Supplementary information

for

Dual H-bond activation of NHC-Au(I)-Cl complexes with amide functionalized side-arms assisted by H-bond donor substrates or acid additives

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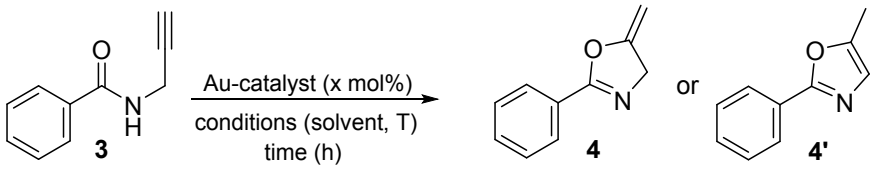
General remarks

Unless otherwise specified, all commercial materials were used as received without further purification. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded using Bruker Avance Neo 400 and 500 spectrometers. ^{1}H spectra were referenced to tetramethylsilane (TMS, 0.0 ppm) or to CD_2Cl_2 (5.32 ppm) and are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = heptet, m = multiplet). Chemical shifts of the $^{13}C\{^{1}H\}$ NMR spectra were measured relative to $CDCl_3$ (77.16 ppm), CD_2Cl_2 (53.84 ppm) or to d_6-DMSO (39.52 ppm). HR-Mass spectral data was acquired with Bruker Daltonics microTOF LC spectrometer. Water content in CD_2Cl_2 was measured with Mettler Toledo DL32 Karl Fischer Coulometer. Column chromatographic purifications were performed on Merck Silica gel 60 (230 – 400 mesh). The eluent is quoted in volume ratios (v1:v2). Analytical thin-layer chromatography analysis (TLC) was performed on silica gel 60 F 254 precoated plates (0.25 mm thickness) visualized with UV light at 254 nm.

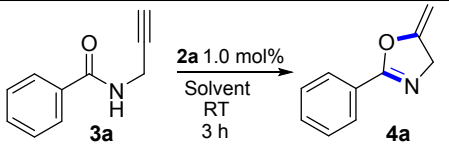
Table S1. Au-catalyzed cycloisomerization of *N*-(prop-2-yn-1-yl)benzamide **3** to oxazoline **4** (or oxazole **4'**) in literature



Entry[ref]	Catalysts (loading)	Conditions		Time (h)	Yield (%) of **4**
		Solvent	Temp (°C)		
1[1]	$AuCl_3$ (5 mol%)	CH_2Cl_2	20	12	>95 (**4'**)
2[1]	$AuCl_3$ (5 mol%)	MeCN	45	15	>95 (**4'**)
3[2]	IPrAuCl, $AgNTf_2$ (0.5 mol%)	CD_2Cl_2	r.t.	24	92
4[3]	PPh_3AuNTf_2 (2 mol%)	CH_2Cl_2	r.t.	24	91
5[4]	[(IPr)Au(Pyr)](PF_6) (5 mol%)	CH_2Cl_2 (dry)	r.t	4	77
6[5]	$IPrAuNTf_2$ (5 mol%), $Fe(acac)_3$(20 mol%)	Acetone	r.t	12	77
7[6]	bis-*N*,*N*'-(9-alkylfluorenyl)NHC$AuCl_3$, $AgNTf_2$ (2 mol%)	CH_2Cl_2	r.t	15	87 (79:8; **4**:**4'**)
8[7]	phosphine/H-bond donor amide ligand AuCl (5 mol%)	CH_2Cl_2	r.t	24	36
9[8]	ArBISKITPHOSAuCl, AgOTf (2 mol%)[a]	CH_2Cl_2	r.t.	1.5	98
10[9]	Unsymmetrical Au(I) NHC complex, $AgNTf_2$ (0.1 mol%)	CD_2Cl_2	r.t.	7 days	97
11[10]	P_2W-Ph_3PAuCl/H_5 (2 mol%)	CH_2Cl_2	r.t.	3	91
12[11]	(Ph_3P)AuCl, Na[$Me_3NM_{12}Cl_{11}$] (2 mol%)	CD_2Cl_2	r.t.	3	92
13[12]	Boron organo-Au(I) (2 mol%)	CH_2Cl_2	r.t.	11	98
14[13]	JohnPhos-Au-Ts[$C(CN)_2$] (4 mol%) JohnPhos-AuCl, AgOTf (4 mol%)	CH_2Cl_2	70	3 1	83 84
15[14]	MIC-AuCl (1 mol%), $AgSbF_6$ (1 mol%)[b] or $Cu(OTf)_2$ (5 mol%)	CH_2Cl_2	r.t.	62	94 92
16[15]	SBA-15@$Ph_3PAuOTf$ (2 mol%)	CH_2Cl_2	r.t	1.5	98
17[16]	HAAC-AuCl, $AgPF_6$ (0.1 mol%)[c]	CD_2Cl_2	r.t.	3 days	88
18[17]	T-Shaped Gold→Stiborane Complex-SbF_6 (3 mol%)	$CDCl_3$	r.t.	7.5	100
19[4]	[(IPr)$AuCl_2$(Pyr)](PF_6) (5 mol%)	CH_2Cl_2(dry)	45	12	76 (7:93; **4**:**4'**)
20[4]	[(I^tBu)$AuCl_2$(Pyr)](PF_6) (5 mol%)	CH_2Cl_2(dry)	45	1.5	75 (37:63; **4**:**4'**)

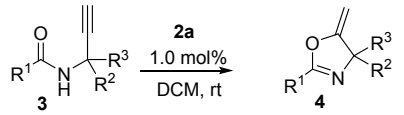
a) KITPHOS= 12-phenyl-9,10-dihydro-9,10-ethenoanthracene phosphine
b) MIC= 1,2,3-Triazol-5-ylidenes mesoionic carbine
c) HAAC= Hydrazino Amino Acyclic Carbene

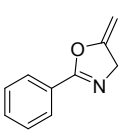
Table S2 Solvent screening



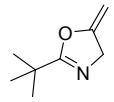
Entry	Solvent	Yield[a] [%] of **4a**
1	CD_2Cl_2	95
2	$CDCl_3$	84
3	d_8-Toluene	22
4	d_6-Acetone	trace
5	CD_3OD	trace
6	CD_3CN	trace

[a] Determined by ^{1}H NMR using trimethoxybenzene as internal standard.

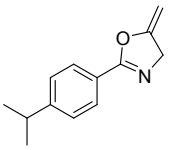




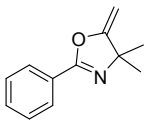
4a: 98%, 3 h



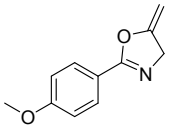
4b: 98%, 2 h



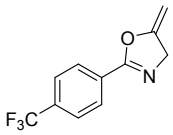
4c: 93%, 3 h



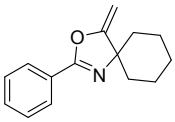
4d: 94%, 5 h



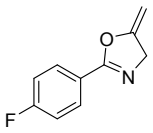
4e: 89%, 24 h



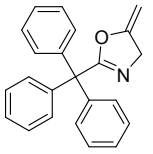
4f: 21%, 4 h



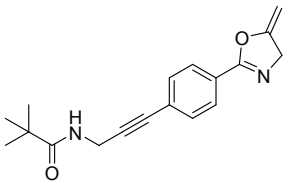
4h: 97%, 7 h



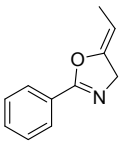
4i: 83%, 8 h



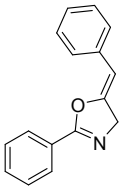
4g: 96 %, 20 h



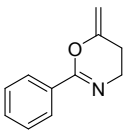
4j: 93%, 24 h[a]



4k: no reaction



4l: no reaction



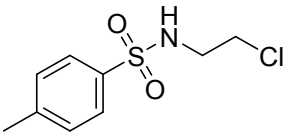
4m: no reaction

Scheme S1. Complete substrate scope in oxazoline synthesis with isolated yields. [a] Catalyst loading 3.0 mol%. [b] Water content in all reactions 150 ppm.

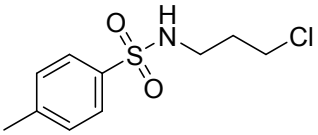
Synthesis of amides and sulfonamides

General procedure

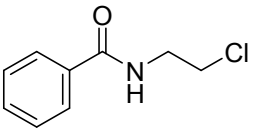
2-Chloroethyl or 2-chloropropyl amine hydrochloride and the corresponding acid chloride (1.1 equiv.) were dissolved in DCM (10 ml). Triethylamine (2.1 equiv.) was added dropwise on ice bath. The reaction was stirred for 4 hours in room temperature. The mixture was diluted with 20 ml of DCM, washed with aqueous NH_4Cl and $NaHCO_3$ solutions and dried with $MgSO_4$. After evaporating the solvent, the product was used without further purification or was purified by flash chromatography with hexane and ethyl acetate (5:1) as eluent.



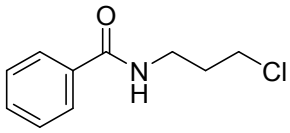
N-(2-chloroethyl)-4-methylbenzenesulfonamide (S1). Product was used without further purification. Pale yellow solid, yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.32 (dd, *J* = 8.6, 0.8 Hz, 2H), 5.05 (t, *J* = 6.7 Hz, 0H), 3.55 (t, *J* = 5.8 Hz, 2H), 3.30 (q, *J* = 6.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.95, 136.98, 130.00, 127.16, 44.77, 43.66, 21.67. Spectral data in accordance with literature.[18]



N-(2-chloropropyl)-4-methylbenzenesulfonamide (S2). Product was used without further purification. Colorless oil, yield 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 4.73 (s, 1H), 3.56 (t, *J* = 6.2 Hz, 2H), 3.11 (t, *J* = 6.6 Hz, 2H), 2.43 (s, 3H), 1.94 (p, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.74, 136.80, 129.93, 127.20, 41.95, 40.48, 32.34, 21.65. Spectral data in accordance with literature.[18]



N-(2-chloro-ethyl)-benzamide (S3). Product was purified by flash chromatography with hexane and ethyl acetate (5:1) as eluent. Pale yellow solid, yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.57 – 7.47 (m, 1H), 7.49 – 7.39 (m, 2H), 6.68 (s, 1H), 3.83 – 3.77 (m, 2H), 3.73 (ddd, *J* = 6.2, 5.0, 1.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.79, 134.19, 131.88, 128.77, 127.10, 44.21, 41.80. The spectral data is in accordance with literature.[19]



N-(2-chloro-propyl)-benzamide (S4). Product was purified by flash chromatography with hexane and ethyl acetate (5:1) as eluent. White solid, yield 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.71 (m, 2H), 7.56 – 7.44 (m, 1H), 7.45 – 7.35 (m, 2H), 6.70 (s, 1H), 3.66 – 3.56 (m, 4H), 2.10 (p, *J* = 6.5 Hz, 2H).

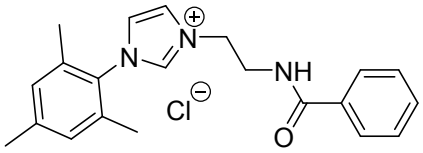
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.95, 134.47, 131.62, 128.66, 127.01, 42.81, 37.75, 32.15.

MS (ESI, positive mode): calcd. for $[C_{10}H_{13}ClNO, M+H]^+$ m/z 198.0680; found 198.0680.

Synthesis of imidazole salts **L1a**, **L1b**, **L2a** and **L2b**

General procedure

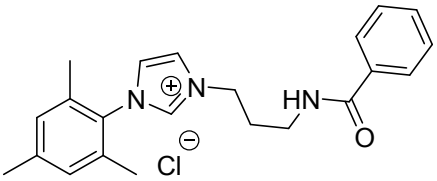
2,4,6-Trimethylphenylimidazole (1.2 equiv.) and corresponding chloride were refluxed in toluene for 2 days. Reaction mixture was cooled down to room temperature and the precipitated salt was filtered and washed with toluene. The salt was used without further purification or was purified by flash chromatography with DCM and methanol (10:1) as eluent.



Imidazole salt L1a. The product was used without further purification. Pale white solid, yield 68%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (d, *J* = 7.0 Hz, 1H), 9.35 (t, *J* = 5.8 Hz, 1H), 8.10 (t, *J* = 6.3 Hz, 2H), 8.00 (d, *J* = 10.6 Hz, 1H), 7.40 (dtd, *J* = 36.8, 7.4, 4.9 Hz, 3H), 7.05 (q, *J* = 1.9 Hz, 1H), 6.88 (d, *J* = 4.1 Hz, 2H), 5.10 (q, *J* = 4.9 Hz, 2H), 4.11 (p, *J* = 5.5 Hz, 2H), 2.28 (s, 3H), 1.81 (s, 6H).

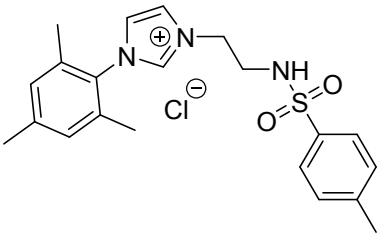
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.82, 141.35, 138.28, 134.26, 132.84, 131.68, 130.58, 129.76, 128.38, 127.90, 123.69, 123.04, 49.09, 39.06, 21.10, 17.20.

MS (ESI, positive mode): calcd. for $[C_{21}H_{24}N_3O, M\text{-}Cl]^+$ m/z 334.1914; found 334.1902

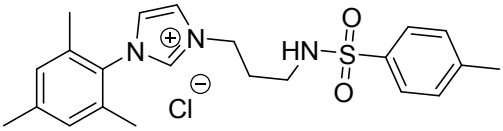


Imidazole salt L1b. Product was purified by flash chromatography with dichloromethane and methanol (10:1) as eluent. Pale brown solid, yield 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (t, *J* = 1.6 Hz, 1H), 9.25 (t, *J* = 5.7 Hz, 1H), 8.14 – 8.07 (m, 2H), 8.05 (t, *J* = 1.7 Hz, 1H), 7.41 – 7.27 (m, 3H), 7.06 (t, *J* = 1.7 Hz, 1H), 6.93 (s, 2H), 4.68 (t, *J* = 6.0 Hz, 2H), 3.47 (q, *J* = 5.7 Hz, 2H), 2.43 – 2.31 (m, 2H), 2.28 (s, 3H), 1.98 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.34, 141.42, 138.58, 134.28, 133.82, 131.40, 130.82, 129.98, 128.39, 127.98, 123.71, 123.21, 48.01, 35.91, 30.82, 21.20, 17.61.
MS (ESI, positive mode): calcd. for $[C_{22}H_{26}N_3O, M\text{-}Cl]^+$ m/z 348.2070; found 348.2055



Imidazole salt L2a. Product was purified by flash chromatography with dichloromethane and methanol (10:1) as eluent. Pale brown solid, yield 85%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (t, *J* = 1.5 Hz, 1H), 8.43 (t, *J* = 6.2 Hz, 1H), 8.20 (t, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 1.8 Hz, 1H), 6.95 (s, 2H), 4.94 – 4.76 (m, 2H), 3.37 (q, *J* = 6.3 Hz, 2H), 2.36 (s, 3H), 2.32 (s, 3H), 2.05 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.39, 141.57, 138.94, 137.12, 134.72, 130.77, 130.00, 129.87, 127.06, 123.33, 123.17, 49.03, 42.84, 21.64, 21.26, 17.76.
MS (ESI, positive mode): calcd. for $[C_{21}H_{26}N_3O_2S, M\text{-}Cl]^+$ m/z 384.1740; found 384.1725.

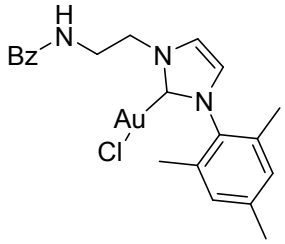


Imidazole salt L2b. Product was purified by flash chromatography with dichloromethane and methanol (10:1) as eluent. Brown solid, yield 51%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (t, *J* = 1.6 Hz, 1H), 8.05 (t, *J* = 1.8 Hz, 1H), 7.98 (t, *J* = 6.0 Hz, 1H), 7.84 – 7.73 (m, 2H), 7.23 (dd, *J* = 8.5, 0.8 Hz, 2H), 7.13 (t, *J* = 1.8 Hz, 1H), 6.98 (s, 2H), 4.80 (t, *J* = 6.3 Hz, 2H), 2.99 (q, *J* = 5.5 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H), 2.32 – 2.26 (m, 2H), 2.04 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00, 141.32, 138.56, 137.14, 134.54, 130.92, 129.94, 129.73, 127.28, 123.56, 123.28, 47.89, 39.61, 30.34, 21.64, 21.24, 17.71.
MS (ESI, positive mode): calcd. for $[C_{22}H_{28}N_3O_2S, M\text{-}Cl]^+$ m/z 398.1897; found 398.1886.

Synthesis of NHC-Au(I) complexes

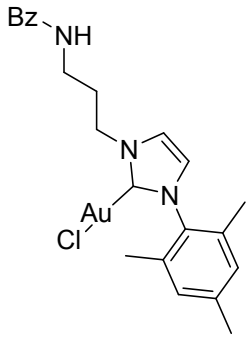
General procedure

The corresponding imidazole salt and Ag_2O (0.7 equiv.) were stirred in DCM at room temperature for 6 hours. Me_2SAuCl (1.0 equiv.) was added and the mixture was stirred at room temperature for 2 hours. After evaporating most of the solvent, hexane was added and the pure product precipitated. Product was collected by filtration and dried in vacuo.



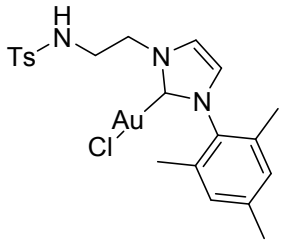
Gold complex 1a. Pale yellow solid, yield 86%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.81 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.59 – 7.47 (m, 1H), 7.43 (tt, *J* = 6.6, 1.6 Hz, 2H), 7.33 (d, *J* = 2.0 Hz, 1H), 6.98 (s, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.79 (t, *J* = 6.0 Hz, 1H), 4.55 (t, *J* = 6.0 Hz, 2H), 3.97 (q, *J* = 6.0 Hz, 2H), 2.34 (s, 3H), 1.91 (s, 6H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.06, 167.76, 140.16, 135.36, 135.19, 134.05, 132.08, 129.55, 128.93, 127.48, 122.88, 121.79, 51.04, 40.54, 21.26, 17.86.
MS (ESI, positive mode): calcd. for $[C_{21}H_{23}AuN_3O, M\text{-}Cl]^+$ m/z 530.1507; found 530.1501.
Found: C, 44.1; H, 4.2; N 7.1%. $C_{21}H_{23}AuClN_3O$ requires C, 44.6; H, 4.1; N 7.4%.



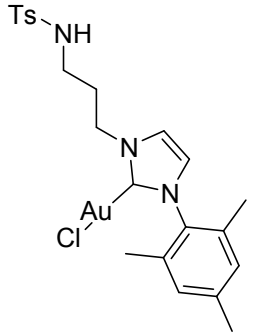
Gold complex 1b. Pale yellow solid, yield 86%.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.28 (s, 1H), 7.02 (s, 2H), 6.92 (s, 1H), 5.21 – 5.02 (m, 1H), 4.34 (t, *J* = 6.7 Hz, 2H), 2.96 (q, *J* = 6.3 Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H), 2.14 (p, *J* = 6.6 Hz, 2H), 1.98 (s, 6H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.78, 167.83, 140.19, 135.31, 135.23, 134.46, 131.84, 129.61, 128.87, 127.54, 122.86, 121.62, 48.91, 36.48, 31.49, 21.28, 17.95.
MS (ESI, positive mode): calcd. for $[C_{22}H_{25}AuN_3O, M\text{-}Cl]^+$ m/z 544.1658; found 544.1677.
Found: C, 45.4; H, 4.3; N 6.8%. $C_{22}H_{25}AuClN_3O$ requires C, 45.6; H, 4.35; N 7.25%.



Gold complex 2a. White solid, yield 84%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.33 (d, *J* = 1.9 Hz, 0H), 7.05 – 7.01 (m, 1H), 6.95 (d, *J* = 2.0 Hz, 0H), 4.84 (t, *J* = 6.3 Hz, 0H), 4.40 (t, *J* = 5.9 Hz, 1H), 3.44 (q, *J* = 6.3 Hz, 1H), 2.44 (s, 2H), 2.36 (s, 1H), 2.03 (s, 3H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.21, 144.61, 140.29, 136.75, 135.40, 135.31, 130.40, 129.66, 127.41, 122.58, 122.52, 51.30, 44.22, 21.69, 21.30, 18.01.
MS (ESI, positive mode): calcd. for $[C_{21}H_{25}AuN_3O_2S, M\text{-}Cl]^+$ m/z 580.1328; found 580.1332.
Found: C, 41.3; H, 4.2; N 6.8; S 5.4%. $C_{21}H_{25}AuClN_3O_2S$ requires C, 40.95; H, 4.1; N 6.8; S 5.2%



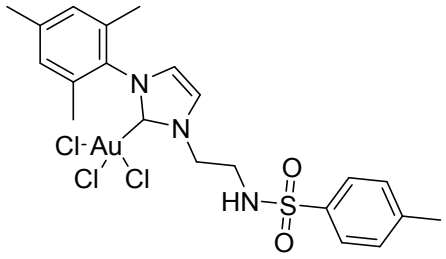
Gold complex 2b. Pale yellow solid, yield 86%.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.28 (s, 1H), 7.02 (s, 2H), 6.92 (s, 1H), 5.21 – 5.02 (m, 1H), 4.34 (t, *J* = 6.7 Hz, 2H), 2.96 (q, *J* = 6.3 Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H), 2.14 (p, *J* = 6.6 Hz, 2H), 1.98 (s, 6H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.80, 144.20, 140.23, 136.88, 135.30, 135.27, 130.25, 129.62, 127.45, 122.73, 121.73, 48.62, 40.24, 31.49, 21.66, 21.29, 17.92.
MS (ESI, positive mode): calcd. for $[C_{22}H_{27}AuN_3O_2S, M\text{-}Cl]^+$ m/z 594.1484 ; found 594.1490.

Oxidation of Au complexes

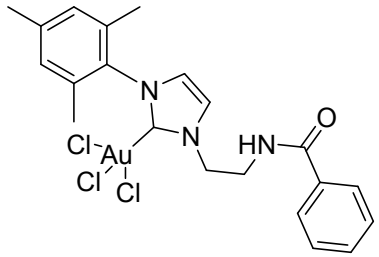
General procedure

The corresponding Au(I) (0.2 mmol) complex was dissolved in DCM (5 ml) and $PhICl_2$ (1 equiv.) was added. The mixture was covered from light and stirred in room temperature overnight. Hexane was added to the mixture and the precipitated Au(III) complex was filtered using a celite pad. After evaporation of solvents no further purification was needed.



Gold complex 8a. Pale yellow solid, yield 92%

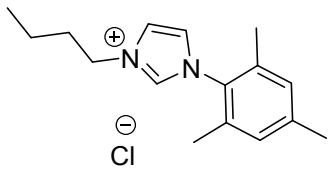
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.80 – 7.69 (m, 2H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 2.0 Hz, 1H), 7.05 (s, 2H), 4.85 (t, *J* = 6.2 Hz, 1H), 4.68 – 4.50 (m, 2H), 3.55 (q, *J* = 5.9 Hz, 2H), 2.45 (s, 3H), 2.37 (s, 3H), 2.15 (s, 6H).
^{13}C NMR (126 MHz, DMSO) δ 143.05, 140.16, 138.22, 137.03, 135.37, 132.49, 129.84, 129.37, 126.70, 126.52, 125.82, 49.97, 42.31, 21.04, 20.67, 17.97.
MS (ESI, positive mode): calcd. for $[C_{21}H_{25}AuCl_2N_3O_2S, M\text{-}Cl]^+$ m/z 650.0710 ; found 650.0705.



Gold complex 8b. Bright yellow solid, yield 92%

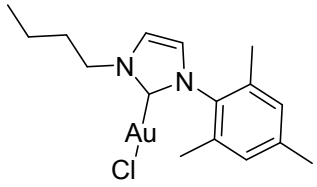
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.79 – 7.71 (m, 2H), 7.59 – 7.49 (m, 2H), 7.49 – 7.40 (m, 2H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.03 (s, 2H), 6.75 (t, *J* = 5.9 Hz, 1H), 4.74 (t, *J* = 6.4 Hz, 2H), 4.12 (q, *J* = 6.3 Hz, 2H), 2.36 (s, 3H), 2.08 (s, 6H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 168.30, 142.45, 141.50, 135.85, 133.79, 132.60, 132.33, 130.14, 128.99, 127.39, 126.14, 125.10, 50.37, 39.59, 21.28, 18.54.
MS (ESI, positive mode): calcd. for $[C_{21}H_{23}AuCl_2N_3O, M\text{-}Cl]^+$ m/z 600.0884 ; found 600.0878.
Found: C, 39.5; H, 3.8; N 6.3%. $C_{21}H_{23}AuCl_3N_3O$ requires C, 39.6; H, 3.6; N 6.6%

Imidazole salt L6 and Gold Complexes 6a-6b

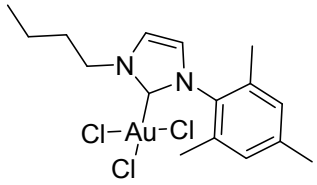


2,4,6-Trimethylphenylimidazole (1.2 equiv., 1.0 g) and *n*-butyl chloride (0.41 g) were refluxed in toluene (5 ml) for 4 days. Reaction mixture was cooled down to room temperature toluene was evaporated. The crude product was purified by flash chromatography using DCM and methanol (20:1) as eluent. Pale brown oil, yield 249 mg (20%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (t, *J* = 1.6 Hz, 1H), 7.98 (t, *J* = 1.7 Hz, 1H), 7.19 (t, *J* = 1.8 Hz, 1H), 6.90 (s, 2H), 4.59 (t, *J* = 7.2 Hz, 2H), 2.24 (s, 3H), 1.97 (s, 6H), 1.89 (dq, *J* = 9.9, 7.3 Hz, 2H), 1.38 – 1.23 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.01, 138.24, 134.16, 130.83, 129.73, 123.37, 123.17, 49.93, 32.34, 21.03, 19.32, 17.50, 13.49.
MS (ESI, positive mode): calcd. for $[C_{16}H_{23}N_2$, M-Cl$]^+$ m/z 243.1856 ; found 243.1864



Gold Complex 6a. The complex was synthesized according to the general procedure. White foamy solid, yield 89%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 1.9 Hz, 1H), 6.95 (q, *J* = 0.8 Hz, 2H), 6.88 (d, *J* = 1.9 Hz, 1H), 4.29 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 2.00 (s, 6H), 1.96 – 1.84 (m, 2H), 1.48 – 1.31 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.80, 139.68, 134.91, 134.87, 129.46, 122.21, 120.51, 51.32, 33.18, 21.20, 19.71, 17.87, 13.80.
Spectral data is in accordance with the literature.[20]

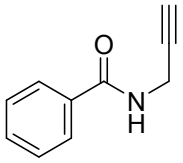


Gold Complex 6b. The complex was synthesized according to the general procedure. Pale yellow foamy solid, yield 60%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.1 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 6.98 (s, 2H), 4.42 (t, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.14 (s, 6H), 2.10 – 1.99 (m, 2H), 1.47 (h, *J* = 7.4 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.94, 141.10, 135.55, 132.39, 130.01, 125.52, 123.42, 51.58, 32.20, 21.25, 19.83, 18.58, 13.73.
MS (ESI, positive mode): calcd. for $[C_{18}H_{25}AuCl_2N_3$, M-Cl+MeCN$]^+$ m/z 550.1086 ; found 550.1076

Preparation of propargylamide substrates

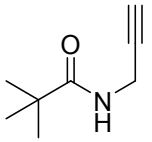
General procedure

Corresponding acid chloride (10 mmol) was dissolved in 25 ml of DCM. The solution was cooled with an ice bath. Amine (10 mmol) was added dropwise followed by dropwise addition of TEA (20 mmol). The ice bath was removed and mixture was mixed in room temperature for 6 hours. After the mixing 20 ml of DCM was added and the organic phase was extracted with saturated NH_4Cl, $NaHCO_3$ and brine. The organic phase was dried with $MgSO_4$ and after evaporation of the solvent, the product was purified by flash chromatography using hexane and ethyl acetate (5:1) as eluent.



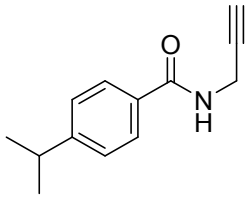
N-(prop-2-yn-1-yl)benzamide (3a). White solid, yield 91%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.78 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.49 – 7.42 (m, 2H), 6.49 (s, 1H), 4.22 (dd, *J* = 5.4, 2.6 Hz, 2H), 2.32 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.25, 134.31, 132.08, 128.96, 127.36, 80.18, 71.56, 29.90.
Spectral data is in accordance with the literature.[21]



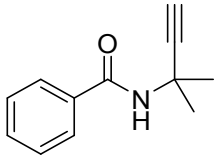
2,2-dimethyl-N-(prop-2-ynyl)propionamide (3b). White solid, yield 92%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.84 (s, 1H), 3.98 (dd, *J* = 5.3, 2.5 Hz, 2H), 2.25 (t, *J* = 2.6 Hz, 1H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 178.15, 80.59, 71.18, 38.85, 29.52, 27.57.
The spectral data is in accordance with the literature.[21]



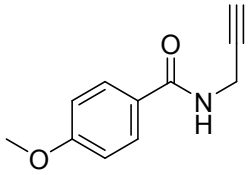
4-isopropyl-N-(prop-2-yn-1-yl)benzamide (3c). White solid, yield 83%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.76 – 7.66 (m, 2H), 7.34 – 7.24 (m, 2H), 6.60 (s, 1H), 4.21 (dd, *J* = 5.4, 2.5 Hz, 2H), 2.96 (hept, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 167.25, 153.51, 131.80, 127.47, 127.05, 80.32, 71.49, 34.48, 29.85, 23.89.
MS (ESI, positive mode): calcd. for $[C_{13}H_{16}NO, M+H]^+$+ m/z 202.1232 ; found 202.1266.



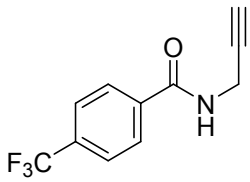
N-(2-methylbut-3-yn-2-yl)benzamide (3d). White solid, yield 85%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.80 – 7.68 (m, 2H), 7.54 – 7.48 (m, 1H), 7.48 – 7.38 (m, 2H), 6.25 (s, 1H), 2.41 (s, 1H), 1.73 (s, 6H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 166.60, 135.46, 131.79, 128.89, 127.17, 87.66, 69.32, 48.18, 29.29.
The spectral data is in accordance with the literature.[22]



4-methoxy-N-(prop-2-yn-1-yl)benzamide (3e). Beige solid, yield 90%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.75 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.41 (s, 1H), 4.20 (dd, *J* = 5.4, 2.6 Hz, 2H), 3.84 (s, 3H), 2.31 (t, *J* = 2.5 Hz, 1H).

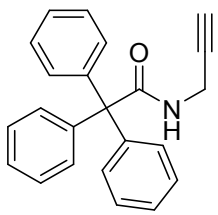
^{13}C NMR (126 MHz, CD_2Cl_2) δ 166.68, 162.85, 129.17, 126.53, 114.13, 80.40, 71.44, 55.82, 29.83.
The spectral data is in accordance with the literature.[22]



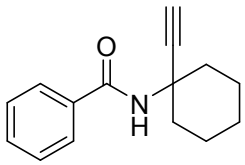
4-(trifluoromethyl)-N-(prop-2-yn-1-yl)benzamide (3f). White solid, yield 86%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.92 (dt, *J* = 8.1, 0.8 Hz, 2H), 7.72 (dt, *J* = 8.2, 0.8 Hz, 2H), 6.64 (s, 2H), 4.24 (dd, *J* = 5.4, 2.6 Hz, 2H), 2.34 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 166.08, 137.71, 133.51 (q, *J* = 32.5 Hz), 128.25, 127.98, 126.03 (q, *J* = 3.7 Hz), 124.19 (q, *J* = 272.3 Hz), 79.73, 71.90, 30.10.

The spectral data is in accordance with the literature.[3]

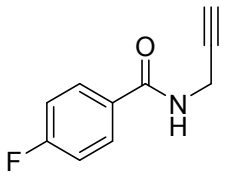


2,2,2-triphenyl-N-(prop-2-yn-1-yl)acetamide (3g). White solid, yield 84%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.43 – 7.13 (m, 15H), 6.10 – 5.97 (m, 1H), 4.08 (dd, *J* = 5.5, 2.5 Hz, 2H), 2.25 (t, *J* = 2.5 Hz, 1H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 173.26, 143.63, 130.90, 128.33, 127.48, 79.86, 71.40, 67.88, 30.05.
The spectral data is in accordance with the literature.[23]



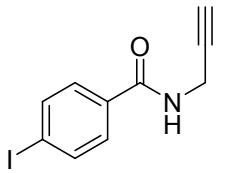
N-(1-ethynylcyclohexyl)benzamide (3h). White solid, yield 91%.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.82 – 7.63 (m, 2H), 7.59 – 7.48 (m, 1H), 7.47 – 7.38 (m, 2H), 6.12 (s, 1H), 2.47 (s, 1H), 2.26 – 2.18 (m, 2H), 1.91 (ddd, *J* = 13.3, 10.4, 3.7 Hz, 2H), 1.76 – 1.60 (m, 5H), 1.39 – 1.29 (m, 1H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 166.39, 135.69, 131.75, 128.90, 127.18, 86.12, 71.52, 52.27, 37.35, 25.68, 22.87.
The spectral data is in accordance with the literature.[24]



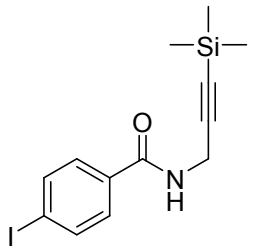
4-fluoro-N-(prop-2-yn-1-yl)benzamide (3i). White solid, yield 81%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.82 – 7.79 (m, 2H), 7.12 (t, *J* = 8.7 Hz, 2H), 6.62 (s, 1H), 4.21 (dd, *J* = 5.4, 2.6 Hz, 2H), 2.32 (t, *J* = 2.5 Hz, 1H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 166.27, 165.24 (d, *J* = 251.4 Hz), 130.58 (d, *J* = 3.1 Hz), 129.83 (d, *J* = 9.0 Hz), 115.93 (d, *J* = 22.0 Hz), 80.08, 71.63, 29.97.
The spectral data is in accordance with the literature.[25]



4-iodo-N-(prop-2-yn-1-yl)benzamide (S5). White solid, yield 85%.

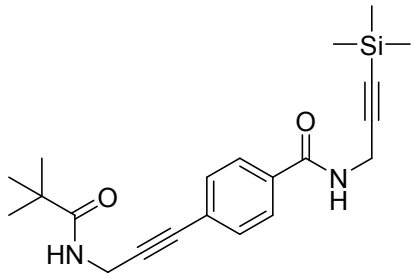
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.30 (s, 2H), 4.25 (dd, *J* = 5.2, 2.6 Hz, 3H), 2.30 (t, *J* = 2.6 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.43, 138.03, 133.26, 128.73, 99.02, 79.34, 72.27, 30.01.
The spectral data is in accordance with the literature.[26]



4-iodo-N-(3-(trimethylsilyl)prop-2-yn-1-yl)benzamide (S6). The product was synthesized according to the procedure from Rahaim et al. [27] A round-bottom flask was charged with zinc triflate (0.05 mmol, 0.018 g) and sealed with a septum under an atmosphere of argon. An argon inlet was attached followed by the sequential addition of dry CH_2Cl_2 (4.2 mL), dry triethylamine (1.5 mmol, 0.209 mL), **S5** (1 mmol, 0.285 g), and TMSOTf (1.5 mmol, 0.271 mL). The reaction was stirred until complete as judged by TLC after 8 hours. The reaction was quenched with saturated NH_4Cl. The mixture was extracted with ether; the aqueous layer was back extracted with ether, and the combined organics were dried, filtered, and concentrated. The crude material was then subjected to flash chromatography using hexane and ethyl acetate (3:1) as eluent. Pale yellow solid, yield 76%.

