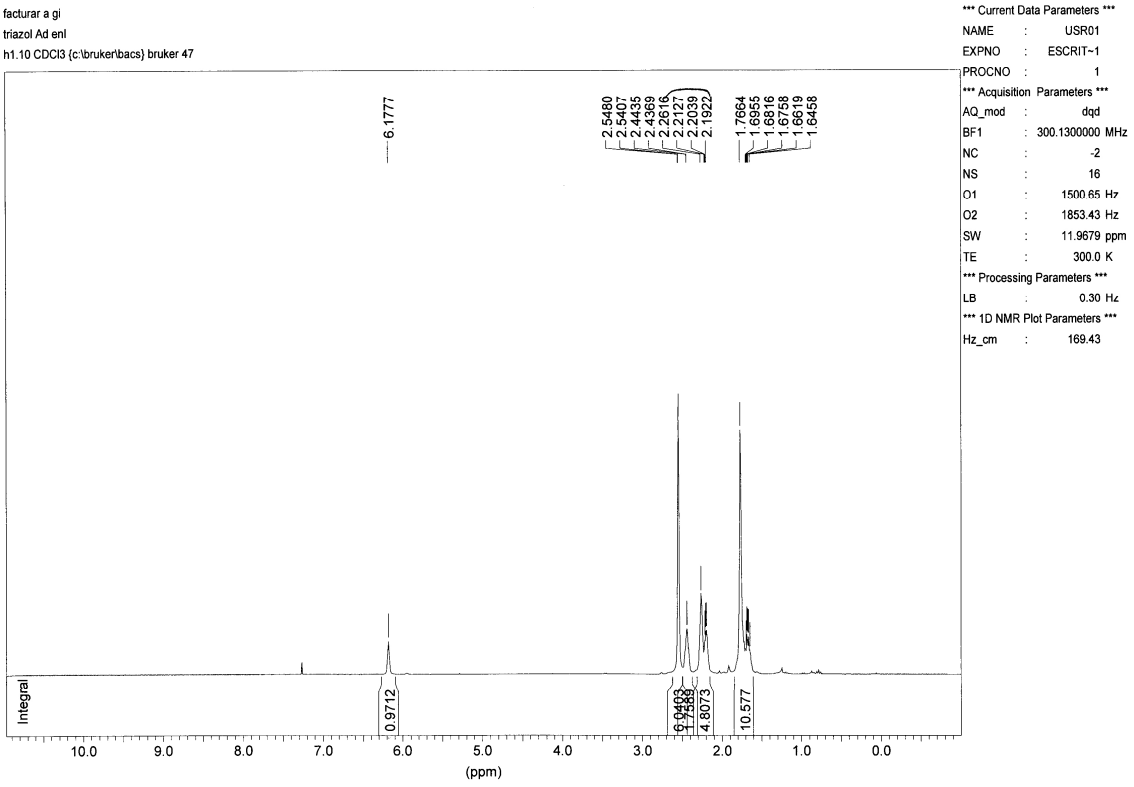


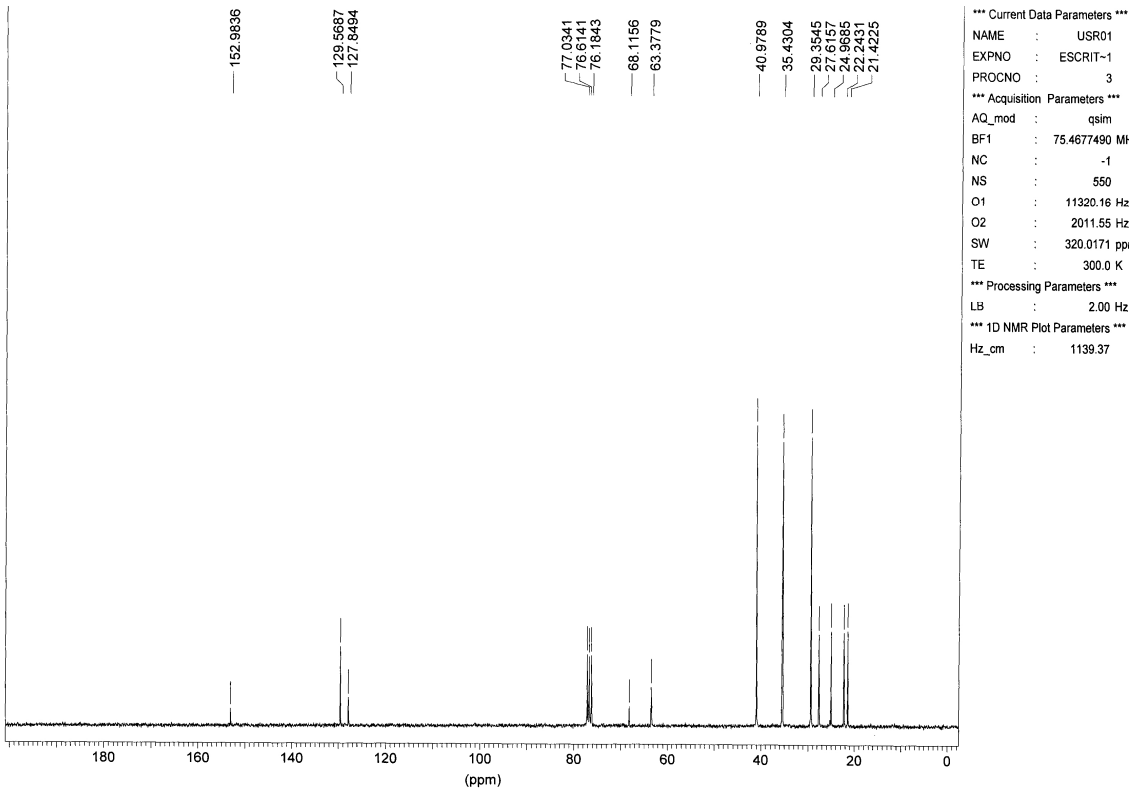




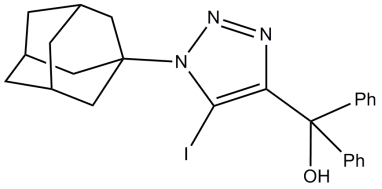
1-adamantyl-4-cyclohexenyl-5-iodo-1H-1,2,3-triazole (9c)

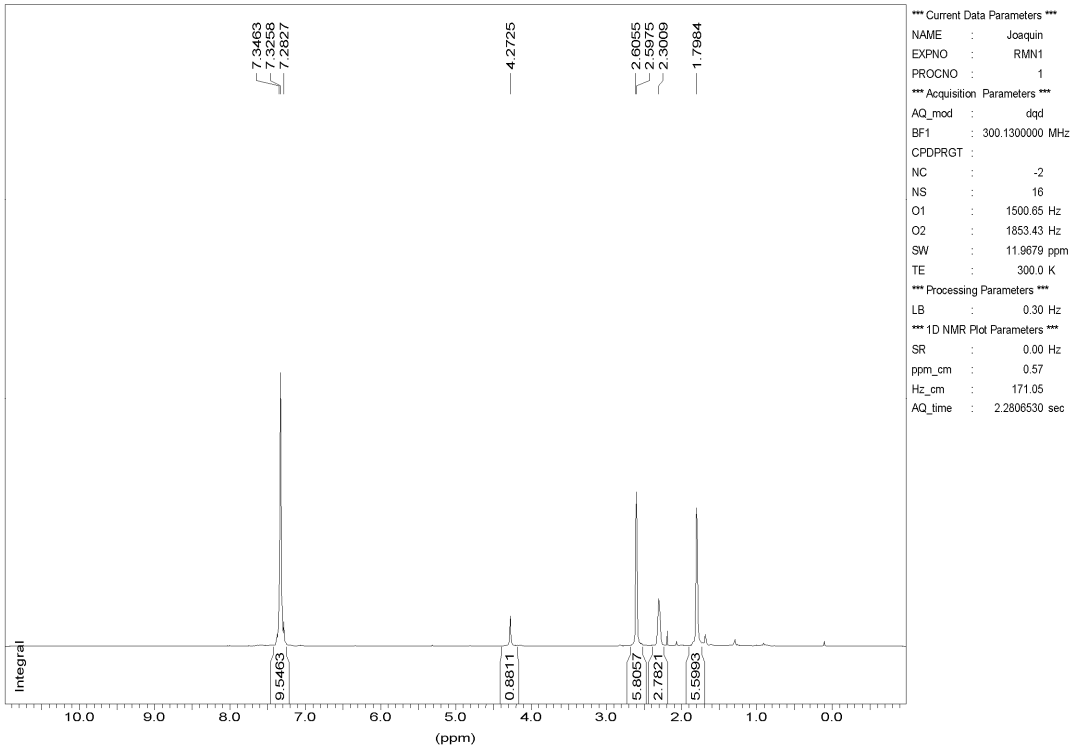


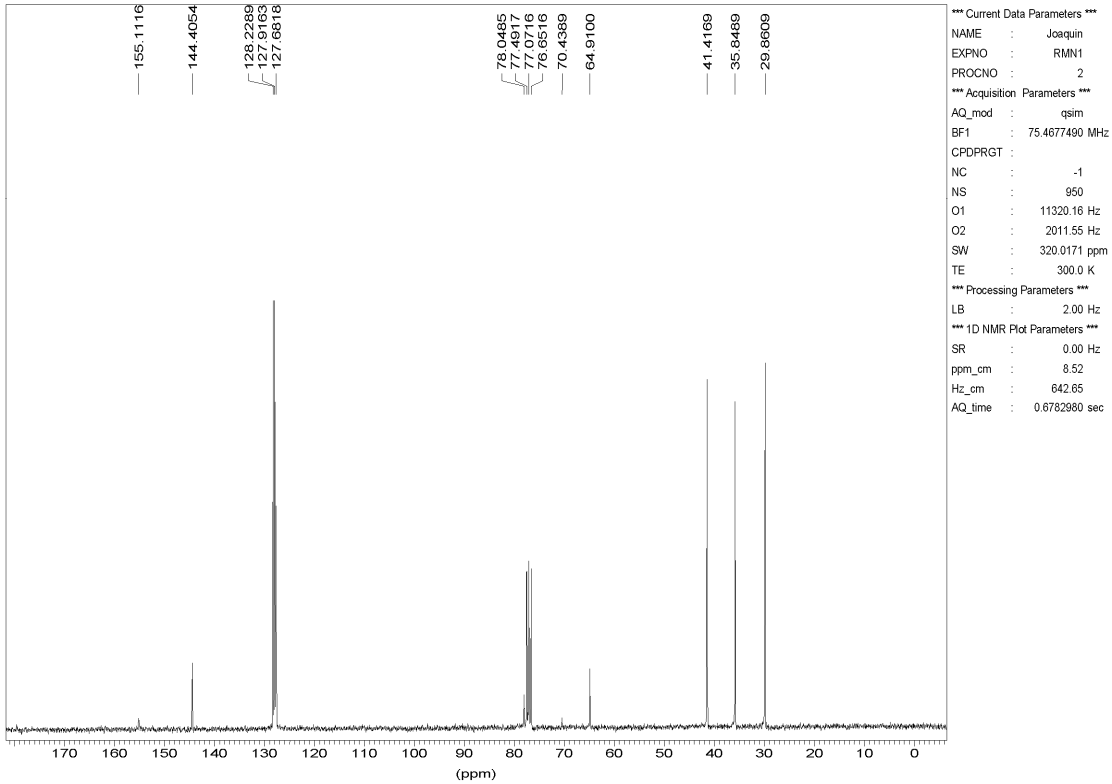




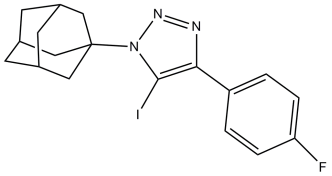
(1-Adamantyl-5-iodo-1-1H-1,2,3-triazol-4-yl)diphenylmethanol (9d)