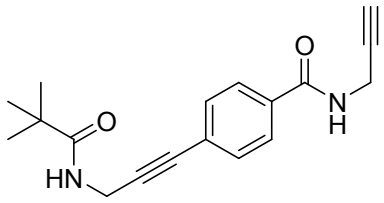
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.42 (t, *J* = 5.2 Hz, 1H), 4.25 (d, *J* = 5.1 Hz, 2H), 0.16 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.29, 137.90, 133.36, 128.76, 100.92, 98.86, 89.11, 31.01, -0.06.

MS (ESI, positive mode): calcd. for $[C_{13}H_{17}INOSi, M+H]^+$ m/z 358.0119; found 358.0136.



4-(3-pivalamidoprop-1-yn-1-yl)-N-(3-(trimethylsilyl)prop-2-yn-1-yl)benzamide (S7). A round-bottom flask was charged with $(PPh_3)_2PdCl_2$ (0.015 mmol, 0.011 g), CuI (0.015 mmol, 0.003 g), **S6** (0.28 mmol, 0.10 g) and **3b** (0.28 mmol, 0.039 g) and sealed with a septum under an atmosphere of argon. An argon inlet was attached followed by the sequential addition of DIPEA (0.19 ml) and dry DMF (5 ml). The reaction was stirred in 80 ^{o}C for 4 hours and after poured in an extraction funnel with cold water and EtOAc (30 ml). The organic phase was washed three times with water and once with brine. The organic phase was dried with $MgSO_4$. After evaporating the solvent, the product was purified by flash chromatography using hexane and ethyl acetate (1:1) as eluent. Beige solid, yield 60%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 6.27 (d, *J* = 5.1 Hz, 1H), 5.87 (s, 1H), 4.28 (t, *J* = 5.8 Hz, 4H), 1.23 (s, 9H), 0.18 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.21, 166.24, 133.56, 132.06, 127.16, 126.30, 100.98, 89.20, 87.88, 82.66, 38.89, 31.06, 30.35, 27.65, -0.04.
MS (ESI, positive mode): calcd. for $[C_{21}H_{28}N_2NaO_2Si, M+Na]^+$ m/z 391.1812; found 391.1809.



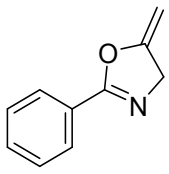
4-(3-pivalamidoprop-1-yn-1-yl)-N-(prop-2-yn-1-yl)benzamide (3j). S7 (0.27 mmol, 0.10 g) was dissolved in DCM (5 ml). TBAF (0.4 equiv.) was added and the mixture turned immediately brown. After stirring the mixture in room temperature for 20 minutes, the mixture was poured in an extraction funnel and washed twice with water and once with brine. The organic phase was dried with $MgSO_4$. After evaporating the solvent, the product was purified by flash chromatography using hexane and ethyl acetate (1:1) as eluent. Beige solid, yield 89%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 6.52 (t, *J* = 5.2 Hz, 1H), 5.89 (s, 1H), 4.21 (d, *J* = 5.1 Hz, 2H), 4.18 (dd, *J* = 5.3, 2.5 Hz, 2H), 2.21 (t, *J* = 2.5 Hz, 1H), 1.17 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.27, 166.47, 133.41, 132.03, 127.19, 126.33, 87.93, 82.58, 79.50, 72.07, 38.88, 30.32, 29.96, 27.63.
MS (ESI, positive mode): calcd. for $[C_{18}H_{21}N_2O_2, M+H]^+$ m/z 297.1598; found 297.1594.

Catalytic cyclization of propargyl amides

General procedure

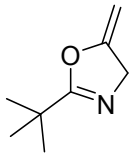
Propargyl amide (0.31 mmol) was dissolved in 1 ml of DCM (measured water content 150 ppm). The catalyst (1 mol%) was added and the mixture was mixed in room temperature. The progress was monitored by TLC and once the starting material was not observed the product was purified by flash chromatography using hexane and ethyl acetate (5:1) as eluent.



2-phenyl-5-methylene-4,5-dihydrooxazole (4a). Reaction time 3 h, colorless oil, yield 98%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.78 (dd, *J* = 8.2, 1.1 Hz, 3H), 7.56 – 7.50 (m, 1H), 7.49 – 7.42 (m, 2H), 6.49 (s, 2H), 4.22 (dd, *J* = 5.4, 2.6 Hz, 3H), 2.32 (t, *J* = 2.6 Hz, 1H).

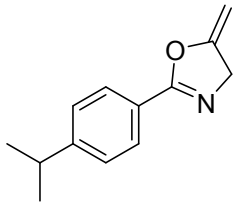
^{13}C NMR (126 MHz, CD_2Cl_2) δ 163.72, 159.59, 132.13, 128.91, 128.27, 127.34, 83.64, 58.17.

The spectral data is in accordance with the literature.[28]



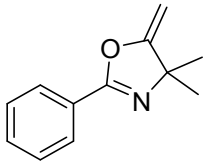
2-tert-butyl-5-methylene-4,5-dihydrooxazole (4b). Reaction time 2 h, colorless oil, yield 98%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.59 (td, *J* = 3.0, 2.5 Hz, 1H), 4.40 – 4.31 (m, 2H), 4.21 (q, *J* = 2.5 Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 173.62, 160.34, 82.37, 57.75, 33.64, 27.51.The spectral data is in accordance with the literature.[25]



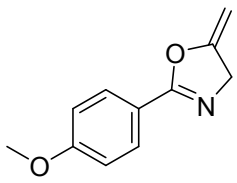
2-(4-isopropylphenyl)-5-methylene-4,5-dihydrooxazole (4c). Reaction time 3 h, pale brown oil, yield 93%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 4.80 (q, *J* = 3.0 Hz, 1H), 4.63 (t, *J* = 2.9 Hz, 2H), 4.34 (q, *J* = 2.7 Hz, 1H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.27 (s, 3H), 1.26 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.90, 159.10, 153.21, 128.22, 126.74, 124.45, 83.63, 57.87, 34.35, 23.87.

MS (ESI, positive mode): calcd. for $[C_{13}H_{16}NO, M+H]^{+}$+ m/z 202.1232 ; found 202.1230.



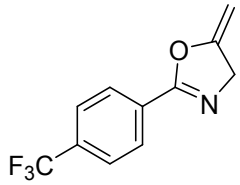
4,4-dimethyl-5-methylene-2-phenyl-4,5-dihydrooxazole (4d). Reaction time 5 h, colorless oil, yield 94%.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.05 – 7.87 (m, 2H), 7.55 – 7.49 (m, 1H), 7.45 (ddt, *J* = 8.4, 6.8, 1.2 Hz, 2H), 4.73 (d, *J* = 2.8 Hz, 1H), 4.26 (d, *J* = 2.8 Hz, 1H), 1.42 (s, 6H).
^{13}C NMR (126 MHz, CD_2Cl2) δ 167.61, 158.82, 130.97, 127.87, 127.32, 126.40, 81.29, 68.54, 28.89.
The spectral data in accordance with literature.[22]



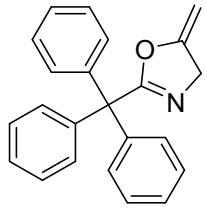
2-(4-methoxyphenyl)-5-methylene-4,5-dihydrooxazole(4e). Reaction time 24 h, white solid, yield 89%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.94 – 7.86 (m, 2H), 6.98 – 6.89 (m, 2H), 4.77 (q, *J* = 3.0 Hz, 1H), 4.59 (t, *J* = 2.8 Hz, 2H), 4.34 (q, *J* = 2.6 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.42, 162.88, 159.77, 130.01, 119.73, 114.25, 83.23, 58.11, 55.80.
The spectral data is in accordance with the literature.[22]



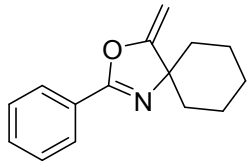
2-(4-(trifluoromethyl)phenyl)-4,5-dihydro-5-methyleneoxazole (4f). Reaction time 4 h, white solid, yield 21%. The reaction did not proceed further and decomposition of the catalyst was noticed when the reaction mixture turned dark. 70% of the starting material was recovered. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.16 – 8.03 (m, 2H), 7.75 – 7.66 (m, 2H), 4.84 (q, *J* = 3.0 Hz, 1H), 4.66 (t, *J* = 2.9 Hz, 2H), 4.42 (q, *J* = 2.7 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 162.68, 159.32, 133.42 (q, *J* = 32.7 Hz), 130.81, 125.89 (q, *J* = 3.9 Hz), 124.29 (q, *J* = 272.4 Hz), 128.75, 84.29, 58.33.
The spectral data is in accordance with the literature.[3]



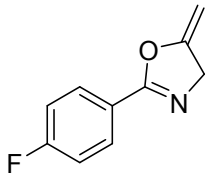
5-methylene-2-trityl-4,5-dihydrooxazole (4g). Reaction time 20 h, white solid, yield 96%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 15H), 4.71 (q, *J* = 3.0 Hz, 1H), 4.65 (t, *J* = 2.8 Hz, 2H), 4.34 (q, *J* = 2.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.71, 158.69, 142.72, 130.35, 127.85, 127.19, 83.94, 61.74, 57.64.
MS (ESI, positive mode): calcd. for $[C_{23}H_{20}NO, M+H]^+$ m/z 326.1539; found 326.1535.



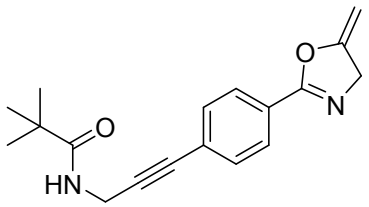
4-methylene-2-phenyl-3-oxa-1-azaspiro[4.5]dec-1-ene (4h) Reaction time 7 h, colorless oil, yield 97%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.53 – 7.44 (m, 1H), 7.47 – 7.38 (m, 2H), 4.75 (d, *J* = 2.7 Hz, 1H), 4.24 (d, *J* = 2.7 Hz, 1H), 1.98 – 1.82 (m, 2H), 1.82 – 1.72 (m, 3H), 1.72 – 1.62 (m, 2H), 1.62 – 1.50 (m, 2H), 1.49 – 1.34 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.42, 159.30, 131.48, 128.45, 128.22, 127.51, 82.58, 72.07, 39.28, 25.73, 22.21.
The spectral data is in accordance with the literature.[29]



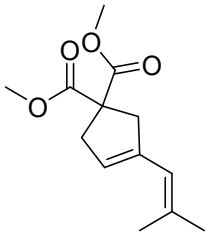
2-(4-fluorophenyl)-5-methylene-4,5-dihydrooxazole (4i). Reaction time 8 h, yellow solid, yield 83 %.

^{1}H NMR (400 MHz, CD_2Cl_2) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.90 (m, 1H), 7.16 – 7.05 (m, 1H), 4.79 (q, *J* = 3.0 Hz, 1H), 4.68 – 4.59 (m, 1H), 4.35 (q, *J* = 2.7 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.05, 164.05, 162.86, 158.90, 130.42, 123.14, 115.88, 115.70, 84.00, 57.86.
The spectral data is in accordance with the literature.[25]

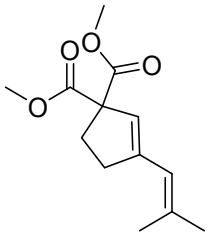


N-(3-(4-(5-methylene-4,5-dihydrooxazol-2-yl)phenyl)prop-2-yn-1-yl)pivalamide (4j). The synthesis was performed with a catalyst loading of 3 mol%. Due to poor solubility of the substrate, the amount of DCM was increased to 3 ml. The product was purified by flash chromatography using hexane and ethyl acetate (1:1) as eluent. Yellow solid, yield 93%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 5.88 (s, 1H), 4.74 (q, *J* = 3.0 Hz, 1H), 4.57 (q, *J* = 1.9, 1.2 Hz, 2H), 4.29 (dq, *J* = 5.0, 2.7 Hz, 1H), 4.21 (d, *J* = 5.1 Hz, 2H), 1.16 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.25, 163.35, 158.66, 132.20, 131.92, 128.00, 126.29, 87.96, 84.23, 82.82, 57.81, 38.85, 30.34, 27.60.
MS (ESI, positive mode): calcd. for $[C_{18}H_{21}N_2O_2, M+H]^+$ m/z 297.1598; found 297.1594.

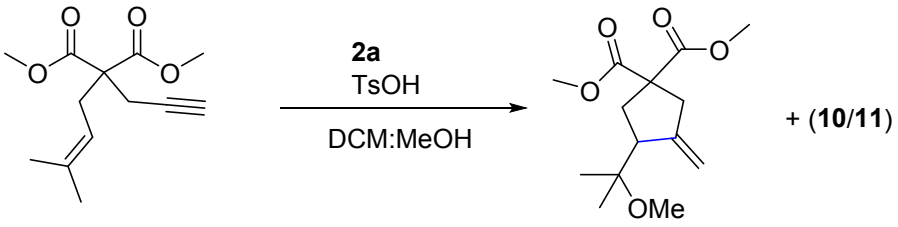


Dimethyl 3-(2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (10). Not isolated. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.79 – 5.70 (m, 1H), 5.44 – 5.34 (m, 1H), 3.71 (s, 7H), 3.18 – 3.14 (m, 2H), 3.05 – 2.97 (m, 2H), 1.82 (s, 3H), 1.79 (s, 3H). Spectral data is in accordance with the literature.[30]



Dimethyl 3-(2-methylprop-1-enyl)cyclopent-2-ene-1,1-dicarboxylate (11). Not isolated ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.85 (td, *J* = 1.4, 0.7 Hz, 1H), 5.64 – 5.56 (m, 1H), 3.73 (s, 6H), 2.72 – 2.60 (m, 2H), 2.54 – 2.43 (m, 2H), 1.88 (s, 3H), 1.85 (s, 3H). Spectral data is in accordance with the literature.[31]

Table S3. Screening for conditions for the cyclication of enynes in the presence of a nucleophile.



9a **12a**

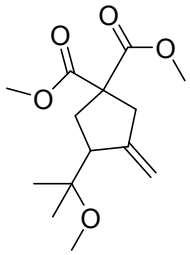
Entry	DCM:MeOH	Catalyst loading [mol%]	TsOH loading [mol%]	Time	Yield **12**:**10+11** [%][a]
1	10:1	1	1	1 h	20:32
2	1:1	1	1	1 h	35:6
3	3:1	1	5	40 min	65:2
4	3:1	2	5	10 min	98:0
5	3:1	-	5	1 h	n.r.

[a]Determined by ^{1}H NMR using trimethoxybenzene as an internal standard.

Catalytic cyclization of enynes in the presence of a nucleophile

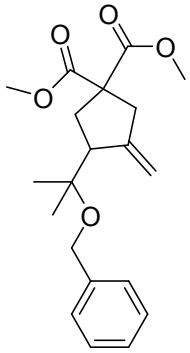
General procedure

Enyne (0.2 mmol) was dissolved in a mixture of DCM and alcohol (0.7 ml, 3:1). The catalyst (2 mol%) and the acid additive (5 mol%) were added and the mixture was mixed in room temperature. The progress was monitored by TLC and once the starting material was not observed the product was purified by flash chromatography using hexane and ethyl acetate (20:1) as eluent.



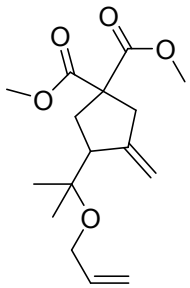
Dimethyl 3-(2-methoxypropan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (12a). Colorless oil, yield 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 – 5.00 (m, 1H), 5.01 – 4.94 (m, 1H), 3.73 (d, *J* = 0.7 Hz, 3H), 3.72 (d, *J* = 0.7 Hz, 3H), 3.18 (d, *J* = 0.7 Hz, 3H), 2.99 – 2.76 (m, 3H), 2.55 (ddd, *J* = 13.5, 8.5, 1.8 Hz, 1H), 2.00 (dd, *J* = 13.5, 9.3 Hz, 1H), 1.18 (s, 3H), 1.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.10, 171.99, 148.28, 110.61, 76.82, 58.65, 52.79, 52.76, 49.19, 49.09, 43.45, 36.07, 22.70, 22.26. Spectral data is in accordance with the literature.[30]



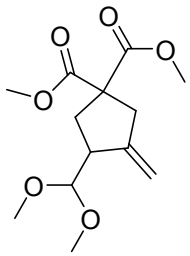
Dimethyl 3-(2-benzyloxypropan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (12b). Colorless oil, yield 30%. In addition, a mixture of **10** and **11** was isolated in 55%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 5H), 5.14 – 4.95 (m, 2H), 4.46 (d, *J* = 1.5 Hz, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 3.03 – 2.78 (m, 3H), 2.62 (ddd, *J* = 13.4, 8.5, 2.0 Hz, 1H), 2.12 (dd, *J* = 13.5, 9.3 Hz, 1H), 1.30 (s, 3H), 1.24 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.20, 172.09, 148.32, 139.70, 128.38, 127.31, 127.19, 110.93, 77.48, 63.63, 58.76, 52.88, 52.83, 50.16, 43.64, 36.19, 23.40, 22.85.
MS (ESI, positive mode): calcd. for $[C_{20}H_{26}NaO_5, M+Na]^+$ m/z 369.1672; found 369.1671.



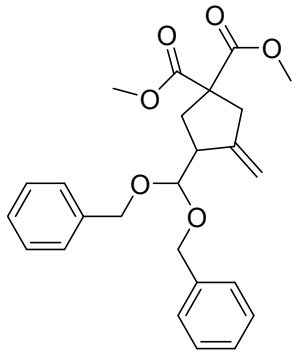
Dimethyl 3-(2-allyloxypropan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (12c). Yellow oil, yield 74%. In addition, a mixture of **10** and **11** was isolated in 20%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (ddt, *J* = 17.3, 10.4, 5.2 Hz, 1H), 5.27 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.10 (dq, *J* = 10.4, 1.6 Hz, 1H), 5.06 – 4.96 (m, 2H), 3.97 – 3.85 (m, 2H), 3.73 (s, 3H), 3.72 (s, 3H), 2.96 – 2.81 (m, 3H), 2.57 (ddd, *J* = 13.5, 8.4, 1.9 Hz, 1H), 2.04 (dd, *J* = 13.4, 9.4 Hz, 1H), 1.22 (s, 3H), 1.16 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.15, 172.07, 148.26, 135.89, 115.60, 110.80, 77.12, 62.55, 58.71, 52.85, 52.82, 49.77, 43.59, 36.13, 23.33, 22.80.
MS (ESI, positive mode): calcd. for $[C_{16}H_{24}NaO_5, M+Na]^+$ m/z 319.1516; found 319.1515.



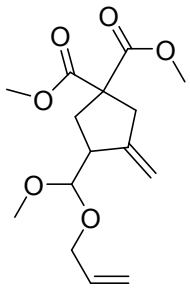
Dimethyl 3-dimethoxymethyl-4-methylenecyclopentane-1,1-dicarboxylate (12d). Yellow oil, yield 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 – 5.06 (m, 1H), 5.04 – 5.02 (m, 1H), 4.26 (d, *J* = 6.4 Hz, 1H), 3.73 (d, *J* = 1.3 Hz, 6H), 3.38 (s, 3H), 3.36 (s, 3H), 3.01 – 2.88 (m, 3H), 2.61 – 2.50 (m, 1H), 2.13 (dd, *J* = 13.4, 9.2 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.19, 171.98, 147.30, 109.45, 106.80, 58.58, 54.14, 54.06, 52.88, 52.82, 44.72, 41.93, 35.38.
Spectral data is in accordance with the literature.[32]



Dimethyl 3-dibenzyloxymethyl-4-methylenecyclopentane-1,1-dicarboxylate (12e). Colorless oil, yield 51%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 10H), 5.11 (q, *J* = 2.2 Hz, 1H), 5.03 (q, *J* = 2.3 Hz, 1H), 4.73 – 4.53 (m, 5H), 3.72 (s, 3H), 3.70 (s, 3H), 3.11 (dtt, *J* = 8.9, 6.8, 3.0 Hz, 1H), 3.03 – 2.88 (m, 2H), 2.69 – 2.56 (m, 1H), 2.24 (dd, *J* = 13.5, 9.3 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.23, 171.97, 147.17, 138.08, 137.98, 128.56, 128.52, 127.95, 127.88, 127.80, 127.76, 109.85, 103.99, 68.38, 68.23, 58.64, 52.94, 52.85, 45.18, 42.06, 35.52.
MS (ESI, positive mode): calcd. for $[C_{25}H_{28}NaO_6, M+Na]^+$ m/z 447.1778; found 447.1782.

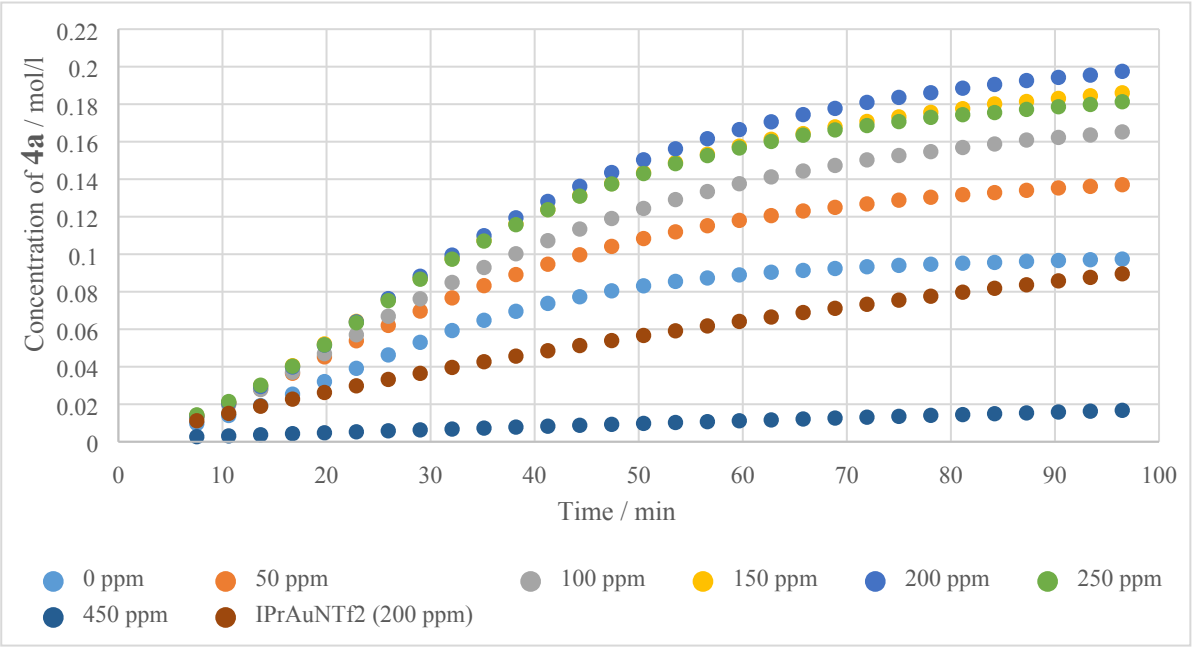


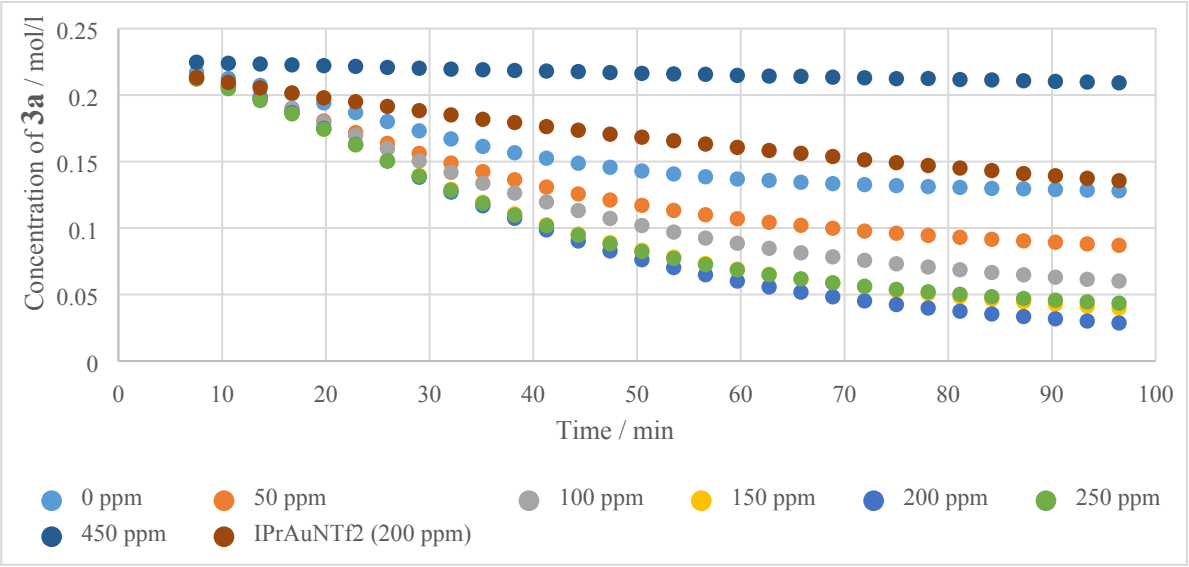
Dimethyl 3-(allyloxy)-(methoxy)methyl-4-methylenecyclopentane-1,1-dicarboxylate (12f). Colorless oil, yield 68%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 – 5.82 (m, 1H), 5.29 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.17 (dq, *J* = 10.4, 1.5 Hz, 1H), 5.05 (dq, *J* = 17.6, 2.0 Hz, 2H), 4.38 (d, *J* = 6.4 Hz, 1H), 4.19 – 3.99 (m, 2H), 3.72 (d, *J* = 0.8 Hz, 7H), 3.37 (s, 3H), 3.02 – 2.88 (m, 3H), 2.56 (ddd, *J* = 13.7, 8.2, 1.4 Hz, 1H), 2.15 (dd, *J* = 13.6, 9.3 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.17, 171.95, 147.22, 134.54, 116.84, 109.48, 105.38, 67.72, 58.57, 53.82, 52.85, 52.80, 44.87, 41.93, 35.45.
MS (ESI, positive mode): calcd. for $[C_{15}H_{22}NaO_6, M+Na]^+$ m/z 321.1309; found 321.1320.

Monitoring the formation of oxazoline with varying the sample water content

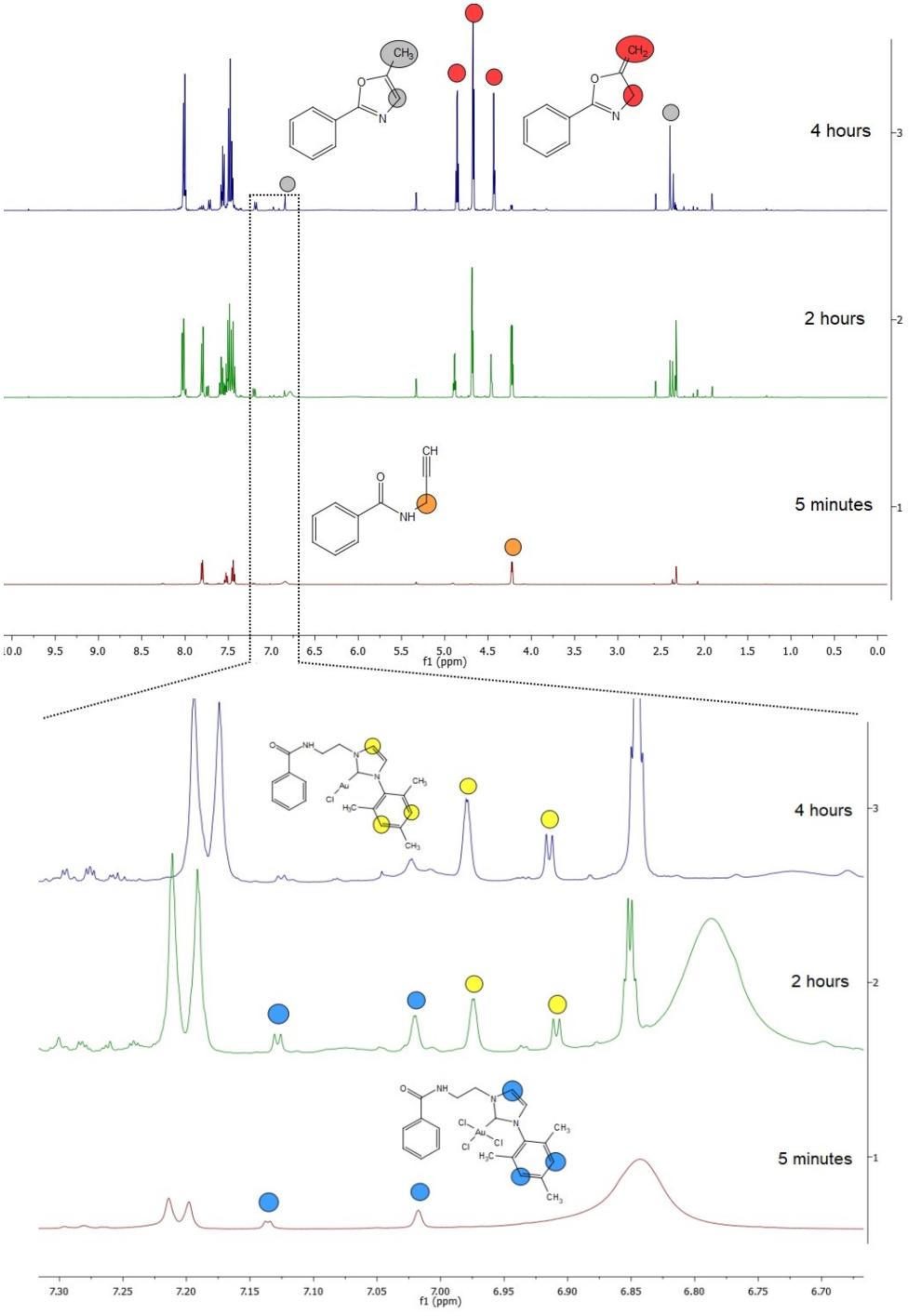
CD_2Cl_2 was dried on 4 Å molecular sieves over 2 days. Dry CD_2Cl_2 was used to prepare stock solutions of **2a** and N-(prop-2-yn-1-yl)benzamide **3a**. Dry mesitylene was added in the substrate stock solution as an internal standard. NMR tubes were loaded in a glovebox. Substrate stock solution was added to an NMR tube followed by varied amounts of dry and wet CD_2Cl_2. The ppm values for the series were 0, 50, 100, 150, 200 and 300 ppm. Substrate concentration in the sample was 0.226 M. Catalyst concertation was 0.0023 M in all reactions. The catalyst stock solution was added last and the tube was transferred from the glovebox to the NMR spectrometer. The experiment was started 6 minutes after addition of the catalyst. One measurement cycle lasted 184 seconds.