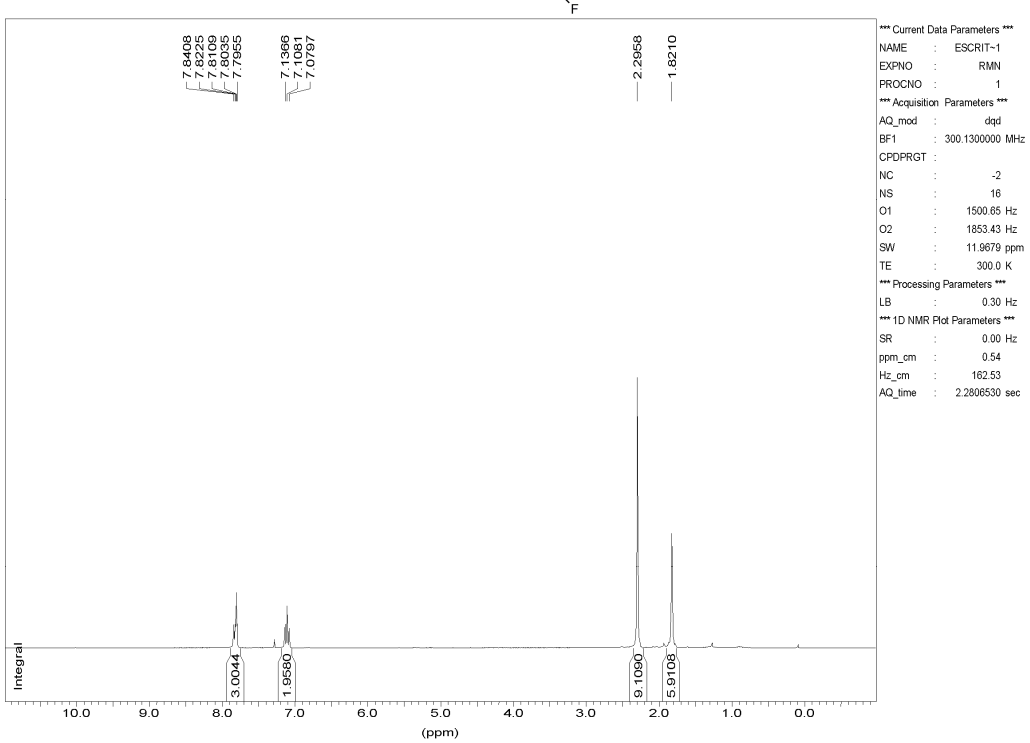


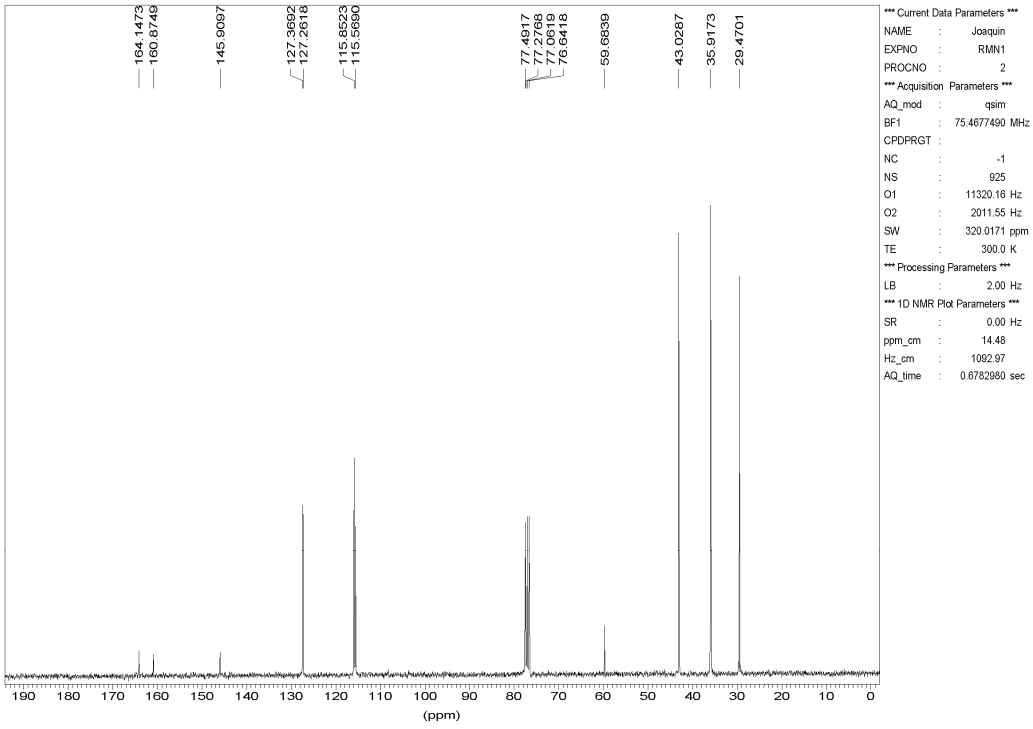




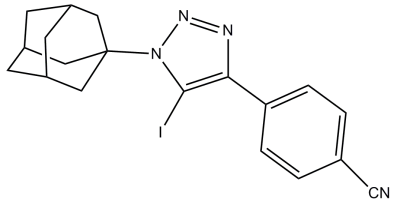
1-adamantyl-4-(4-fluorophenyl)-5-iodo-1H-1,2,3-triazole (9e)