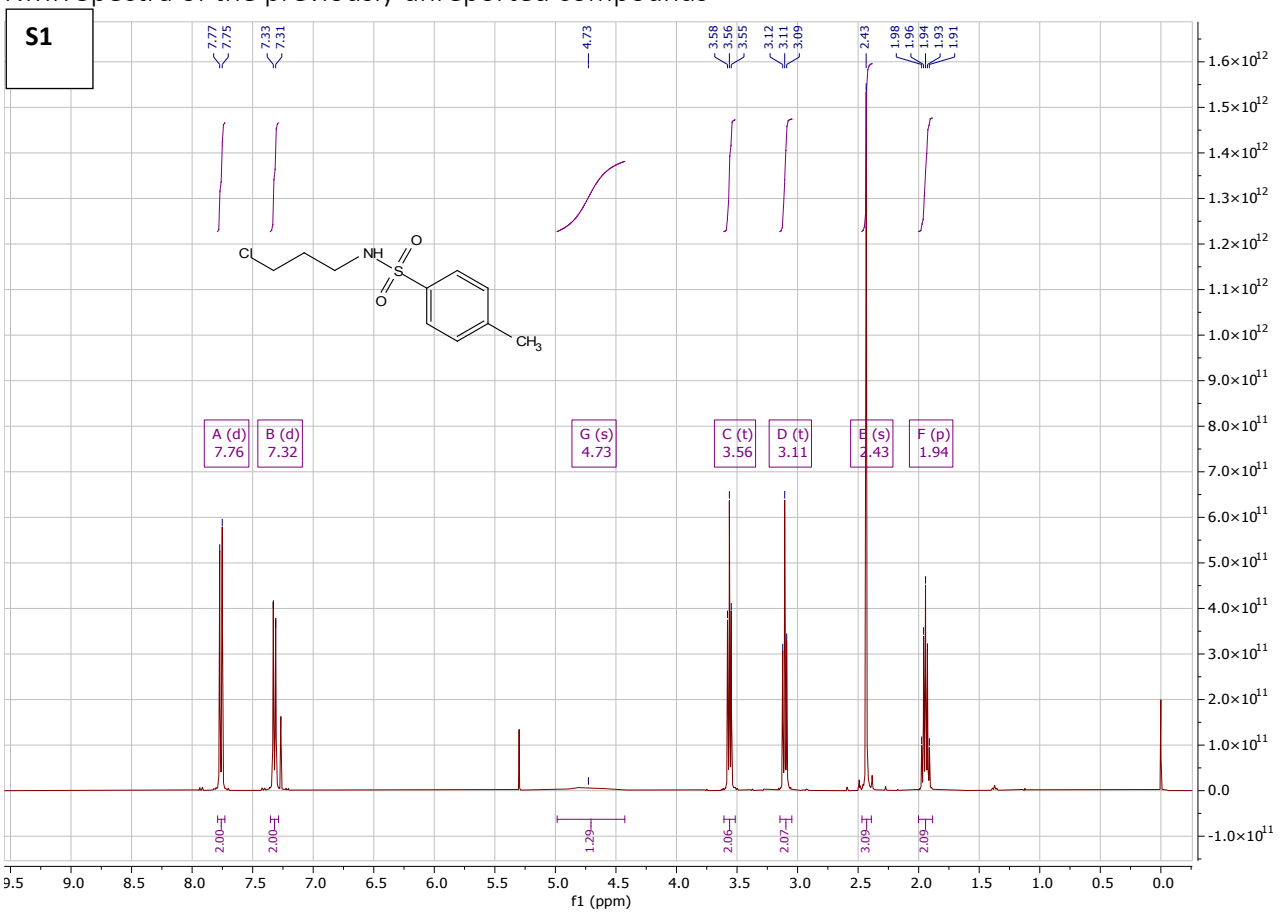


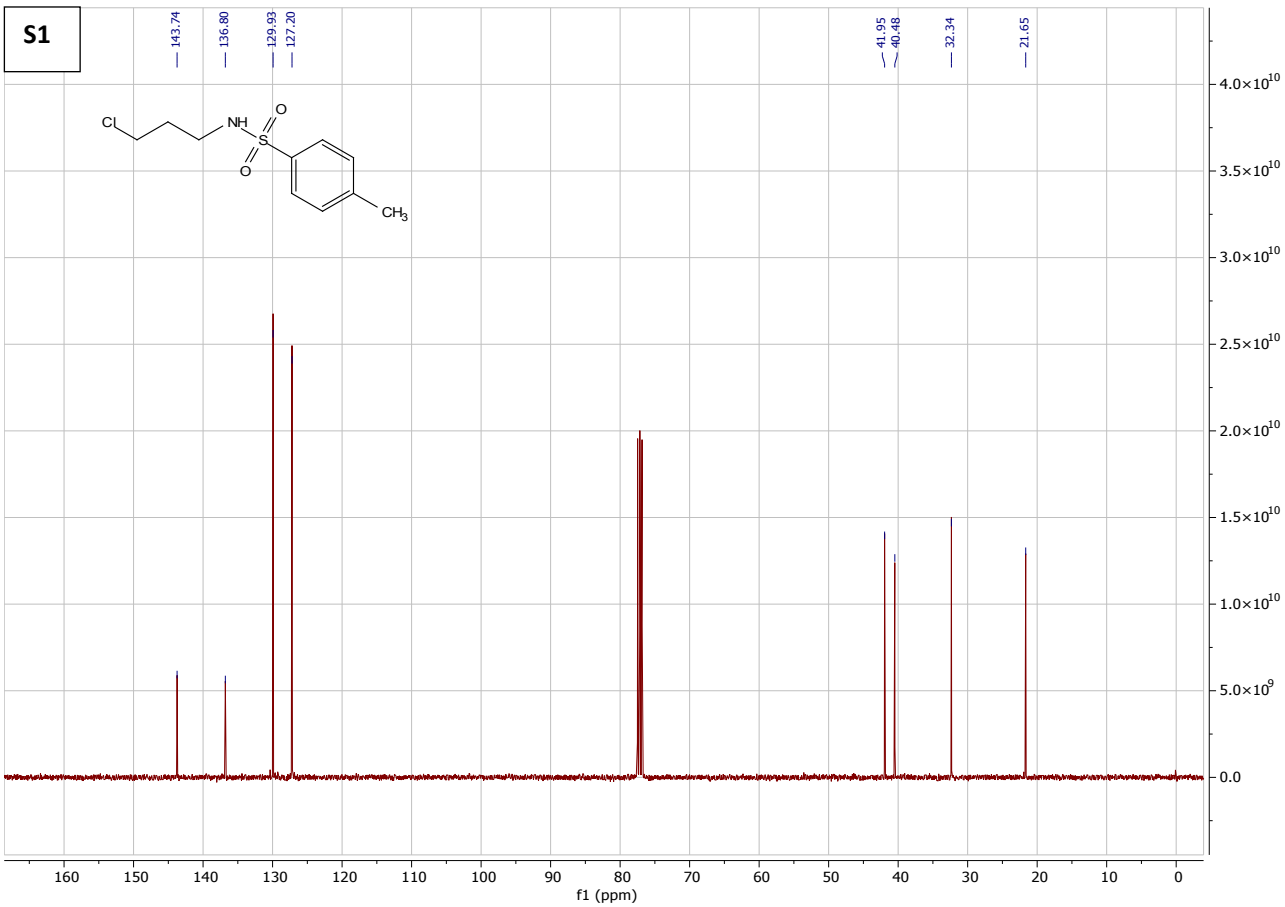
The effect of an acid additive to Au(III) complex

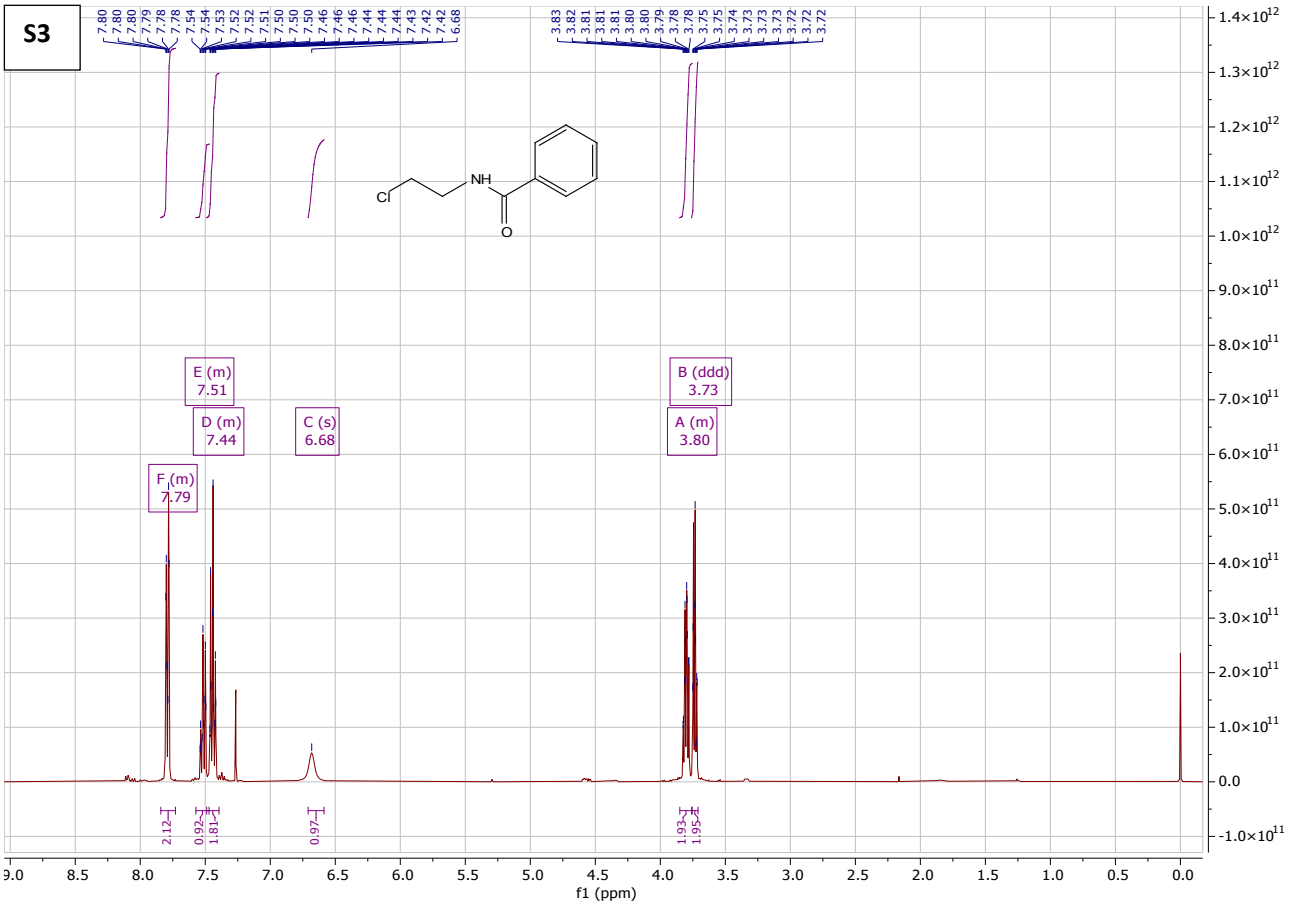
To study the effect of acid additives to Au(III) complex **8b**, the reaction from **3a** to **4a** was performed in the presence of *p*-TsOH (5 mol%). The reaction started very slowly, after 2h, however, 59% of **3a** was converted to **4a**. At the same time, the signal intensities belonging to Au(III) complex **8b** were reduced (blue dots) and new signals belonging to Au(I) complex **1a** (yellow dots) appeared in the spectrum (below). When the reaction was complete after 4 hours, majority the gold complex signals can be assigned to corresponding Au(I) complex. We will in future studies focus on details of this reduction process.

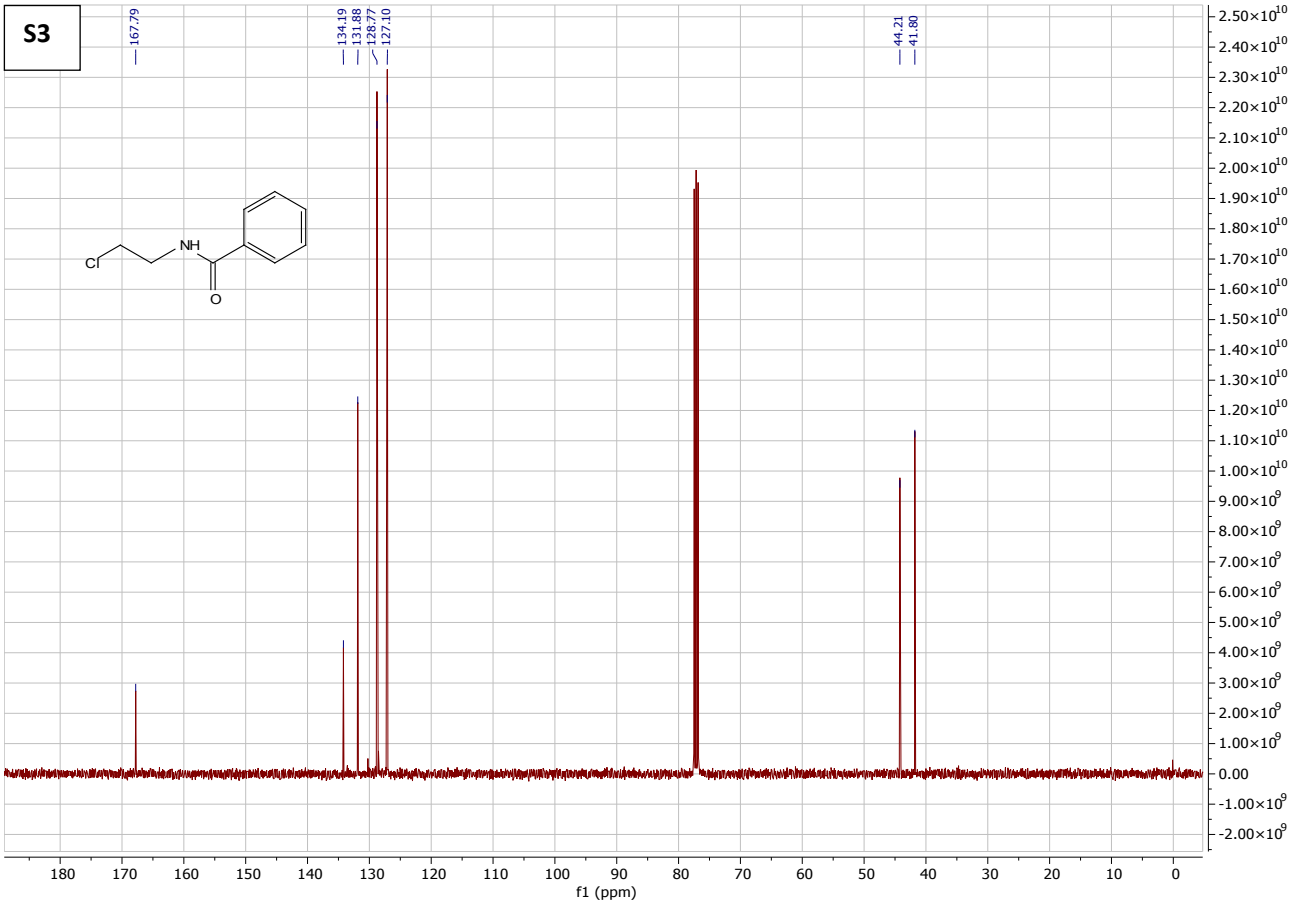


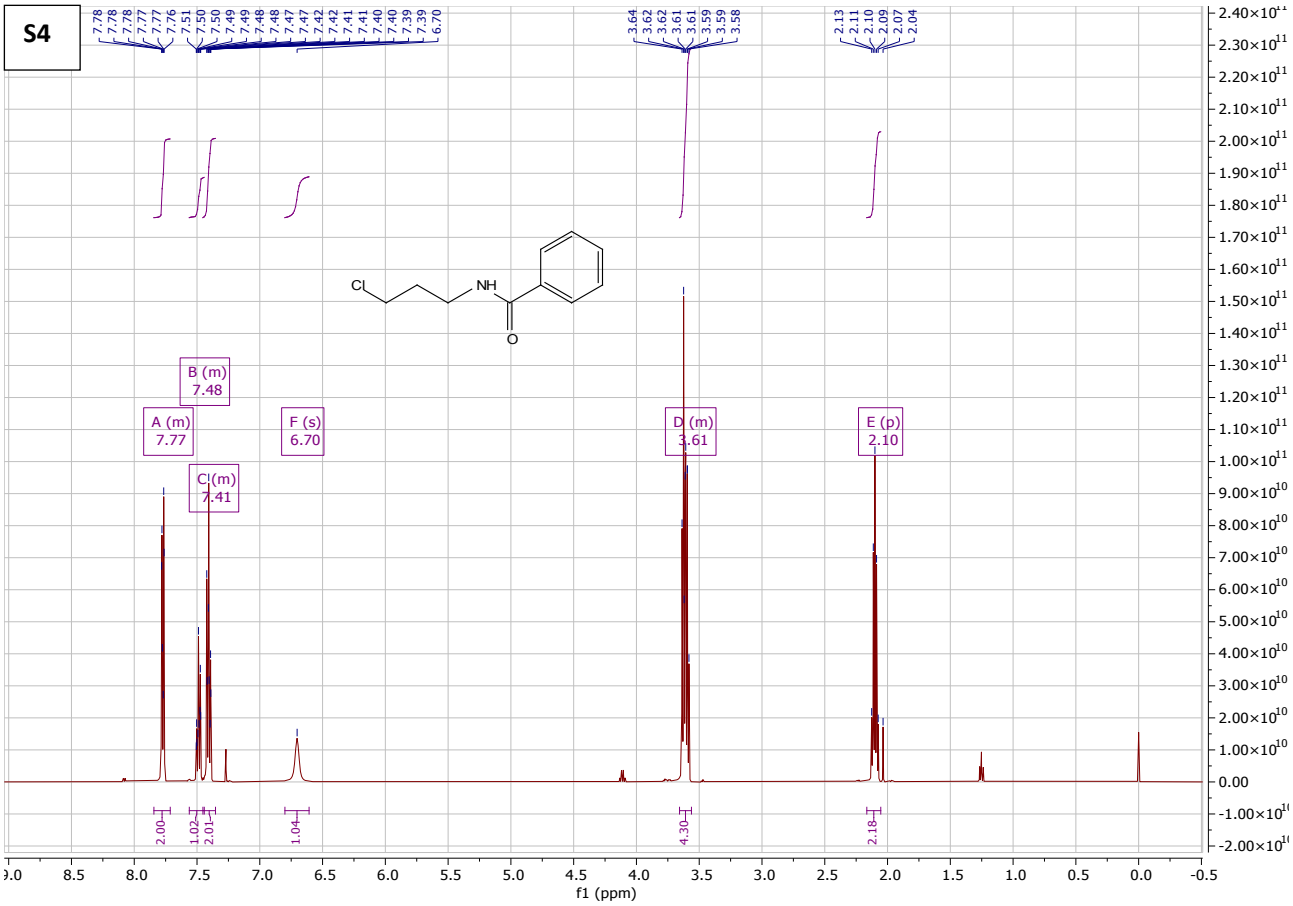
NMR Spectra of the previously unreported compounds

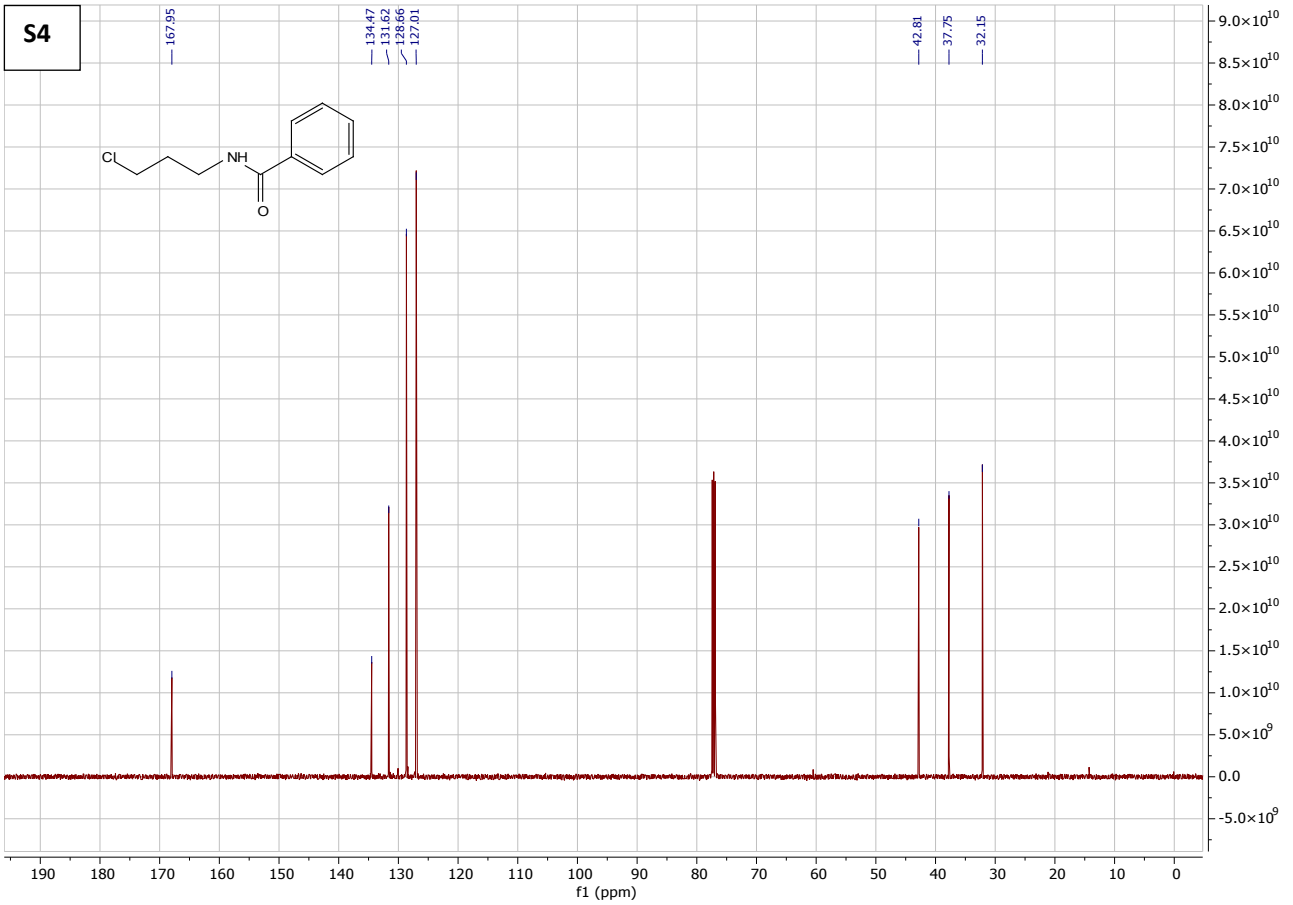


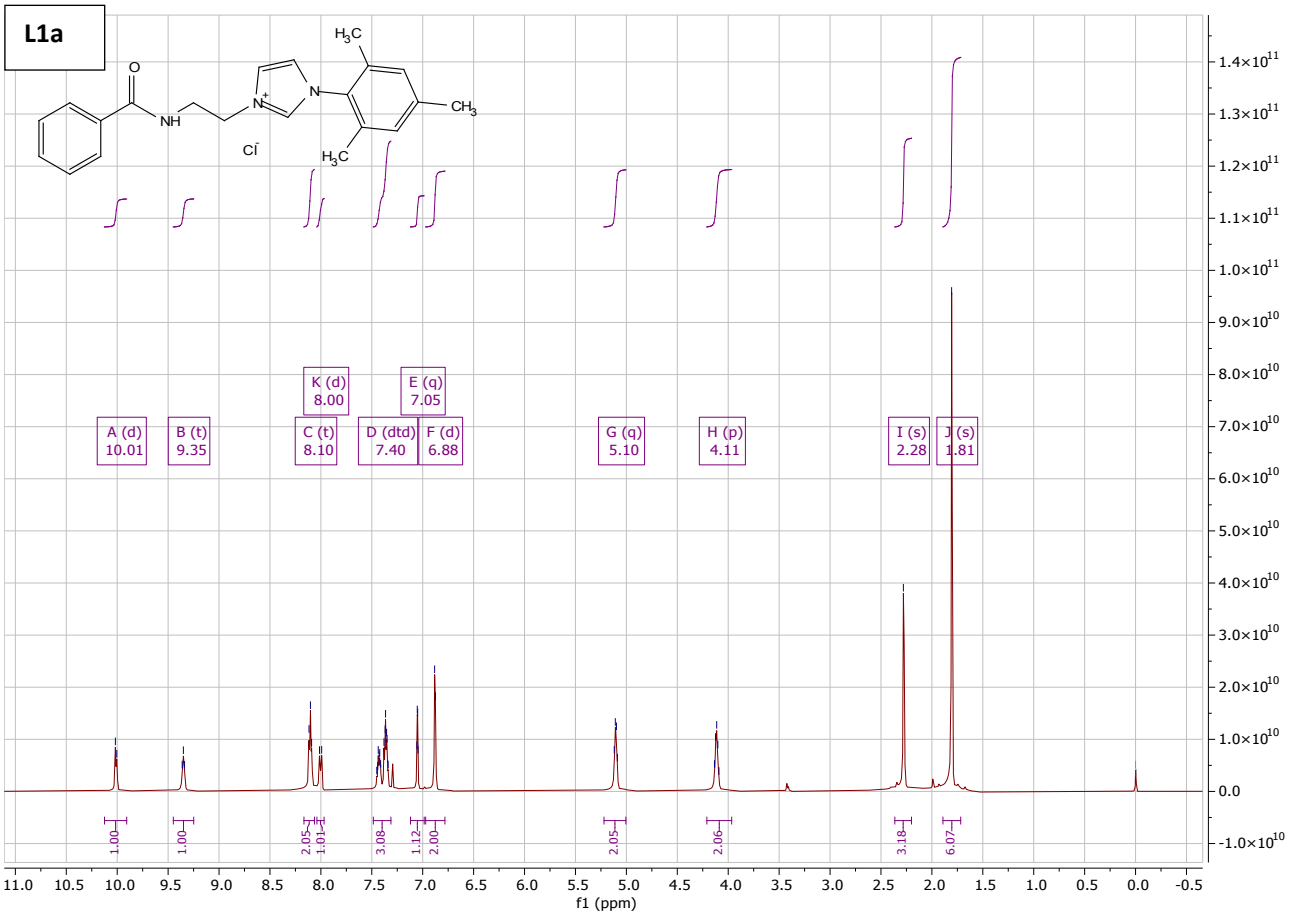


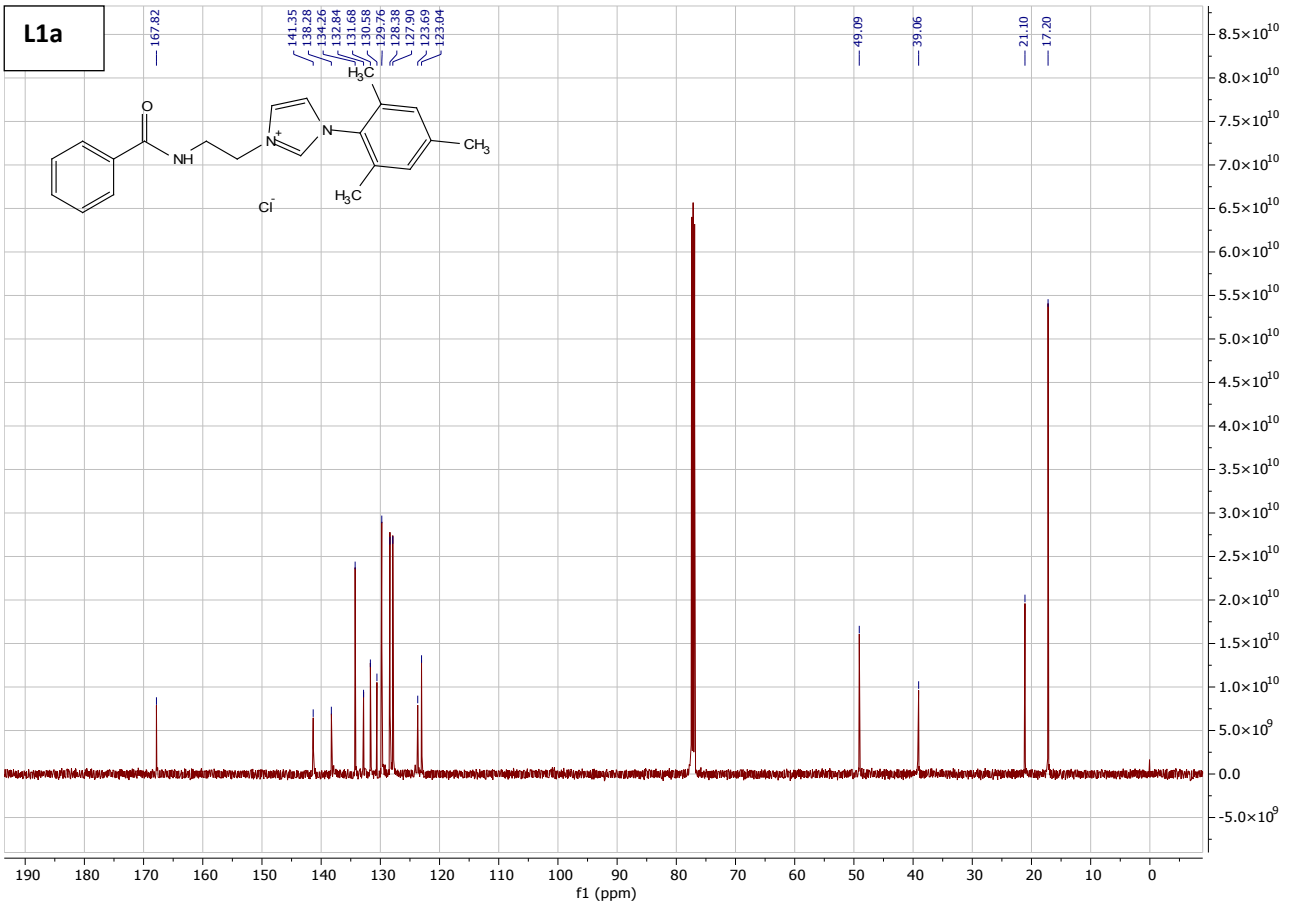

S3
E (m) 7.51
D (m) 7.44
C (s) 6.68
F (m) 7.79
B (ddd) 3.73
A (m) 3.80
f1 (ppm)

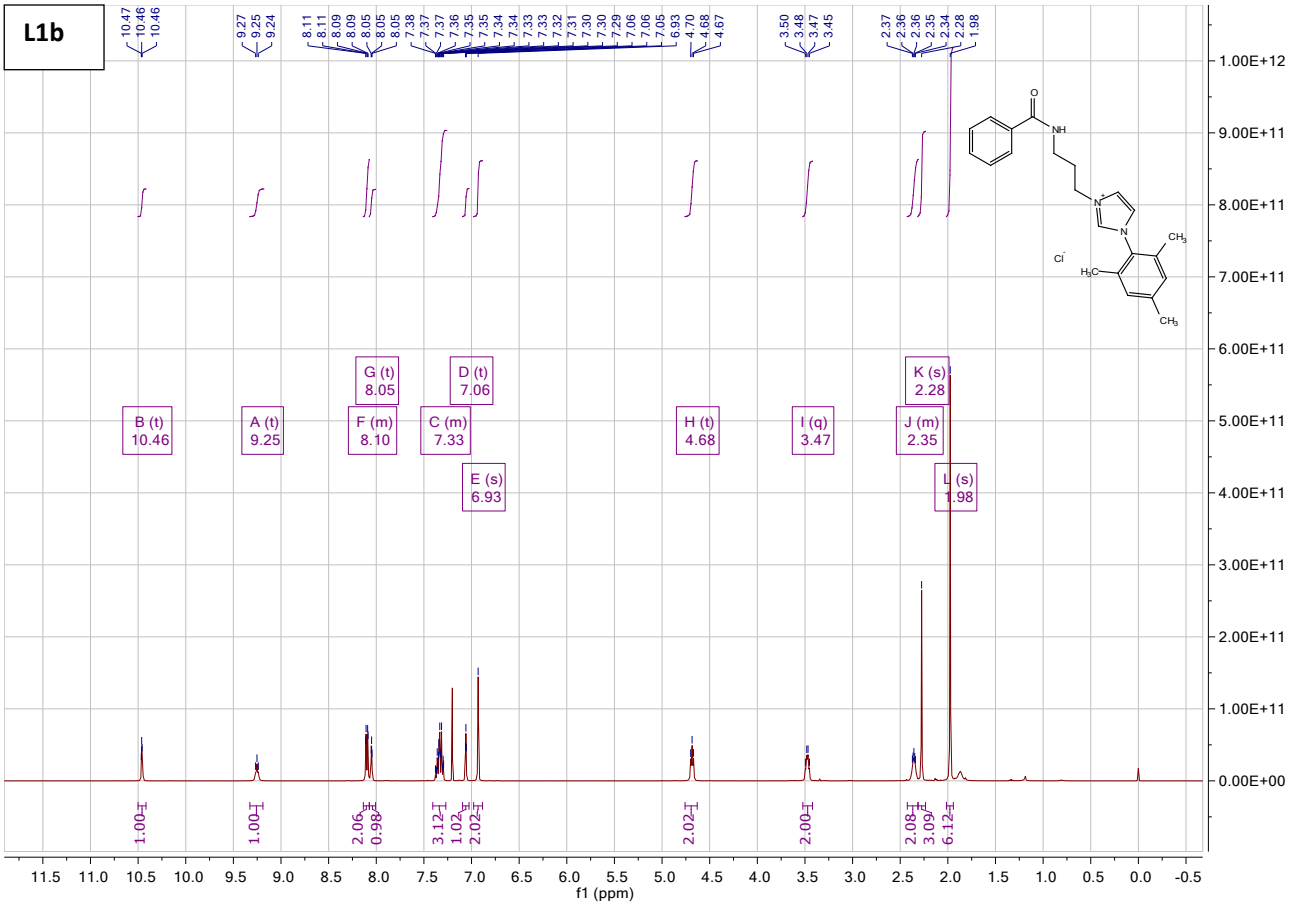

S3
167.79
134.19
131.88
128.77
127.10
44.21
41.80
f1 (ppm)

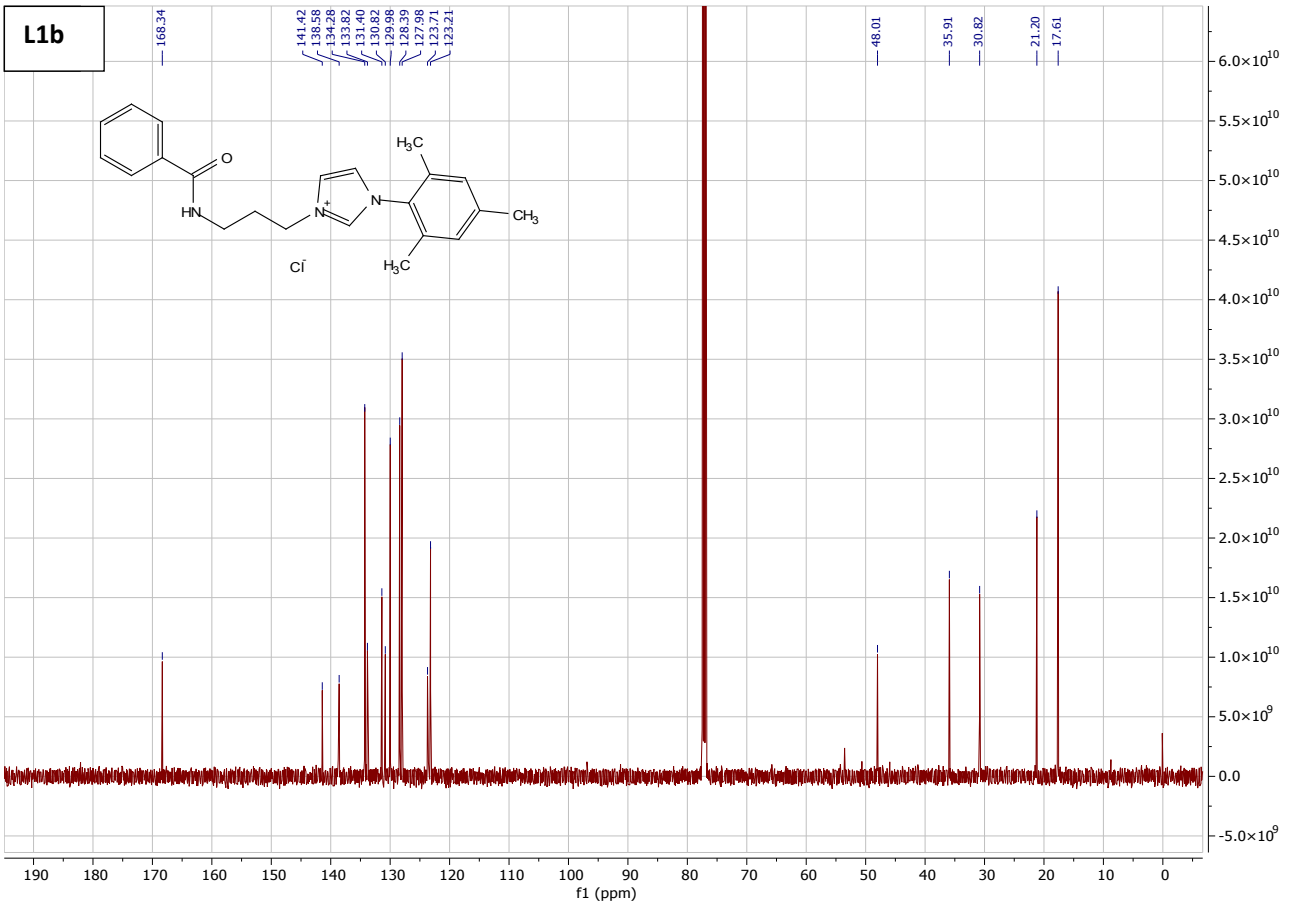

S4
B (m)
7.48
A (m)
7.77
C (m)
7.41
F (s)
6.70
D (m)
3.61
E (p)
2.10
f1 (ppm)


S4
167.95
134.47
131.62
128.66
127.01
42.81
37.75
32.15
f1 (ppm)

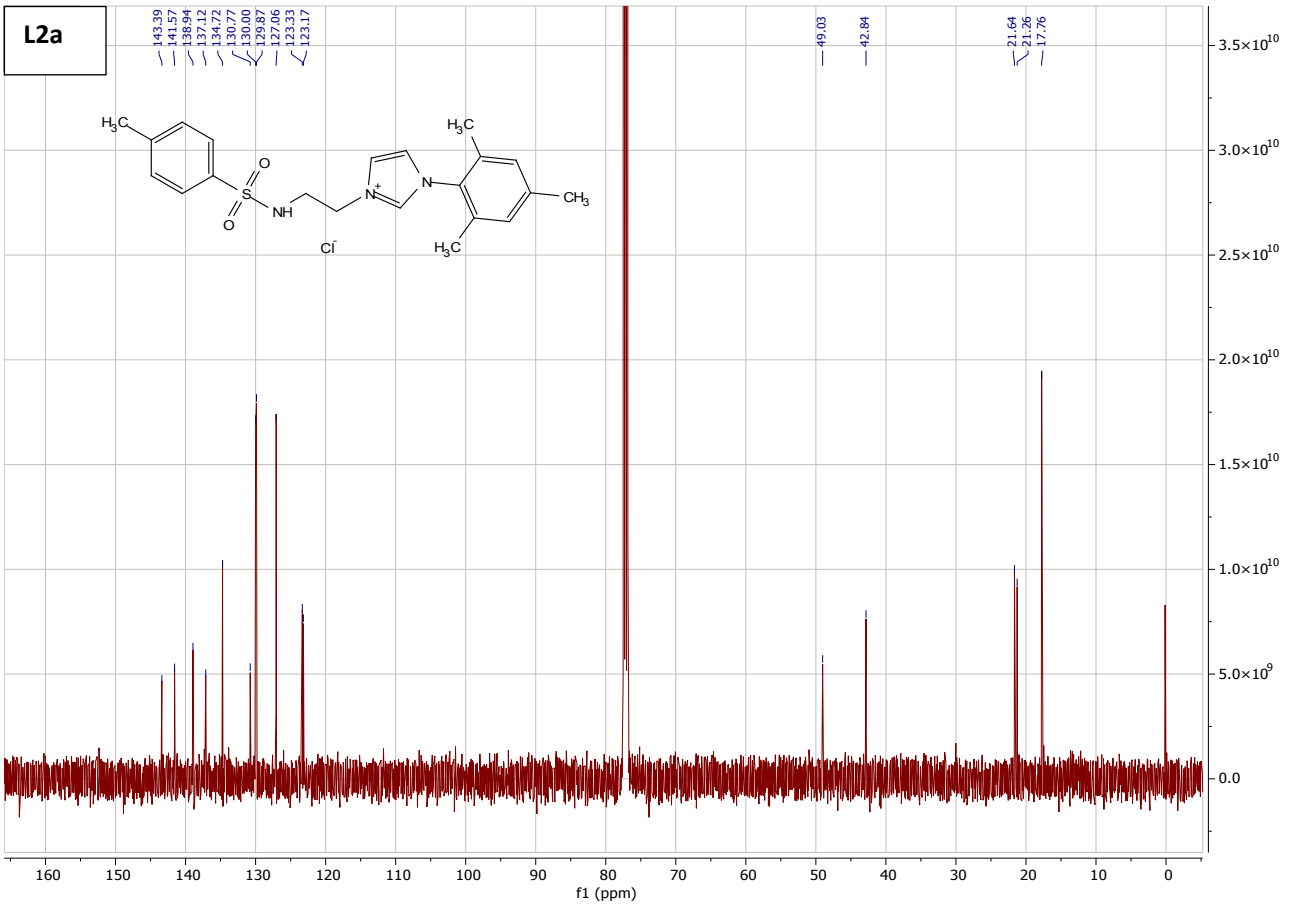

L1a
A (d) 10.01
B (t) 9.35
C (t) 8.10
K (d) 8.00
D (dtd) 7.40
E (q) 7.05
F (d) 6.88
G (q) 5.10
H (p) 4.11
I (s) 2.28
J (s) 1.81
f1 (ppm)

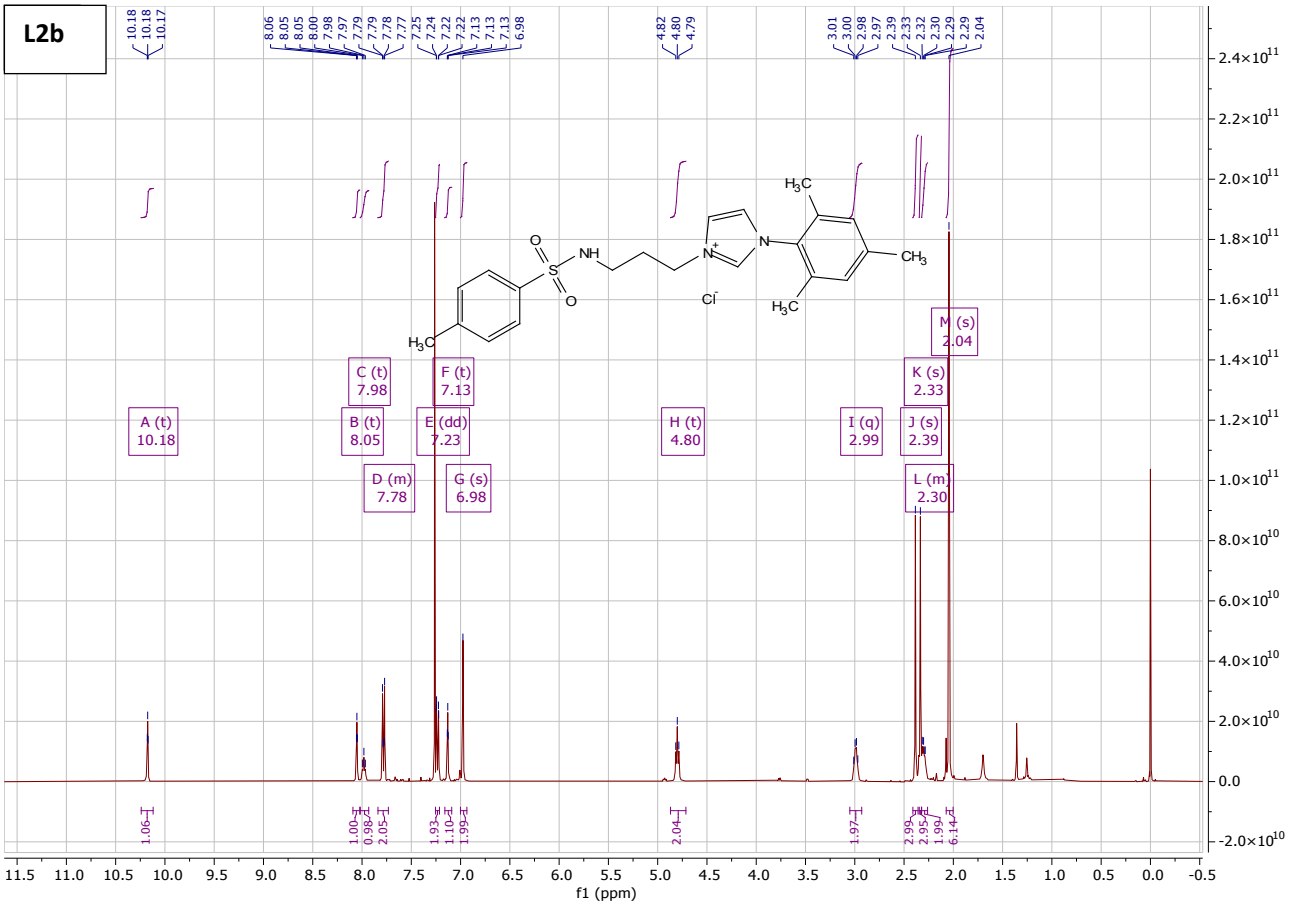

L1a
167.82
141.35
138.28
134.26
132.84
131.68
130.58
129.76
128.38
127.90
123.69
123.04
49.09
39.06
21.10
17.20
f1 (ppm)

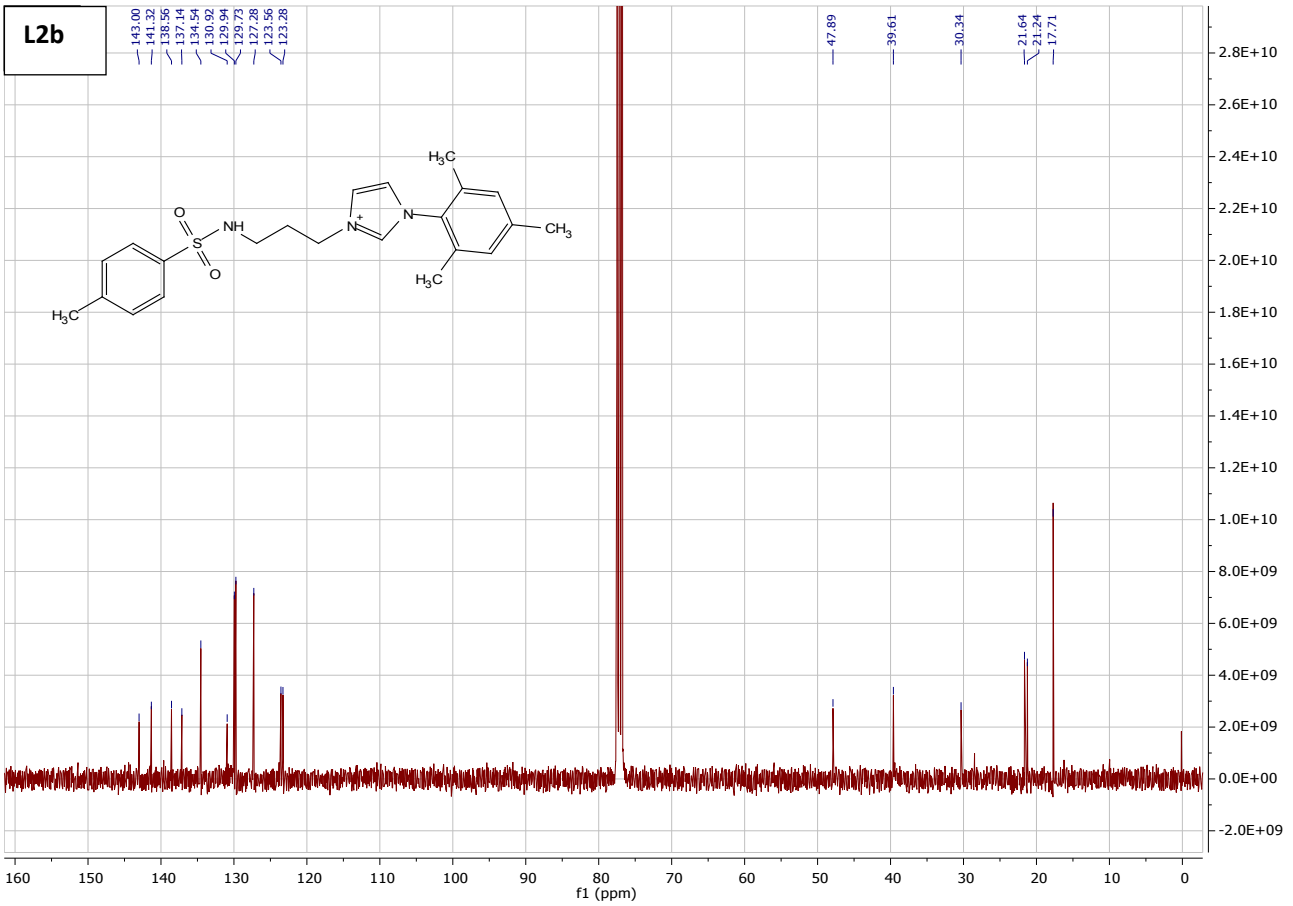

L1b
B (t) 10.46
A (t) 9.25
G (t) 8.05
F (m) 8.10
C (m) 7.33
D (t) 7.06
E (s) 6.93
H (t) 4.68
I (q) 3.47
K (s) 2.28
J (m) 2.35
L (s) 1.98
f1 (ppm)

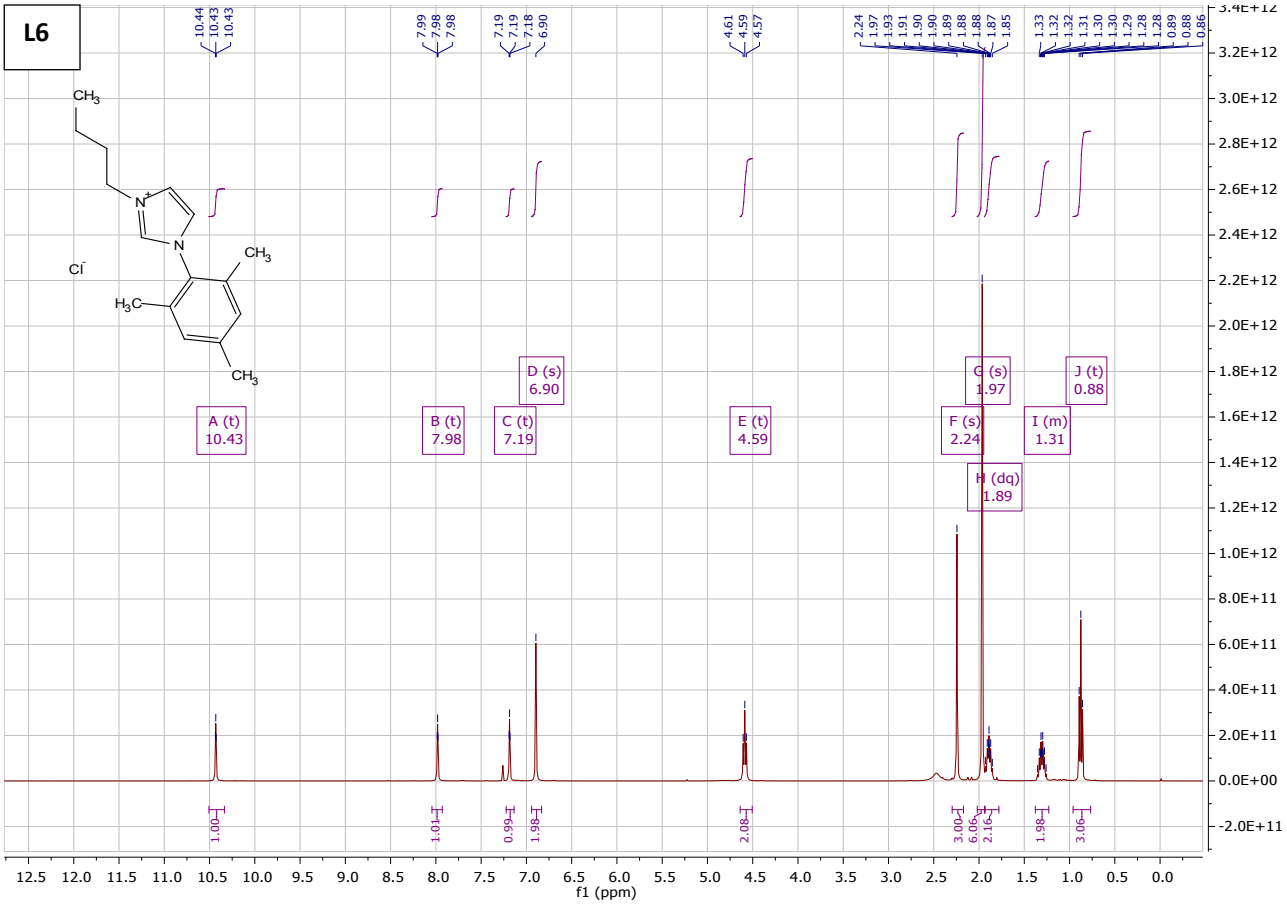

L1b
168.34
141.42
138.58
134.28
133.82
131.40
130.82
129.98
128.39
127.98
123.71
123.21
48.01
35.91
30.82
21.20
17.61
f1 (ppm)

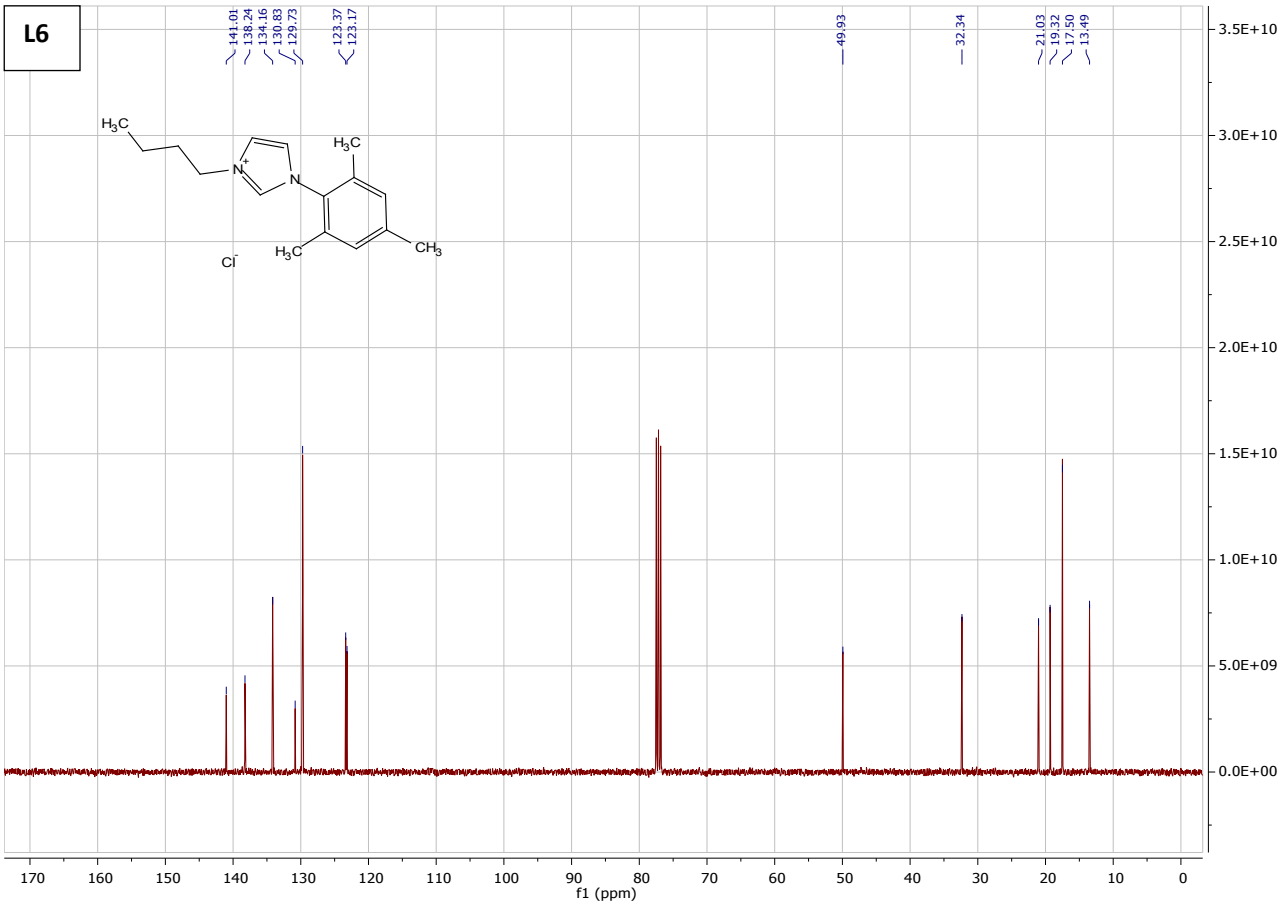

L2a
A (t) 9.78
B (t) 8.43
C (t) 8.20
D (d) 7.71
E (d) 7.21
F (t) 7.12
G (s) 6.95
H (m) 4.88
I (q) 3.37
J (s) 2.36
K (s) 2.32
L (s) 2.05
f1 (ppm)

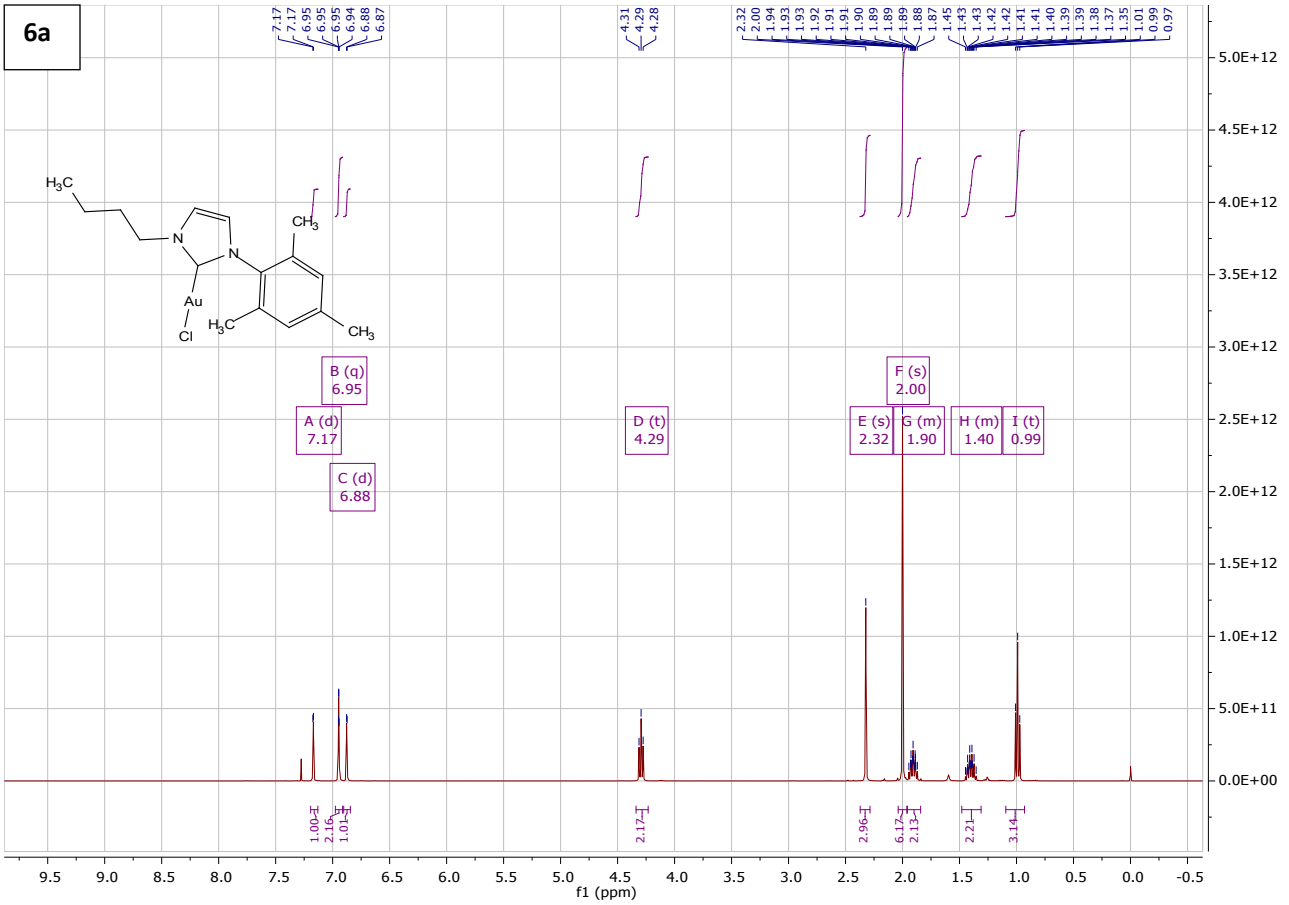

L2a
f1 (ppm)

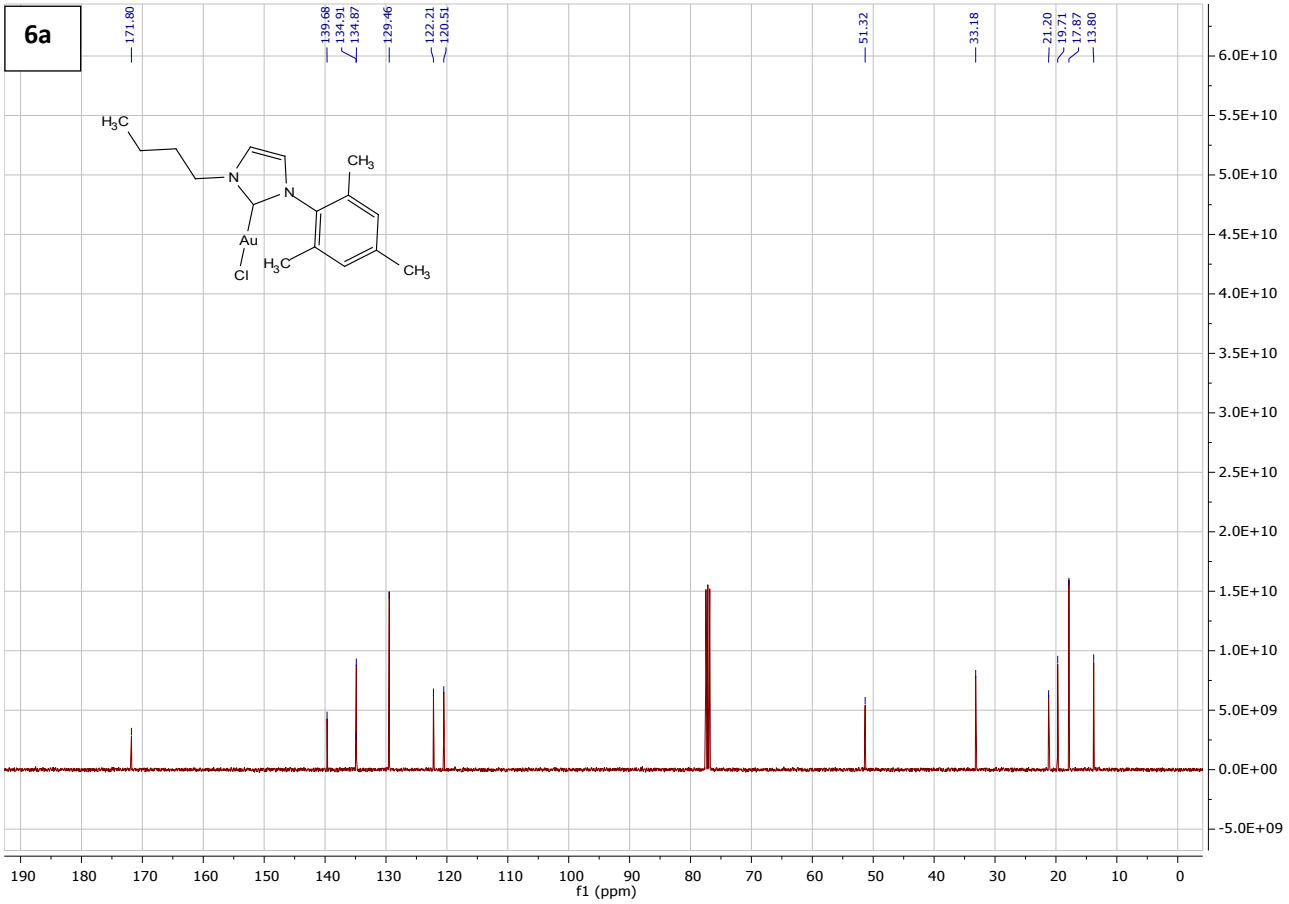

L2b
A (t) 10.18
B (t) 8.05
C (t) 7.98
D (m) 7.78
E (dd) 7.23
F (t) 7.13
G (s) 6.98
H (t) 4.80
I (q) 2.99
J (s) 2.39
K (s) 2.33
L (m) 2.30
M (s) 2.04
f1 (ppm)

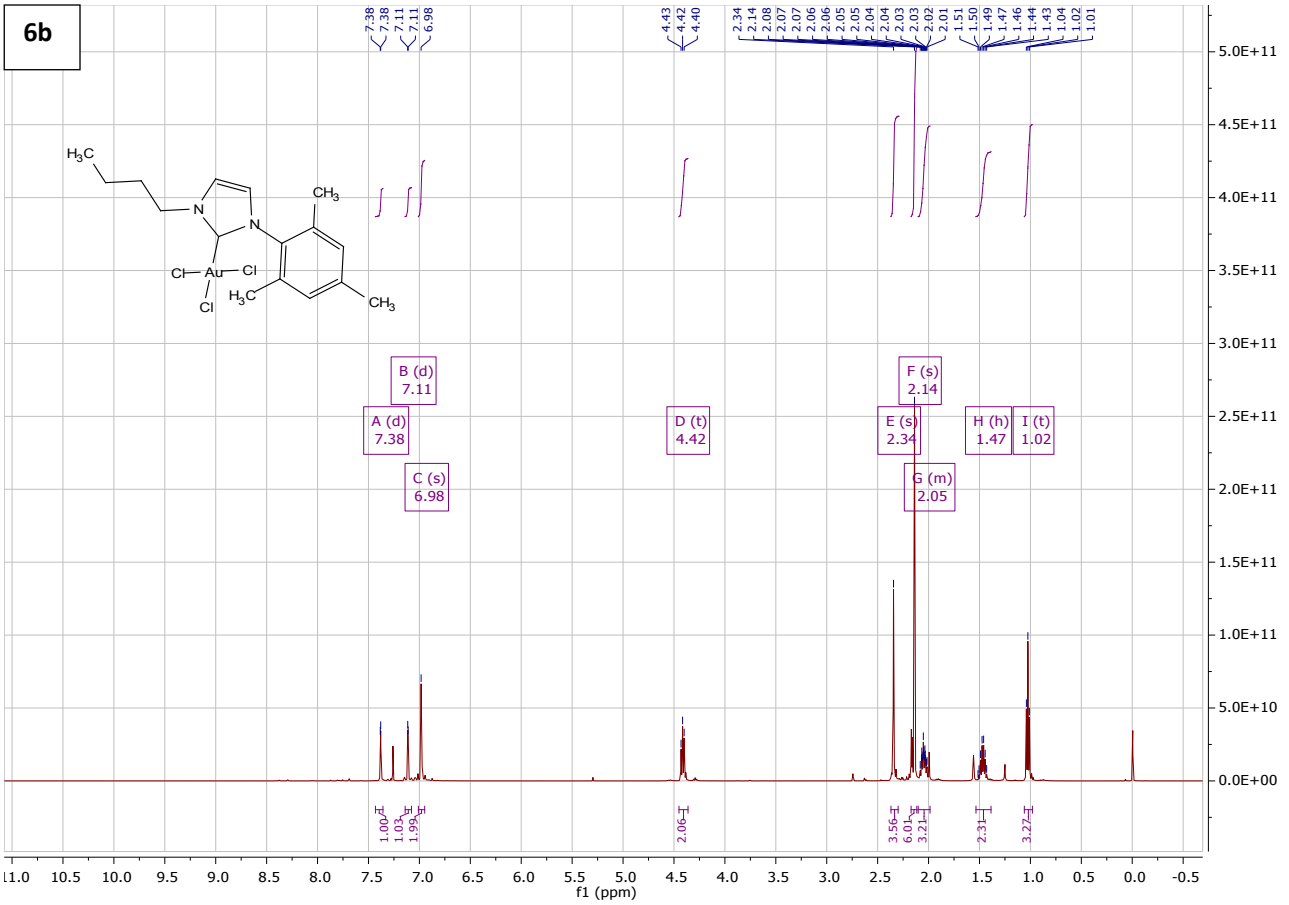

L2b
f1 (ppm)

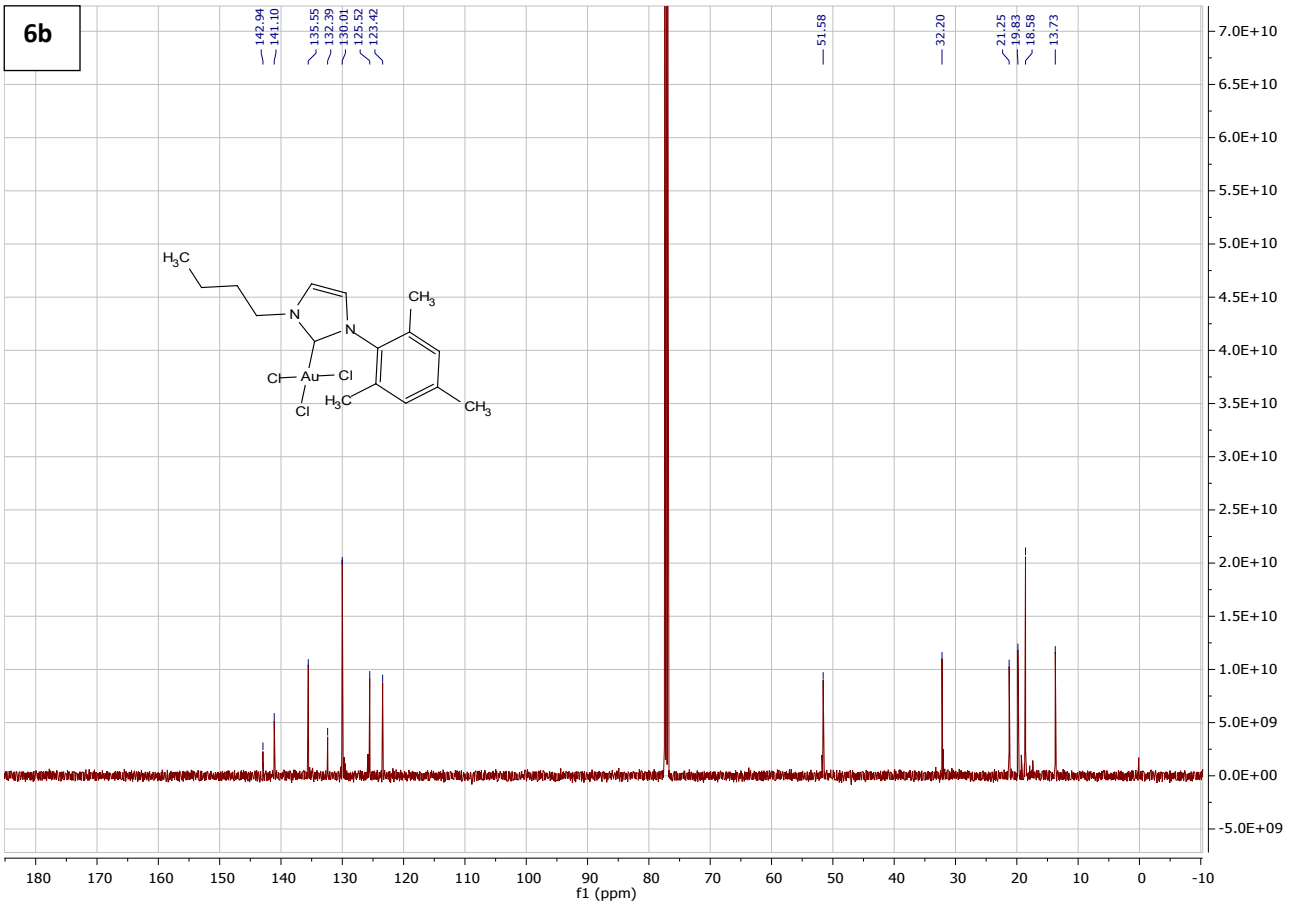

L6
A (t) 10.43
B (t) 7.98
C (t) 7.19
D (s) 6.90
E (t) 4.59
F (s) 2.24
G (s) 1.97
H (dq) 1.89
I (m) 1.31
J (t) 0.88
f1 (ppm)