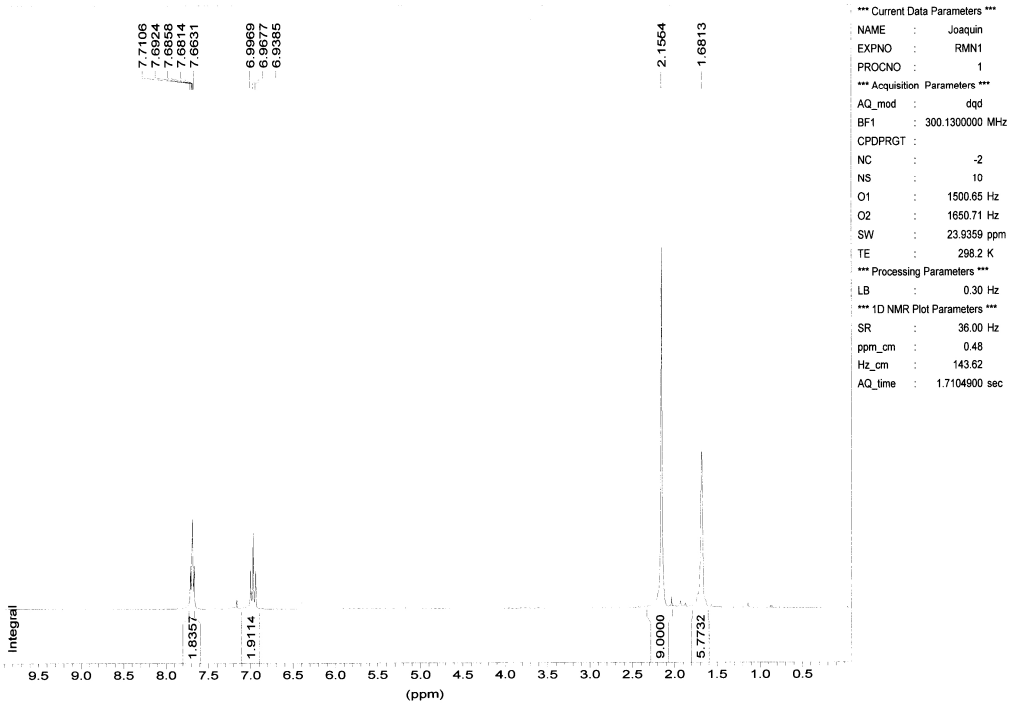




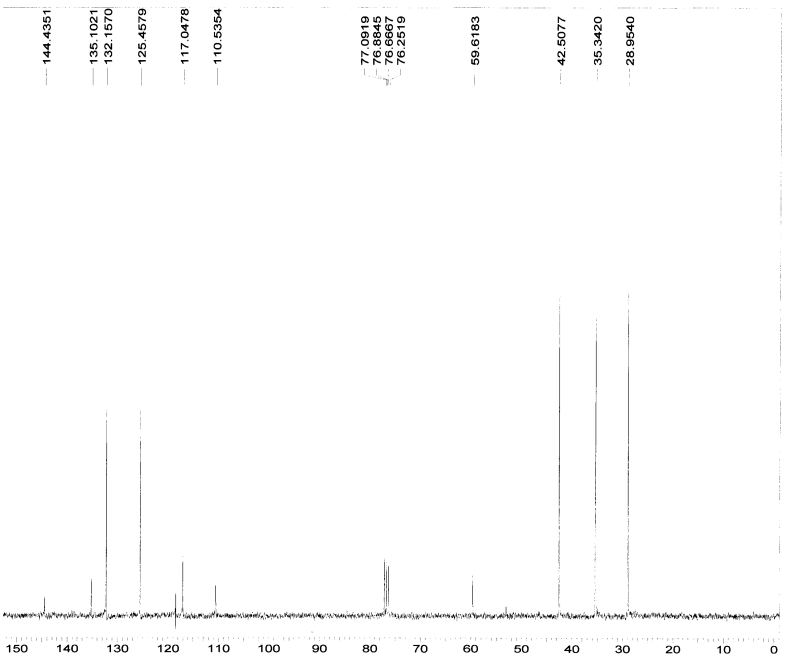


4-(1-adamantyl-5-iodo-1H-1,2,3-triazol-4-yl)benzonitrile (9f)



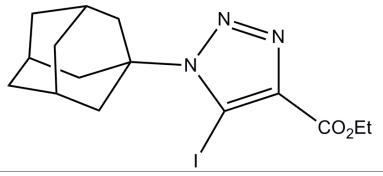


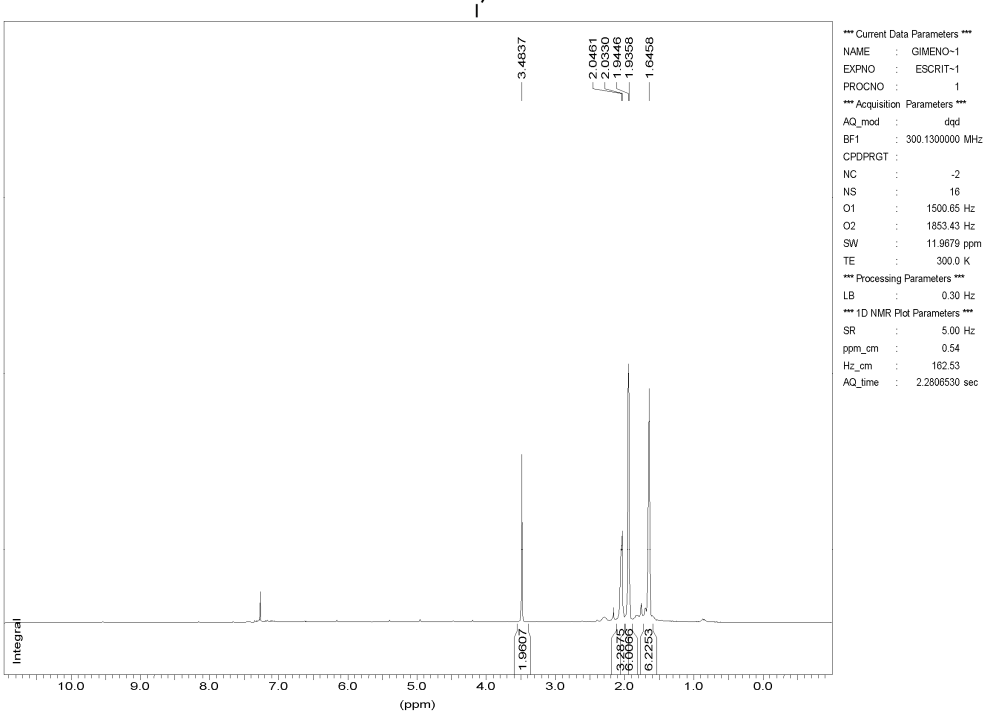
*** Current Data Parameters ***
NAME : Joaquin
EXPNO : RMN1
PROCNO : 1
*** Acquisition Parameters ***
AQ_mod : dqd
BF1 : 300.1300000 MHz
CPDPRGT :
NC : -2
NS : 10
O1 : 1500.65 Hz
O2 : 1650.71 Hz
SW : 23.9359 ppm
TE : 298.2 K
*** Processing Parameters ***
LB : 0.30 Hz
*** 1D NMR Plot Parameters ***
SR : 36.00 Hz
ppm_cm : 0.48
Hz_cm : 143.62
AQ_time : 1.7104900 sec