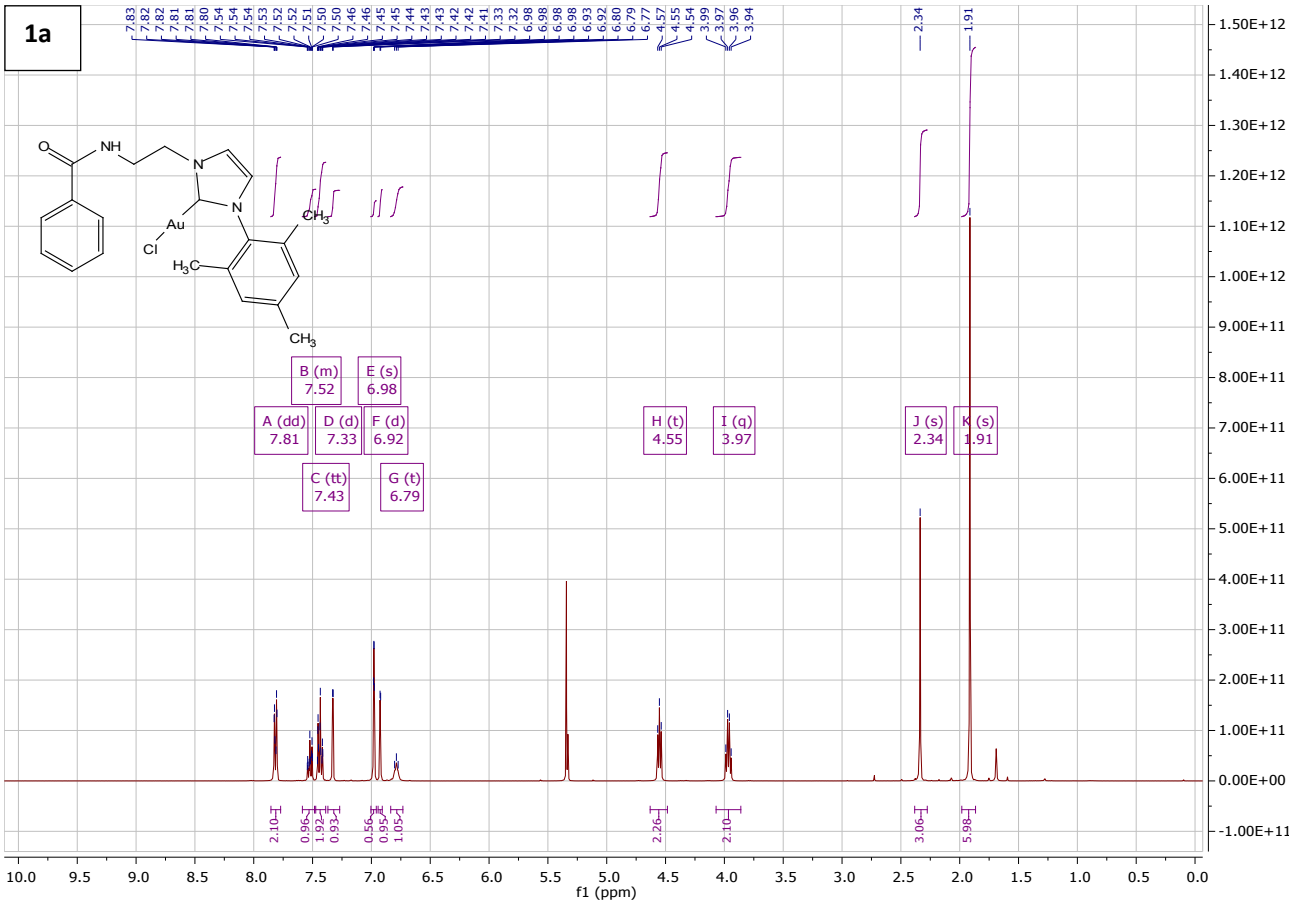

L6
f1 (ppm)

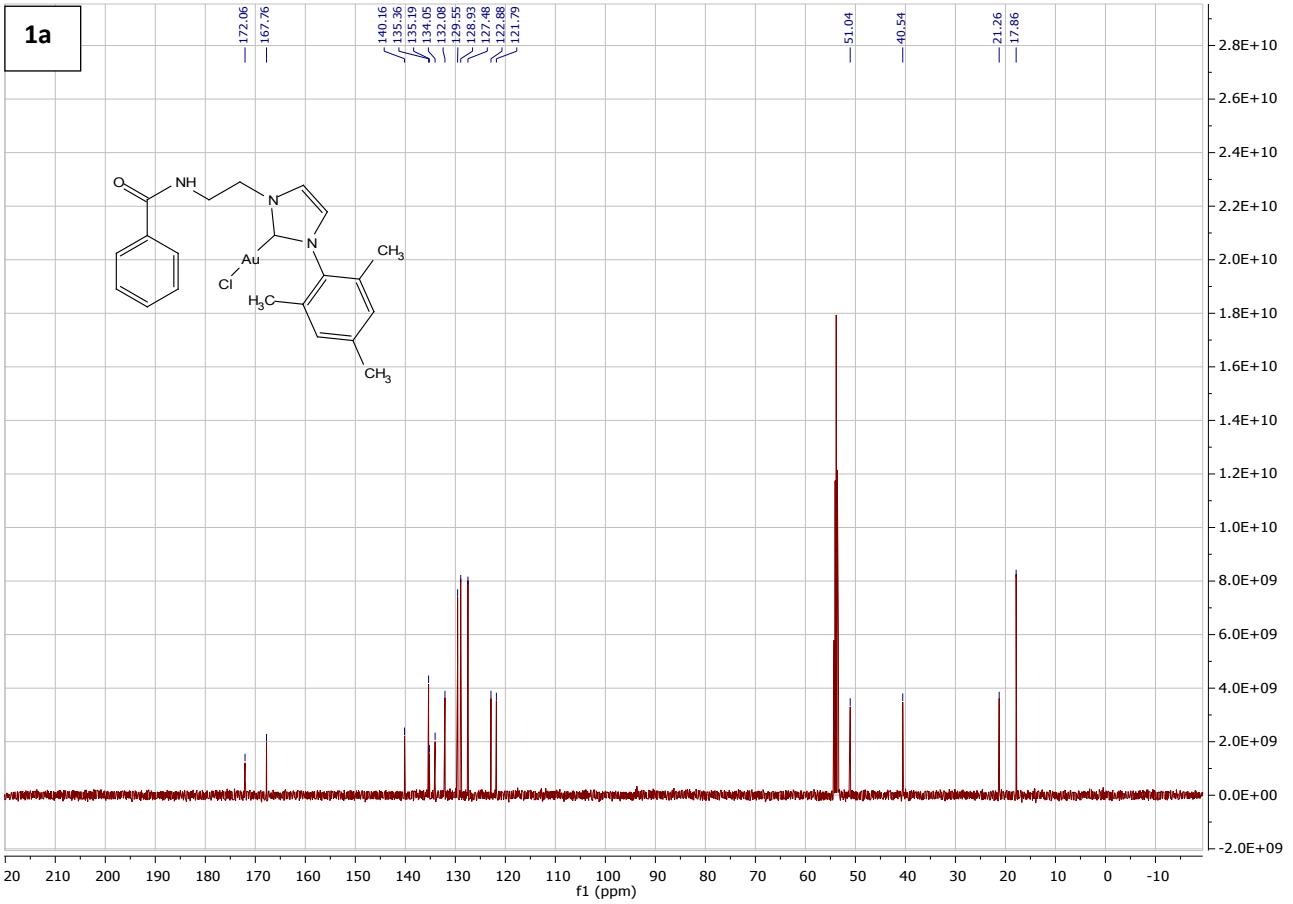

6a
B (q) 6.95
A (d) 7.17
C (d) 6.88
D (t) 4.29
F (s) 2.00
E (s) 2.32
G (m) 1.90
H (m) 1.40
I (t) 0.99
f1 (ppm)

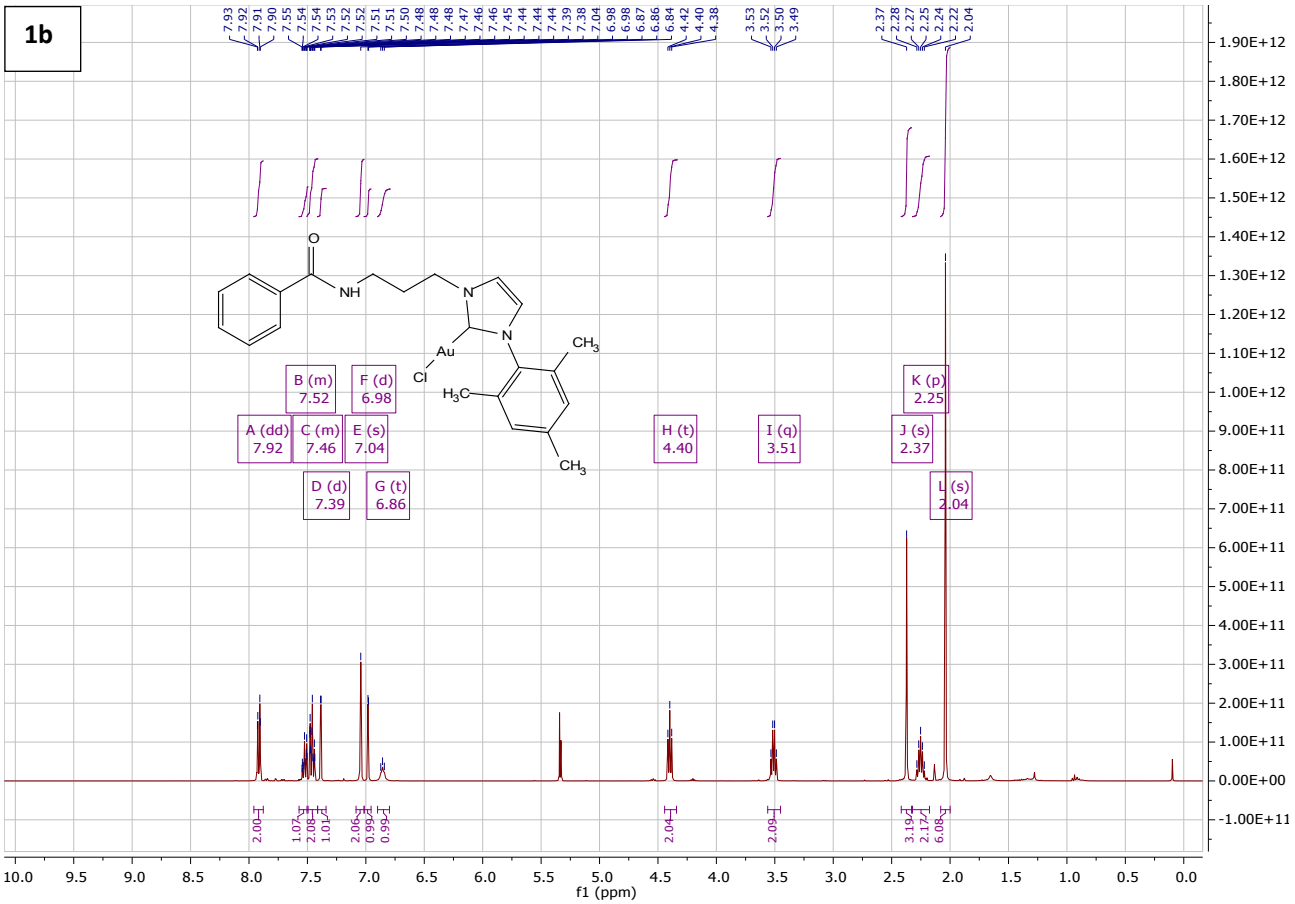

6a
f1 (ppm)

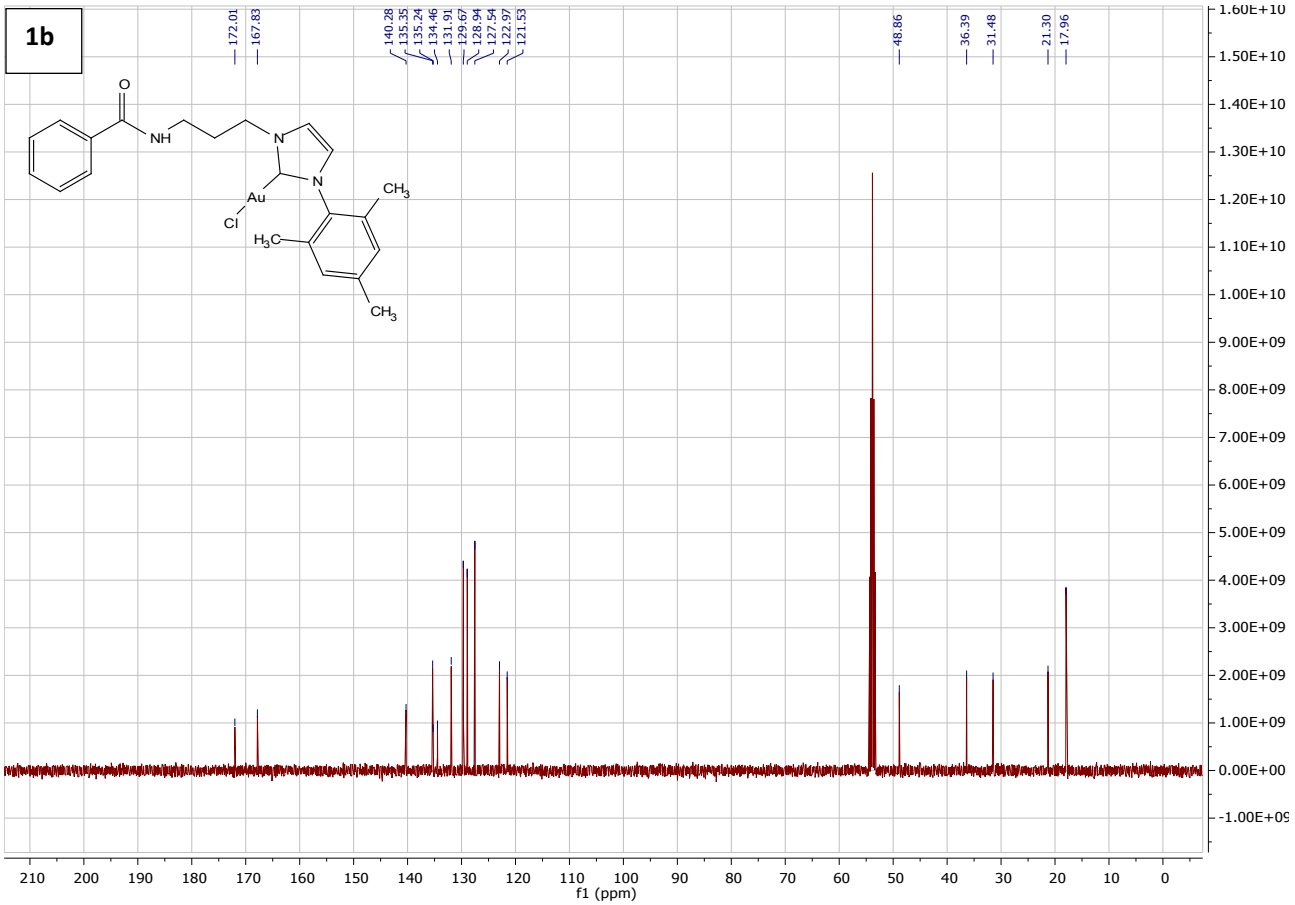

6b
B (d) 7.11
A (d) 7.38
C (s) 6.98
D (t) 4.42
F (s) 2.14
E (s) 2.34
G (m) 2.05
H (h) 1.47
I (t) 1.02
f1 (ppm)


6b
f1 (ppm)


1a
B (m) 7.52
E (s) 6.98
A (dd) 7.81
D (d) 7.33
F (d) 6.92
C (tt) 7.43
G (t) 6.79
H (t) 4.55
I (q) 3.97
J (s) 2.34
K (s) 1.91
f1 (ppm)


1a
f1 (ppm)


1b
B (m) 7.52
F (d) 6.98
A (dd) 7.92
C (m) 7.46
E (s) 7.04
D (d) 7.39
G (t) 6.86
H (t) 4.40
I (q) 3.51
K (p) 2.25
J (s) 2.37
L (s) 2.04
f1 (ppm)


1b
172.01
167.83
140.28
135.35
135.24
134.46
131.91
129.67
128.94
127.54
122.97
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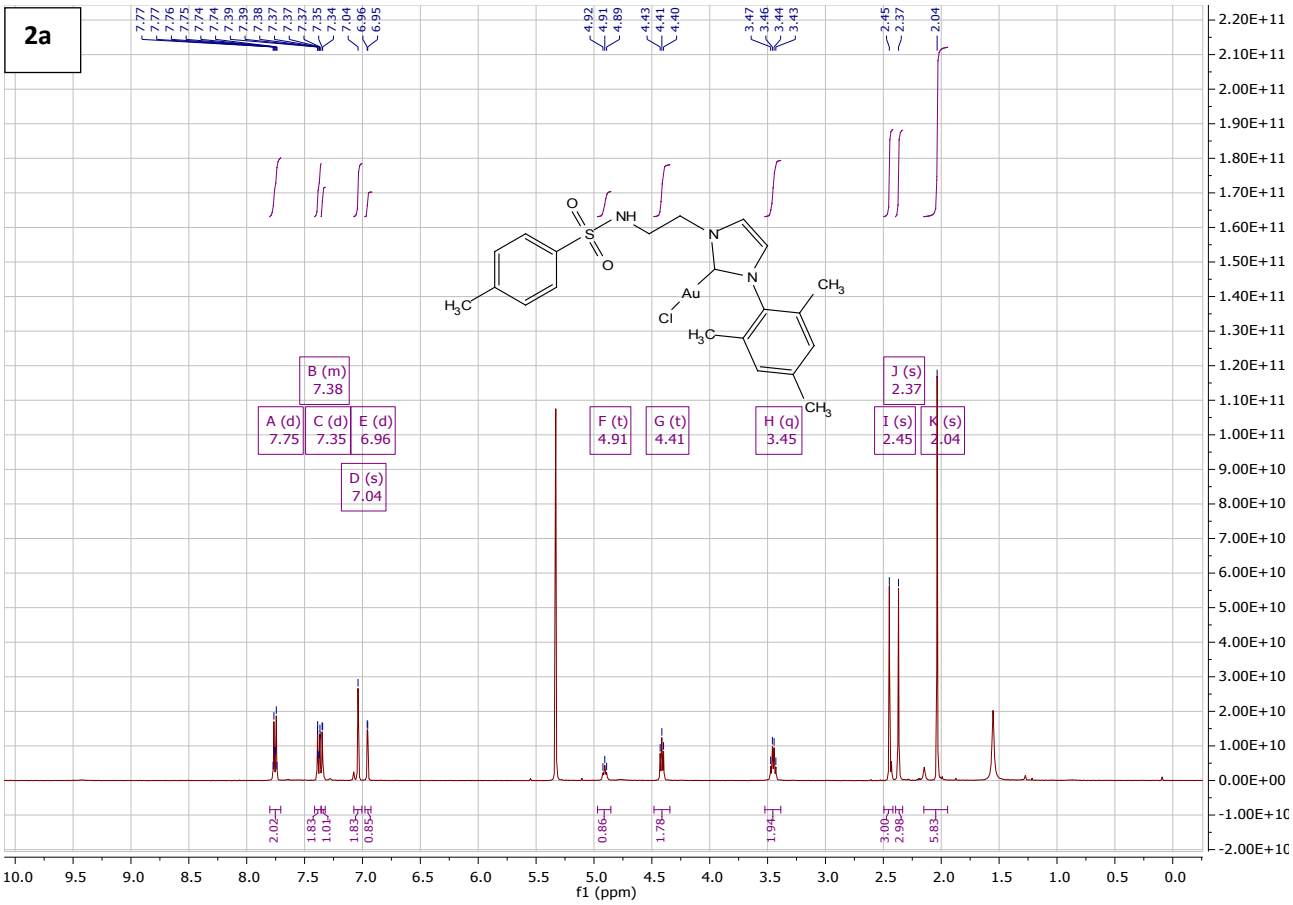
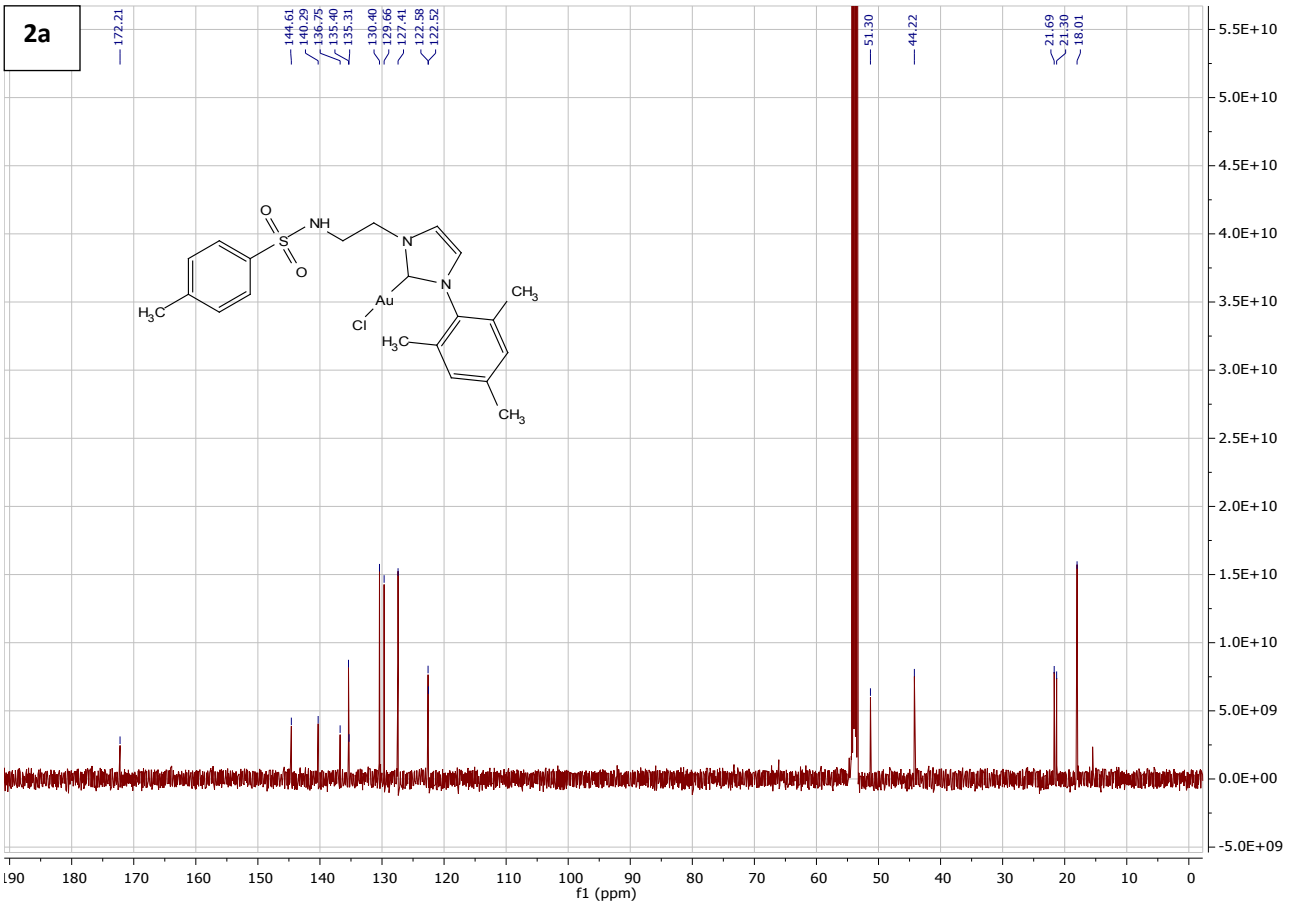
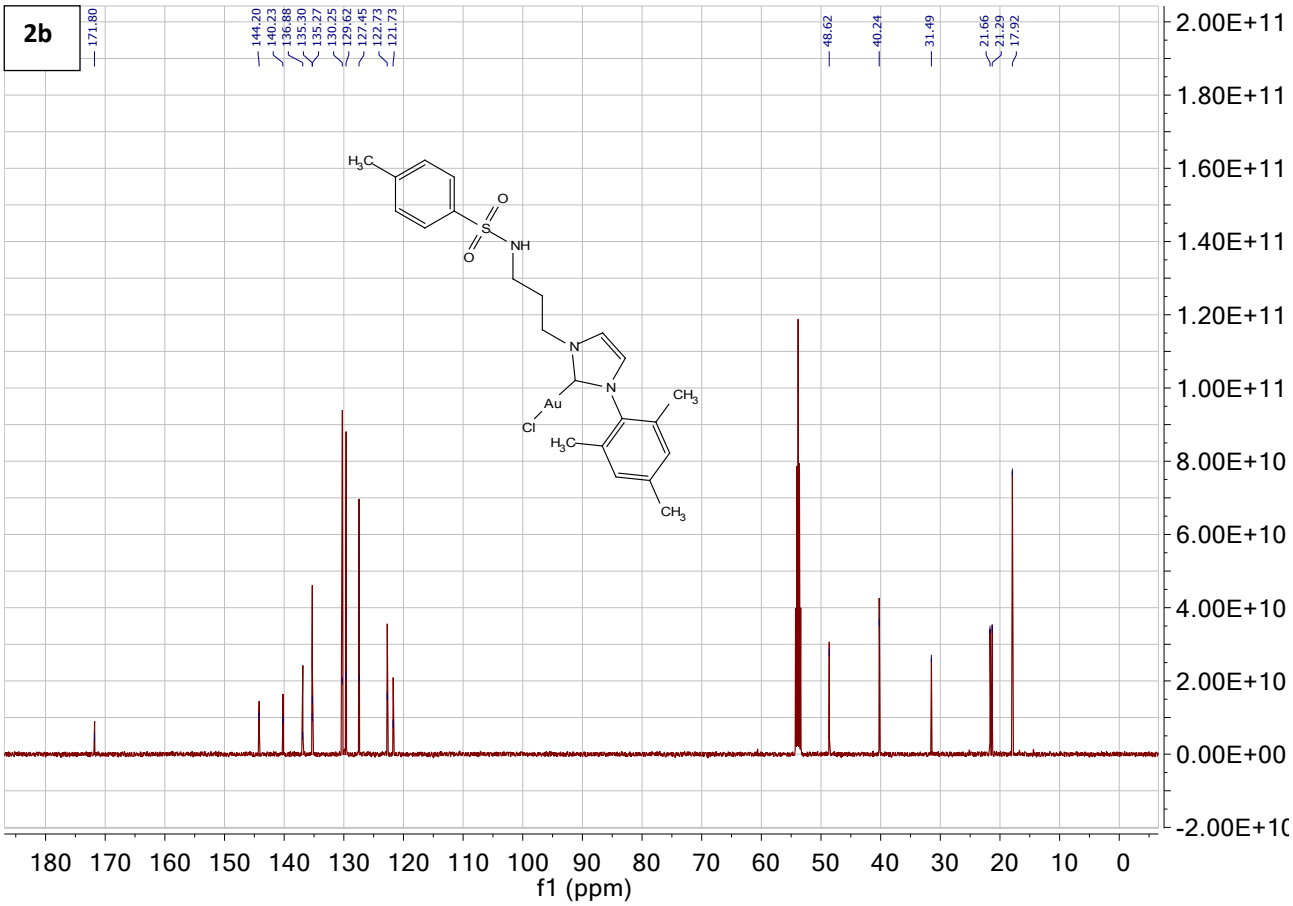
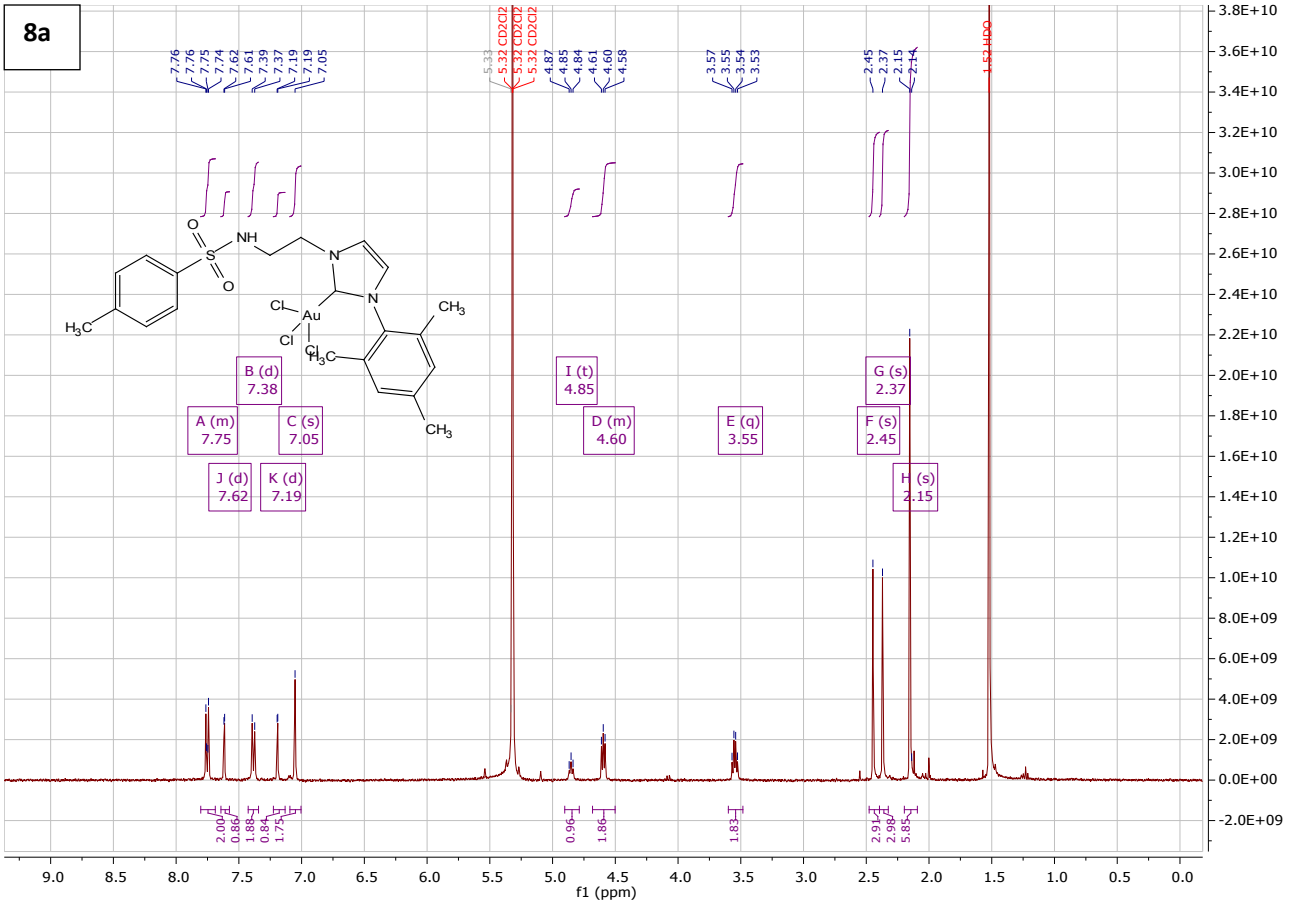
48.86
36.39
31.48
21.30
17.96
f1 (ppm)

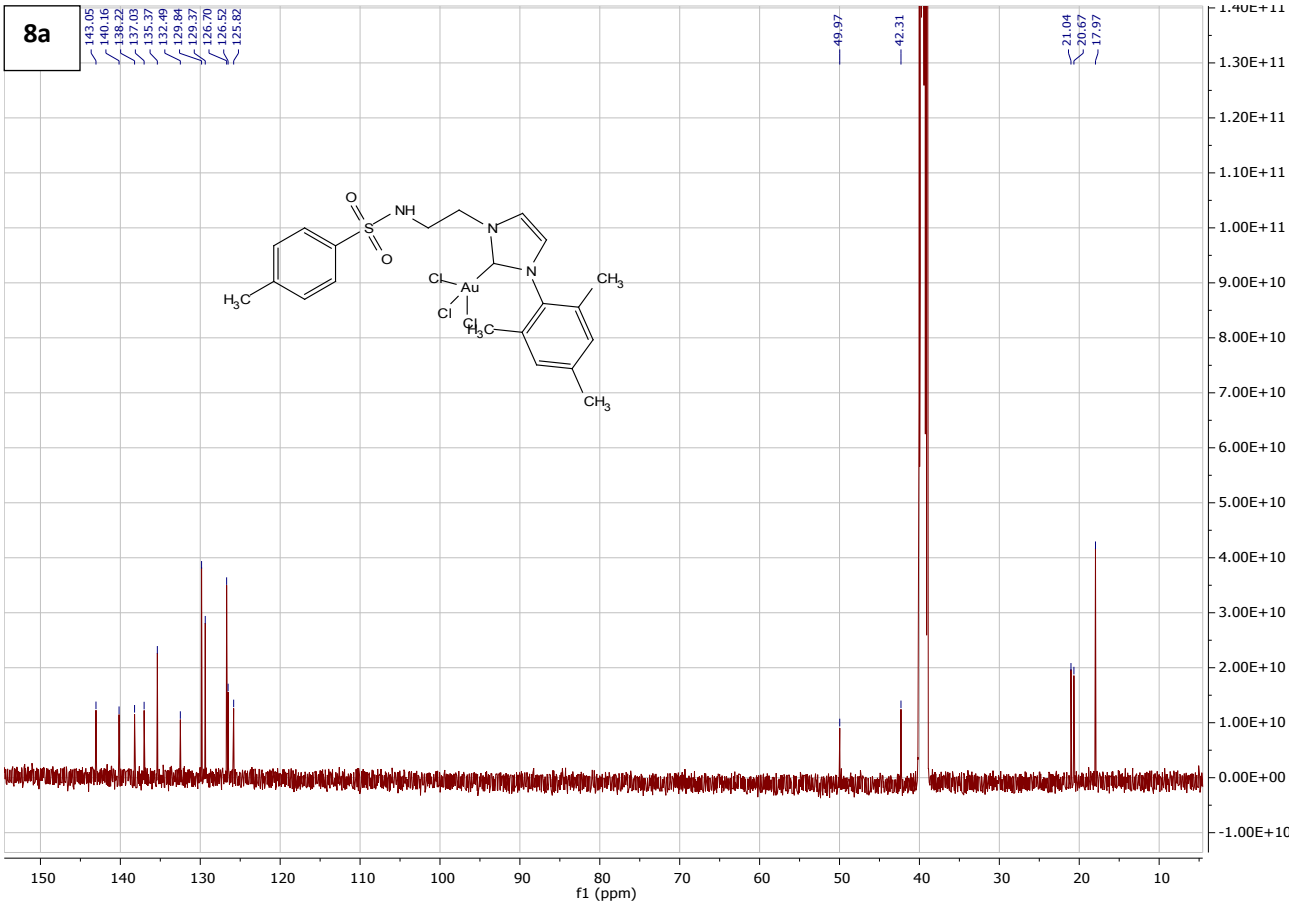

2a
7.77
7.77
7.76
7.75
7.74
7.74
7.39
7.38
7.37
7.37
7.37
7.35
7.34
7.04
6.96
6.95
4.92
4.91
4.89
4.43
4.41
4.40
3.47
3.46
3.44
3.43
2.45
2.37
2.04
B (m) 7.38
A (d) 7.75
C (d) 7.35
E (d) 6.96
D (s) 7.04
F (t) 4.91
G (t) 4.41
H (q) 3.45
J (s) 2.37
I (s) 2.45
K (s) 2.04
2.02
1.83
1.01
1.83
0.85
0.86
1.78
1.94
3.00
2.98
5.83
f1 (ppm)

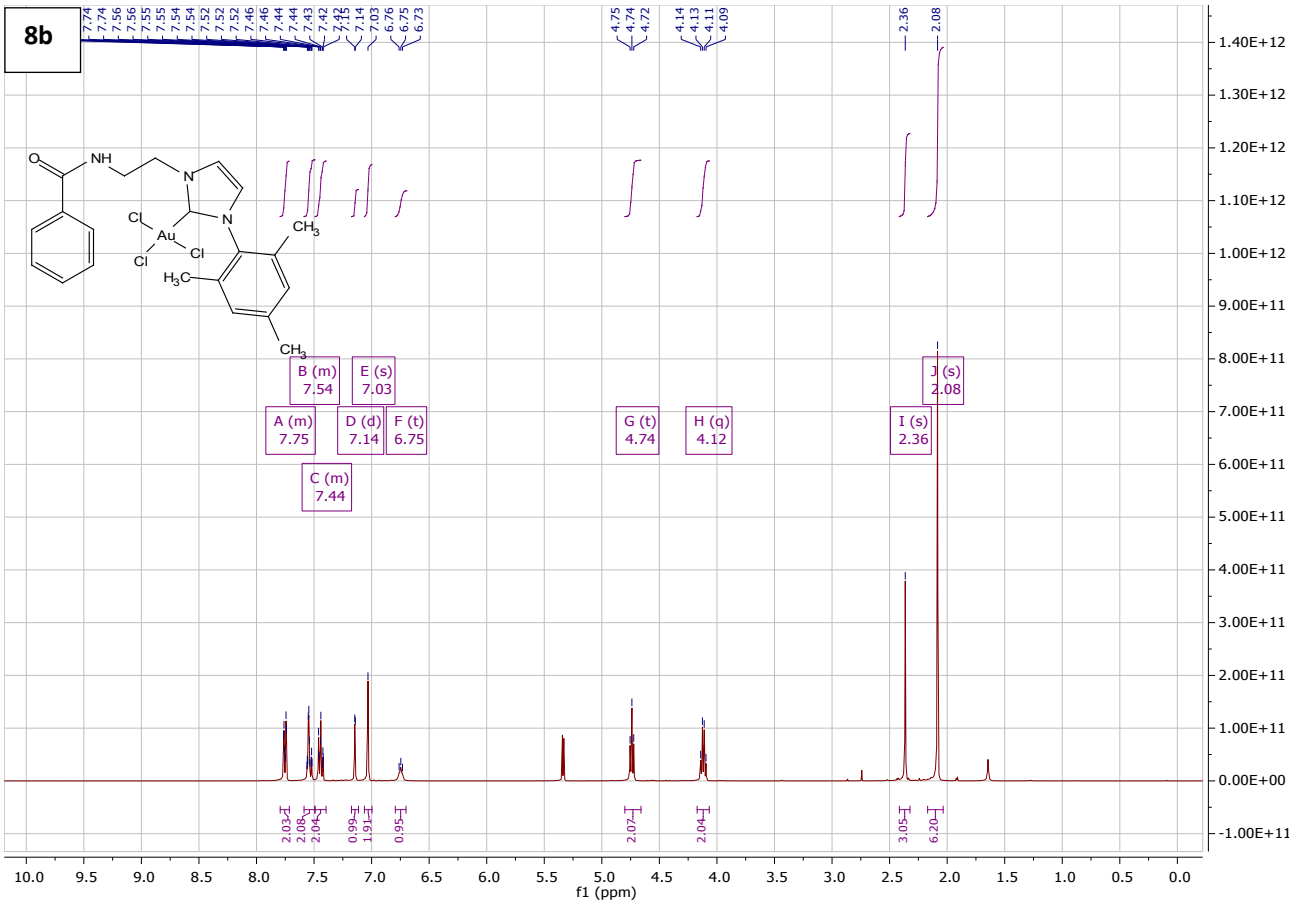

2a
172.21
144.61
140.29
136.75
135.40
135.31
130.40
129.66
127.41
122.58
122.52
51.30
44.22
21.69
21.30
18.01
f1 (ppm)

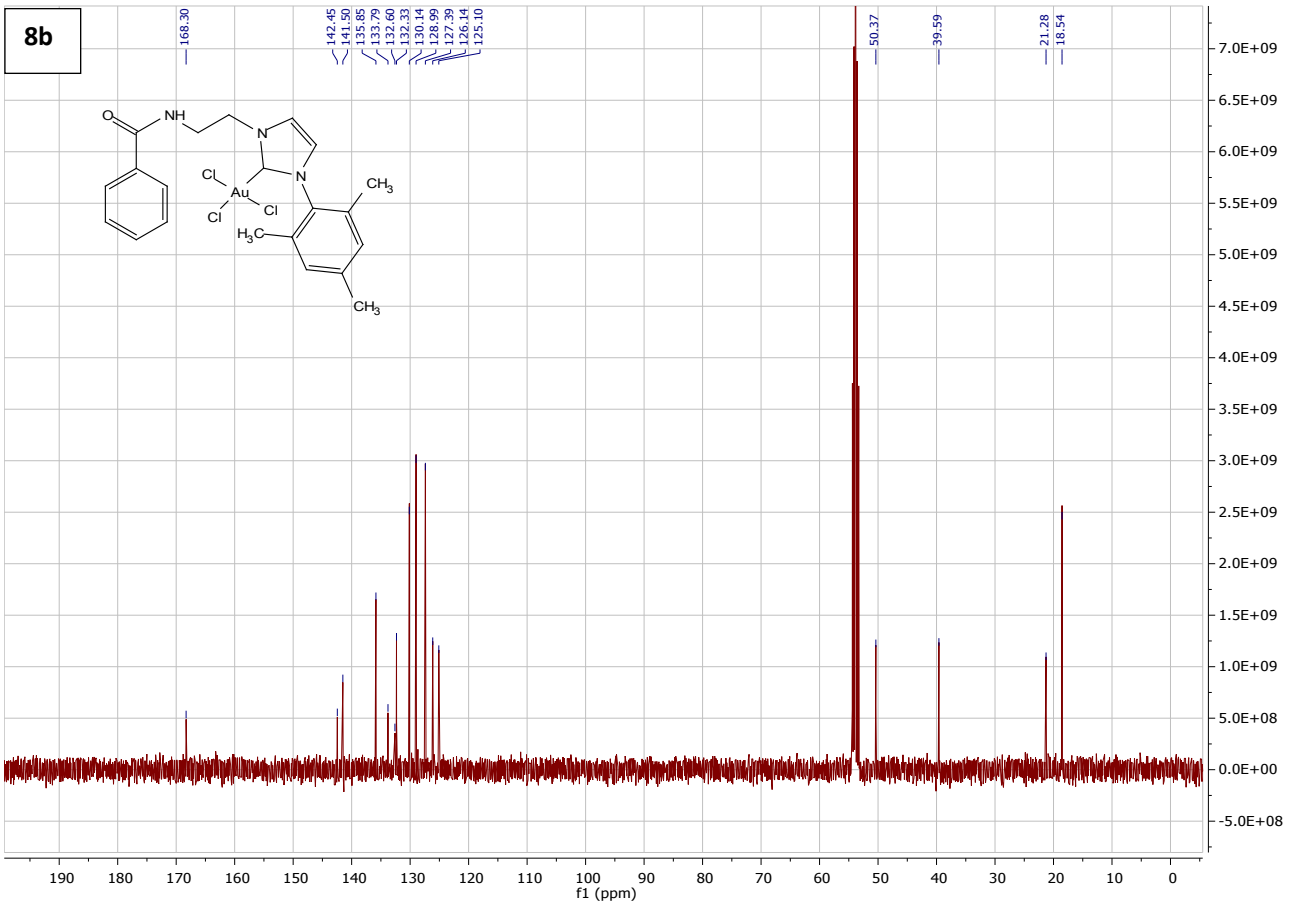

2b
f1 (ppm)

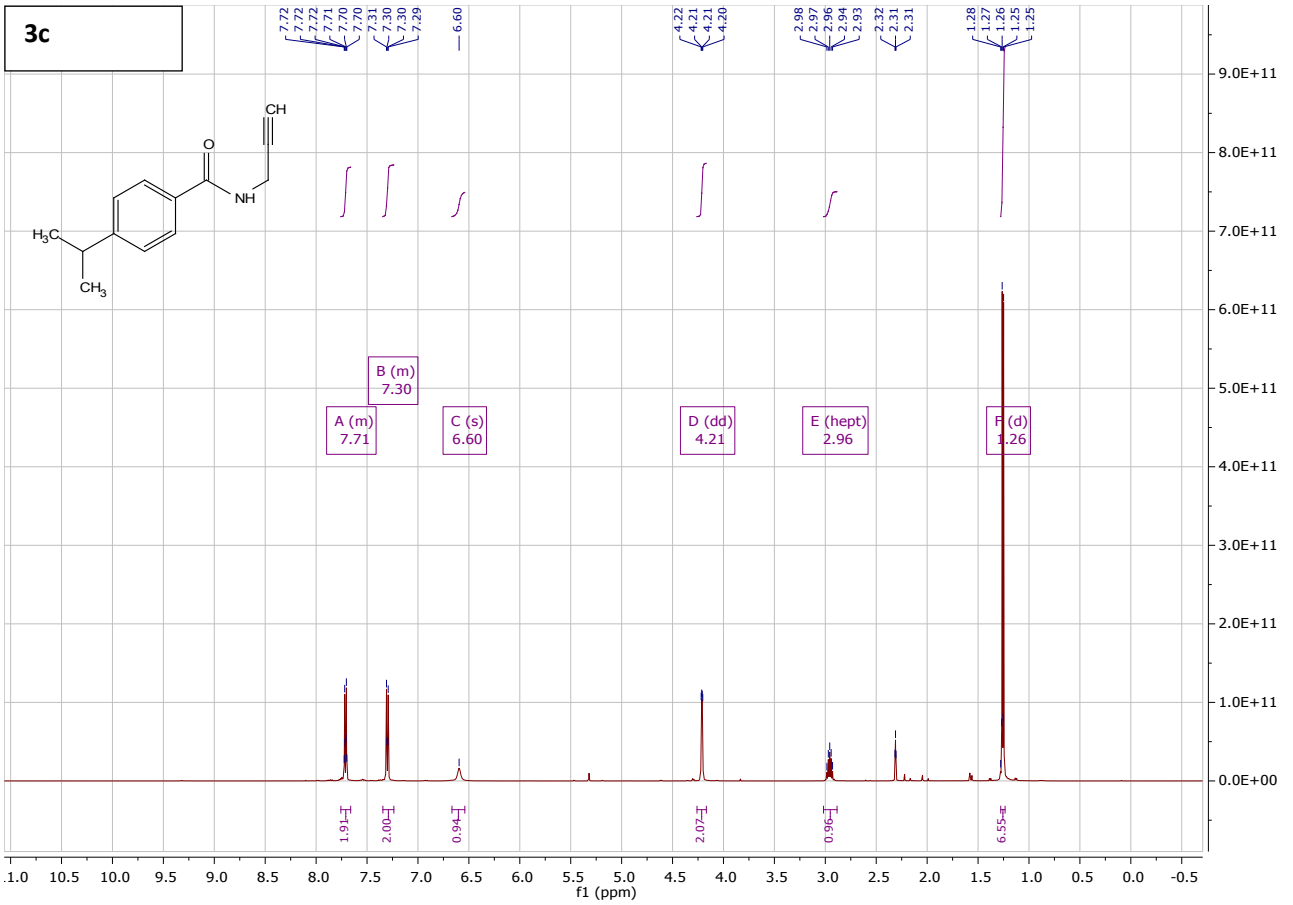

2b
f1 (ppm)

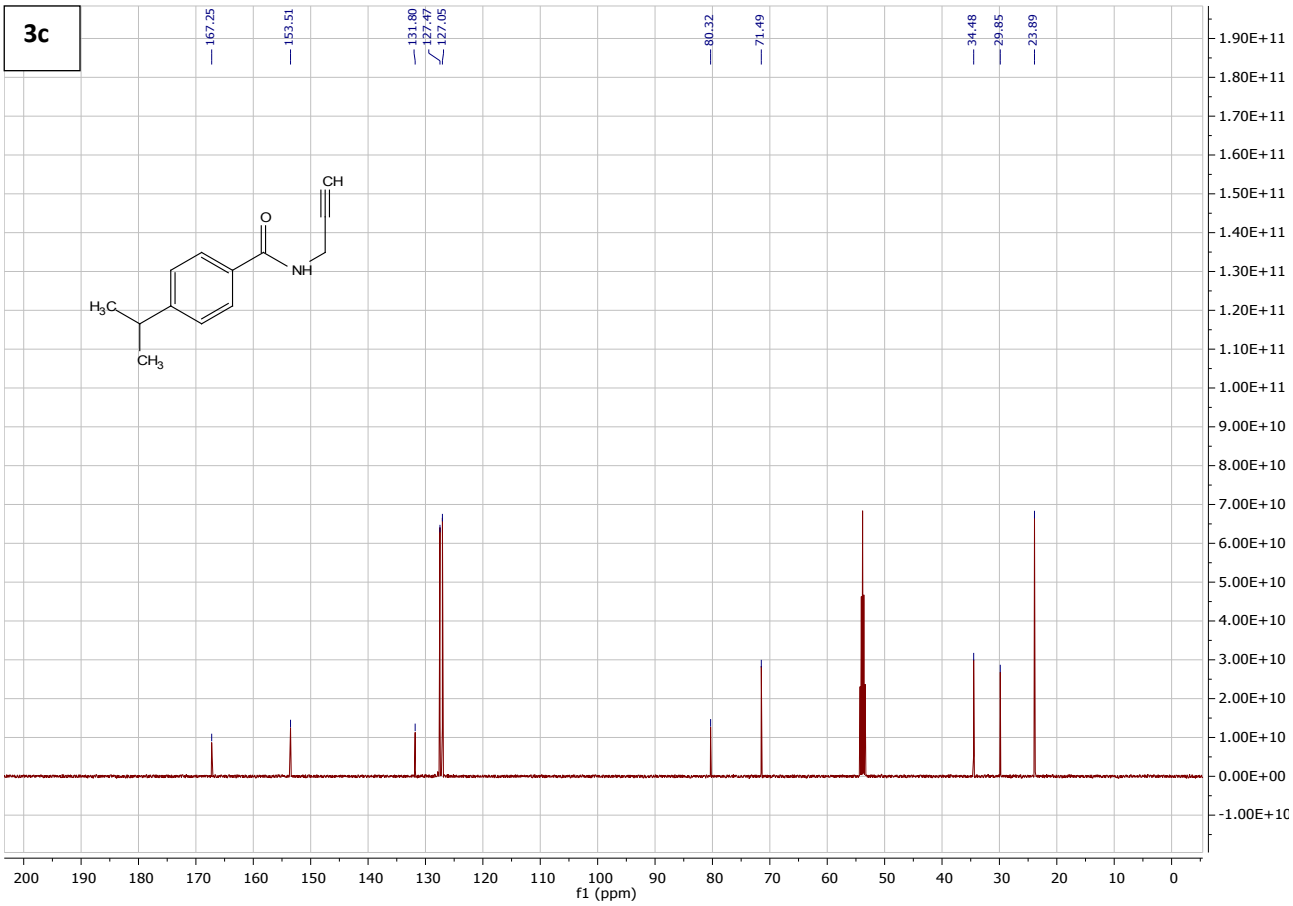

8a
7.76
7.76
7.75
7.74
7.62
7.61
7.39
7.37
7.19
7.19
7.05
5.33
5.32 CD2Cl2
5.32 CD2Cl2
5.32 CD2Cl2
4.87
4.85
4.84
4.61
4.60
4.58
3.57
3.55
3.54
3.53
2.45
2.37
2.15
2.14
1.53 H2O
B (d) 7.38
I (t) 4.85
G (s) 2.37
A (m) 7.75
C (s) 7.05
D (m) 4.60
E (q) 3.55
F (s) 2.45
J (d) 7.62
K (d) 7.19
H (s) 2.15
2.00
0.86
1.88
0.84
1.75
0.96
1.86
1.83
2.91
2.98
5.85
f1 (ppm)

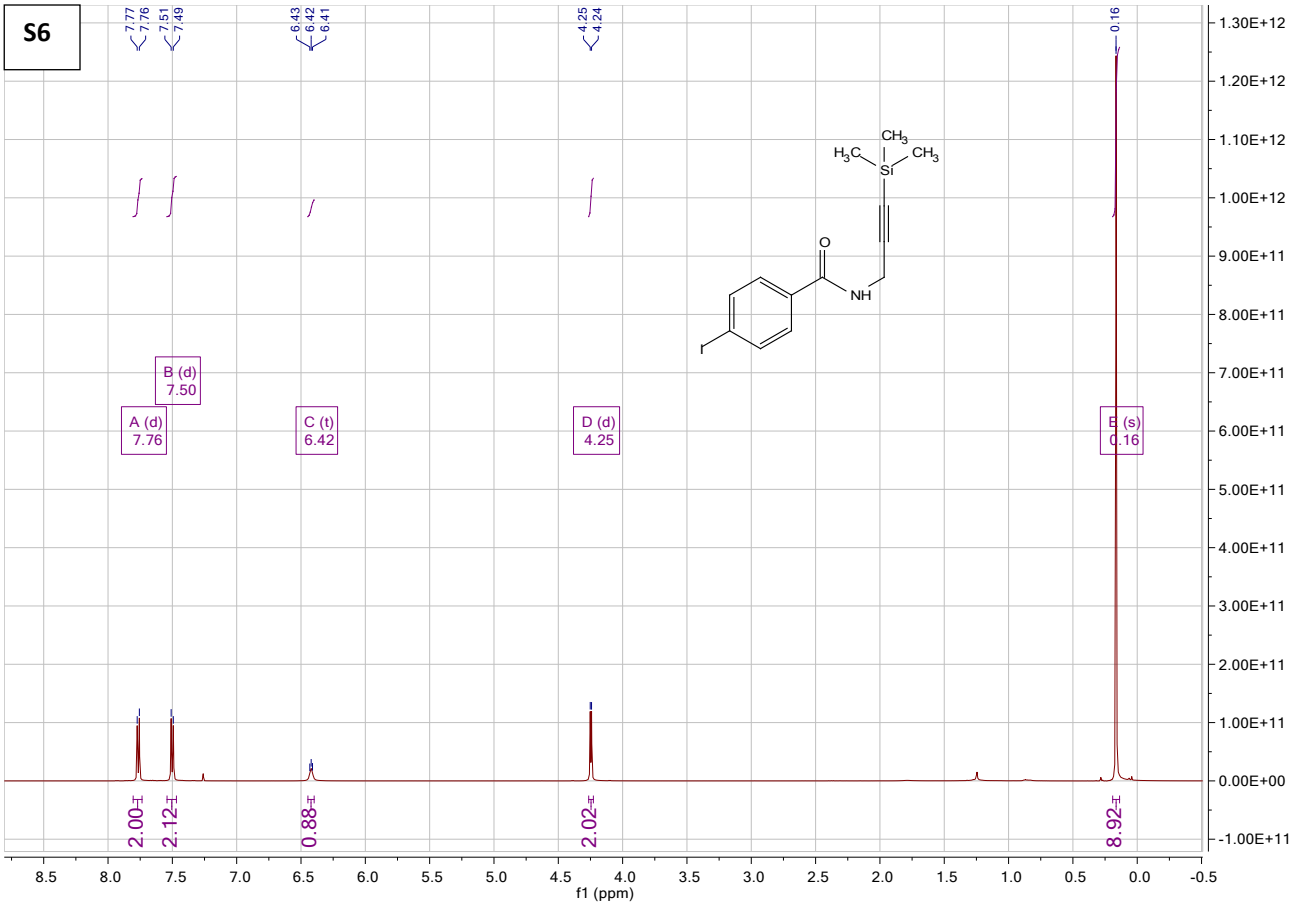

8a
143.05
140.16
138.22
137.03
135.37
132.49
129.84
129.37
126.70
126.52
125.82
49.97
42.31
21.04
20.67
17.97
f1 (ppm)

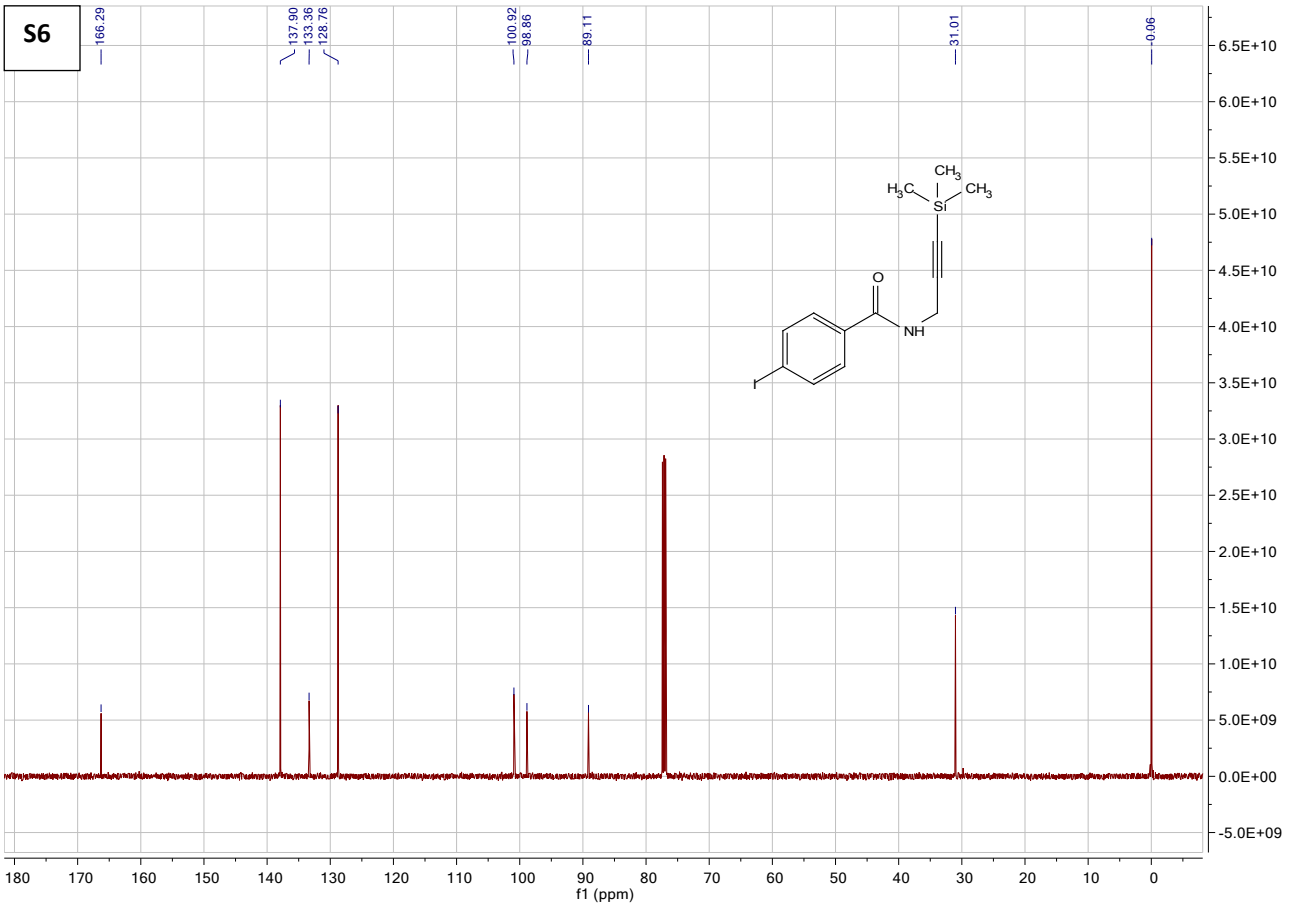

8b
B (m) 7.54
E (s) 7.03
J (s) 2.08
A (m) 7.75
D (d) 7.14
F (t) 6.75
G (t) 4.74
H (q) 4.12
I (s) 2.36
C (m) 7.44
f1 (ppm)

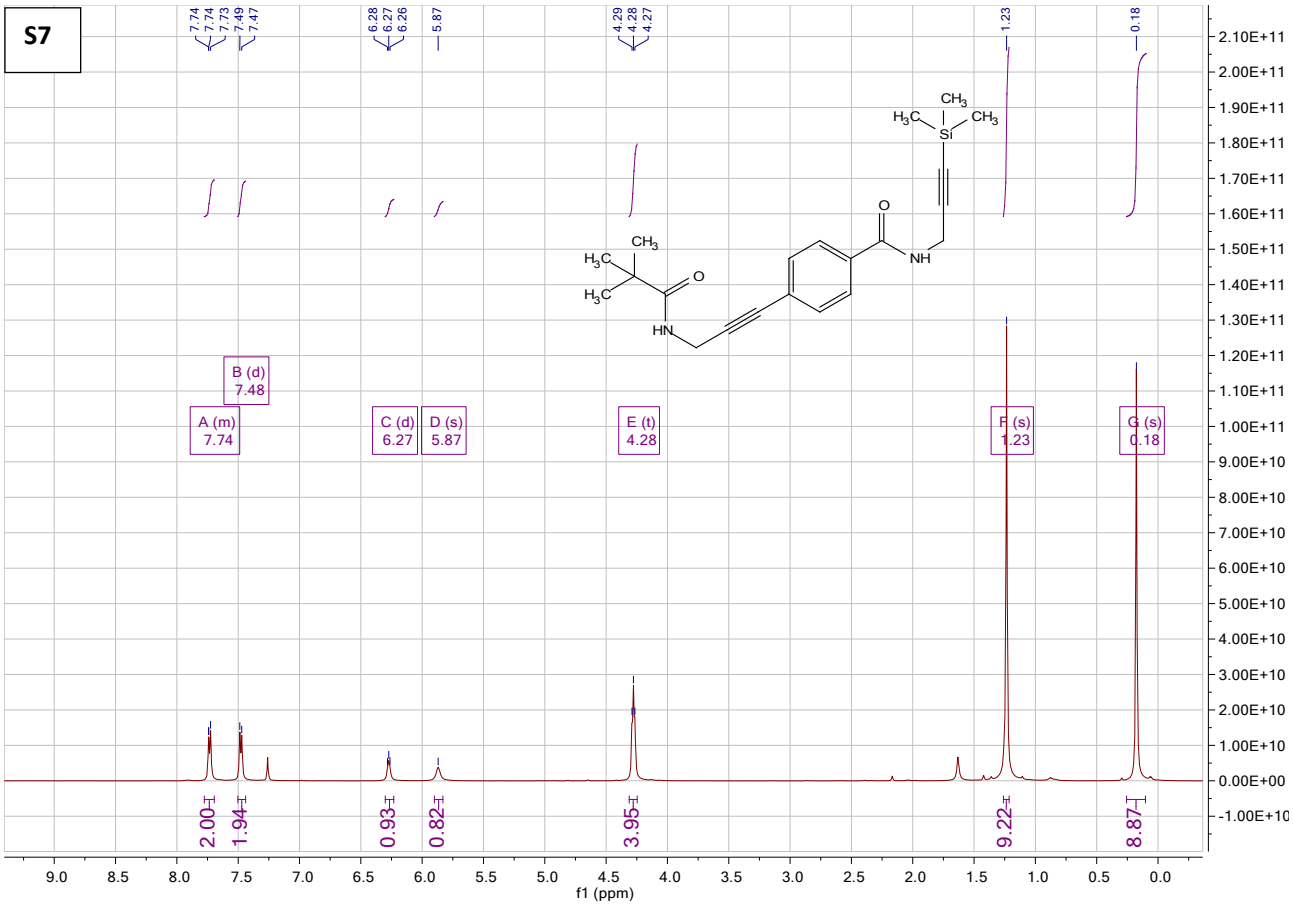

8b
f1 (ppm)

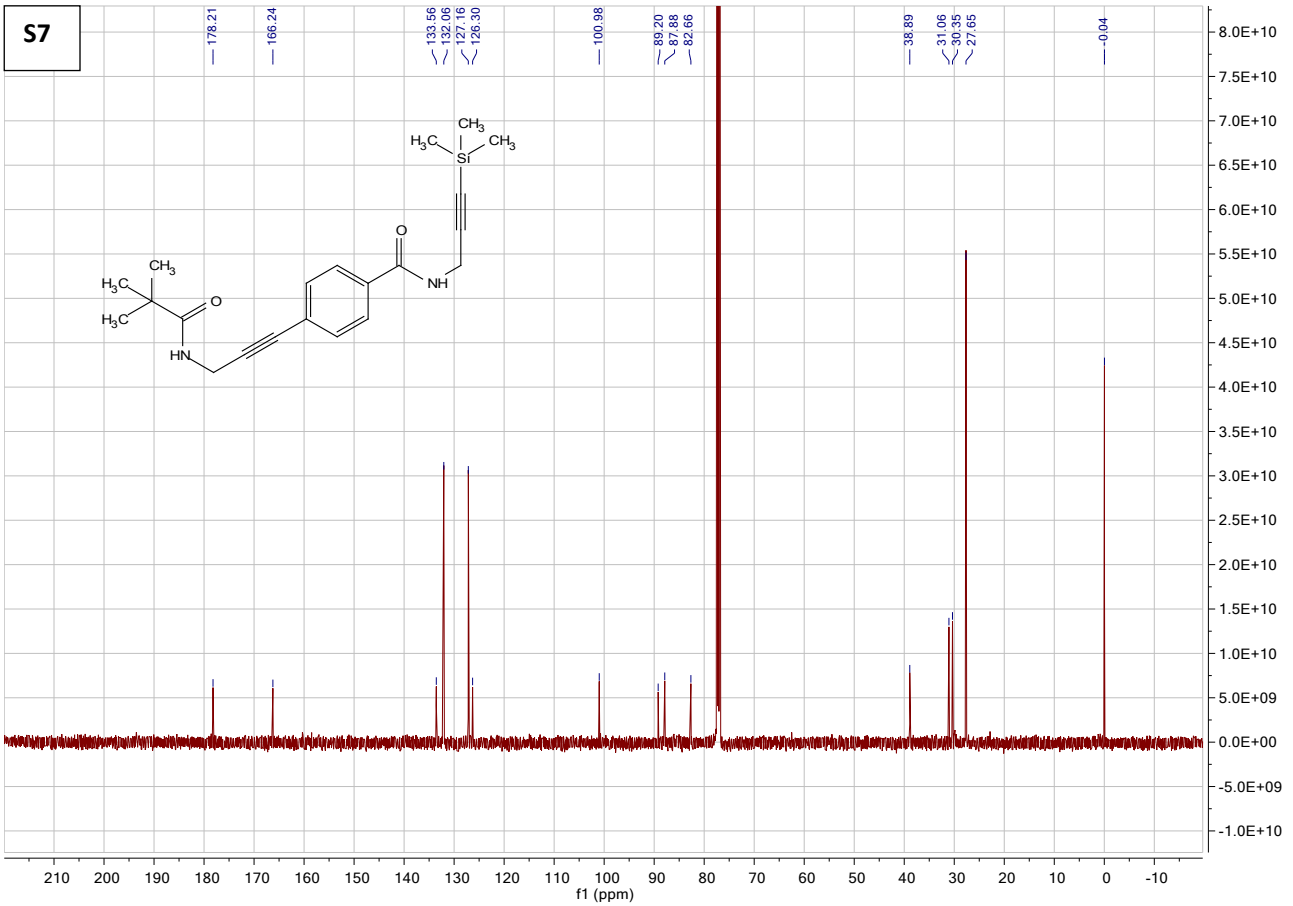

3c
7.72
7.72
7.72
7.71
7.70
7.70
7.31
7.30
7.30
7.29
6.60
4.22
4.21
4.21
4.20
2.98
2.97
2.96
2.94
2.93
2.32
2.31
2.31
1.28
1.27
1.26
1.25
1.25
CH
O
NH
H3C
CH3
B (m)
7.30
A (m)
7.71
C (s)
6.60
D (dd)
4.21
E (hept)
2.96
F (d)
1.26
1.91
2.00
0.94
2.07
0.96
6.55
f1 (ppm)

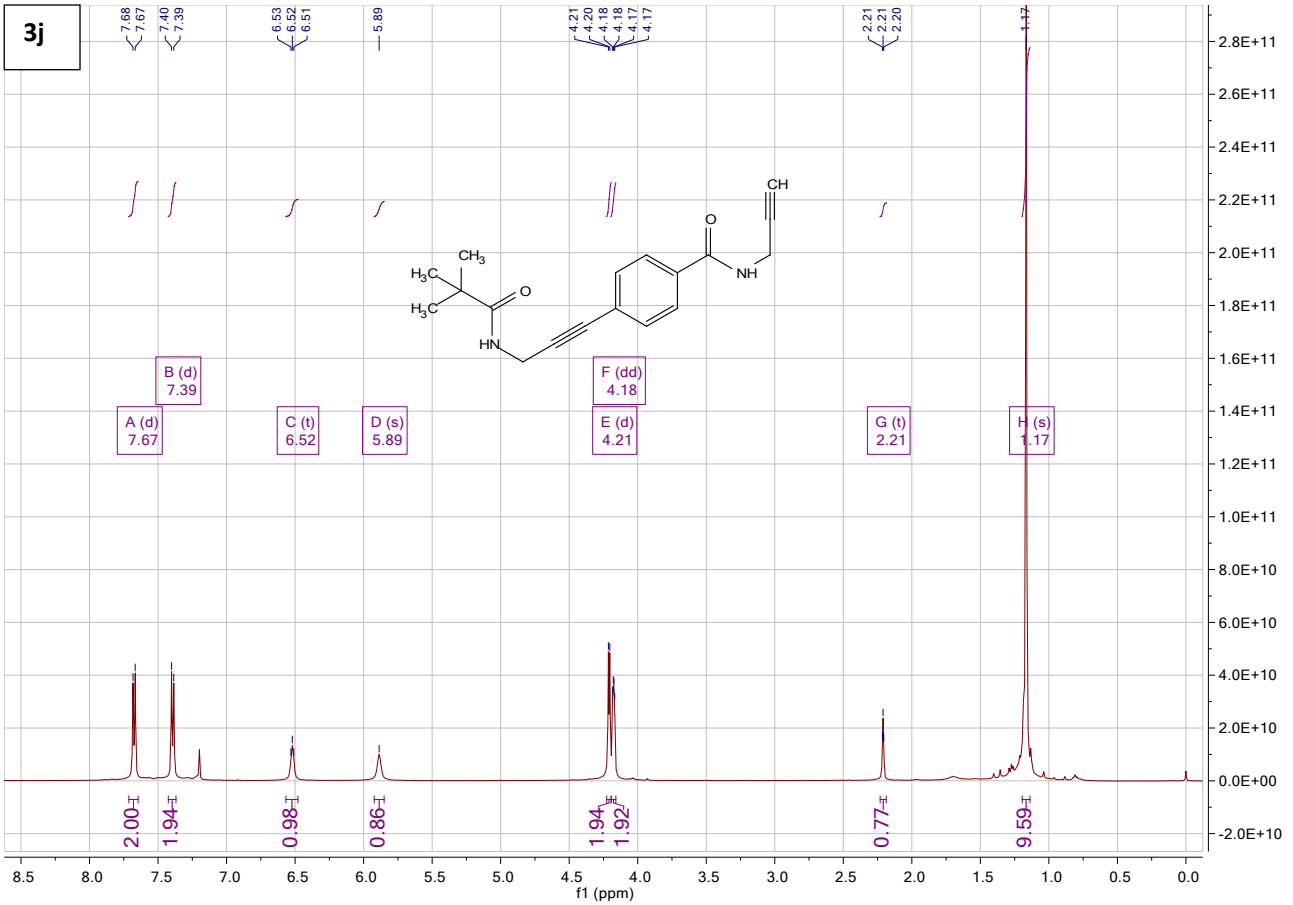

3c
167.25
153.51
131.80
127.47
127.05
80.32
71.49
34.48
29.85
23.89
CH
O
NH
H3C
CH3
f1 (ppm)