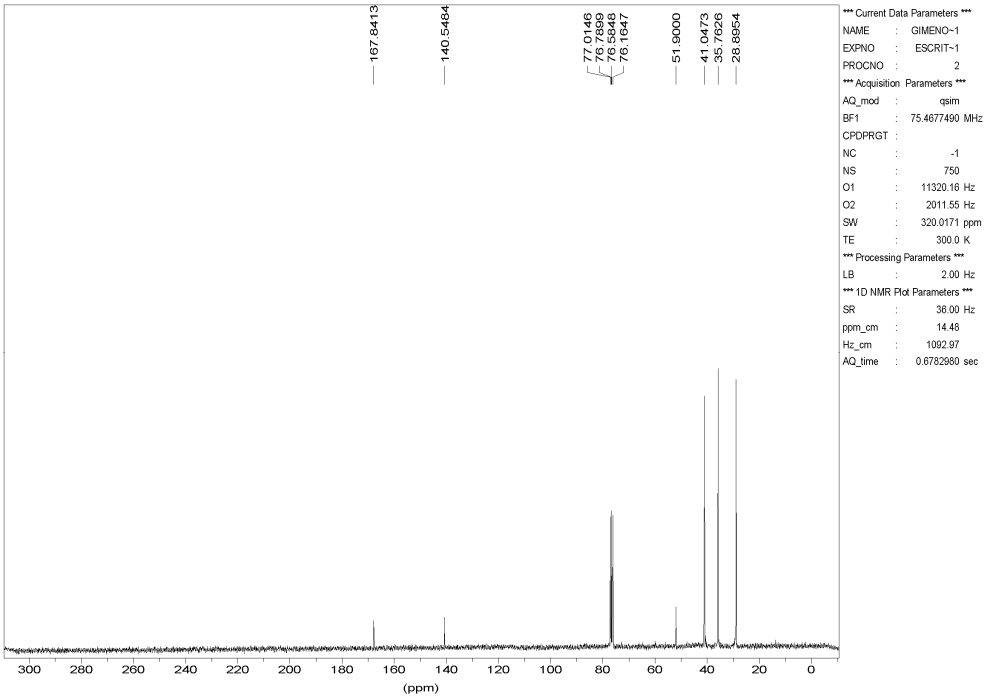
*** Current Data Parameters ***
NAME : Joaquin
EXPNO : RMN1
PROCNO : 3
*** Acquisition Parameters ***
AQ_mod : qsim
BF1 : 75.4576910 MHz
CPDPRGT :
NC : -1
NS : 46
O1 : 11318.17 Hz
O2 : 1200.36 Hz
SW : 339.7557 ppm
TE : 298.9 K
*** Processing Parameters ***
LB : 2.00 Hz
*** 1D NMR Plot Parameters ***
SR : 36.00 Hz
ppm_cm : 7.17
Hz_cm : 541.34
AQ_time : 0.6389760 sec

ethyl 1-adamantyl-5-iodo-1H-1,2,3-triazole-4-carboxylate (9g)





*** Current Data Parameters ***
NAME : GIMENO~1
EXPNO : ESCRIT~1
PROCNO : 1
*** Acquisition Parameters ***
AQ_mod : dqd
BF1 : 300.1300000 MHz
CPDPRGT :
NC : -2
NS : 16
O1 : 1500.65 Hz
O2 : 1853.43 Hz
SW : 11.9679 ppm
TE : 300.0 K
*** Processing Parameters ***
LB : 0.30 Hz
*** 1D NMR Plot Parameters ***
SR : 5.00 Hz
ppm_cm : 0.54
Hz_cm : 162.53
AQ_time : 2.2806530 sec



*** Current Data Parameters ***
NAME : GIMENO~1
EXPNO : ESCRIT~1
PROCNO : 2
*** Acquisition Parameters ***
AQ_mod : qsim
BF1 : 75.4677490 MHz
CPDPRGT :
NC : -1
NS : 750
O1 : 11320.16 Hz
O2 : 2011.55 Hz
SW : 320.0171 ppm
TE : 300.0 K
*** Processing Parameters ***
LB : 2.00 Hz
*** 1D NMR Plot Parameters ***
SR : 36.00 Hz
ppm_cm : 14.48
Hz_cm : 1092.97
AQ_time : 0.6782980 sec

X-Ray Crystal Structure Determination of Compounds 3 and 7a.

Crystals suitable for X-ray diffraction analysis were obtained, for **3**, by slow diffusion of hexane into a saturated solution of the complex in acetone, and for **7a**, by slow evaporation of a saturated solution of the triazole in dichloromethane. The most relevant crystal and refinement data are collected in Table S.I.-2.

For **3** diffraction data were recorded on a Nonius KappaCCD single crystal diffractometer, using Mo-Kα radiation (λ= 0.71073 Å). Images were collected at a 30 mm fixed crystal-detector distance, using the oscillation method, with 1º oscillation and 35 s exposure time per frame. Data collection strategy was calculated with the program Collect[7] (Bruker, **2004**). Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack[8] (Otwinowski & Minor, **1997**). A semi-empirical absorption correction was applied using the program SORTAV[9] (Blessing, **1995**).

For **7a** data collection was performed on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-Kα radiation (λ = 1.5418 Å). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1º oscillation and (1.5 – 3 s) variable exposure time per image. Data collection strategy was calculated with the program CrysAlis Pro CCD.[10] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[10] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[10]

In all cases the software package WINGX[11] was used for space group determination, structure solution and refinement. The structure for the complex **3** was solved by Patterson interpretation and phase expansion using DIRDIF,[12] and for **7a** was solved by direct methods using SIR2004[13]

Isotropic least-squares refinement on F^2 using SHELXL97[14] was performed. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined**.** The H atoms were geometrically located and their coordinates were refined riding on their parent atoms for **3**. For **7a** the coordinates of H atoms were found from different Fourier maps and

included in a refinement with isotropic parameters. The function minimized was $([\Sigma w F_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP\ ]$ (a and b values are collected in Table?) with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}\ (F_o^2, 0) + 2F_c^2)/3$.

Atomic scattering factors were taken from the International Tables for X-Ray Crystallography International.[15] Geometrical calculations were made with PARST.[16] (Nardelli, 1983). The crystallographic plots were made with PLATON.[17]

Table ESI-2 Crystal data and structure refine for compounds **3** and **7a**

	3	**7a**
Empirical formula	$CuC_{20}H_{44}F_6N_8P_5O_4S_2$	$C_{15}H_{12}IN_3S$
Formula weight	857.15	393.24
Temperature/K	293(2)	100(2)
Wavelength/Å	0.71073	1.84184
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/C$
a/Å; α/°	10.4612(2); 80.696(1)	14.5177(2); 90
b/Å; β/°	11.6733(2); 70.225(1)	7.2359(1); 101.588(2)
c/Å; γ/	15.4752(2); 83.182(1)	14.3593(2); 90(1)
Z	2	4
Volume/Å^3	1750.69(5)	1477.68(4)
Calculated density/Mg m^{-3}	1.626	1.768
μ/mm^{-1}	1.045	18.284
F(000)	884	768
Crystal size/mm	0.25 x 0.22 x 0.15	0.055 x 0.112 x 0.198
θ range/°	1.41 to 25.39	3.11 to 73.87
Index ranges	$-11 \le h \le 12$, $-13 \le k \le 14$, $0 \le l \le 18$	$-17 \le h \le 17$, $-7 \le k \le 8$, $-17 \le l \le 12$
No. of reflns. collected	6395	6667
No. of unique reflns.	6394 (R(int) = 0.0000]	2903 (R(int) = 0.0297]
Completeness to θ_{max}	99.2	97.4
No. of parameters/restraints	419/0	229/0
Goodness-of-fit on F^2	1.166	1.038
Weight function (a, b)	0.0803, 0.4186	0.0748, 0
R_1 $[I > 2\sigma(I)]^a$	0.0420	0.0357
wR_2 $[I > 2\sigma(I)]^a$	0.1269	0.0.0959
Largest diff. peak and hole/e Å^{-3}	1.232 and -1.047	0.928 and -1.786

[a] $R_1 == \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

References

(1) a) D. J. Daigle, A. B. Pepperman Jr., S. L. Vail *Heterocycl. Chem.* 1974, **11**, 407. b) For the synthesis of compound **2** we followed the experimental procedure previously described by Majoral and co-workers for the preparation of PTA iminophosphorane derivatives in: M. Benhammou, R. Kraemer, H. Germa, J. P. Majoral, J. Navech, *Phosphorus and Sulfur,* 1982, **14**, 105.