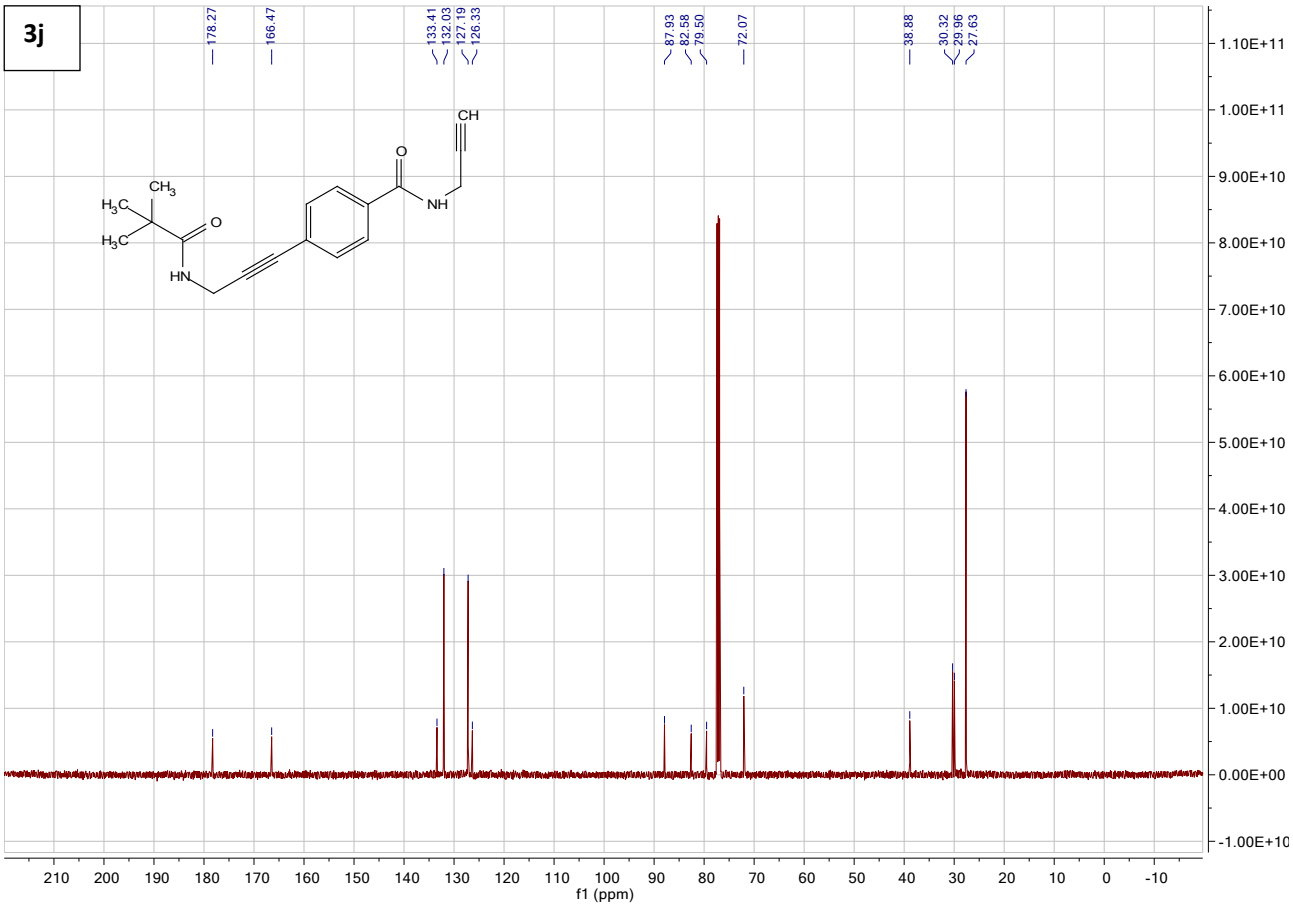

S6
7.77
7.76
7.51
7.49
6.43
6.42
6.41
4.25
4.24
0.16
B (d)
7.50
A (d)
7.76
C (t)
6.42
D (d)
4.25
E (s)
0.16
2.00
2.12
0.88
2.02
8.92
f1 (ppm)


S6
166.29
137.90
133.36
128.76
100.92
98.86
89.11
31.01
0.06
f1 (ppm)

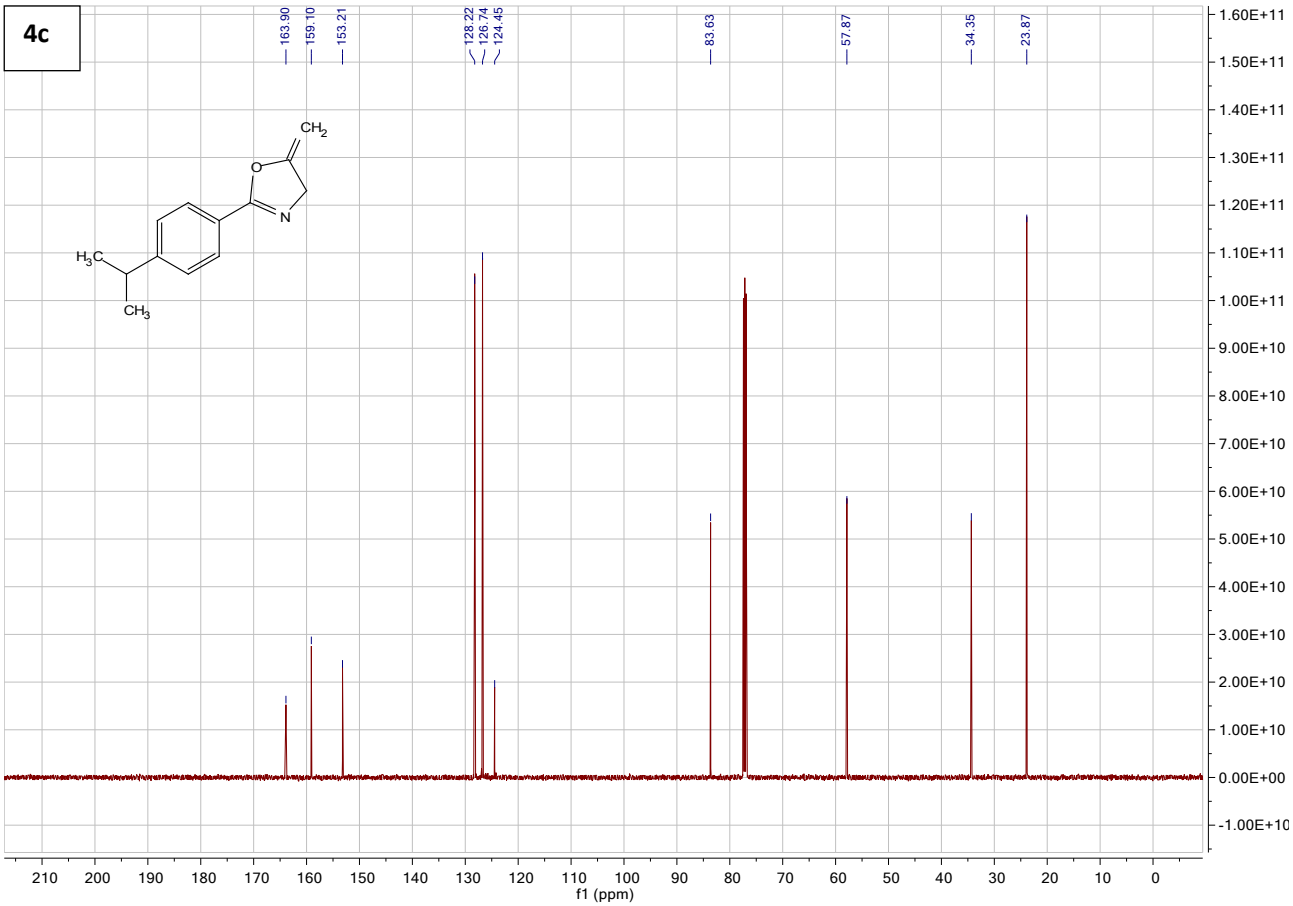

S7
7.74
7.74
7.73
7.49
7.47
6.28
6.27
6.26
5.87
4.29
4.28
4.27
1.23
0.18
B (d)
7.48
A (m)
7.74
C (d)
6.27
D (s)
5.87
E (t)
4.28
F (s)
1.23
G (s)
0.18
2.00
1.94
0.93
0.82
3.95
9.22
8.87
f1 (ppm)

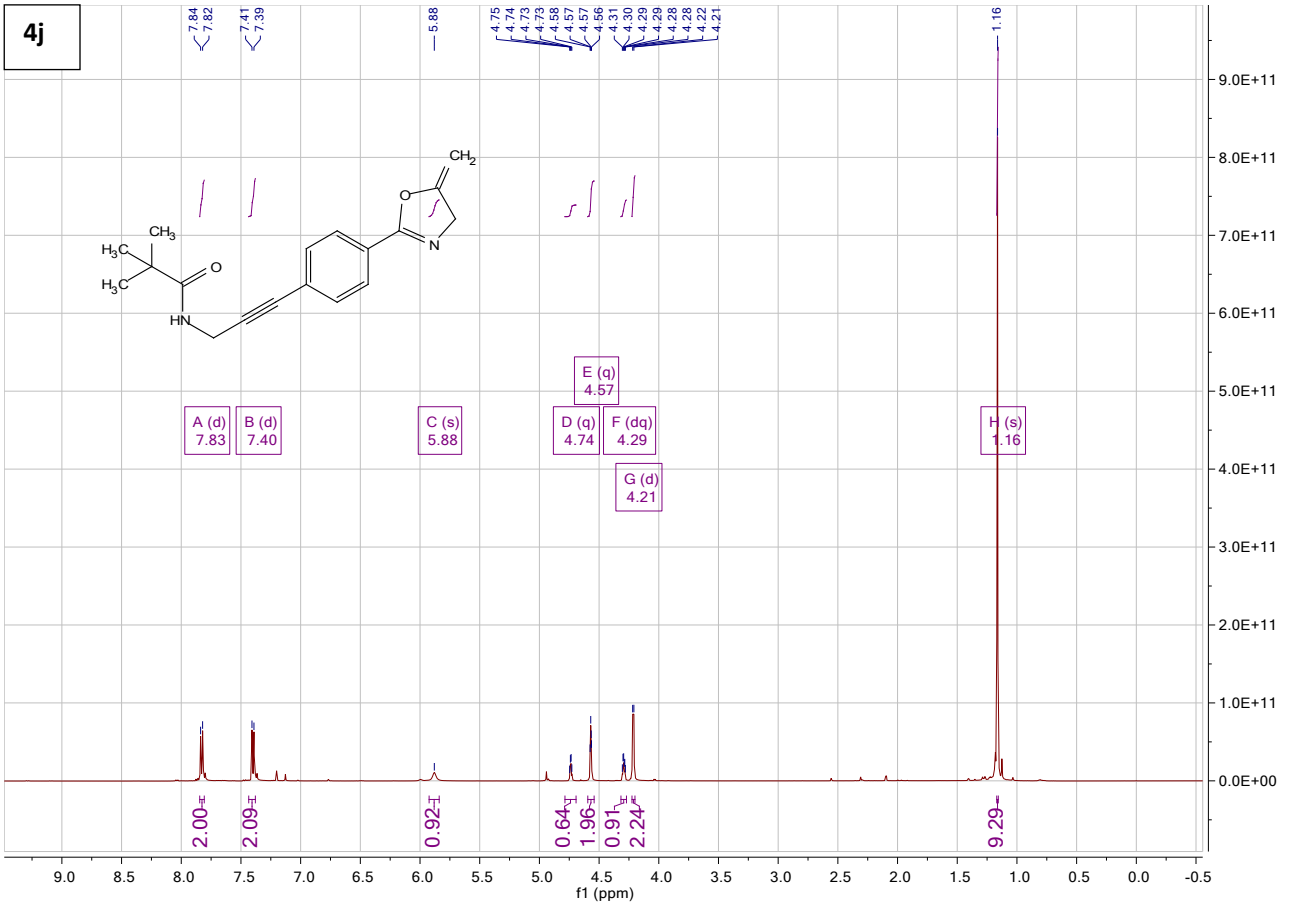

S7
178.21
166.24
133.56
132.06
127.16
126.30
100.98
89.20
87.88
82.66
38.89
31.06
30.35
27.65
-0.04
f1 (ppm)

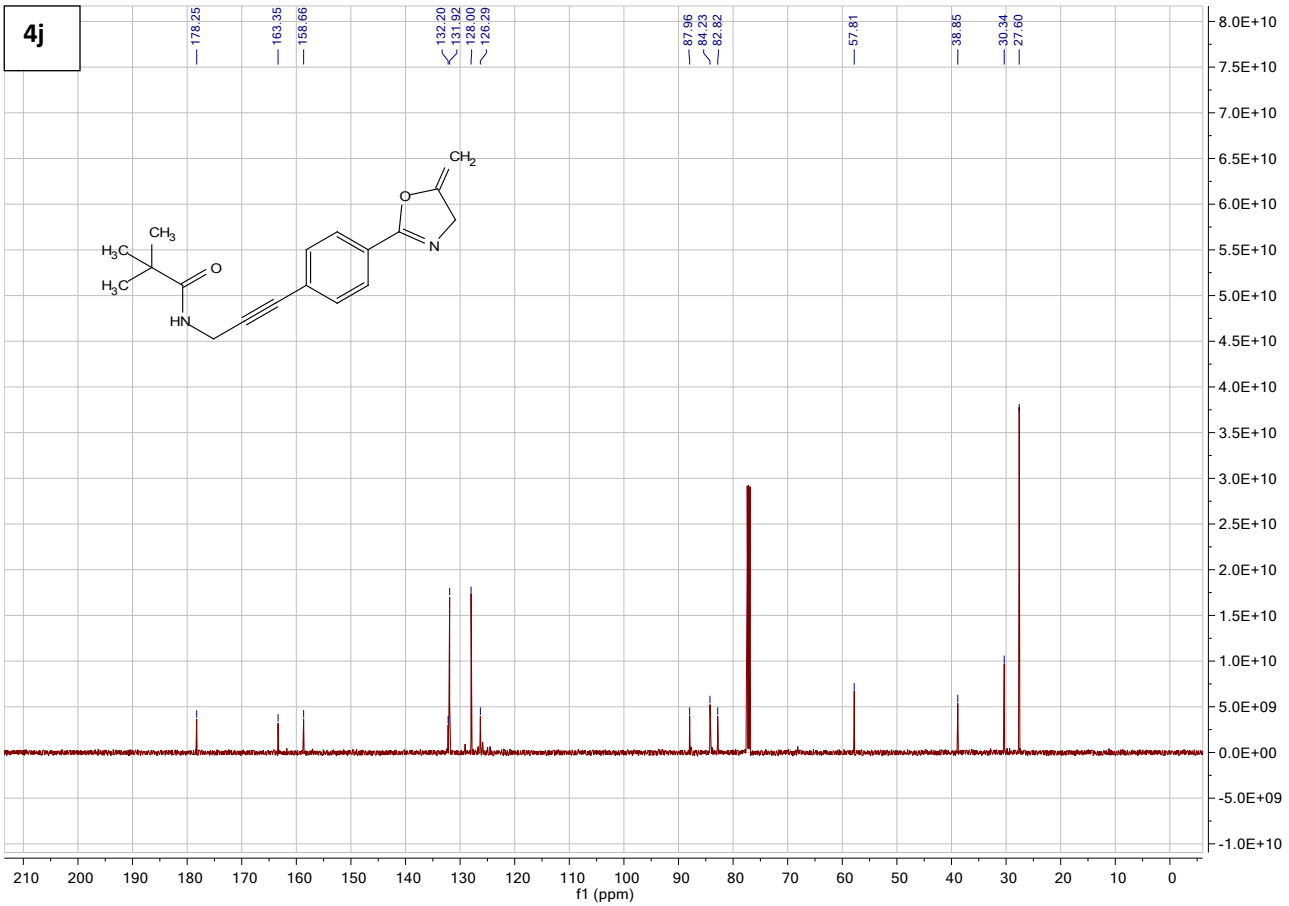

3j
7.68
7.67
7.40
7.39
6.53
6.52
6.51
5.89
4.21
4.20
4.18
4.17
2.21
2.20
1.17
B (d)
7.39
A (d)
7.67
C (t)
6.52
D (s)
5.89
F (dd)
4.18
E (d)
4.21
G (t)
2.21
H (s)
1.17
2.00
1.94
0.98
0.86
1.94
1.92
0.77
9.59
f1 (ppm)

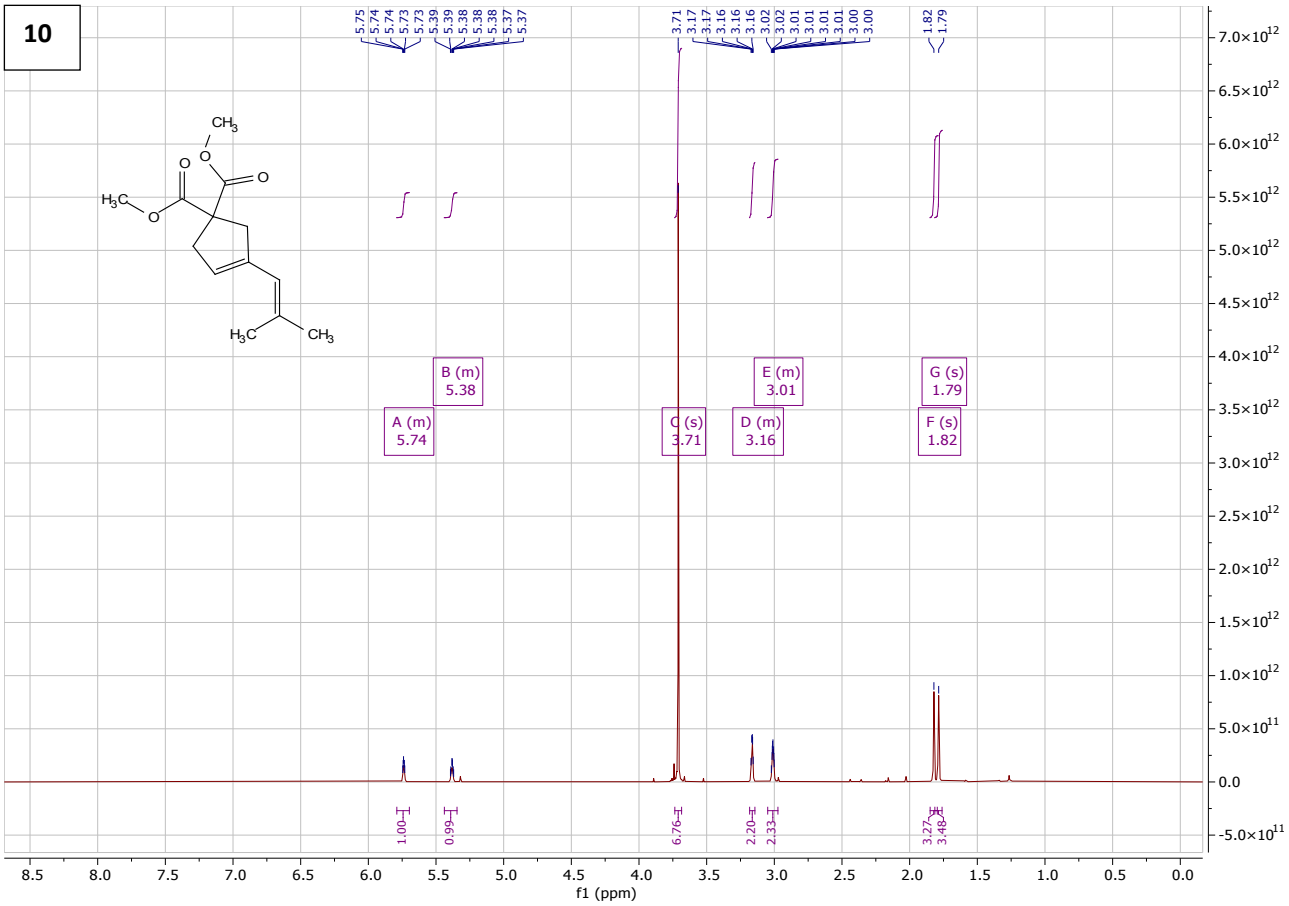

3j
178.27
166.47
133.41
132.03
127.19
126.33
87.93
82.58
79.50
72.07
38.88
30.32
29.96
27.63
f1 (ppm)

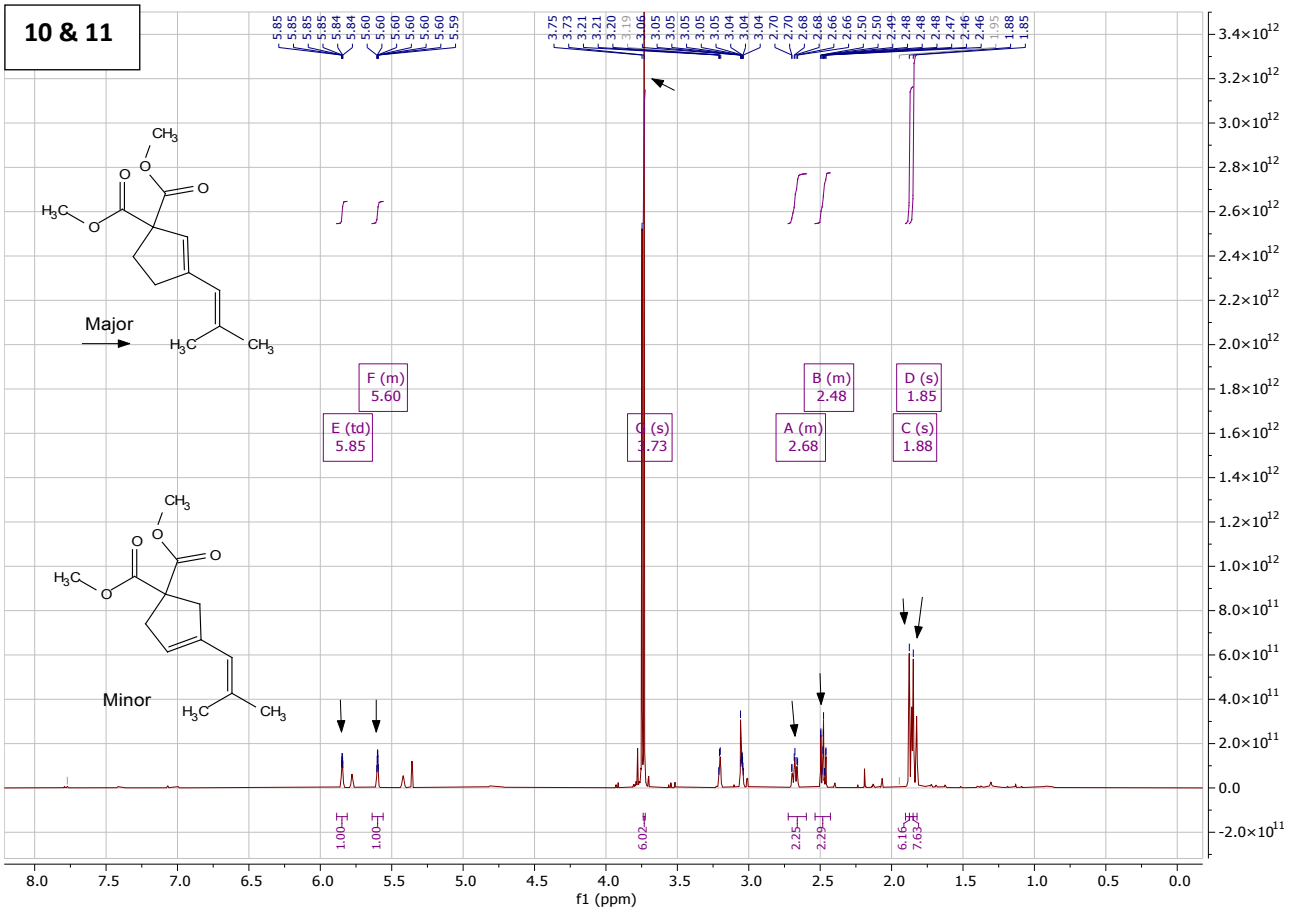

4c
7.90
7.90
7.89
7.88
7.30
7.28
4.81
4.80
4.80
4.79
4.64
4.63
4.63
4.35
4.35
4.34
4.34
2.99
2.98
2.97
2.95
2.94
2.93
2.91
1.27
1.26
CH2
O
N
H3C
CH3
A (m)
7.89
B (d)
7.29
D (t)
4.63
C (q)
4.80
E (q)
4.34
F (hept)
2.95
H (s)
1.26
G (s)
1.27
2.00
2.14
1.05
2.09
1.04
1.08
3.09
3.14
f1 (ppm)

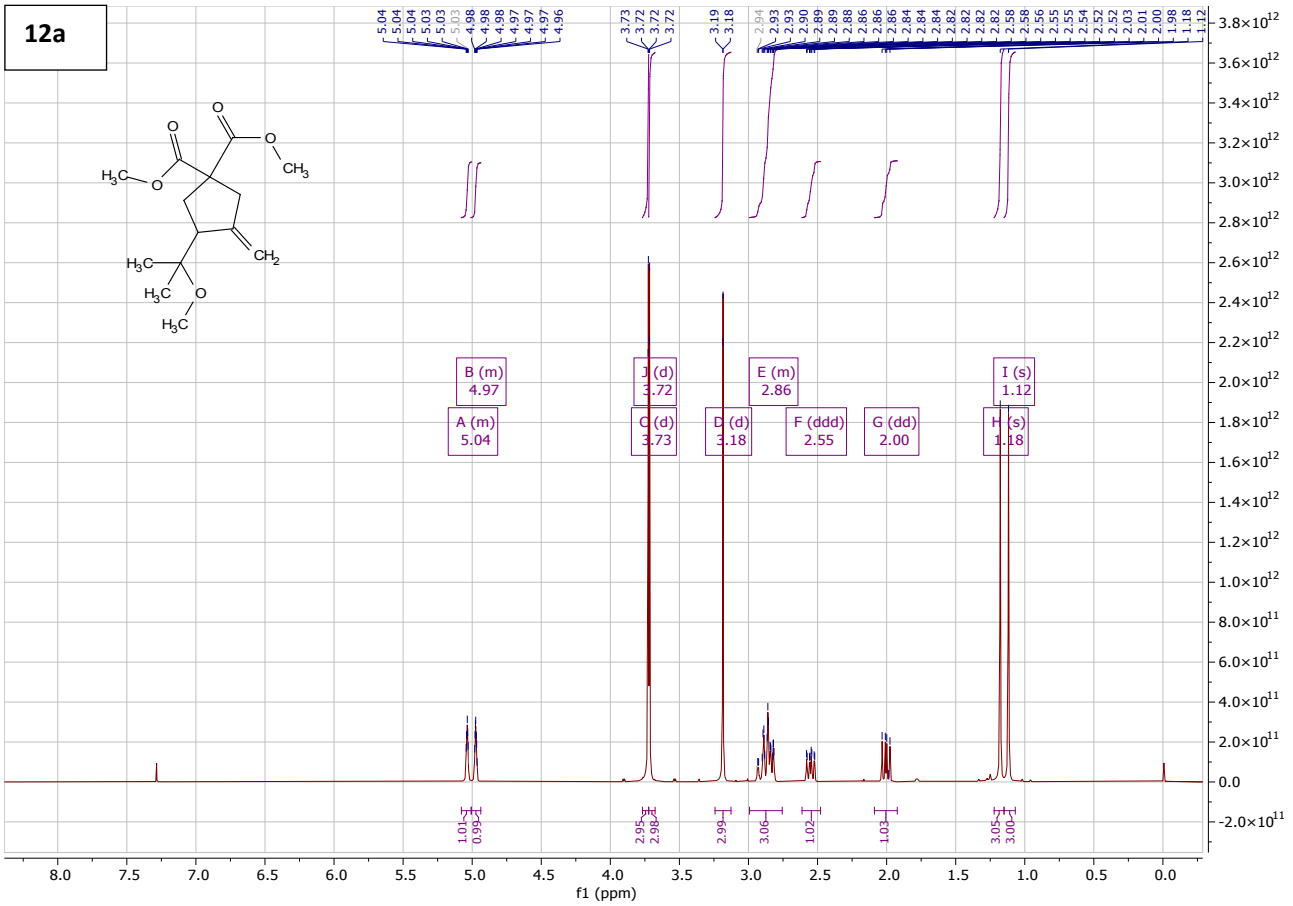

4c
163.90
159.10
153.21
128.22
126.74
124.45
83.63
57.87
34.35
23.87
CH2
O
N
H3C
CH3
f1 (ppm)

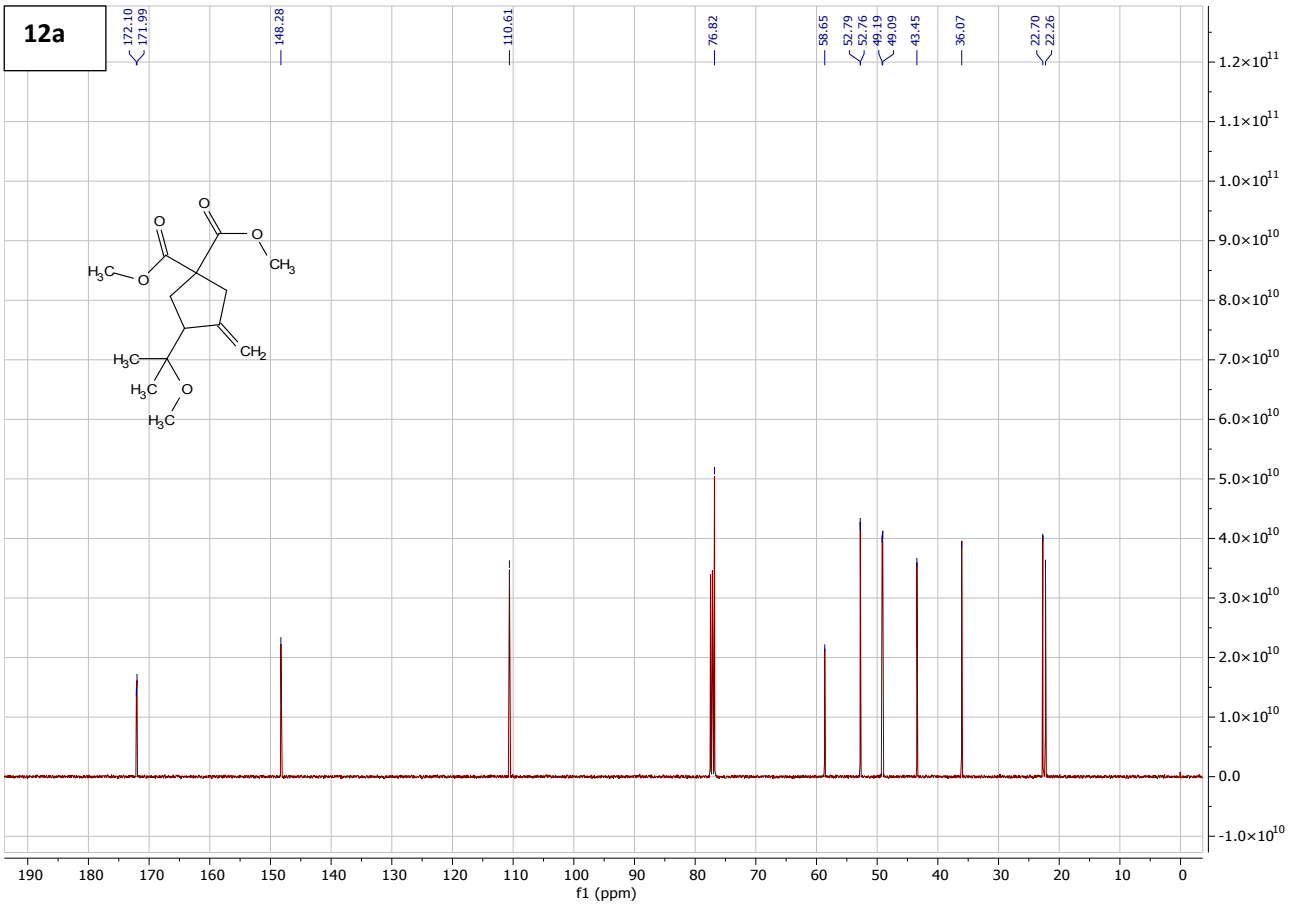

4j
7.84
7.82
7.41
7.39
5.88
4.75
4.74
4.73
4.58
4.57
4.56
4.31
4.30
4.29
4.29
4.28
4.28
4.22
4.21
1.16
CH2
O
N
CH3
H3C
H3C
O
HN
E (q)
4.57
A (d)
7.83
B (d)
7.40
C (s)
5.88
D (q)
4.74
F (dq)
4.29
G (d)
4.21
H (s)
1.16
2.00
2.09
0.92
0.64
1.96
0.91
2.24
9.29
f1 (ppm)

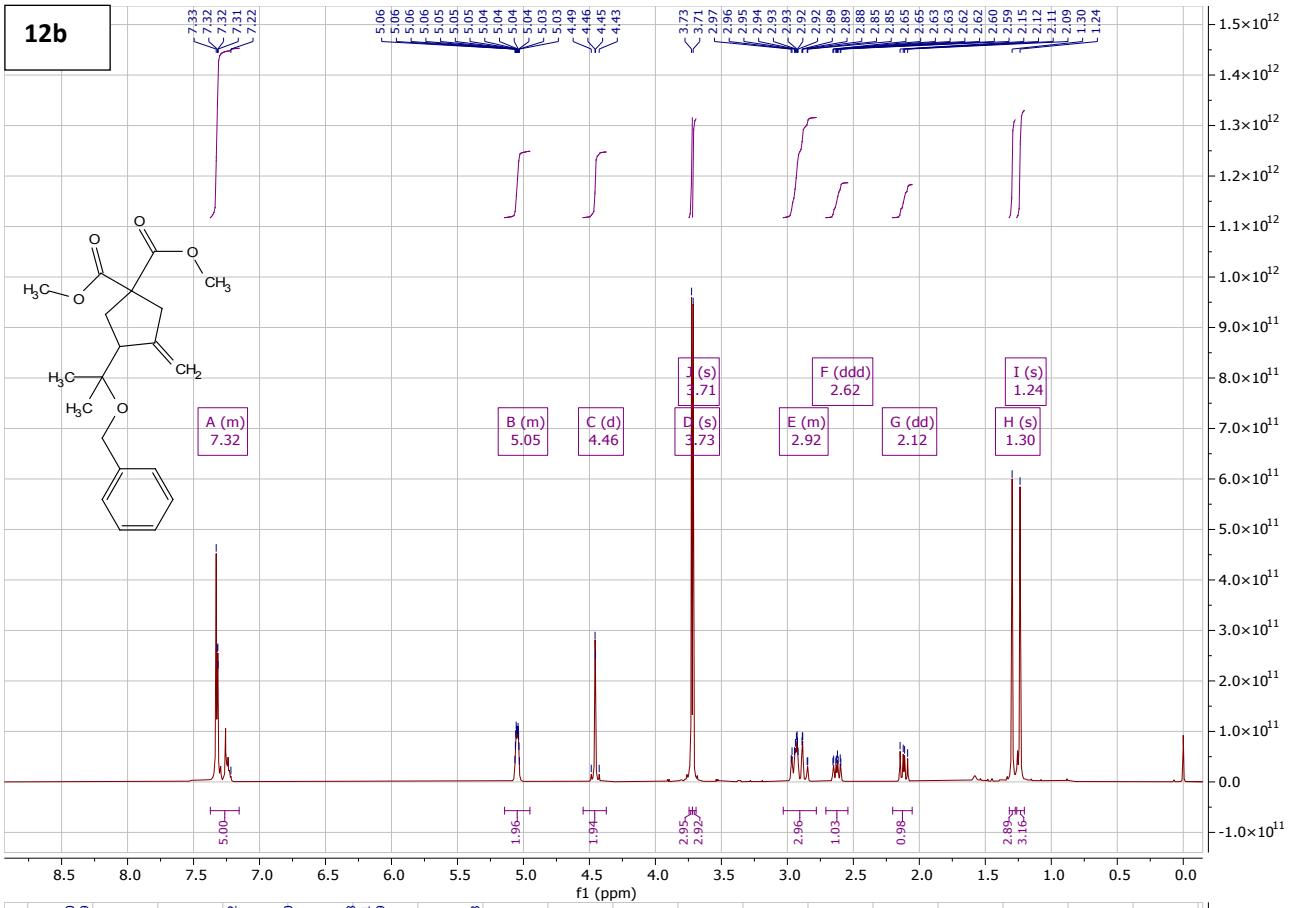

4j
178.25
163.35
158.66
132.20
131.92
128.00
126.29
87.96
84.23
82.82
57.81
38.85
30.34
27.60
CH2
O
N
CH3
H3C
H3C
O
HN
f1 (ppm)

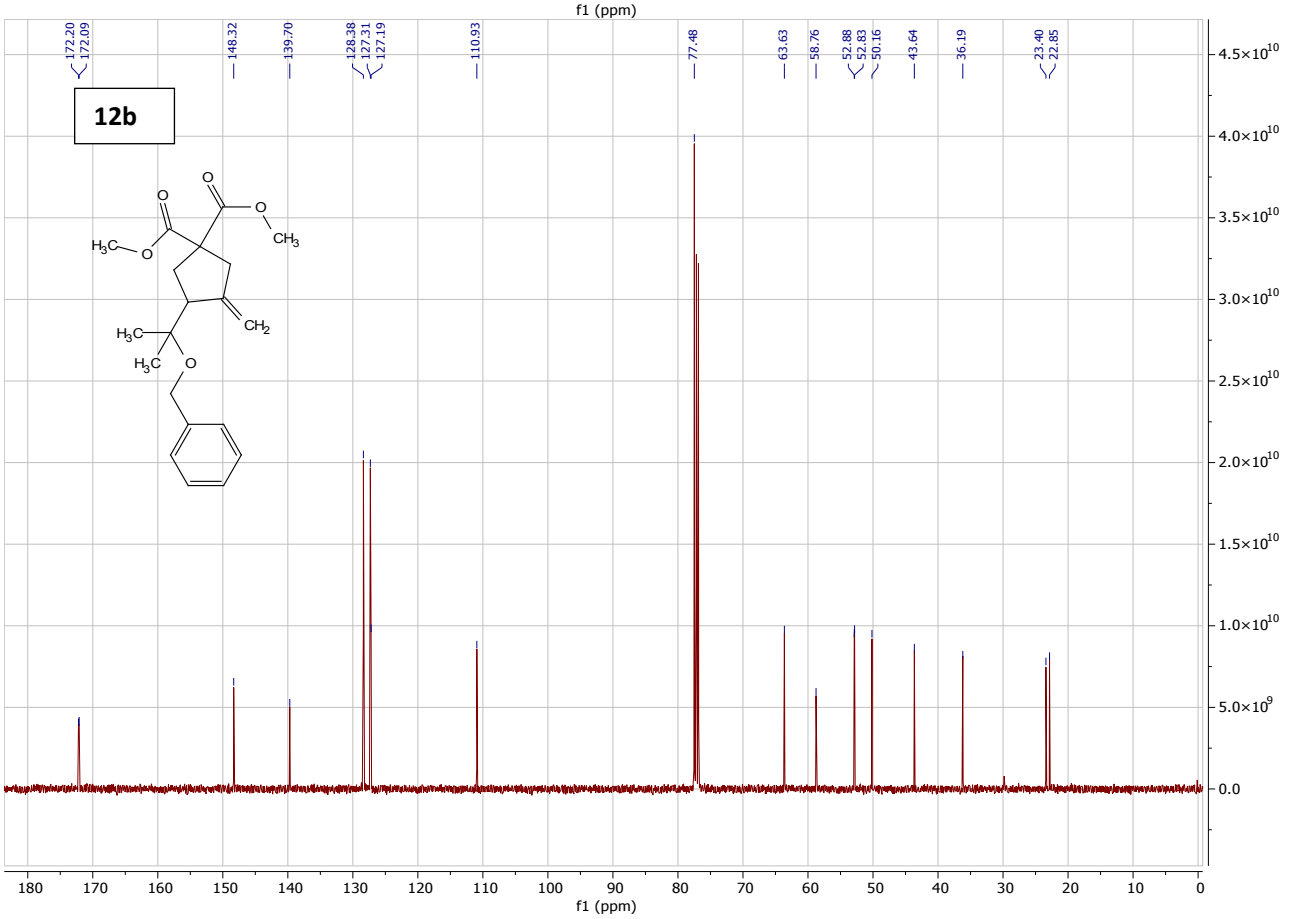

10
B (m)
5.38
A (m)
5.74
C (s)
3.71
E (m)
3.01
D (m)
3.16
G (s)
1.79
F (s)
1.82
f1 (ppm)

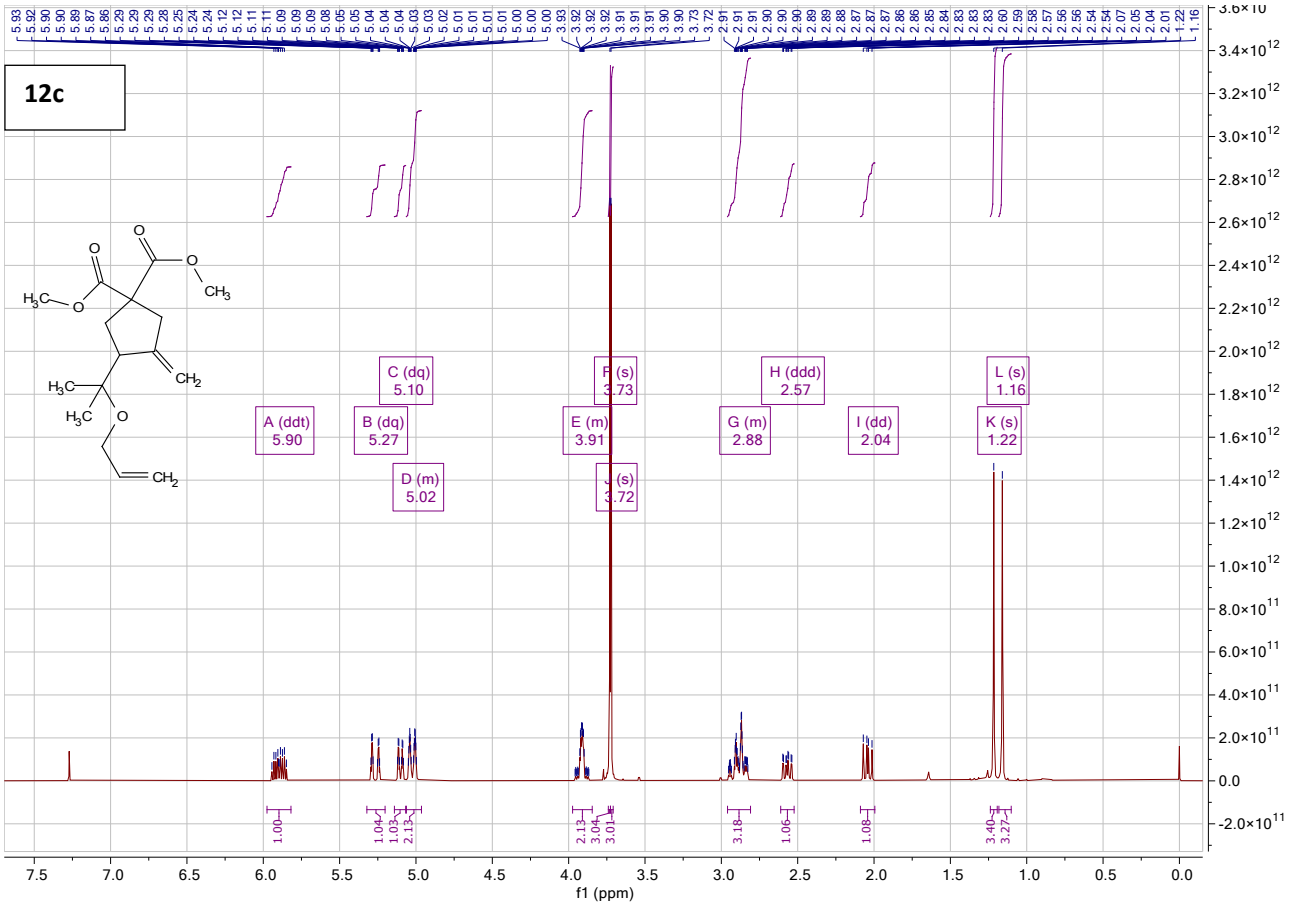

10 & 11
Major
Minor
F (m)
5.60
E (td)
5.85
C (s)
3.73
B (m)
2.48
A (m)
2.68
D (s)
1.85
C (s)
1.88
f1 (ppm)

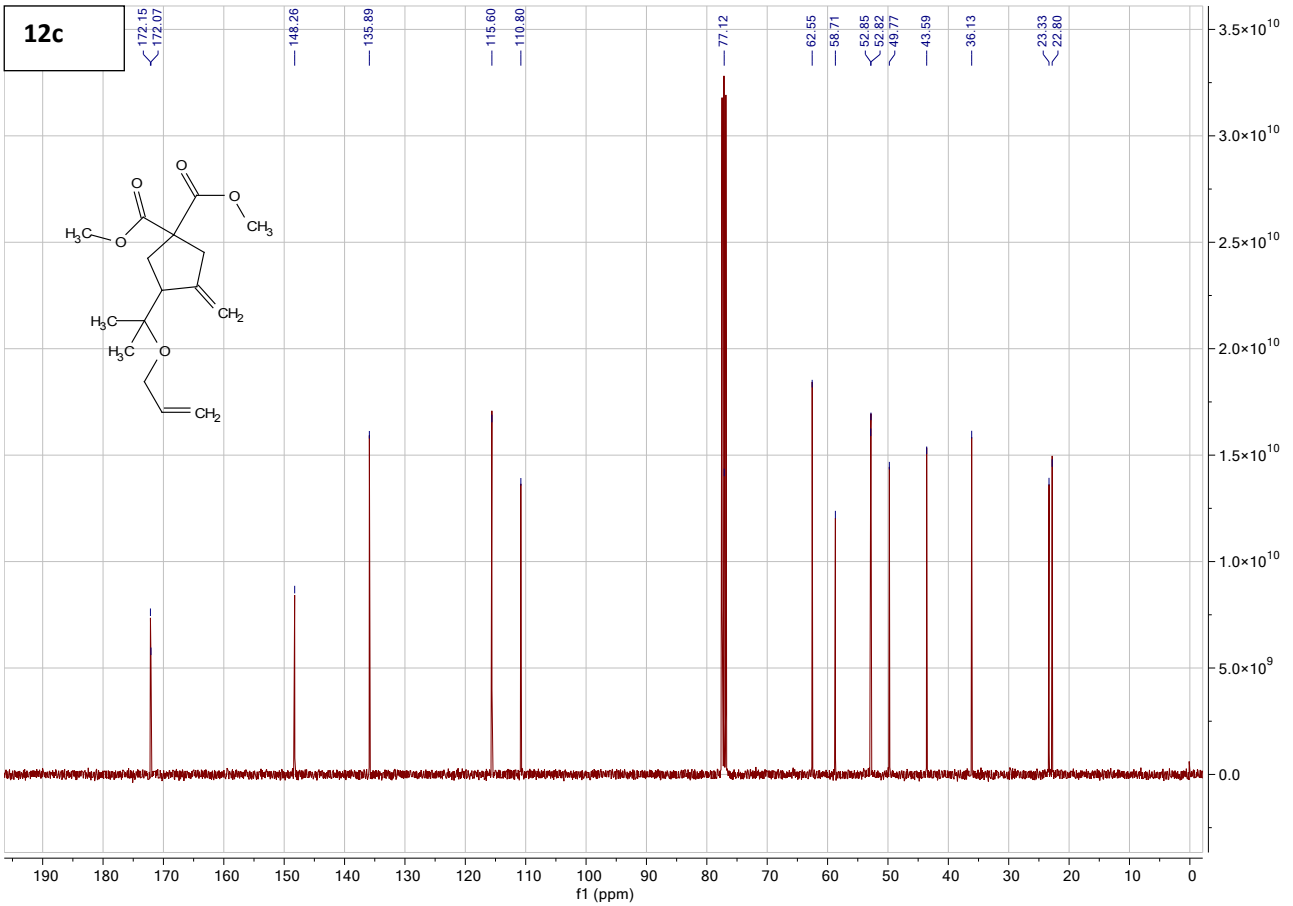

12a
B (m) 4.97
A (m) 5.04
J (d) 3.72
G (d) 3.73
D (d) 3.18
E (m) 2.86
F (ddd) 2.55
G (dd) 2.00
I (s) 1.12
H (s) 1.18
f1 (ppm)

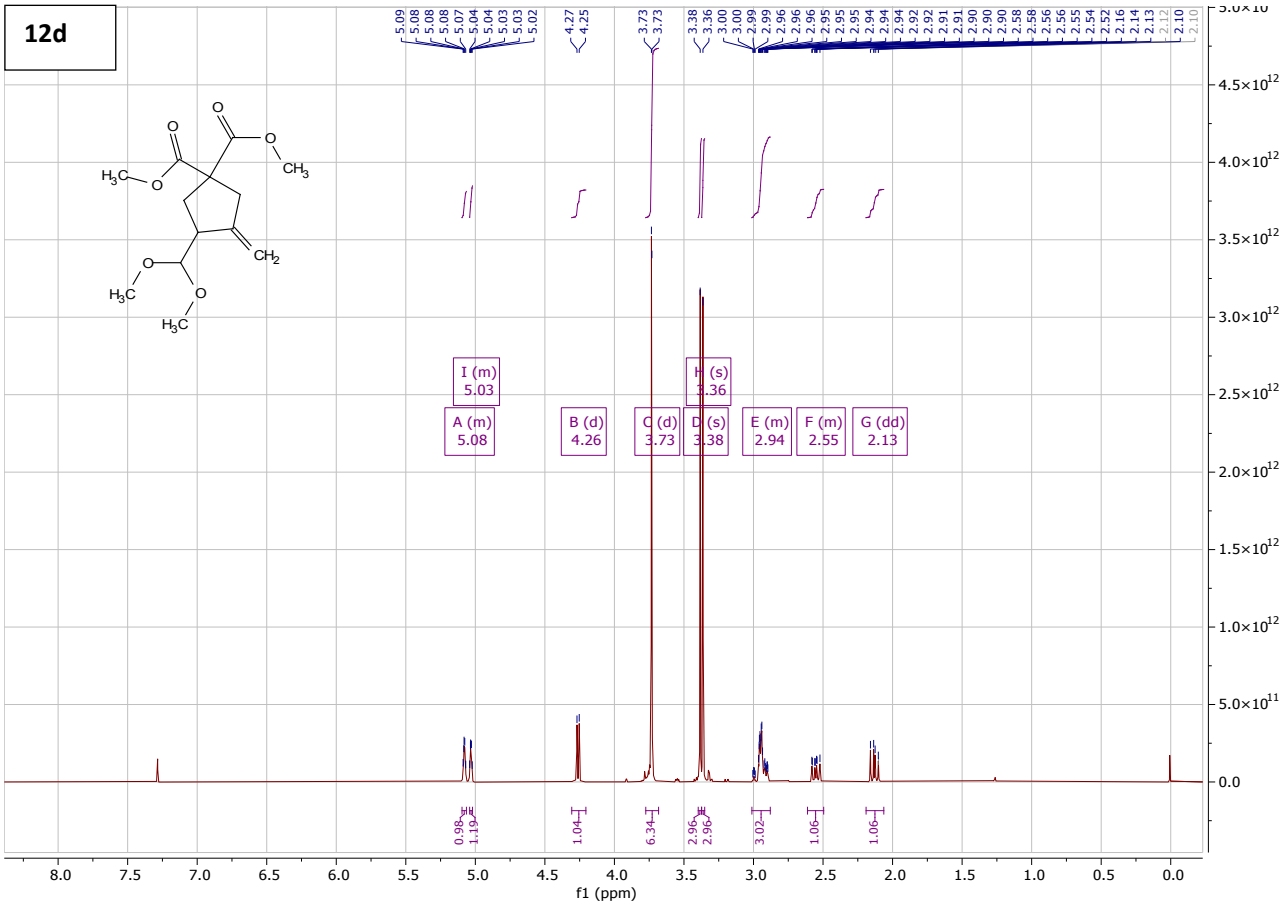

12a
172.10
171.99
148.28
110.61
76.82
58.65
52.79
52.76
49.19
49.09
43.45
36.07
22.70
22.26
f1 (ppm)

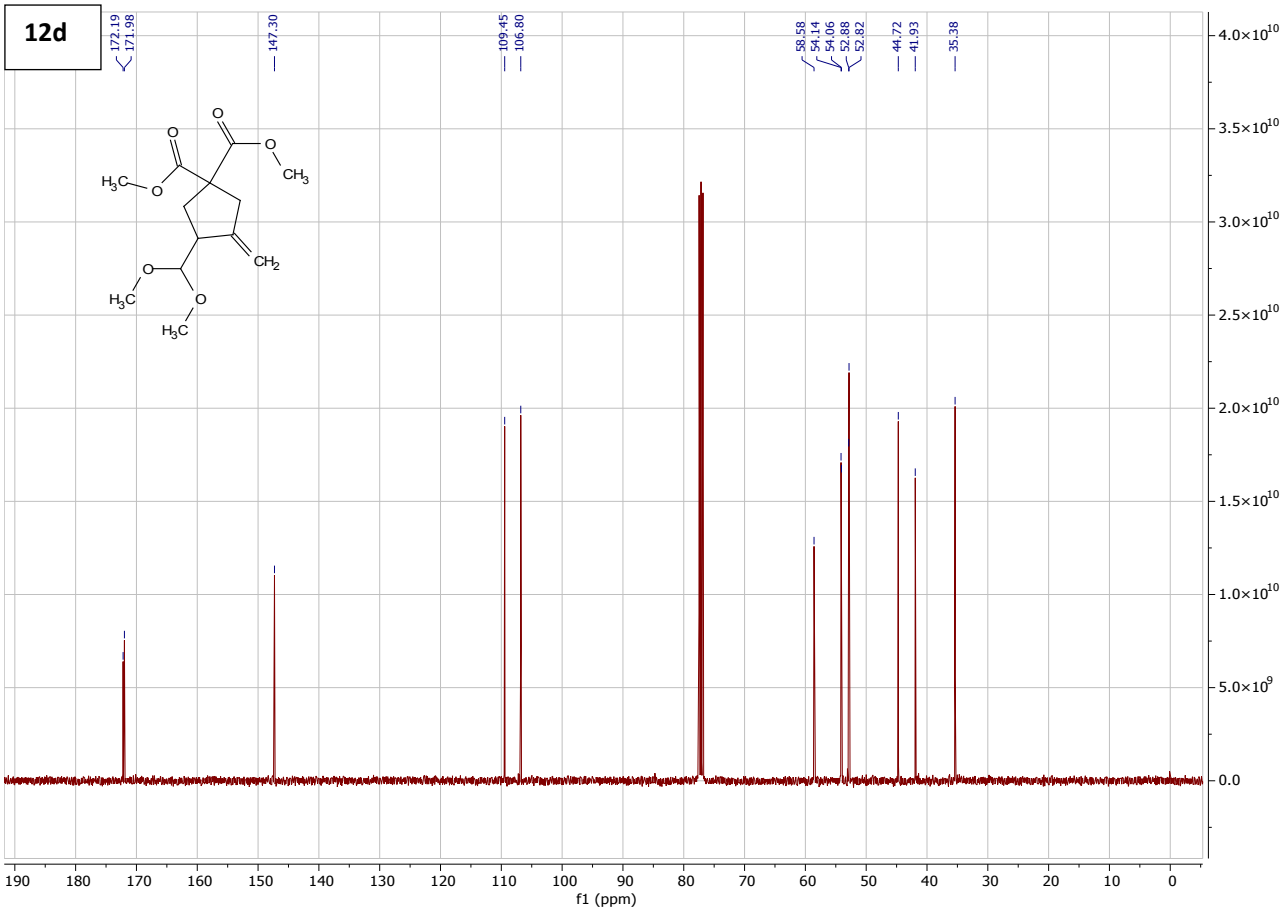

12b
A (m) 7.32
B (m) 5.05
C (d) 4.46
D (s) 3.73
E (m) 2.92
F (ddd) 2.62
G (dd) 2.12
H (s) 1.30
I (s) 1.24
f1 (ppm)

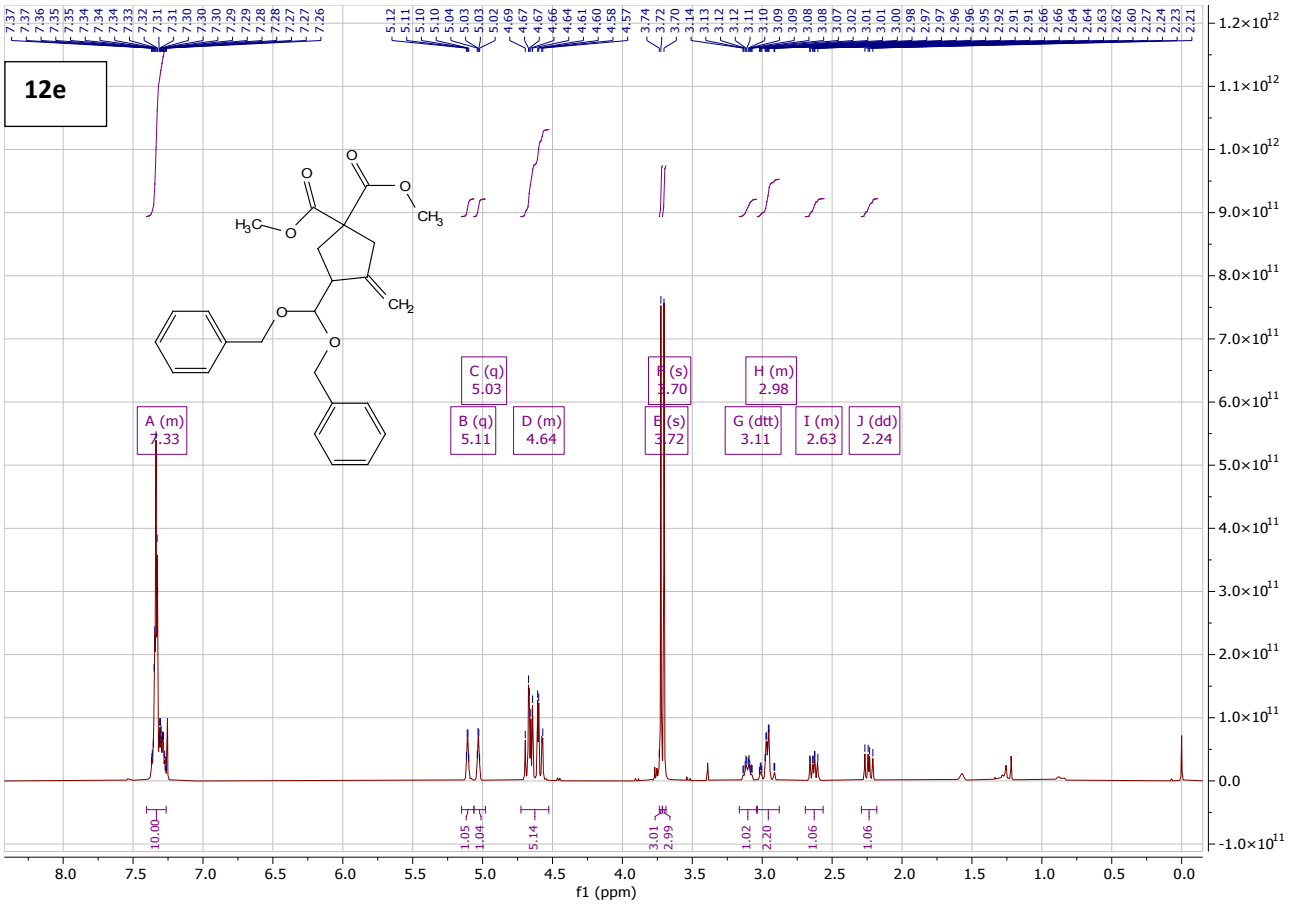

12b
f1 (ppm)

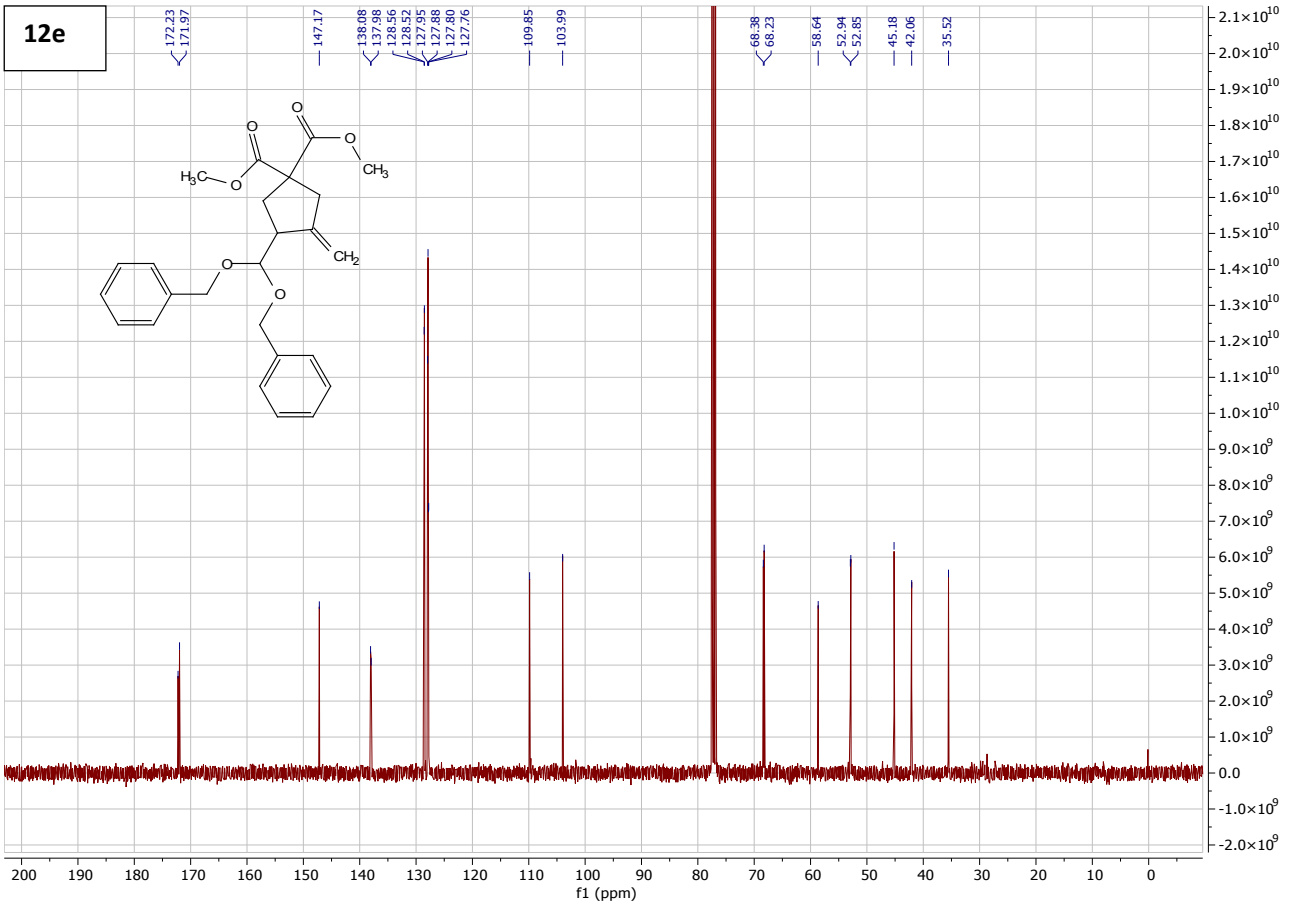

12c
A (ddt) 5.90
B (dq) 5.27
C (dq) 5.10
D (m) 5.02
E (m) 3.91
F (s) 3.73
G (m) 2.88
H (ddd) 2.57
I (dd) 2.04
K (s) 1.22
L (s) 1.16
f1 (ppm)

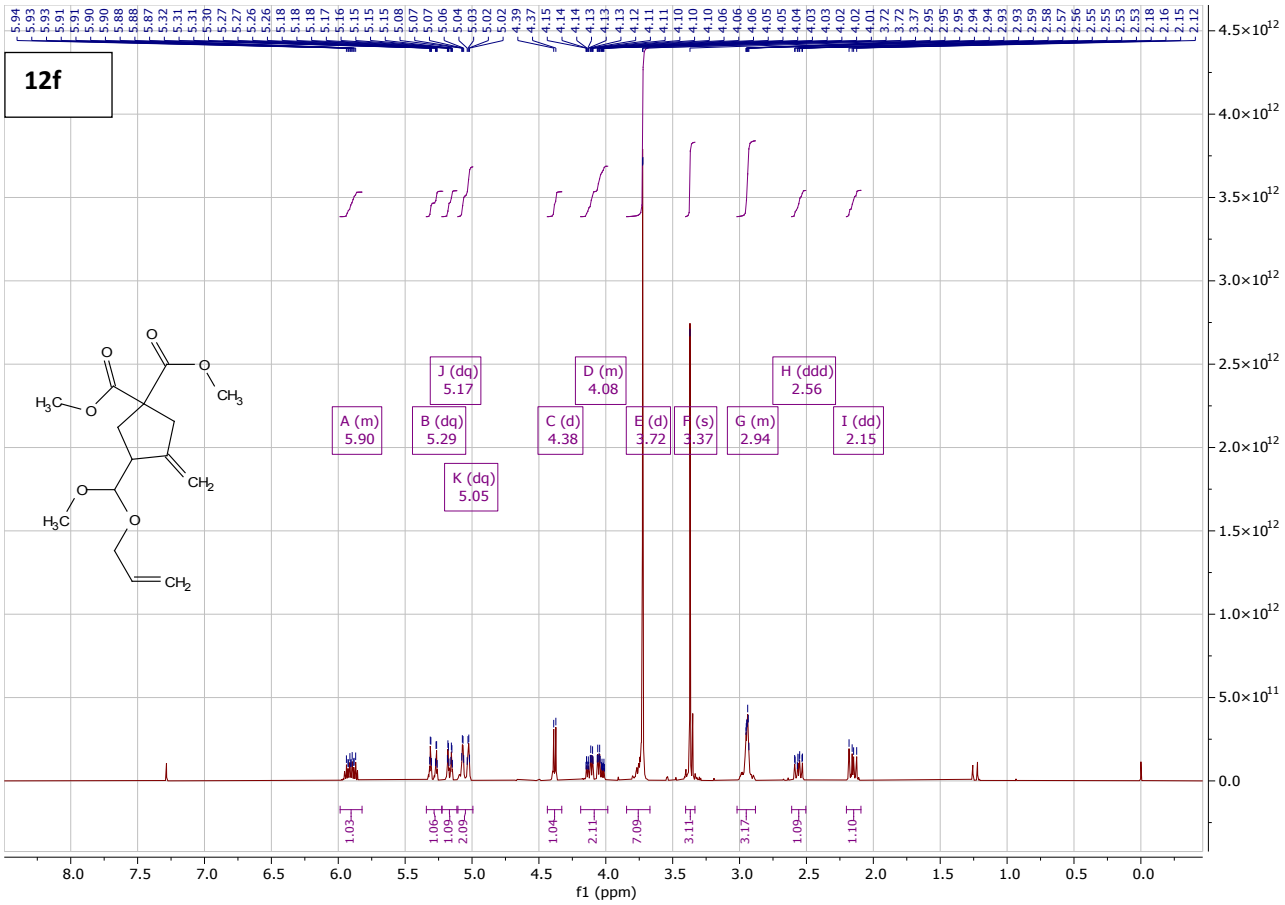

12c
172.15
172.07
148.26
135.89
115.60
110.80
77.12
62.55
58.71
52.85
52.82
49.77
43.59
36.13
23.33
22.80
f1 (ppm)

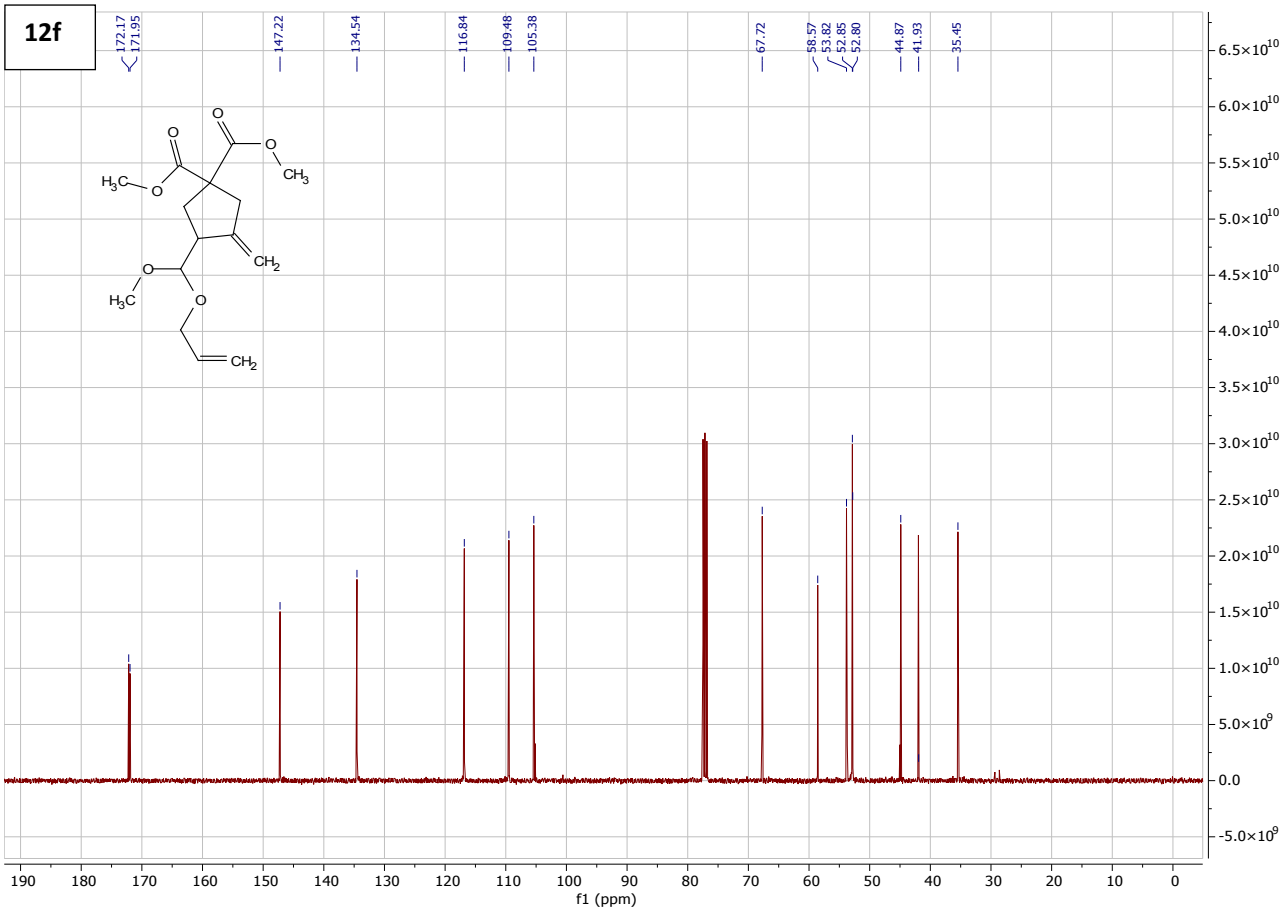

12d
I (m) 5.03
H (s) 3.36
A (m) 5.08
B (d) 4.26
C (d) 3.73
D (s) 3.38
E (m) 2.94
F (m) 2.55
G (dd) 2.13
f1 (ppm)


12d
f1 (ppm)


12e
A (m) 7.33
B (q) 5.11
C (q) 5.03
D (m) 4.64
E (s) 3.72
F (s) 3.70
G (dtt) 3.11
H (m) 2.98
I (m) 2.63
J (dd) 2.24
f1 (ppm)


12e
172.23
171.97
147.17
138.08
137.98
128.56
128.52
127.95
127.88
127.80
127.76
109.85
103.99
68.38
68.23
58.64
52.94
52.85
45.18
42.06
35.52
f1 (ppm)


12f
A (m) 5.90
B (dq) 5.29
J (dq) 5.17
K (dq) 5.05
C (d) 4.38
D (m) 4.08
E (d) 3.72
F (s) 3.37
G (m) 2.94
H (ddd) 2.56
I (dd) 2.15
f1 (ppm)


12f
172.17
171.95
147.22
134.54
116.84
109.48
105.38
67.72
58.57
53.82
52.85
52.80
44.87
41.93
35.45
f1 (ppm)

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