(2) A. A. Khodak, V. A. Gilyarov, M. I. Kabachnik, *Zh. Obshch. Kim.* 1974, **44**, 27.

(3) R. F. C. Brown, F. W. Eastwood, K. J. Harrington, G. L. McMullen, *Aust. J. Chem.* 1974, **27**, 2393.

(4) a) G. Garcia-Muñoz, R. Madroñero, M. Rico, M. C. Saldaña, *J. Heterocycl. Chem.*, 1969, **6**, 921. b) G. M. Pawar, B. Bantu, J. Weckesser, S. Blechert, K. Wurst, M. R. Buchmeiser, *Dalton Trans.*, 2009, 9043. c) N. Candelon, D. Lastécouères, A. K. Diallo, J. Ruiz Aranzaes, D. Astruc, J.-M Vincent, *Chem. Commun.*, 2008, 741. d) J. Deng, Y. Wu, Q.-Y. Chen, *Synthesis* 2005, 2730. e) I. S. Park, M. S. Kwon, Y. Kim, J. S. Lee, J. Park, *Org. Lett.*, 2008, **10**, 497. f) S. T. Abu-Orabi, M. Adnan Atfah, I. Jibril, F. M. Mari'i, A. Al-Sheikh Ali, *J. Heterocycl. Chem.*, 1989, **26**, 1461. g) T. Sasaki, S. Eguchi, M. Yamaguchi, T. Esaki, *J. Org. Chem.*, 1981, **46**, 1800. h) K. Kamata, Y. Nakagawa, K. Yamaguchi, N. Mizuno, *J. Am. Chem. Soc.*, 2008, **130**, 15304.

(5) a) 1-iodo-phenylacetylene: J. E. Hein, J. C. Tripp, L. B. Krasnova, K. B. Sharpless, V. V. Fokin, *Angew. Chem. Int. Ed.*, 2009, **48**, 8018. b) 1-iodo-hexyne and 1-fluoro-4-(iodoethynyl)benzene: J. Yan, J. Li, D. Cheng, *Synlett*, 2007, 2442. c) 1-(iodoethynyl)cyclohex-1-ene: F. Bellina, A. Carpita, L. Mannocci, R. Rossi, *Eur. J. Org. Chem.*, 2004, 2610. d) G. Jaeger, E. Klauke, W. Brandes, P. E. Frohberger, *Ger. Offen.*, 1979, 23. e) 4-(iodoethynyl)benzonitrile: H. Abe, H. Suzuki, *Bull. Chem. Soc. Japan*, 1999, **72**, 787. f) ethyl 3-iodopropiolate: T. Jefrey, *J. Chem. Soc., Chem. Commun.* 1988, 909.

(6) P. Dinér, T. Andersson, J. Kjellén, K. Elbing, S. Hohmann, M. Grøtli, *New J. Chem.*, 2009, 1010.

(7) Bruker 2004. *Collect* data collection software. Bruker AXS, Delft, The Netherlands.

(8) Z. Otwinowski, W. Minor, *Methods Enzymol.,* 1997, **276**, 307.

(9) SORTAV. R.H. Blessing, *Acta Cryst.* 1995, **A51**, 33.

(10) *CrysAlis^{Pro} CCD, CrysAlis^{Pro} RED.* Oxford Diffraction Ltd., Abingdon, Oxfordshire, U.K. 2008.

(11) L. Farrugia, J. *J. Appl. Crystallogr.* 1999, **32**, 837.

(12) P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *The DIRDIF Program System*; Technical Report of the Crystallographic Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1999.

(13) M. C. Burla, R. Caliandro, M Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *SIR2004, J. Appl. Cryst.* 2005, **38**, 381.

(14) G. M. Sheldrick, *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(15) *Tables for X-Ray Crystallography*; Kynoch Press; Birminghan, U.K., 1974; Vol. IV (present distributor: Kluwer Academic Publishers; Dordrecht, The Netherlands).

(16) PARST . M. Nardelli, *Comput. Chem.* 1983, **7**, 95.

(17) A. L. Spek, *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht, The Netherlands, 2007.